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PREFACE

In investigating the highly different phenomena in nature, scientists have always tried to find some fundamental principles that can explain the variety from a basic unity. Today they have not only shown that all the various kinds of matter are built up from a rather limited number of atoms, but also that these atoms are constituted of a few basic elements of building blocks. It seems possible to understand the innermost structure of matter and its behavior in terms of a few elementary particles: electrons, protons, neutrons, photons, etc., and their interactions. Since these particles obey not the laws of classical physics but the rules of modern quantum theory of wave mechanics established in 1925, there has developed a new field of "quantum science" which deals with the explanation of nature on this ground.

Quantum chemistry deals particularly with the electronic structure of atoms, molecules, and crystalline matter and describe it in terms of electronic wave patterns. It uses physical and chemical insight, sophisticated mathematics, and high-speed computers to solve the wave equations and achieve its results. Its goals are great, but perhaps the new field can better boast of its conceptual framework than of its numerical accomplishments. It provides a unification of the natural sciences that was previously inconceivable, and the modern development of cellular biology shows that the life sciences are now, in turn, using the same basis. "Quantum biology" is a new field which describes the life processes and the functioning of the cell on a molecular and submolecular level.

Quantum chemistry is hence a rapidly developing field which falls between the historically established areas of mathematics, physics, chemistry, and biology. As a result there is a wide diversity of backgrounds among those interested in quantum chemistry. Since the results of the research are reported in periodicals of many different types, it has become increasingly difficult for both the expert and the nonexpert to follow the rapid development in this new borderline area.

The purpose of this serial publication is to try to present a survey of the current development of quantum chemistry as it is seen by a number of the internationally leading research workers in various countries. The authors have been invited to give their personal points of view of the subject freely and without severe space limitations. No attempts have been made to avoid overlap—on the contrary, it has seemed desirable to have certain important research areas reviewed from different points of view. The response from the authors has been so encouraging that an eighth volume is now being prepared.

The editor would like to thank the authors for their contributions which give an interesting picture of the current status of selected parts of quantum chemistry. The topics covered in this volume range from the treatment of symmetry properties and molecular integrals over the study of atoms and small molecules to polyatomic molecules and biological systems; special attention is paid to the Hartree–Fock approximation and to new methods for solving the Schrödinger wave equation. Problems related to solvent effects and thermochemistry are also treated. Some of the papers emphasize studies in fundamental quantum theory and others computational techniques.

It is our hope that the collection of surveys of various parts of quantum chemistry and its advances presented here will prove to be valuable and stimulating, not only to the active research workers but also to the scientist in neighboring fields of physics, chemistry, and biology, who are turning to the elementary particles and their behavior to explain the details and innermost structure of their experimental phenomena.

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Rotation and Translation of Regular and Irregular Solid Spherical Harmonics*

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I. Introduction

A. Transformation of Orbitals: Regular Spherical Harmonics

Quantum-mechanical calculations of molecular properties and reactions usually require at the very beginning the introduction of atomic orbitals (AO's) which are centered on the nuclei of the different atoms of the investigated molecule or molecular complex. Each atomic orbital is a certain mathematical function of the coordinates of one electron with respect to a coordinate system which has its origin in the nucleus of the considered atom. *Ab initio* calculations have to deal with large numbers of molecular integrals which contain products of such AO's. To simplify the mathematical treatment or to make it even possible, it is important to investigate the problem of the optimum relative orientation of the different "atomic coordinate systems" with respect to each other. This problem is closely related to the problem of the transformation properties of the basis orbitals and their products if the atomic coordinate systems are rotated or translated in different ways. These transformation properties are not only important for derivations of analytical formulas, but also for solving the task of performing a calculation in a practical way. In fact, also the sequence in which the transformation operations are carried out is of considerable importance.

These problems have not found much systematic investigation. Some workers, who evaluated independently molecular integrals for *ab initio* calculations instead of relying on published results and thus were confronted with these problems, have occasionally discussed some aspects of this matter. This was the case especially when single-center expansions were applied, since such expansions require the translation of all functions to the one center in question. However, formulas which could be used in a general way have not been published, and the problem of optimization of such mathematical means and procedures has received only little attention. Accordingly, there are only a few remarks in the literature that hint at problems of this kind, as the following one:

"Since the orbitals which make up a charge distribution may be located at arbitrary spatial points with arbitrary relative orientations, provision must be made for both translational and rotational transformations of the coordinate systems.... A key feature of the method actually used is the choice of the order in which axial rotations and translations are performed; an optimum choice can lead to an order-of-magnitude less computational effort than a less fortunate choice" (Harris and Michels, 1966).

If one imagines that the atomic coordinate systems are attached to the atoms which constitute the molecule, it is clear that there are many possibilities of arranging these coordinate systems in the different molecules. For instance, orthogonal atomic coordinate systems may be attached to the atoms in such a way that all z axes direct to the same point which may be a center of the molecule. The atomic coordinate systems could also be arranged in such a way that their respective x, y, and z axes are parallel. In addition many other arrangements can be imagined. The advantages and disadvantages of the different arrangements of the atomic coordinate systems can be tested only by applying them to practical problems.

It turns out that the last-mentioned arrangement with parallel x, parallel y, and parallel z axes of the different atomic coordinate systems appears to have the greatest advantages for practical purposes. (For this arrangement, the term "parallel coordinate systems" will be used in the sequel.) This is partly based upon the fact that a vector is a mathematical quantity which is independent of the location of the origin of the coordinate system, i.e., a vector (which as usual may be envisaged as a pointing arrow of certain length) can be displaced arbitrarily in space provided its direction and length (absolute value) remain unchanged. Another reason why it is advantageous to use parallel atomic coordinate systems is the following. Since the nuclei of a polyatomic molecule in general do not lie on a straight line, the vector connecting two different centers (" origins "), will, in general, not coincide with an axis of one of those two ("parallel, shifted") atomic coordinate systems. However, by a simple rotation of both coordinate systems carried out at the same time in the same way, it is possible to achieve a relative position of both coordinate systems in which, for instance, both z axes coincide with and point to the same direction as the vector which connects both origins. In this "lined-up position of the atomic coordinate systems" (as it will be called in the sequel) one can make use of many formulas which have been derived for such a case as, for instance, in former investigations of diatomic molecules. The effect of such a rotation of the coordinate systems may then be investigated once and for all; this allows the best generalization of already known relationships. On the other side, one may look for generalizations of certain formulas by starting with the "lined-up" position and by turning both coordinate systems into a general not "lined-up," but "parallel and shifted" position by applying the same rotation to both coordinate systems. The latter procedure would be inverse to the former.

For practical purposes one needs especially the rotation of a function about a fixed center, the translation of a function from one center to another one, and the splitting of a one-centered function into such functions which originate at two other centers. Being able to carry out these operations, one can always consider more than two centers and build up step-by-step the whole molecule.

Due to the basic importance of the rotations, more attention will be paid to the angular parts of the atomic orbitals. For the present, the radial parts of the AO's will be included in the consideration as powers of r. This leads to the examination of the transformation properties of the regular solid spherical harmonics. These functions are contained in Slater-type AO's as well as in Gauss-type AO's with directional dependence. For the examination of the properties of the transformation under rotations, the radial parts of the considered orbitals are arbitrary. The consideration of the behavior of specific radial dependences under translation will be postponed to a later investigation. The application of the formulas derived in this paper to the calculation of multicenter integrals proved that considerable help is provided by using transformation properties of solid spherical harmonics.

The behavior of the solid spherical harmonics under *rotations* is, of course, the same as that of the surface spherical harmonics, and as such it is, as usually remarked, "well known." However, by using formulas which are given in the literature it becomes evident that utmost care is necessary to avoid mistakes, the reason being in the first place that a great variety of phase definitions are in use which makes it difficult to adopt formulas. Other reasons are a number of misprints or inconsistencies even in standard textbooks which may be misleading when, for instance, figures do not match the text, an explanation is missing whether the axes of a coordinate system or the shape of a function of the coordinates is rotated (two operations that are inverse to each other), or when co- and contravariant sets are not distinguished properly, and so on. For the following and for a uniform notation and treatment, it is therefore necessary to discuss the behavior of the aforementioned functions under rotations.

Much less is known about the behavior of the solid spherical harmonics under *translations*. Some useful and, to the knowledge of the authors, new formulas are derived here. Some of the known formulas, which are scattered and not too accessible in the literature, are derived consistently in a new way and in agreement with the rest of the present mathematical treatment. Thereby the expressions can be simplified, incorrect summation limits can be corrected, uniform phase definitions can be introduced, etc. This uniform treatment makes use of the laws of rotations and may, therefore, provide a better insight into the physical meaning of the derived relationships, since the similarities with the coupling of angular momenta become manifest.

The formulas derived to describe the transformation properties of solid spherical harmonics under rotations and translations have been found useful for the calculation of molecular integrals. The present investigation implies that the use of *parallel* atomic coordinate systems is of advantage for the calculation of quantum-mechanical molecular integrals, particularly if the important concept of charge-density distributions is used. It also proves to be advantageous to work with complex AO's. So far, one used in a somewhat biased attitude almost exclusively real AO's, since this is possible due to the reality of the Hamilton operator and appeared to be more convenient. However, many of the intermediate steps of the necessary mathematical operations may be formulated in a better and more compact way for complex atomic orbitals. Therefore, complex spherical harmonics will be used in this article. The relationships between integrals over real and those over complex orbitals are discussed in the next article in this volume (Steinborn, 1973).

B. Transformation of Operators: Irregular Spherical Harmonics

The main difficulties of quantum-mechanical theories are due to operators which may be considered as special cases of irregular solid spherical harmonics. Therefore, the investigation of the properties of these functions can be of considerable help and importance in a twofold way: On the one hand, it makes possible the simplification and evaluation of molecular integrals as mentioned above; on the other hand, it is useful if correlated wave functions are used which depend explicitly on r_{12}. A link with the problems considered here is given by the fact that with the help of the developed formulas, and according to $|\mathbf{r}_{12}| = |\mathbf{r}_1 - \mathbf{r}_2|$, an expansion in powers of r_{12} may be changed into an expansion whose terms contain products of quantities which depend only on $\mathbf{r}_1$ or $\mathbf{r}_2$, respectively.

In their classical work on the hydrogen molecule, Heitler and London (1927) could evaluate the exchange integral only approximately. Sugiura (1927) succeeded in its analytical evaluation by applying the *Neumann expansion* (see Rüdenberg, 1951)

$$\frac{1}{r_{12}} = \frac{4}{R} \sum_{\lambda=0}^{\infty} \sum_{\nu=-\lambda}^{\lambda} (-1)^{\nu} \frac{(\lambda - |\nu|)!}{(\lambda + |\nu|)!} P_{\lambda}^{|\nu|}(\xi_<) Q_{\lambda}^{|\nu|}(\xi_>)$$
$$\cdot \mathcal{P}_{\lambda}^{|\nu|}(\eta_1) \mathcal{P}_{\lambda}^{|\nu|}(\eta_2) e^{i\nu(\varphi_1 - \varphi_2)},$$

where $1/r_{12}$ is expressed in *elliptical coordinates* ξ, η, φ. Since then these coordinates were often applied in the theory of molecular integrals, especially, of course, to diatomic molecules which exhibit the appropriate symmetry.

As an alternative, the expansion about a single center was investigated. The developed single-center expansion methods are essentially based upon the *Laplace expansion* (see Condon and Shortley, 1953)

$$\frac{1}{r_{12}} = \sum_{\lambda=0}^{\infty} \frac{r_<^{\lambda}}{r_>^{\lambda+1}} \frac{2}{2\lambda+1} \sum_{\nu=-\lambda}^{\lambda} \mathscr{P}_\lambda^{\nu}(\cos\theta_1)\mathscr{P}_\lambda^{\nu}(\cos\theta_2)e^{i\nu(\varphi_1-\varphi_2)},$$

where $1/r_{12}$ is expressed in *spherical coordinates* r, θ, φ with respect to an origin 0 where $\mathbf{r}_1$ and $\mathbf{r}_2$ are centered:

$$\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1 = \mathbf{r}_{02} - \mathbf{r}_{01}.$$

This expansion is simpler than the Neumann expansion but of course less adapted to many problems. Several modifications of these expansions were specified, especially to get rid of the necessity to distinguish between $r_<$ and $r_>$, and to make a factorization possible (Roberts, 1966, 1969; Cressy and Ruedenberg, 1969).

Another development is represented by the so-called *bipolar expansions* which decompose r_{12} according to

$$\mathbf{r}_{12} = \mathbf{R}_{AB} - \mathbf{r}_{A1} + \mathbf{r}_{B2}.$$

Then, r_{12} is expanded with respect to the two centers A and B which are separated from each other by a distance R_{AB}: Hence, bipolar expansions contain functions which depend upon the coordinates of $\mathbf{r}_{A1}$ and $\mathbf{r}_{B2}$ as well as $\mathbf{R}_{AB}$, i.e., $(r_{A1}, \theta_{A1}, \varphi_{A1})$, $(r_{B2}, \theta_{B2}, \varphi_{B2})$, $(R_{AB}, \Theta_{AB}, \Phi_{AB})$. The bipolar expansion of $1/r_{12}$ was given by Carlson and Rushbrooke (1950) and by Buehler and Hirschfelder (1951, 1952):

$$\frac{1}{r_{12}} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \sum_{m=-n_<}^{n_<} B_{n_1,n_2}^{|m|}(r_{A1}, r_{B2}, R_{AB}) \cdot P_{n_1}^{|m|}(\cos\theta_{A1})P_{n_2}^{|m|}(\cos\theta_{B2})e^{im(\varphi_{B2}-\varphi_{A1})};$$

$$n_< = \min(n_1, n_2).$$

The drawback to this important formula is the decomposition of the configuration space into different regions with complicated boundary surfaces, since the coefficients $B_{n_1,n_2}^{|m|}$, which contain the radial dependencies, have four different functional forms in the following four regions I–IV (see Fig. 1)

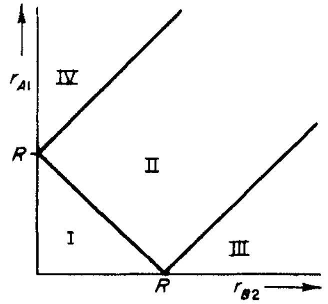


Fig. 1

I: $R > r_{A1} + r_{B2}$
II: $|r_{A1} - r_{B2}| \leq R \leq r_{A1} + r_{B2}$
III: $r_{B2} > R + r_{A1}$
IV: $r_{A1} > R + r_{B2}$

Obviously, the four regions I–IV to be distinguished in the r_{A1}, r_{B2} plane correspond to the following four possible cases which describe the situation of two spheres being centered at A or B with radii r_{A1} or r_{B2}, respectively: They may either be separated (I) or penetrate each other (II), or one sphere may contain the other one completely (III or IV, respectively).

Ruedenberg (1967) gave the bipolar expansion of an essentially arbitrary function of r_{12}, i.e., $g(r_{12})$, by means of Fourier transformation which produces the radial expansion coefficients as integrals over spherical Bessel functions. These integrals were evaluated for $g(r_{12}) = r_{12}^{-1}$ by expansion of the spherical Bessel functions into Laguerre polynomials whereby Salmon, Birss, and Ruedenberg (1968) achieved the following expression:

$$\frac{1}{r_{12}} = \sum_{n_1 l_1 m_1} \sum_{n_2 l_2 m_2} F_{n_1 l_1 m_1, n_2 l_2 m_2}(R_{AB}, \Theta_{AB}, \Phi_{AB})$$
$$\cdot\, Y_{l_1}^{m_1}(\theta_{A1}, \varphi_{A1}) f_{n_1 l_1}(r_{A1}) Y_{l_2}^{m_2}(\theta_{B2}, \varphi_{B2}) f_{n_2 l_2}(r_{B2}).$$

The corresponding integrals for more general functions $g(r_{12})$ were investigated by Taylor (1969).

In the sequel polypolar or *multicenter expansions* will be derived. The final formulas will contain the bipolar expansions as special cases and are more advantageous for quantum-mechanical calculations because of their greater flexibility. It will be shown that for regular and irregular solid spherical harmonics one may formulate expressions of the kind

$$f_n(\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3 + \cdots) = \sum_i \sum_j \sum_k \cdots f_i(\mathbf{r}_1) f_j(\mathbf{r}_2) f_k(\mathbf{r}_3) \cdots,$$

which may have many different meanings. Special applications are translations of functions and certain multicenter expansions that are useful for the evaluation of quantum-mechanical multicenter energy integrals.

II. Solid Spherical Harmonics

This section does not contain an introduction to the theory of spherical harmonics. It merely presents in a coherent manner certain relations which are to be used in the sequel.

A. Legendre Functions

1. Legendre Polynomials

The Coulomb potential between two points $\mathbf{r}_1$ and $\mathbf{r}_2$,

$$r_{12}^{-1} = (r_1{}^2 + r_2{}^2 - 2r_1 r_2 \cos\theta_{12})^{-1/2}, \tag{1}$$

satisfies the Laplace equations

$$\Delta_1 r_{12}^{-1} = \Delta_2\, r_{12}^{-1} = 0. \tag{2}$$

Take $\mathbf{r}_1 = \mathbf{r} = (x, y, z)$ and $\mathbf{r}_2 = (0, 0, t)$. Then r_{12}^{-1} can be written as

$$r_{12}^{-1} = [x^2 + y^2 + (z - t)^2]^{-1/2} \tag{3}$$

or as

$$r_{12}^{-1} = r^{-1}[1 + \rho^2 - 2\rho\cos\theta]^{-1/2} \tag{4}$$

with

$$\rho = t/r, \qquad \cos\theta = z/r. \tag{5}$$

Assuming $t < r$, the expression of Eq. (4) can be expanded in powers of ρ,

$$[1 + \rho^2 - 2\rho\cos\theta]^{-1/2} = \sum_{l=0}^{\infty} \rho^l P_l(\cos\theta). \tag{6}$$

The functions $P_l(\cos\theta)$, appearing as coefficients in this expansion, are defined as Legendre polynomials. Alternatively one derives from Eq. (3) that

$$\begin{aligned} r_{12}^{-1} &= \sum_{l=0}^{\infty} \{\partial^l[x^2 + y^2 + (z - t)^2]^{-1/2}/\partial t^l\}_{t=0}(t^l/l!) \\ &= \sum_l \{\partial^l[x^2 + y^2 + z^2]^{-1/2}/\partial z^l\}(-1)^l t^l/l! \\ &= \sum_l \rho^l \left\{\frac{(-1)^l r^l}{l!}\frac{\partial^l r^{-1}}{\partial z^l}\right\}, \end{aligned} \tag{7}$$

whence one has also

$$P_l(\cos\theta) = \frac{(-1)^l r^{l+1}}{l!}\frac{\partial^l r^{-1}}{\partial z^l}. \tag{8}$$

By virtue of Eq. (8) and the Laplace equation (2), it follows that

$$\Delta\{r^{-l-1}P_l(\cos\theta)\} = 0. \tag{9}$$

Now in spherical coordinates (see Fig. 2)

$$\begin{aligned} x &= r\sin\theta\cos\varphi, \\ y &= r\sin\theta\sin\varphi, \\ z &= r\cos\theta, \\ x^2+y^2+z^2 &= r^2, \end{aligned} \tag{10}$$

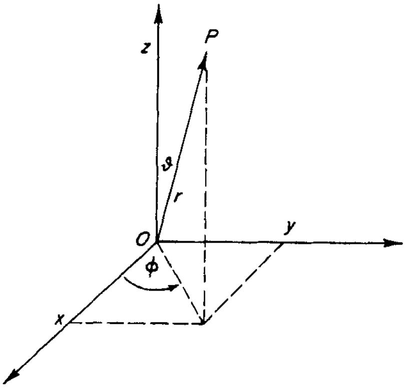


Fig. 2

the Laplacian Δ is given by

$$\Delta = \frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{1}{r^2}\mathbf{L}^2 \tag{11}$$

where $\mathbf{L}^2$ is the operator

$$\mathbf{L}^2 = -\frac{1}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\varphi^2}\right]. \tag{12}$$

From this it can be seen that the Legendre polynomials satisfy the differential equation

$$(1-\zeta^2)\frac{d^2P_l(\zeta)}{d\zeta^2} - 2\zeta\frac{dP_l(\zeta)}{d\zeta} + l(l+1)P_l(\zeta) = 0 \tag{13}$$

with

$$\zeta \equiv \cos\theta = z/r. \tag{14}$$

From the definitions Eq. (6) or Eq. (8) one finds that

$$P_0(\zeta) = 1, \qquad P_l(\zeta = 1) = 1, \tag{15}$$

and, for instance,

$$\begin{aligned} P_1(\zeta) &= \zeta, & P_3(\zeta) &= \frac{1\cdot 3\cdot 5}{3!}\left(\zeta^3 - \frac{3}{5}\zeta\right), \\ P_2(\zeta) &= \frac{1\cdot 3}{2!}\left(\zeta^2 - \frac{1}{3}\right), & P_4(\zeta) &= \frac{1\cdot 3\cdot 5\cdot 7}{4!}\left(\zeta^4 - \frac{6}{7}\zeta^2 + \frac{3}{35}\right). \end{aligned} \tag{16}$$

It may be shown (see Hobson, 1931) that the general formula is given by

$$P_l(\zeta) = \frac{(2l)!}{2^l(l!)^2}\left[\zeta^l - \frac{l(l-1)}{2(2l-1)}\zeta^{l-2} + \frac{l(l-1)(l-2)(l-3)}{2\cdot 4\cdot(2l-1)(2l-3)}\zeta^{l-4} - + \cdots\right], \tag{17}$$

$$P_l(\zeta) = \sum_{\lambda=0}^{\Lambda}(-1)^\lambda \frac{(2l-2\lambda)!}{2^l\lambda!(l-\lambda)!(l-2\lambda)!}\zeta^{l-2\lambda} \tag{18}$$

where $\Lambda = l/2$ for even l, but $\Lambda = (l-1)/2$ for odd l. Since l is an integer ($l \geq 0$), one has

$$\begin{aligned} \left(\frac{d}{d\zeta}\right)^l[(\zeta^2-1)^l] &= \left(\frac{d}{d\zeta}\right)^l\left[\sum_{\lambda=0}^{l}(-1)^\lambda\binom{l}{\lambda}\zeta^{2l-2\lambda}\right] \\ &= \sum_{\lambda=0}^{\Lambda}(-1)^\lambda \frac{l!}{\lambda!(l-\lambda)!}\,\frac{(2l-2\lambda)!}{(l-2\lambda)!}\zeta^{l-2\lambda}. \end{aligned} \tag{19}$$

This furnishes Rodrigues' formula of the Legendre polynomials

$$P_l(\zeta) = \frac{1}{2^l l!}\left(\frac{d}{d\zeta}\right)^l(\zeta^2-1)^l. \tag{20}$$

The $P_l(\zeta)$ obey the orthogonality relations

$$\int_{-1}^{1} d\zeta\, P_k(\zeta)P_l(\zeta) = [\tfrac{1}{2}(2l+1)]^{-1}\delta_{k,l}. \tag{21}$$

The following formula, which expands powers of ζ in a series of polynomials $P_l(\zeta)$, is also due to Legendre:

$$\zeta^l = a_l P_l(\zeta) + a_{l-2}P_{l-2}(\zeta) + \cdots + \begin{cases} a_0 & \text{for even } l, \\ a_1 P_1(\zeta) & \text{for odd } l. \end{cases} \tag{22}$$

According to Eq. (17) is $a_l = 2^l\binom{2l}{l}^{-1}$. The indices λ of a_λ proceed in even steps; of course, if l is even (odd), the power ζ^l will be expanded in terms of even (odd) functions. Because of Eq. (21), one has

$$a_\lambda = \tfrac{1}{2}(2\lambda + 1)A_{l,\lambda}, \qquad A_{l,\lambda} = \int_{-1}^{1} d\zeta\, \zeta^l P_\lambda(\zeta). \tag{23}$$

With the help of the differential equation (13) one finds the recursion formulas

$$\lambda(\lambda + 1)A_{l,\lambda} = l(l + 1)A_{l,\lambda} - l(l - 1)A_{l-2,\lambda}. \tag{24}$$

Since $A_{l,l} = 2^{l+1}(l!)^2/(2l + 1)!$, this leads to the expressions

$$a_\lambda = 2^\lambda(2\lambda + 1)\frac{l!}{(l + \lambda + 1)!}\,\frac{[\frac{1}{2}(l + \lambda)]!}{[\frac{1}{2}(l - \lambda)]!}; \qquad l - \lambda = \text{even}; \tag{25}$$

$$a_\lambda = 2^\lambda\,\frac{2\lambda + 1}{\lambda + 1}\binom{\frac{1}{2}(l + \lambda)}{\lambda}\binom{l + \lambda + 1}{\lambda + 1}^{-1}; \qquad l - \lambda = \text{even}. \tag{26}$$

Obviously, $a_\lambda = 0$ if $(l - \lambda)$ is odd or negative; see Whittaker and Watson (1963).

2. *Associated Legendre Functions*

The associated Legendre functions are defined by

$$P_l^m(\zeta) = (1 - \zeta^2)^{m/2}(d/d\zeta)^m P_l(\zeta), \qquad (1 - \zeta^2)^{m/2} = (\sin\theta)^m. \tag{27}$$

It is obvious that

$$P_l(-\zeta) = (-1)^l P_l(\zeta), \qquad P_l^{(m)}(-\zeta) = (-1)^{l+m}P_l^{(m)}(\zeta), \tag{28}$$

where $P_l^{(m)}$ denotes the mth derivative of P_l with respect to ζ. If Eq. (13) is differentiated m times, the new equation may be written as

$$\left[(1 - \zeta^2)\frac{d^2}{d\zeta^2} - 2\zeta\frac{d}{d\zeta} + l(l + 1) - \frac{m^2}{1 - \zeta^2}\right]P_l^m(\zeta) = 0. \tag{29}$$

If this equation is written with different indices and multiplied crosswise by $P_{l'}^m$ or P_l^m respectively, the subtraction of both equations yields

$$\frac{d}{d\zeta}\left[(1 - \zeta^2)\left(P_{l'}^m\frac{dP_l^m}{d\zeta} - P_l^m\frac{dP_{l'}^m}{d\zeta}\right)\right] + (l - l')(l + l' + 1)P_l^m P_{l'}^m = 0. \tag{30}$$

By integration one obtains from the differential equation the following relations (see Morse and Feshbach, 1953):

$$\int_{-1}^{1} d\zeta\, P_l^m(\zeta)\, P_{l'}^m(\zeta) = 0 \qquad \text{for} \quad l \neq l', \tag{31}$$

$$\int_{-1}^{1} d\zeta\, \frac{P_l^m(\zeta) P_l^{m'}(\zeta)}{1-\zeta^2} = 0 \qquad \text{for} \quad m \neq m'. \tag{32}$$

By partial integration and with the help of differential equation (29) one finds (see Whittaker and Watson, 1963) that

$$\int_{-1}^{1} d\zeta (P_l^{m+1}(\zeta))^2 = (l-m)(l+m+1) \int_{-1}^{1} d\zeta (P_l^m(\zeta))^2. \tag{33}$$

By repeating the same procedure one obtains the connection with Eq. (21) and finally the orthogonality relation

$$\int_{-1}^{1} d\zeta\, \mathscr{P}_l^m(\zeta) \mathscr{P}_{l'}^m(\zeta) = \delta_{l,l'} \tag{34}$$

where the normalized associated Legendre functions (specified by script letters) are defined as

$$\mathscr{P}_l^m(\zeta) = (-1)^m \left[\frac{2l+1}{2} \frac{(l-m)!}{(l+m)!}\right]^{1/2} P_l^m(\zeta). \tag{35}$$

For the $P_l^m(\zeta)$ one has—corresponding to Eqs. (17), (18)—the expansion

$$P_l^m(\zeta) = \frac{(l+m)!}{2^m \cdot m!(l-m)!}(1-\zeta^2)^{m/2}\left\{\zeta^{l-m} - \frac{(l-m)(l-m-1)}{(2m+2)2}\zeta^{l-m-2} \cdot (1-\zeta^2) + \frac{(l-m)\cdots(l-m-3)}{(2m+2)(2m+4)\cdot 2\cdot 4}\zeta^{l-m-4}(1-\zeta^2) + \cdots\right\}. \tag{36}$$

For other expansions confer, for instance, Magnus-Oberhettinger (1948).

By differentiating both sides of Eq. (6) with respect to ζ (where $\zeta = \cos\theta$) and multiplying by $(\sin\theta)^m$ one obtains the generating function of the power series whose coefficients are the associated Legendre functions (Hobson, 1931):

$$\frac{1\cdot 3\cdot 5\cdot\cdots\cdot(2m-1)\rho^m(1-\zeta^2)^{m/2}}{(1+\rho^2-2\rho\zeta)^{m+1/2}} = \sum_{l=m}^{\infty} \rho^l P_l^m(\zeta); \qquad \rho < 1. \tag{37}$$

B. Surface Harmonics

1. Definitions by Angular Momentum Operators

It is desirable to introduce surface spherical harmonics by utilizing the quantum-mechanical formalism of angular momentum, since then the meaning of phase definitions becomes apparent.

The angular momentum operator

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}, \qquad \mathbf{p} = \frac{\hbar}{i}\frac{\partial}{\partial \mathbf{r}} \tag{38}$$

has the Cartesian components L_x, L_y, and L_z where

$$L_z = -i(x\,\partial/\partial y - y\,\partial/\partial x), \qquad L_x = -i(y\,\partial/\partial z - z\,\partial/\partial y),$$
$$L_y = -i(z\,\partial/\partial x - x\,\partial/\partial z), \tag{39}$$

which obey the commutation relations

$$[L_x, L_y]_- = iL_z, \qquad [L_y, L_z]_- = iL_x, \qquad [L_z, L_x]_- = iL_y. \tag{40}$$

(Here we use $\hbar = 1$.) It is $\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2$. The eigenvectors $|lm\rangle$ of the commuting operators $\mathbf{L}^2$ and L_z solve the equations

$$\mathbf{L}^2|lm\rangle = l(l+1)|lm\rangle, \qquad L_z|lm\rangle = m|lm\rangle. \tag{41}$$

Since orbital angular momenta will be considered, l and m are integers, where m may assume values between $-l$ and $+l$:

$$l = 0, 1, 2, 3, 4, 5, 6, \ldots$$
$$m = -l, -l+1, -l+2, \ldots, l-1, l. \tag{42}$$

Blatt and Weisskopf (1952) have added interesting comments on this subject.

In spherical coordinates r, θ, φ, the operators $\mathbf{L}^2$ and L_z are given by

$$\mathbf{L}^2 = -\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right], \tag{43}$$

$$L_z = -i\,\partial/\partial\varphi. \tag{44}$$

The eigenvalue equations (41) are a pair of differential equations whose (normalized) solutions are the surface harmonics

$$|lm\rangle = Y_l^m(\theta, \varphi) = \mathscr{P}_l^m(\cos\theta)e^{im\varphi}(2\pi)^{-1/2} \tag{45}$$

which contain the variables θ and φ separately. Since the operator $\mathbf{L}^2$ of Eq. (43) equals the one of Eq. (12), any function $\mathscr{P}_l^m(\zeta)$ obeys the differential equation (29) and, therefore, may be obtained as the power series solution of this equation, leading to expressions as given above. However, for specifying the surface harmonics it is more elegant and transparent to consider the effect of the non-Hermitian so-called shift operators

$$L_+ = L_x + iL_y, \qquad L_- = L_x - iL_y, \tag{46}$$

which, applied to an eigenfunction Y_l^m of $\mathbf{L}^2$ and L_z, change its upper index m by 1 according to

$$\begin{aligned} L_\pm Y_l^m(\theta, \varphi) &= e^{i\delta_\pm}[(l \mp m)(l \pm m + 1)]^{1/2} Y_l^{m\pm 1} \\ &= e^{i\delta_\pm}[l(l+1) - m(m \pm 1)]^{1/2} Y_l^{m\pm 1}. \end{aligned} \tag{47}$$

Because of the restriction imposed on all possible m due to Eq. (42), one has

$$L_+ \mathscr{P}_l^l(\cos\theta) e^{il\varphi} = 0, \qquad L_- \mathscr{P}_l^{-l}(\cos\theta) e^{-il\varphi} = 0. \tag{48}$$

These equations contain the arbitrary phase factor $e^{i\delta_\pm}$. Since in spherical coordinates

$$L_\pm = e^{\pm i\varphi}\left(\pm\frac{\partial}{\partial\theta} + i\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\varphi}\right), \tag{49}$$

the condition $L_+ Y_l^l = 0$ leads to the differential equation

$$\left(\frac{\partial}{\partial\theta} - l\frac{\cos\theta}{\sin\theta}\right)\mathscr{P}_l^l(\cos\theta) = 0, \tag{50}$$

which requires

$$\mathscr{P}_l^l(\cos\theta) = \text{const}\cdot(\sin\theta)^l. \tag{51}$$

To obtain a value 1 for the normalization integral of the surface spherical harmonics, one must have

$$Y_l^l(\theta, \varphi) = e^{i\eta}\left[\frac{(2l+1)!}{2}\right]^{1/2} \frac{1}{2^l l!}(\sin\theta)^l \frac{e^{il\varphi}}{(2\pi)^{1/2}}; \tag{52}$$

$e^{i\eta}$ is another arbitrary phase factor.

The phase conventions

$$e^{i\delta_\pm} = 1, \qquad e^{i\eta} = (-1)^l, \tag{53}$$

which are due to Condon and Shortley and are widely used, will be employed in the present article. This facilitates the application of shift operators. Then, the surface harmonics $Y_l^m(\theta, \varphi)$ are determined by

$$\mathscr{P}_l^m(\zeta) = (-1)^m \left[\frac{2l+1}{2}\frac{(l-m)!}{(l+m)!}\right]^{1/2} (1-\zeta^2)^{m/2} \left(\frac{d}{d\zeta}\right)^{l+m} \frac{1}{2^l l!}(\zeta^2-1)^l \tag{54}$$

if their φ dependence, according to their definition in Eq. (45), is given by $e^{im\varphi}/(2\pi)^{1/2}$. The surface harmonics are orthogonal and normalized according to

$$\int d\Omega \; Y_l^{m*}(\theta, \varphi) Y_{l'}^{m'}(\theta, \varphi) = \delta_{ll'}\delta_{mm'} \tag{55}$$

$$\int d\Omega = \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta = \int_0^{2\pi} d\varphi \int_{-1}^{1} d\zeta \tag{56}$$

and with respect to Eq. (34). The notations are the same as those used in other sections of this investigation. Hence, one can factor the functions as usual in the following manner:

$$Y_l^m(\theta, \varphi) = \mathscr{P}_l^m(\zeta) e^{im\varphi}(2\pi)^{-1/2}, \qquad \begin{array}{l} \zeta = \cos\theta, \\ -1 \le \zeta \le 1, \\ -l \le m \le l; \end{array} \tag{57}$$

$$\mathscr{P}_l^m(\zeta) = (-1)^m N_l^m P_l^m(\zeta), \tag{58}$$

$$N_l^m = \left[\frac{2l+1}{2}\frac{(l-m)!}{(l+m)!}\right]^{1/2}, \tag{59}$$

$$P_l^m(\zeta) = (1-\zeta^2)^{m/2} \left(\frac{d}{d\zeta}\right)^{l+m} \frac{1}{2^l l!}(\zeta^2-1)^l. \tag{60}$$

The associated Legendre function of Eq. (60) is reduced to the Legendre polynomial if $m = 0$,

$$P_l(\zeta) = \frac{1}{2^l l!}\left(\frac{d}{d\zeta}\right)^l (\zeta^2-1)^l. \tag{61}$$

All expressions hold for positive as well as for negative m. However, $\mathscr{P}_l^m(\zeta)$ and $\mathscr{P}_l^{-m}(\zeta)$ are then no longer independent of each other. Of course, one may write

$$P_l^m(\zeta) = (1-\zeta^2)^{m/2} \left(\frac{d}{d\zeta}\right)^m P_l(\zeta) \tag{62}$$

only for $m \geq 0$. The quantity N_l^m, defined by Eq. (59), represents the normalization factor.

2. *Symmetry Relationships*

Because of (Hobson, 1931, Rose, 1957).

$$\frac{(l-m)!}{(l+m)!}(\zeta^2-1)^m\left(\frac{d}{d\zeta}\right)^{l+m}(\zeta^2-1)^l=\left(\frac{d}{d\zeta}\right)^{l-m}(\zeta^2-1)^l, \tag{63}$$

the relations

$$P_l^{-m}(\zeta)=(-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(\zeta), \tag{64}$$

$$\mathcal{P}_l^{-m}(\zeta)=(-1)^m\mathcal{P}_l^m(\zeta) \tag{65}$$

hold and lead to the important relation

$$Y_l^{-m}(\theta,\varphi)=(-1)^m Y_l^{m*}(\theta,\varphi). \tag{66}$$

The "parity" of $P_l^m(\zeta)$ is $(-1)^{l+m}$:

$$P_l^m(-\zeta)=(-1)^{l+m}P_l^m(\zeta). \tag{67}$$

Therefore, $P_l^m(0)=0$ if $(l-m)$ is odd; for $\zeta=0$, since $P_l^m(0)=P_l^{(m)}(0)$, only the term with $l-2k=m$ survives in the expansion of $P_l^{(m)}(\zeta)$, if $(l-m)$ is even; cf. Eq. (18). Hence

$$\begin{aligned} &P_l^m(0)=0 && \text{if}\quad l-m=\text{odd},\\ &P_l^m(0)=(-1)^k\frac{1}{2^l k!}\frac{(l+m)!}{(k+m)!} && \text{if}\quad l-m=2k=\text{even}. \end{aligned} \tag{68}$$

It is clear that

$$P_l^m(\pm 1)=(\pm 1)^l\,\delta_{m,0}, \tag{69}$$

$$\mathcal{P}_l^m(\pm 1)=(\pm 1)^l[\tfrac{1}{2}(2l+1)]^{1/2}\,\delta_{m,0}, \tag{70}$$

and hence

$$Y_l^m(0,\varphi)=[\tfrac{1}{2}(2l+1)]^{1/2}(2\pi)^{-1/2}\,\delta_{m,0}, \tag{71}$$

$$Y_l^0(\theta,0)=[\tfrac{1}{2}(2l+1)]^{1/2}(2\pi)^{-1/2}P_l(\cos\theta). \tag{72}$$

The parity of the surface harmonics is $(-1)^l$, since a reflection of space in the origin, which means $(\theta,\varphi)\to(\pi-\theta,\varphi+\pi)$, has the effect

$$Y_l^m(\theta,\varphi)\to Y_l^m(\pi-\theta,\varphi+\pi)=(-1)^l\,Y_l^m(\theta,\varphi) \tag{73}$$

so that

$$Y_l^m(\theta, \varphi) \rightarrow (-1)^l Y_l^m(\theta, \varphi) \quad \text{if} \quad \mathbf{r} \rightarrow -\mathbf{r}. \tag{74}$$

The surface harmonics may easily be expressed in Cartesian coordinates with the help of

$$\cos\theta = z/r, \qquad (\sin\theta)\, e^{\pm i\varphi} = (x \pm iy)/r \tag{75}$$

(see Ballhausen, 1962). The addition theorem is given by (Condon and Shortley, 1953)

$$\begin{aligned} Y_l^0(0, 0)\, Y_l^0(\Theta, 0) &= (4\pi)^{-1}(2l + 1)P_l(\cos\Theta) \\ &= \sum_{m=-l}^{l} Y_l^{m*}(\mathbf{r}_1)\, Y_l^m(\mathbf{r}_2) \end{aligned} \tag{76}$$

where each of the two vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ connects the center of the unit sphere with a point on its surface and both vectors make an angle Θ with each other, viz.

$$\begin{aligned} (\mathbf{r}_1 \cdot \mathbf{r}_2) &= \cos\Theta \\ &= \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\varphi_1 - \varphi_2). \end{aligned} \tag{77}$$

With $\Theta = 0$ this yields

$$\sum_{m=-l}^{l} |\, Y_l^m(\mathbf{r})|^2 = [Y_l^0(0, 0)]^2 = (4\pi)^{-1}(2l + 1). \tag{78}$$

The application of the shift operators, as defined by Eq. (47), furnishes recursion relations which allow the expression of certain relationships which contain functions $\mathcal{P}_l^m(\zeta)$ or $Y_l^m(\theta, \varphi)$ respectively, by new relationships in terms of equivalent functions with greater or smaller indices like $m \pm 1$ or $l \pm 1$. For expressions

$$m\zeta\mathcal{P}_l^m(\zeta), \qquad \partial\mathcal{P}_l^m(\cos\theta)/\partial\theta, \qquad \zeta Y_l^m, \qquad (\sin\theta)\mathcal{P}_l^m(\zeta) \tag{79}$$

see, for instance, Condon and Shortley (1953). For expressions of the kind

$$\cos\theta \sin\theta\, \mathcal{P}_l^m(\zeta), \qquad \sin^2\theta\, \mathcal{P}_l^m(\zeta), \qquad \cos^2\theta\, \mathcal{P}_l^m(\zeta) \tag{80}$$

see, for instance, Bethe and Salpeter (1957). Recursion relations for the $P_l^m(\zeta)$ are given by Edmonds (1957).

3. *Phase Conventions*

There are many definitions for the eigenfunction of an electron in a central field and, therefore, for surface harmonics. Most of the definitions, which differ from those $Y_l^m(\theta, \varphi) = [Y_l^m(\theta, \varphi)]_{\mathrm{CS}}$ employed by Condon and Shortley (1953), belong to one of the following groups (b)–(f).

(a) If Condon and Shortley's phase convention is chosen, the eigenfunctions Y_l^m of the operators $\mathbf{L}^2$ and L_z have negative phases for positive odd m, but positive phases for all other m.

In this $[Y_l^m]_{\mathrm{CS}}$ basis the $\mathbf{L}^2$ and L_z are diagonal and the nonvanishing matrix elements of L_x, $\langle m|L_x|m \pm 1\rangle$, are real and positive. This means also that the nonvanishing matrix elements of L_y are imaginary, since

$$\begin{aligned} \langle m|L_x|m+1\rangle &= \langle m+1|L_x|m\rangle \\ &= i\langle m+1|L_y|m\rangle \\ &= -i\langle m|L_y|m+1\rangle \\ &= \tfrac{1}{2}[(l-m)(l+m+1)]^{1/2}, \\ \langle m|L_z|m\rangle &= m. \end{aligned} \tag{81}$$

Condon–Shortley's phase convention is now commonly used.

The same phase convention for the Y_l^m as the one used by Condon and Shortley is employed, for instance, by Blatt and Weisskopf (1952), Rose (1957), Edmonds (1957), but also by van der Waerden (1932), Rose (1955), Wigner (1959), Fano and Racah (1959), Slater (1960), Heine (1960), Griffith (1961), Ballhausen (1962), Brink and Satchler (1962), Messiah (1963 a,b), Judd (1963), Watanabe (1966), and other authors.

Just another way of writing the above mentioned expressions is

$$\mathscr{P}_l^m(\zeta) = \varepsilon_m \left[\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\zeta), \tag{82}$$

$$\varepsilon_m = (-1)^{(|m|+m)/2} = i^{|m|+m} = \begin{cases} (-1)^m & \text{if } m \geq 0 \\ 1 & \text{if } m < 0, \end{cases} \tag{83}$$

and, as used above,

$$P_l^{|m|}(\zeta) = (1-\zeta^2)^{|m|/2}(d/d\zeta)^{|m|}P_l(\zeta), \tag{84}$$

where $P_l(\zeta)$ is given by Eq. (61). Then the Y_l^m, which are defined by Eq. (57), are still given in Condon–Shortley phases if the normalized associated Legendre functions $\mathscr{P}_l^m(\zeta)$ are given by Eq. (82). Furthermore, all formulas which contain those Y_l^m hold for all possible values of m although ε_m is different for the two different cases $m \geq 0$ and $m < 0$. The connection between the two ways of writing the formulas in Condon–Shortley's phases is given by

$$P_l^{-|m|}(\zeta) = (-1)^m \frac{(l-|m|)!}{(l+|m|)!} P_l^{|m|}(\zeta). \tag{85}$$

This leads to

$$(-1)^m P_l^m(\zeta) = p_l^m P_l^{|m|}(\zeta) \tag{86}$$

with

$$p_l^m = \begin{cases} (-1)^m & \text{if} \quad m \geq 0 \\ \dfrac{(l-|m|)!}{(l+|m|)!} = \dfrac{(l+m)!}{(l-m)!} & \text{if} \quad m < 0 \end{cases}. \tag{87}$$

(b) Bethe (1933) and likewise Bethe and Salpeter (1957) as well as Rose (1937) suppress a factor $(-1)^m$ in the definition given by Eq. (57), since they define

$$e^{i\delta_\pm} = -1, \qquad e^{i\eta} = (-1)^{2l} = +1. \tag{88}$$

Therefore

$$[\mathscr{P}_l^m(\zeta)]_{\text{Bethe}} = (-1)^m [\mathscr{P}_l^m(\zeta)]_{\text{CS}}. \tag{89}$$

The other definitions remain unchanged. Therefore, Eq. (66) still holds. The same definitions as those used by Bethe are employed by Hirschfelder, Curtiss, and Bird (1954) who define $e^{i\delta_\pm} = -1$ and write, cf. Eq. (83),

$$\begin{aligned} [Y_l^m]_{\text{HCB}} &= i^{|m|-m} \varepsilon_m [Y_l^m]_{\text{CS}}, \\ &= (-1)^m [Y_l^m]_{\text{CS}}. \end{aligned} \tag{90}$$

(c) Some authors prefer to derive the associated Legendre functions $\mathscr{P}_l^m$ as series expansions which solve the respective differential equations. Since Eq. (29) contains m^2, they define

$$\mathscr{P}_l^m(\zeta) = \mathscr{P}_l^{-m}(\zeta) = \left[\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\zeta) \tag{91}$$

with $P_l^m = P_l^{|m|}$ and apply Eq. (84). This yields

$$[Y_l^m]_c = \left[\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\zeta) \frac{e^{im\varphi}}{(2\pi)^{1/2}}. \tag{92}$$

Then, instead of Eq. (66), one has

$$[Y_l^m(\theta, \varphi)]_c^* = [Y_l^{-m}(\theta, \varphi)]_c. \tag{93}$$

This corresponds to

$$[Y_l^m]_c = \varepsilon_m [Y_l^m]_{CS}, \qquad [Y_l^l]_c = (-1)^l [Y_l^l]_{CS}. \tag{94}$$

A consequence of this definition is that the Y_l^m containing formulas do not hold for all values of m as this was the case for Condon–Shortley's convention as well as for Bethe's.

Differences of the kind discussed here caused much trouble in the early times of quantum mechanics. Ufford and Shortley (1932) discussed the difference between a basis of u functions and a basis of v functions. Their u basis corresponds to $[Y_l^m]_c$, their v basis corresponds to $[Y_l^m]_{CS}$.

The omission of the phase factor ε_m in the definition of the $[Y_l^m]_c$ requires, for instance, using, together with $e^{i\eta} = 1$, the definitions

$$e^{i\delta_+} = \begin{cases} -1, & m \geq 0, \\ 1, & m < 0, \end{cases} \qquad e^{i\delta_-} = \begin{cases} -1, & m > 0, \\ 1, & m \leq 0, \end{cases} \tag{95}$$

which effect the expressions produced by the shift operators. These definitions are chosen by Schiff (1955). The $[Y_l^m]_c$ are also applied by some authors who do not specify the shift operators, like, for instance, Pauling and Wilson (1935), Herzberg (1950), Margenau and Murphy (1956), Hamermesh (1962), and also Eyring, Walter, and Kimball (1944) who, however, quote contradictorily Condon–Shortley phases corresponding to Eq. (53).

(d) Landau and Lifshitz (1965) choose

$$e^{i\delta_\pm} = +1, \qquad e^{i\eta} = (-i)^l, \tag{96}$$

so that their surface spherical harmonics Y_l^m are given by

$$[Y_l^m]_d = i^l [Y_l^m]_{CS}. \tag{97}$$

Since $e^{i\eta}$ is no longer real, it follows

$$[Y_l^{-m}]_d = (-1)^{l+m} [Y_l^{m*}]_d. \tag{98}$$

This choice of the phases has advantages in the theory of time reversal; cf. Messiah (1963b), Edmonds (1957), Fano and Racah (1959), Tinkham (1964). In addition, this phase convention yields real coefficients

$$A_l(r) = [4\pi(2l + 1)]^{1/2} j_l(kr) \tag{99}$$

in the expansion of a plane wave in spherical waves,

$$e^{ikz} = \sum_{l=0}^{\infty} A_l(r)[Y_l^0(\theta)]_{\mathrm{d}}. \tag{100}$$

On this subject see Blatt-Weisskopf (1952), Messiah (1963a), Fano and Racah (1959). The $j_l(kr)$ of Eq. (99) are spherical Bessel functions.

(e) Sometimes it is useful to apply real surface spherical harmonics. Bethe (1929), for instance, used the basis functions

$$2^{1/2}[\mathscr{P}_l^m(\cos\theta)]_{\mathrm{Bethe}}\begin{cases}\cos m\varphi\\ \sin m\varphi,\end{cases} \tag{101}$$

which are advantageous in ligand field theory although nowadays complex Y_l^m are also widely used in this theory. The main advantage of these real basis functions of Eq. (101) is their property that they may change sign if the positive and negative directions of an axis are interchanged, but do not transform into each other; the latter case may only occur if different axes are exchanged. Another reason why real functions are popular is certainly the fact that they can be drawn.

Birss (1964) listed explicitly the basis

$$[Y_l^m]_{\mathrm{Birss}} = \begin{cases}\cos m\varphi\, P_l^m(\cos\theta), & (m > 0)\\ P_l(\cos\theta), & (m = 0)\\ \sin(|m|\varphi)\, P_l^{|m|}(\cos\theta) & (m < 0)\end{cases} \tag{102}$$

up to $l = 6$.

The use of real surface spherical harmonics will be discussed more thoroughly in the subsequent article (Steinborn, 1973).

(f) The mathematical literature treats chiefly the Laplacian surface spherical harmonics

$$S_l(\theta, \varphi) = \sum_{m=0}^{l} (A_m \cos m\varphi + B_m \sin m\varphi) P_l^m(\cos\theta), \tag{103}$$

which are the general solutions of the differential equation

$$[\mathbf{L}^2 - l(l+1)]S_l = 0. \tag{104}$$

Therefore, in the mathematical literature the associated Legendre functions P_l^m are more emphasized than the surface spherical harmonics of the kind Y_l^m. Hobson (1931) defined for $\zeta = \cos\theta$

$$[P_l^m(\zeta)]_{\mathrm{H}} = (-1)^m(1 - \zeta^2)^{m/2}(d/d\zeta)^m P_l(\cos\theta) \tag{105}$$

with the common Legendre polynomials $P_l^m(\zeta)$. This definition, which is also employed by other authors (cf. Magnus, Oberhettinger, and Soni, 1966), differs by a factor $(-1)^m$ from the definition used in the present paper. For the moment the associated Legendre functions, which are employed in the present article, will be specified by $[P_l^m(\zeta)]_{\mathrm{CS}}$, although Condon and Shortley do not define the functions P_l^m but only normalized functions $\mathscr{P}_l^m$. Thus

$$[P_l^m(\zeta)]_{\mathrm{H}} = (-1)^m [P_l^m(\zeta)]_{\mathrm{CS}}. \tag{106}$$

The functions $[P_l^m]_{\mathrm{CS}}$ are used in several mathematical texts and handbooks (Jahnke and Emde, 1938; Jahnke, Emde, and Lösch, 1960, Whittaker and Watson, 1963) and by most of the authors who use Condon–Shortley's Y_l^m. (If comparisons are made, it is important to notice the difference between P_l^m and $\mathscr{P}_l^m$.) Different conventions for the P_l^m are discussed by Magnus and Oberhettinger (1948).

Another important relation, which was also introduced by Hobson (1931), is

$$P_l^{-m}(\zeta) = (-1)^m \frac{(l-m)!}{(l+m)!} P_l^m(\zeta) \tag{107}$$

which enables us to express Y_l^m for all values of m by one formula; cf. Magnus and Oberhettinger (1948), Magnus, Oberhettinger, and Soni (1966), Ryshik and Gradstein (1963).

Definitions of the kind $P_l^m = P_l^{-m} = P_l^{|m|}$ were discussed in Section (c) of this article.

This may suffice for the classification of the most important phase definitions of the angular momentum eigenfunctions which are employed in the literature. Phase conventions are essential for any practical application of the relations to be derived in this article.

C. Regular and Irregular Solid Harmonics

Consider a set of N variables

$$\mathbf{x} = x_1, x_2, x_3, \ldots, x_N, \tag{108}$$

which after multiplication by a scaling parameter λ is transferred into a new set:

$$\begin{aligned} \lambda\mathbf{x} = \mathbf{x}' &= \lambda x_1, \lambda x_2, \lambda x_3, \ldots, \lambda x_N \\ &= x_1', x_2', x_3', \ldots, x_N'. \end{aligned} \tag{109}$$

A function $g(\mathbf{x})$ of these N variables is called a harmonic function if it is a solution of the equation

$$\sum_{\nu=1}^{N} (\partial/\partial x_\nu)^2 g(\mathbf{x}) = 0. \tag{110}$$

A *function* $g_\rho(\mathbf{x})$ *is homogeneous of the degree* ρ (*where* ρ *is real, not* necessarily integral), if for all x_ν and λ of the domain of definition of g_ρ the following relationship is valid:

$$g_\rho(\lambda\mathbf{x}) = \lambda^\rho g_\rho(\mathbf{x}). \tag{111}$$

Partial differentiation of this identity with respect to λ yields

$$\begin{aligned}\frac{\partial}{\partial\lambda} g_\rho(\lambda\mathbf{x}) &= \sum_{j=1}^{N} \frac{\partial x_j'}{\partial\lambda}\frac{\partial}{\partial x_j'} g_\rho(\mathbf{x}')\\ &= \sum_{j=1}^{N} x_j \frac{\partial}{\partial x_j'} g_\rho(\mathbf{x}') = \rho\lambda^{\rho-1} g_\rho(\mathbf{x}).\end{aligned} \tag{112}$$

This becomes Euler's equation for homogeneous functions of degree ρ if one chooses $\lambda = 1$:

$$\sum_{j=1}^{N} x_j \frac{\partial}{\partial x_j} g_\rho(\mathbf{x}) = \rho g_\rho(\mathbf{x}). \tag{113}$$

In three dimensions this is reduced to

$$(x\,\partial/\partial x + y\,\partial/\partial y + z\,\partial/\partial z) g_\rho(x, y, z) = \rho g_\rho(x, y, z). \tag{114}$$

Partial differentiation of Eq. (111) with respect to a certain variable will show that the first derivatives of a homogeneous function of degree ρ are homogeneous functions of degree $(\rho - 1)$.

If Eq. (112) is written for the three-dimensional case, and if now ρ is assumed to be an integer, it follows from Eq. (111) that

$$\begin{aligned}\left(\frac{\partial}{\partial\lambda}\right)^\rho g_\rho(x', y', z') &= \left[\left(\frac{\partial x'}{\partial\lambda}\right)\frac{\partial}{\partial x'} + \left(\frac{\partial y'}{\partial\lambda}\right)\frac{\partial}{\partial y'} + \left(\frac{\partial z'}{\partial\lambda}\right)\frac{\partial}{\partial z'}\right]^\rho g_\rho(x', y', z')\\ &= (\rho!) g_\rho(x, y, z).\end{aligned} \tag{115}$$

Since linear scaling parameters λ are used, the quantities $\partial x'/\partial\lambda = x$, etc. are independent of λ, hence $\partial^2 x'/\partial\lambda^2 = 0$, etc.; in Eq. (115), therefore, the operators contained in the bracket (which is to be taken to the ρth power) must only be applied to the function g_ρ outside this bracket. Therefore, to get the expression expanded, one may utilize the trinomial theorem

$$(a+b+c)^n = \sum_{n_1}\sum_{n_2}\sum_{n_3} \frac{n!}{n_1!\,n_2!\,n_3!}\, a^{n_1}b^{n_2}c^{n_3}, \qquad n = n_1 + n_2 + n_3, \tag{116}$$

which follows easily from the binomial theorem. In the space of the indices n_1, n_2, and n_3 the summation runs over all those points on the plane

$$\frac{n_1}{n} + \frac{n_2}{n} + \frac{n_3}{n} = 1 \tag{117}$$

in the positive octant whose coordinates on the axes n_1, n_2, and n_3 are integral. This plane intersects each of the positive axes of this coordinate system in a point which is a distance n apart from the origin. This yields the expression

$$g_\rho(x, y, z) = \sum_{\kappa,\lambda,\mu} c_{\kappa\lambda\mu} x^\kappa y^\lambda z^\mu, \qquad \kappa + \lambda + \mu = \rho, \tag{118}$$

with coefficients

$$c_{\kappa\lambda\mu} = \frac{1}{\kappa!\,\lambda!\,\mu!}\,\frac{\partial^\rho g_\rho(x', y', z')}{\partial x'^\kappa \partial y'^\lambda \partial z'^\mu} = \frac{1}{\kappa!\,\lambda!\,\mu!}\,\frac{\partial^\rho g_\rho(x, y, z)}{\partial x^\kappa \partial y^\lambda \partial z^\mu}. \tag{119}$$

The polynomial of Eq. (118) is a homogeneous function of degree ρ and could have been given without relying on other formulas, since Eq. (119) follows from Eq. (118). However, the derivation given here may illustrate how the most general form of a homogeneous function, which is given by Eq. (118), follows directly from the definition stated by Eq. (111).

In the three-dimensional case the identity of Eq. (110) becomes the Laplace equation

$$\Delta V_l(x, y, z) = 0, \qquad \Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \tag{120}$$

The homogeneous solutions V_l of this potential equation shall be discussed shortly since they will serve as the basis for the following explanations. As is well known, these homogeneous potential functions are the "solid spherical harmonics."

The application of the operator $\partial^{l-2}/\partial x^\kappa\, \partial y^\lambda\, \partial z^\mu$ to Eq. (120) leads with $\kappa + \lambda + \mu = l - 2$ to

$$(\kappa+2)(\kappa+1)c_{\kappa+2,\lambda,\mu} + (\lambda+2)(\lambda+1)c_{\kappa,\lambda+2,\mu} + (\mu+2)(\mu+1)c_{\kappa,\lambda,\mu+2} = 0. \tag{121}$$

With the help of this recursion relation all coefficients $c_{\alpha\beta\gamma}$ may be expressed as linear combinations of those coefficients whose indices α equal either 0 or 1: For $\alpha + \beta + \gamma = l$ there are exactly $(l + 1)$ linearly independent coefficients with $\alpha = 0$, namely

$$c_{0,0,l},\ c_{0,1,l-1},\ c_{0,2,l-2},\ \ldots,\ c_{0,l,0}\,; \tag{122}$$

there are exactly l linearly independent coefficients with $\alpha = 1$, namely

$$c_{1,0,l-1},\ c_{1,1,l-2},\ c_{1,2,l-3},\ \ldots,\ c_{1,l-1,0}. \tag{123}$$

Hence V_l becomes

$$V_l(x, y, z) = \sum_{n=1}^{2l+1} C_n v_{l,n}(x, y, z). \tag{124}$$

The functions $v_{l,n}(x, y, z)$ are certain homogeneous polynomials in x, y, and z of degree l which are, as V_l, solutions of the Laplace equation. They are in fact the solid spherical harmonics which are called "regular" since they consist of polynomials.

The connection with the surface spherical harmonics $Y_l^m(\theta, \varphi)$ becomes apparent by expressing the Laplace equation (120) in spherical coordinates r, θ, φ [see Eq. (10)],

$$\Delta V = \left(\frac{1}{r}\frac{\partial^2}{\partial r^2} r - \frac{\mathbf{L}^2}{r^2}\right) V = 0. \tag{125}$$

The operator $\mathbf{L}^2$ was already identified as the square of the orbital angular momentum operator in Section B1, and its representation in spherical coordinates, which is to be used in Eq. (125), was given by Eq. (12) of Section A as well as by Eq. (43) of Section B. Because of

$$\mathbf{L}^2 Y_l^m(\theta, \varphi) = l(l + 1) Y_l^m(\theta, \varphi), \tag{126}$$

$$\mathbf{L}^2 f(r) = f(r)\mathbf{L}^2, \tag{127}$$

and

$$\left[r \frac{\partial^2}{\partial r^2} r - l(l + 1)\right] f(r) = 0 \tag{128}$$

if

$$f(r) = r^l, \qquad f(r) = r^{-l-1}, \tag{129}$$

the most general solution of the Laplace equation is given by

$$V = \sum_{l,m} (a_{lm} \mathcal{Y}_l^m + b_{lm} \mathcal{Z}_l^m), \tag{130}$$

where the two independent solutions of Eq. (125) are specified by $\mathcal{Y}_l^m$ and $\mathcal{Z}_l^m$. They represent

(a) regular solid spherical harmonics

$$\mathcal{Y}_l^m(\mathbf{r}) = \mathcal{Y}_l^m(r, \theta, \varphi) = r^l Y_l^m(\theta, \varphi), \tag{131}$$

(b) irregular solid spherical harmonics

$$\mathcal{Z}_l^m(\mathbf{r}) = \mathcal{Z}_l^m(r, \theta, \varphi) = \frac{1}{r^{l+1}} Y_l^m(\theta, \varphi). \tag{132}$$

The harmonics depend analytically upon the coordinates of a field point P with respect to a given reference system with origin O, i.e.,the harmonics are centered on this origin. A convenient choice for specifying the location of P are spherical coordinates r, θ, φ [see Eq. (10) and Fig. 2]. However, the argument of each harmonic may also be denoted by the vector $\mathbf{r}$ which connects the origin O with the field point P, directing from O to P, provided that the reference system is given. Then, this shorthand notation leaves no doubt about its meaning.

It has been shown that there are at most $(2l + 1)$ linearly independent regular solid spherical harmonics of degree l which are sufficient to construct any general regular solid spherical harmonic according to Eq. (124). One realizes that there are just $(2l + 1)$ linearly independent surface harmonics Y_l^m which exhibit integral values of m within the range $-l \leq m \leq l$, where $l = 0, 1, 2, 3, \ldots$.

The two independent solutions $\mathcal{Y}_l^m$ and $\mathcal{Z}_l^m$ apparently exist because of the fact that

$$l(l+1) \qquad \text{remains unchanged if} \qquad l \to -(l+1). \tag{133}$$

Special cases of the irregular solid spherical harmonics are the functions

$$\frac{1}{r^{l+1}} Y_l^0(\theta, \phi) = \frac{1}{(2\pi)^{1/2} r^{l+1}} \mathcal{P}_l^0(\zeta) = \text{const.} \frac{\partial^l r^{-1}}{\partial z^l}, \tag{134}$$

which had been considered in Eqs. (8) and (9) of Section A.

III. Transformation of Spherical Harmonics under Rotations

A. Rotations in Coordinate Space

The behavior of spherical harmonics under rotations will be discussed to obtain a set of uniform formulas useful for subsequent considerations.

1. Definitions

Mappings and transformations in the three-dimensional coordinate space may be considered briefly. Consider an orthogonal basis spanned by unit vectors $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ which fulfill the conditions

$$\mathbf{e}_i \cdot \mathbf{e}_j = \delta_{ij}; \qquad i, j = 1, 2, 3. \tag{135}$$

Any vector $\mathbf{x}$ or $\mathbf{r}$ is defined by its coordinates in this basis; these coordinates are denoted by x_1, x_2, x_3 or by x, y, z, respectively:

$$\begin{aligned} \mathbf{x} &= x_1\mathbf{e}_1 + x_2\mathbf{e}_2 + x_3\mathbf{e}_3 = (\mathbf{e}_1\,\mathbf{e}_2\,\mathbf{e}_3)\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \boldsymbol{\mathsf{e}}\boldsymbol{\mathsf{x}}; \\ \mathbf{r} &= x\mathbf{e}_1 + y\mathbf{e}_2 + z\mathbf{e}_3 = (\mathbf{e}_1\,\mathbf{e}_2\,\mathbf{e}_3)\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \boldsymbol{\mathsf{e}}\boldsymbol{\mathsf{r}}. \end{aligned} \tag{136}$$

The row matrix containing the basis vectors is denoted by $\boldsymbol{\mathsf{e}}$; the column matrix containing the components of the vector $\mathbf{x}$ or $\mathbf{r}$ in the basis of the $\mathbf{e}_i$ $(i = 1, 2, 3)$, is denoted by $\boldsymbol{\mathsf{x}}$ or $\boldsymbol{\mathsf{r}}$, respectively:

$$\boldsymbol{\mathsf{e}} = (\mathbf{e}_1\,\mathbf{e}_2\,\mathbf{e}_3); \qquad \boldsymbol{\mathsf{x}} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}; \qquad \boldsymbol{\mathsf{r}} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \tag{137}$$

It is advantageous to collect covariant sets into row vectors and to put contravariant sets into column vectors [see, e.g., Tietz (1955), Hollingsworth (1967), Perlis (1958)]. [The reader is asked to distinguish carefully between symbols of vectors and symbols of row or column matrices, respectively, since the shape of the specifying letters is unfortunately very similar.]

Let $\mathscr{R}$ be an operator transforming every vector $\mathbf{x}$ into its image vector $\mathbf{x}' = \mathscr{R}\mathbf{x}$. Hence, $\mathscr{R}$ causes a mapping of the vector $\mathbf{x}$ onto the vector $\mathbf{x}'$.

Consider rotations about the z axis by an angle α. Positive rotations are counterclockwise if the observer looks along the z axis from its positive end toward the origin. We use only right-handed reference systems.

2. *Transformation of Basis Vectors*

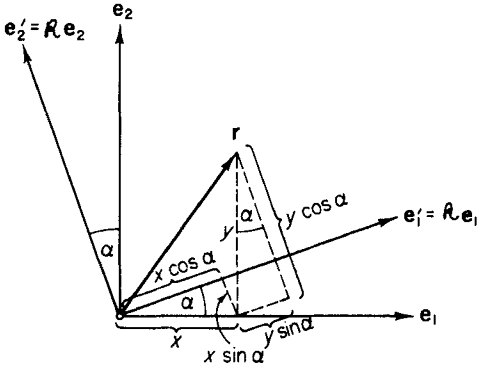


Fig. 3

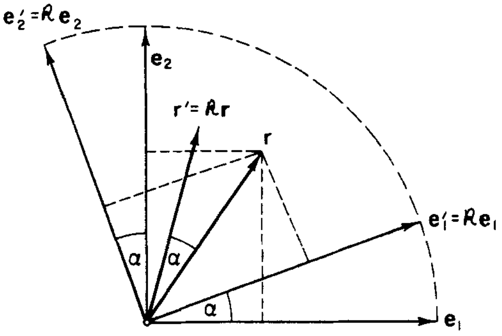


Fig. 4

A forward rotation about the z axis through an angle α (compare Figs. 3 and 4) will be described by

$$\begin{aligned} \mathbf{e}_1' &= \mathcal{R}\mathbf{e}_1 = \mathbf{e}_1\cos\alpha + \mathbf{e}_2\sin\alpha, \\ \mathbf{e}_2' &= \mathcal{R}\mathbf{e}_2 = -\mathbf{e}_1\sin\alpha + \mathbf{e}_2\cos\alpha, \\ \mathbf{e}_3' &= \mathcal{R}\mathbf{e}_3 = \mathbf{e}_3 . \end{aligned} \tag{138}$$

This may be written as

$$\begin{aligned} &(\mathbf{e}_1'\mathbf{e}_2'\,\mathbf{e}_3') = (\mathcal{R}\mathbf{e}_1\,\mathcal{R}\mathbf{e}_2\,\mathcal{R}\mathbf{e}_3) = (\mathbf{e}_1\,\mathbf{e}_2\,\mathbf{e}_3)\mathbf{R}(\alpha), \\ &\qquad\qquad \mathbf{e}' = \mathcal{R}\mathbf{e} = \mathbf{eR}(\alpha); \qquad \mathbf{e}_i' = \sum_j \mathbf{e}_j\,\mathbf{R}_{ji}, \end{aligned} \tag{139}$$

utilizing the 3 × 3 matrix

$$\mathbf{R}(\alpha) = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{140}$$

A backward rotation about the same axis through the same amount, that is to say, through the absolute value of the same angle α, will send each vector $\mathbf{x}$ into an image vector $\mathbf{x}''$ (compare Fig. 5):

$$\mathbf{e}'' = \mathscr{R}^{-1}\mathbf{e} = \mathbf{e}\mathbf{R}^{-1}(\alpha) = \mathbf{e}\mathbf{R}(-\alpha). \tag{141}$$

Since the vectors are real, the matrices are orthogonal:

$$\mathbf{R}^{-1}(\alpha) = \tilde{\mathbf{R}}(\alpha) = \mathbf{R}(-\alpha). \tag{142}$$

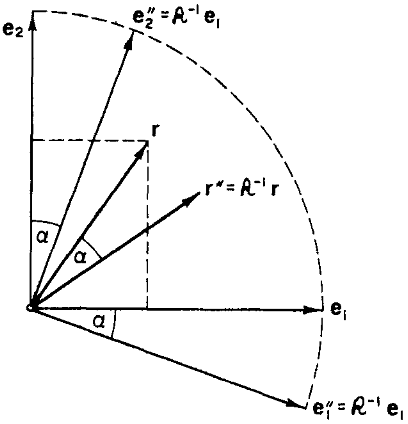


Fig. 5

Of course, the use of a complex basis would produce unitary matrices. $\tilde{\mathbf{R}}$ is the transpose of $\mathbf{R}$.

3. Transformation of Vector Components ("Coordinates")

(a) Consider first the case that the vector $\mathbf{r}$ is fixed, whereas the basis is rotated about $\mathbf{e}_3$: Relative to the basis $\mathbf{e}_1'$, $\mathbf{e}_2'$, $\mathbf{e}_3'$, which is obtained by a forward rotation through an angle α, the vector $\mathbf{r}$ has components $\bar{x}$, $\bar{y}$, $\bar{z}$ with (compare Figs. 3 and 4)

$$\bar{\mathbf{r}} = \mathbf{R}^{-1}\mathbf{r}, \qquad \begin{pmatrix} \bar{x} \\ \bar{y} \\ \bar{z} \end{pmatrix} = \begin{pmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \tag{143}$$

Relative to the basis $\mathbf{e}_1''$, $\mathbf{e}_2''$, $\mathbf{e}_3''$, which is obtained by a backward rotation through an angle $|\alpha|$, the same vector $\mathbf{r}$ has components x', y', z' with (compare Figs. 3 and 5)

$$\mathbf{r}' = \mathbf{R}\mathbf{r}, \qquad \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \tag{144}$$

Both relationships can be expressed by

$$\mathbf{r} = \mathbf{e}\mathbf{r} = (\mathbf{e}\mathbf{R})(\mathbf{R}^{-1}\mathbf{r}) = (\mathbf{e}\mathbf{R}^{-1})(\mathbf{R}\mathbf{r}). \tag{145}$$

(b) Secondly, consider the case that the vector may be rotated, whereas the basis remains fixed: According to Eq. (139) and Eq. (144), the rotated vector $\mathbf{r}'$ has components x', y', z' relative to the original basis $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$:

$$\mathbf{r}' = \mathcal{R}\mathbf{r} = \mathcal{R}\mathbf{e}\mathbf{r} = \mathbf{e}\mathbf{R}\mathbf{r} = \mathbf{e}\mathbf{r}', \qquad \mathbf{r}' = \mathbf{R}\mathbf{r}. \tag{146}$$

It is clear that $\mathbf{r}'$ has the same coordinates relative to the basis $\mathbf{e}_1'$, $\mathbf{e}_2'$, $\mathbf{e}_3'$ as $\mathbf{r}$ has relative to the basis $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$:

$$\mathbf{r}' = \mathcal{R}\mathbf{r} = \mathcal{R}\mathbf{e}\mathbf{r} = \mathbf{e}\mathbf{R}\mathbf{r} = \mathbf{e}'\mathbf{r}. \qquad \mathbf{e}' = \mathbf{e}\mathbf{R}. \tag{147}$$

This corresponds to Eq. (146) if some terms are expressed according to Eq. (139).

If a clockwise rotation of the vector is carried out, the final position of the vector may be specified by $\mathbf{r}''$ (see Fig. 5). This "backward rotated" vector $\mathbf{r}''$ has components $\bar{x}$, $\bar{y}$, $\bar{z}$ relative to the original basis. According to Eqs. (141) and (143), it must hold that

$$\mathbf{r}'' = \mathcal{R}^{-1}\mathbf{r} = \mathcal{R}^{-1}\mathbf{e}\mathbf{r} = \mathbf{e}\mathbf{R}^{-1}\mathbf{r} = \mathbf{e}\bar{\mathbf{r}}, \qquad \bar{\mathbf{r}} = \mathbf{R}^{-1}\mathbf{r}. \tag{148}$$

Naturally, $\mathbf{r}''$ has components x, y, z relative to the basis $\mathbf{e}_1''$, $\mathbf{e}_2''$, $\mathbf{e}_3''$, whence

$$\mathbf{r}'' = \mathcal{R}^{-1}\mathbf{r} = \mathcal{R}^{-1}\mathbf{e}\mathbf{r} = \mathbf{e}\mathbf{R}^{-1}\mathbf{r} = \mathbf{e}''\mathbf{r}, \qquad \mathbf{e}'' = \mathbf{e}\mathbf{R}^{-1}. \tag{149}$$

Comparing the statements of paragraph (a) with those of paragraph (b), we recall the well-known fact that any coordinate transformation

$$\mathbf{r}' = \mathbf{R}\mathbf{r} \tag{150}$$

allows two interpretations: In a *passive interpretation* (alias transformation) it means a backward rotation of the basis vectors, the vector $\mathbf{r}$ being fixed [cf. Eq. (144)]. However, in an *active interpretation* (alibi transformation), it means a forward rotation of the vector when the basis vectors remain fixed [cf. Eq. (146)]. In an equivalent manner one can say that

$$\bar{\mathbf{r}} = \mathbf{R}^{-1}\mathbf{r}, \tag{151}$$

in a passive interpretation, means a forward rotation of the basis vectors if the vector **r** is fixed [cf. Eq. (143)] and, in an active interpretation, means a backward rotation of the vector in a fixed reference system [Eq. (148)].

It is irrelevant which interpretation is chosen. However, if different texts are to be compared, the interpretation of the formulas should be known in order to avoid mistakes.

Equation (139) describes how an operator $\mathscr{R}$ generates a representation matrix **R** by means of a basis $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$:

$$\mathscr{R}\mathbf{e} = \mathbf{e}\mathbf{R}. \tag{152}$$

Since all possible operators which cause rotations of the three-dimensional space form a *group*, the corresponding matrices form a *representation* of this group.

Although the relations given so far describe simple rotations about the z axis, they may easily be extended to the general case of an arbitrary rotation in three-dimensional space. In fact, if the formulas given above are expressed by means of unspecified matrices, these relations may be considered as describing the general case. Such a general rotation can be defined either by the position of the rotation axis (relative to a reference system) and the rotation angle about this axis, or by the Eulerian angles.

For successive rotations, the interpretation becomes important. The relationship

$$\mathbf{r}_{\text{II}} = \mathbf{S}\mathbf{R}\mathbf{r}, \qquad \mathbf{S}\mathbf{R} = \mathbf{T}, \tag{153}$$

means in the passive interpretation: In the first place the basis is rotated by $\mathscr{R}^{-1}$ (e.g., backward), then the rotation of this basis is continued by $\mathscr{S}^{-1}$. It is important to realize that the second rotation is defined with respect to the "new" reference system which was obtained as the final position of the original reference system that was subject to the first rotation. Hence, the total operator is in fact $\mathscr{S}_{\text{fl}}^{-1}\mathscr{R}_{\text{fl}}^{-1}$ where the subscript fl denotes the "floating definition" of these operators. If a floating definition is applied to a sequence of operators, any following rotation will be defined with respect to the final position of the rotated reference system which was just obtained before, but *not* with respect to the fixed and unchanged original reference system which rests in the laboratory. Since in $\mathscr{S}_{\text{fl}}^{-1}\mathscr{R}_{\text{fl}}^{-1}$ the operator $\mathscr{S}_{\text{fl}}^{-1}$ is defined just as $\mathscr{S}^{-1}$ but with respect to a reference system which was rotated by $\mathscr{R}^{-1}$ before—and which differs from the original (laboratory) frame due to this rotation—it follows from the transformation law of operators that

$$\mathscr{S}_{\text{fl}}^{-1} = \mathscr{R}^{-1}\mathscr{S}^{-1}\mathscr{R}. \tag{154}$$

This may be illustrated by Fig. 6: $\mathbf{r}''$ has the same relative position with respect to a basis which is rotated by $\mathscr{A}$ as $\mathbf{r}$ has with respect to the original basis; this fact is used in Eq. (155b). Then, Eq. (155c) follows with the help of Eq. (155a), since $\mathbf{r}$ is arbitrary:

$$\begin{aligned}\mathbf{r}''' &= \mathscr{A}\mathbf{r}' = \mathscr{A}\mathscr{R}\mathbf{r}\\ &= (\mathscr{A}\mathscr{R}\mathscr{A}^{-1})\mathscr{A}\mathbf{r},\end{aligned}\tag{155a}$$

$$\begin{aligned}\mathbf{r}''' &= \mathscr{R}_{\text{fl}}\mathbf{r}'' = \mathscr{R}_{\text{fl}}\mathscr{A}\mathbf{r}\\ &= \mathscr{R}_{\text{fl}}\mathscr{A}_{\text{fl}}\mathbf{r},\end{aligned}\tag{155b}$$

$$\mathscr{A}\mathscr{R} = \mathscr{R}_{\text{fl}}\mathscr{A} = \mathscr{R}_{\text{fl}}\mathscr{A}_{\text{fl}}.\tag{155c}$$

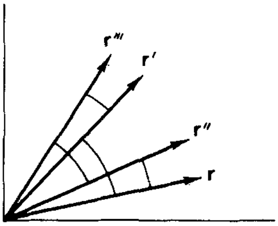


Fig. 6

Hence, rotations defined with respect to "floating bases" are carried out in a reverse sequence compared with rotations defined with respect to a fixed basis. Hence it follows that

$$\mathbf{r} = \mathbf{er} = \mathbf{e}_{\text{II}}\mathbf{r}_{\text{II}} = \mathbf{e}_{\text{II}}\mathbf{SRr}, \qquad \mathbf{e}_{\text{II}} = \mathbf{e}(\mathbf{SR})^{-1},\tag{156}$$

$$\mathbf{e}_{\text{II}} = \mathscr{S}_{\text{fl}}^{-1}\mathscr{R}_{\text{fl}}^{-1}\mathbf{e} = \mathscr{R}^{-1}\mathscr{S}^{-1}\mathbf{e} = \mathbf{eR}^{-1}\mathbf{S}^{-1}.\tag{157}$$

Operators $\mathscr{T} = \mathscr{S}\mathscr{R}$ are represented by matrices $\mathbf{T} = \mathbf{SR}$. Operators $\mathscr{T}^{-1} = \mathscr{R}^{-1}\mathscr{S}^{-1}$ are represented by matrices $\mathbf{T}^{-1} = \mathbf{R}^{-1}\mathbf{S}^{-1}$ according to Eq. (152). Hence, referring to the transformation law given by Eq. (153), the matrices $\mathbf{R}$, $\mathbf{S}$, $\mathbf{T}$, etc., form a *representation* of the rotation group if, in the passive interpretation of the transformation law for the components of a fixed vector, the successive (backward) rotations of the bases are defined with respect to "themselves," i.e., in a "floating" way. Then, the sequence of the rotations is the same as the sequence of the corresponding matrices determined by Eq. (153) if, as usual, the operators in a product are applied from right to left.

The active interpretation makes no difficulties. Quantities which transform linearly and homogeneously like the

$$\begin{Bmatrix}\text{coordinates} & x_1, x_2, x_3 \\ \text{basis vectors} & \mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\end{Bmatrix} \quad \text{form a} \quad \begin{Bmatrix}\text{contravariant} \\ \text{covariant}\end{Bmatrix}\text{set.}$$

Two sets are *cogredient* if they transform in the same way; they are *contragredient* if one set transforms contravariantly whereas the other one transforms covariantly.

B. Rotations in Function Space

The transformations considered here are again spatial symmetry operations which leave distances and angles unchanged; they are rotations about a fixed point. To each rotation of a function $f(r, \theta, \varphi)$ belongs a unitary operator that may be introduced by means of a Taylor expansion and Eq. (44) if z-axis quantization is chosen:

$$e^{\pm i\alpha L_z} f(r, \theta, \varphi) = f(r, \theta, \varphi \pm \alpha). \tag{158}$$

For a given positive rotation through an angle α ($\alpha \geq 0$, real) about the z axis, which in the coordinate space is accomplished by the operator $\mathcal{R}_\alpha$, there are obviously two possibilities for defining an operator which acts upon the function:

$$P_{\mathcal{R}_\alpha} = e^{-i\alpha L_z}, \qquad O_{\mathcal{R}_\alpha} = e^{i\alpha L_z}. \tag{159}$$

Both operators are inverse with respect to each other. Each "main transformation" $\mathcal{R}$ in coordinate space—as it may be called—induces a transformation in function space; however, positive and negative senses of rotations are to be defined separately also in that space.

The two possibilities of choosing a definition according to Eq. (159) divides the authors into two groups. (There is also, unhappily, a third group of authors who equivocate in their usage and will remain nameless.) This choice must be known if formulas are adopted from the literature. In order to decide which definition is used, first of all the sign of α, i.e., the sense of rotation must be given. In addition it is essential to be aware of the kind of interpretation, whether an active or a passive interpretation is used consistently. Finally, if a "rotation of axes" is discussed, it has to be stated whether the rotated axes are vectors of a body-fixed reference system or of a non-body-fixed one. Unfortunately, many texts refer to a rotation of "systems" without specifying whether a non-body-fixed coordinate system or a physical system, i.e., a "body-fixed" reference system is dealt with.

Apart from differences in the phase definitions of basis functions, coupling parameters, etc., which are employed in the literature, some difficulties may arise by the use of different notations by different authors, by referring to either right-handed or left-handed systems, by misprints or even errors, or by the use of different definitions within one reference work. Last, but not least, the Eulerian angles, although being most important and employed throughout in pertinent literature, are used in a discouraging variety of notations and definitions.

Because of this situation it appears appropriate to describe some simple properties of linear transformations which will be used in the sequel. In this section the transformation of functions under rotations will be discussed, making it easier to refer to the literature in order to compare formulas concerning especially the behavior of angular momentum eigenfunctions under transformations. However, because of the restricted space available, we must refrain from discussing the varieties of phase definitions and other assumptions, which are used in literature, as, for instance, those for operators, rotation matrices, coupling parameters, etc., although it is important for any practical work to have such information at hand. For spherical harmonics, those aspects have been discussed above.

$\mathbf{r}$ denotes the column matrix which contains the coordinates x_1, x_2, x_3, whereas $\mathbf{e}$ denotes the row matrix $\mathbf{e} = (\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3)$ which contains the basis vectors $\mathbf{e}_i$, $i = 1, 2, 3$. This definition of Eq. (137) not withstanding, the following self-explaining abbreviations will be used in order to denote arguments of functions in a simple way:

$$f(x, y, z) = f(\mathbf{r}) = f(x_1, x_2, x_3) = f(\mathbf{x}) = f(\mathbf{e} \cdot \mathbf{r}). \tag{160}$$

Due to Eqs. (136) and (137), $\mathbf{r}$ denotes the local vector

$$\mathbf{r} = x_1\mathbf{e}_1 + x_2\mathbf{e}_2 + x_3\mathbf{e}_3$$

which has components $x_i = (\mathbf{e}_i \cdot \mathbf{r})$ with respect to the basis $\mathbf{e}_i$, $i = 1, 2, 3$. Although, according to the aforementioned definitions, the scalar product $\mathbf{e} \cdot \mathbf{r}$ will generally denote the row matrix $(x_1\ x_2\ x_3)$, it is obvious that it will denote the argument (x_1, x_2, x_3) of a function if used in the sense of Eq. (160). Besides its shortness, this way of writing functional dependences has the further advantage of expressing the fact that a simultaneous rotation of the position vector and the basis has no effect:

$$f(\mathbf{e} \cdot \mathbf{r}) = f(\mathscr{R}\mathbf{e} \cdot \mathscr{R}\mathbf{r}) = f(\mathbf{r}). \tag{161}$$

If instead of $\mathbf{e}$ the basis $\mathscr{R}^{-1}\mathbf{e}$ is chosen, there follows either

$$f(\mathscr{R}^{-1}\mathbf{e}\cdot\mathbf{r}) = f(\mathbf{Rr}) \tag{162a}$$

or

$$f(\mathbf{e}\cdot\mathscr{R}\mathbf{r}) = f(\mathbf{Rr}). \tag{162b}$$

The first expression of the function as given by Eq. (162a) corresponds to a passive interpretation of the coordinate transformation which is determined by Eq. (144), whereas the second expression given by Eq. (162b) corresponds to an active interpretation. On replacing the position vector $\mathbf{r}$ by the vector $\mathscr{R}^{-1}\mathbf{r}$ in Eq. (161), one obtains either

$$f(\mathbf{e}\cdot\mathscr{R}^{-1}\mathbf{r}) = f(\mathbf{R}^{-1}\mathbf{r}) \tag{163a}$$

or

$$f(\mathscr{R}\mathbf{e}\cdot\mathbf{r}) = f(\mathbf{R}^{-1}\mathbf{r}). \tag{163b}$$

Again, the two relations correspond to the two possible interpretations of the relationship given by Eq. (151), its active interpretation being formulated by Eq. (163a), its passive one by Eq. (163b).

If the operators P or O, defined in Eq. (159), are applied to a given function f, they will generate new functions which will be denoted by (Pf) or (Of), respectively, or shorter as Pf or Of.

If the operator $P_{\mathscr{R}}$ of Eq. (159) is used in connection with the "main transformation" characterized by $\mathscr{R}$, then we have

$$(P_{\mathscr{R}}f)(\theta, \varphi) = f(\theta, \varphi - \alpha), \tag{164}$$

if $\mathscr{R}$ causes positive rotations about the z axis. For general rotations, there follows

$$P_{\mathscr{R}}f(\mathbf{r}) = f(\mathbf{R}^{-1}\mathbf{r}), \qquad \tilde{\mathbf{r}} = \mathbf{R}^{-1}\mathbf{r}, \tag{165}$$

which can also be written as

$$P_{\mathscr{R}}f(\mathbf{Rr}) = f(\mathbf{r}), \qquad \mathbf{r}' = \mathbf{Rr}. \tag{166}$$

According to Eq. (162), the "new function" has the same value at the point $\mathscr{R}\mathbf{r}$ as the "old function" has at the point $\mathbf{r}$. Hence, $P_{\mathscr{R}}$ causes a positive rotation of the field relative to a fixed reference frame. Since the physical distribution, which is determined by the function f, is rotated, one may also talk about a rotation of a body or a body-fixed reference system. The basis vectors of *this* reference system may be denoted by $\mathbf{e}_1{}^B$, $\mathbf{e}_2{}^B$, $\mathbf{e}_3{}^B$. In contrast, the basis vectors of a non-body-fixed reference frame (which is usually referred to as "fixed in space") shall be specified by $e_1{}^A$, $e_2{}^A$, $e_3{}^A$. If both systems coincide before the rotation is carried out, the "main transformation," which induces $P_{\mathscr{R}}$, is described by

$$\mathscr{R}\mathbf{e}^A = \mathbf{e}^A\mathbf{R} = \mathbf{e}^B. \tag{167}$$

Then, the body-fixed basis vectors, collected into $\mathbf{e}^B$, are rotated and in a new position relative to the "resting" vectors, collected into $\mathbf{e}^A$: The vectors $\mathbf{e}^B$ are expressed by the vectors $\mathbf{e}^A$ by means of relationship Eq. (167).

The inverse rotation, which is determined by

$$\mathscr{R}^{-1}\mathbf{e}^A = \mathbf{e}^A\mathbf{R}^{-1} = \mathbf{e}^B, \tag{168}$$

induces the operator $P_{\mathscr{R}^{-1}}$ which causes a backward rotation of the field (body). It may be noted that the term "body-fixed reference system" means a "reference system embedded in the field."

The equations (167) and (168) have the advantage of being completely independent of the interpretation. They relate only the final relative position of both systems to each other without stating which reference frame has been rotated and which one was resting. A backward rotation of the body (or the shape of the function), which is defined with respect to a fixed reference system, is identical with a forward rotation of this system (which then is no longer fixed in space), if the body is kept fixed. This is true since only the relative position of two reference frames is of interest; any other distinguished reference system does not exist.

According to Eq. (165), the transformed function, depending on the coordinates x, y, z, is given by the original function, depending on the new coordinates $\bar{x}, \bar{y}, \bar{z}$, which are given by Eq. (143). That is to say, in order to obtain the transformed function $(P_{\mathscr{R}}f)$ with the argument (x, y, z), one just may take the original function f and replace the coordinates x, y, z of its argument by the new coordinates $\bar{x}, \bar{y}, \bar{z}$. Since these new coordinates are functions of the old ones according to Eq. (143), a new functional dependence upon the old coordinates arises, viz. the new function. For example:

The three real p functions are given by

$$p_x = [x/r], \qquad p_y = [y/r], \qquad p_z = [z/r]. \tag{169}$$

This covariant set transforms under $\mathscr{R}$, if the operator $P_{\mathscr{R}}$ (not $O_{\mathscr{R}}$) is chosen, like

$$P_{\mathscr{R}}[x/r] = [\bar{x}/r], \qquad P_{\mathscr{R}}[y/r] = [\bar{y}/r], \qquad P_{\mathscr{R}}[z/r] = [\bar{z}/r]. \tag{170}$$

These relations are in agreement with their geometrical meaning.

The operator $O_{\mathscr{R}}$ has the effect

$$(O_{\mathscr{R}}f)(\theta, \varphi) = f(\theta, \varphi + \alpha), \tag{171}$$

$$O_{\mathscr{R}}f(\mathbf{r}) = f(\mathbf{Rr}), \tag{172}$$

$$O_{\mathscr{R}}f(\mathbf{R}^{-1}\mathbf{r}) = f(\mathbf{r}). \tag{173}$$

Hence, $O_{\mathscr{R}}$ causes a forward rotation of a certain reference system, leaving the resting field unchanged. Then, the rotated reference system can be discussed against the body-fixed system which now is fixed in space. This description of the situation is, of course, equivalent to saying $O_{\mathscr{R}}$ effects a backward rotation of the field (the body-fixed reference system) if this rotation is defined with respect to another reference frame fixed in space. For both interpretations, the main transformation is given by

$$\mathscr{R}\mathbf{e}^B = \mathbf{e}^B\mathbf{R} = \mathbf{e}^A. \tag{174}$$

$O_{\mathscr{R}^{-1}}$ belongs to the inverse rotation of a certain (so-called "non-body-fixed") reference system, if the rotation is defined with respect to a reference system which is embedded in the resting field (body). This corresponds to a forward rotation of the field, defined with respect to another reference frame fixed in space. Hence, one has

$$\mathscr{R}^{-1}\mathbf{e}^B = \mathbf{e}^B\mathbf{R}^{-1} = \mathbf{e}^A. \tag{175}$$

One realizes that it is better to avoid the use of the terms "body-fixed" and "fixed in space" in an opposite meaning, since the case that the body rests in the laboratory may be considered as well.

The transformed function is determined by Eq. (172) in case the operator $O_{\mathscr{R}}$ is used. Again, simple tests can be made by means of the p functions given in Eq. (169).

From the given identities it follows easily that

$$P_{\mathscr{R}} = O_{\mathscr{R}^{-1}}, \qquad P_{\mathscr{R}^{-1}} = O_{\mathscr{R}}; \tag{176}$$

$$P_{\mathscr{R}} = O_{\mathscr{R}}^{-1}, \qquad P_{\mathscr{R}}^{-1} = P_{\mathscr{R}^{-1}} = O_{\mathscr{R}}, \qquad O_{\mathscr{R}}^{-1} = O_{\mathscr{R}^{-1}}. \tag{177}$$

According to Eq. (176), the Eqs. (167) and (175) are equivalent, as are Eqs. (168) and (174).

C. Parametrization in Terms of Eulerian Angles

The following derivations are based on operators of the kind $P_{\mathscr{R}}$ which cause a positive rotation of the field.

Operators of the kind $P_{\mathscr{R}}$ are also used in the book by Rose (1957), which contains lucid derivations, although no explicit statement that the field is rotated. Misunderstanding may also arise concerning the distinction between co- and contravariance especially as regards the relationship between real and complex basis functions.

Operators of the type $O_{\mathfrak{R}}$ are used by Edmonds (1957), Rose (1955), Wigner (1959). Edmonds (1957) gives many useful formulas in a concise manner, containing, however, some misprints and contradictions between text, formulas, and figures. Wigner employs right-handed reference systems in the English edition of his work on group theory (Wigner, 1959), but left-handed systems in the German edition (Wigner, 1931).

The rotation of a reference system is in an unequivocal manner defined by the rotation angle δ and the rotation axis whose direction is determined by the unit vector $\mathbf{n}$. A positive rotation advances a right-handed screw along the rotation axis. Since the ("body-fixed") reference system is embedded in the physical system (field), which is rotated, the associate operator is given by $\exp[-i\delta(\mathbf{n}\cdot\mathbf{L})]$. The transformed spherical harmonic is

$$P_{\mathfrak{R}}|lm\rangle = e^{-i\delta\mathbf{n}\cdot\mathbf{L}}|lm\rangle. \tag{178}$$

Just as the original harmonic, it is an eigenfunction of $\mathbf{L}^2$ to the eigenvalue $l(l+1)$,

$$\mathbf{L}^2 P_{\mathfrak{R}}|lm\rangle = l(l+1)P_{\mathfrak{R}}|lm\rangle. \tag{179}$$

This is so, since $\mathbf{L}^2$ commutes with $P_{\mathfrak{R}}$ as can be verified by expanding $\exp[-i\delta(\mathbf{n}\cdot\mathbf{L})]$ into an infinite series. However, since $P_{\mathfrak{R}}$ does not commute with L_z, the transformed function is not an eigenfunction of L_z but a linear combination of eigenfunctions of $\mathbf{L}^2$, denoted by $|lm'\rangle$, with different quantum numbers m':

$$P_{\mathfrak{R}}|lm\rangle = \sum_{m'} |lm'\rangle\langle lm'|e^{-i\delta\mathbf{n}\cdot\mathbf{L}}|lm\rangle. \tag{180}$$

Instead of using $\mathbf{n}$ and δ, it is advantangeous to specify a rotation with the help of Eulerian angles which may be introduced as follows (cf. Figs 7 and 8).

Let the fixed vector $\mathbf{r}$, pointing from the origin to the point P fixed in space, have the Cartesian coordinates x, y, z and the spherical coordinates r, θ, φ with respect to the original basis $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$. Let the very same vector have the Cartesian coordinates $\check{x}$, $\check{y}$, $\check{z}$ and the spherical coordinates $\check{r}$, $\check{\theta}$, $\check{\varphi}$ with respect to the rotated basis $\check{\mathbf{e}}_1$, $\check{\mathbf{e}}_2$, $\check{\mathbf{e}}_3$:

$$\mathbf{r} = \mathbf{er} = \check{\mathbf{e}}\check{\mathbf{r}} = (\mathbf{eR})(\mathbf{R}^{-1}\mathbf{r}). \tag{181}$$

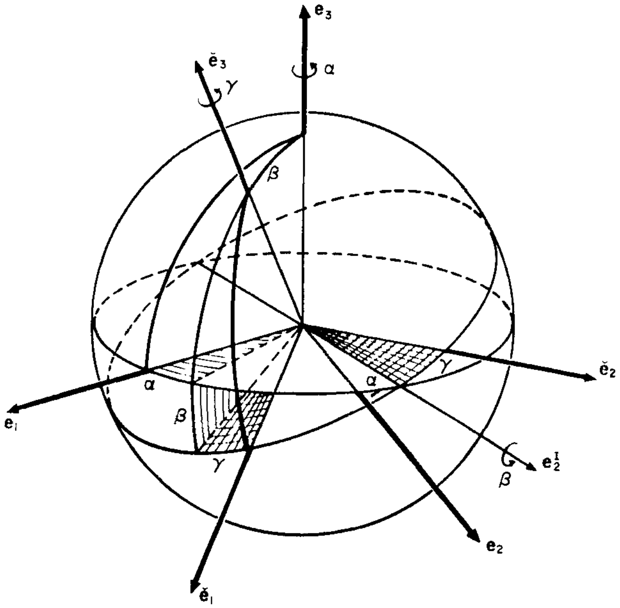

$\mathbf{e}_3$
α
$\check{\mathbf{e}}_3$
γ
β
$\check{\mathbf{e}}_2$
α
γ
α
$\mathbf{e}_1$
β
γ
$\mathbf{e}_2^{I}$
β
$\mathbf{e}_2$
$\check{\mathbf{e}}_1$

Fig. 7

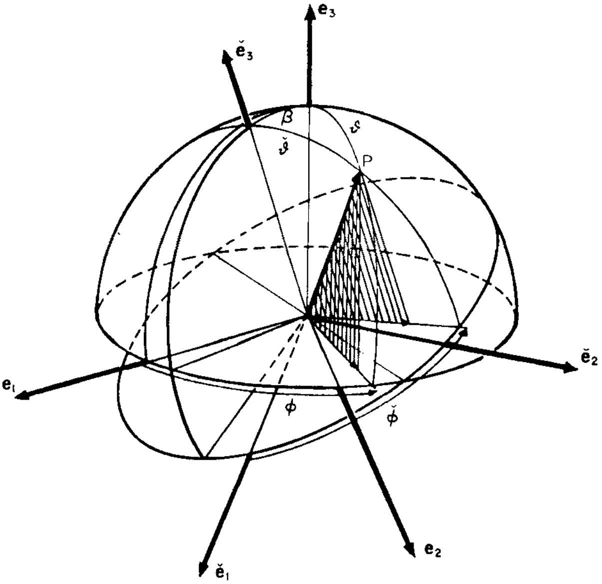

$\mathbf{e}_3$
$\check{\mathbf{e}}_3$
β
ϑ
$\check{\vartheta}$
P
$\check{\mathbf{e}}_2$
$\mathbf{e}_1$
ϕ
$\check{\phi}$
$\mathbf{e}_2$
$\check{\mathbf{e}}_1$

Fig. 8

Since the origin is fixed and pure rotations are considered (implying $\mathbf{r} = \check{\mathbf{r}}$), the final position $\check{\mathbf{e}}$ of the reference frame may be obtained from the original position $\mathbf{e}$ of the reference system with the help of the following three rotations by *Eulerian angles* α, β, γ:

(1) The original reference system $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ is rotated by an angle α about the $\mathbf{e}_3$ axis. The new position is given by the basis vectors $\mathbf{e}_1{}^{\mathrm{I}}$, $\mathbf{e}_2{}^{\mathrm{I}}$, $\mathbf{e}_3{}^{\mathrm{I}}$. The operator $P_{\mathfrak{R}}$, which is associated with this rotation, is given by $\exp(-i\alpha L_z)$. After this first step, one has

$$\mathbf{r} = \mathbf{er} = \mathbf{e}^{\mathrm{I}}\bar{\mathbf{r}}. \tag{182a}$$

(2) Then, the reference system is rotated by an angle β about the new $\mathbf{e}_2{}^{\mathrm{I}}$ axis, yielding the new axes $\mathbf{e}_1{}^{\mathrm{II}}, \mathbf{e}_2{}^{\mathrm{II}}, \mathbf{e}_3{}^{\mathrm{II}}$. According to Eq. (155c), the generating operator is given by

$$e^{-i\beta L_{\bar{y}}} = e^{-i\alpha L_z} e^{-i\beta L_y} e^{i\alpha L_z} \tag{182b}$$

with

$$\mathbf{e}_2{}^{\mathrm{I}} = \mathbf{e}_2{}^{\mathrm{II}}, \qquad \bar{y} = \bar{\bar{y}},$$
$$L_z = (\mathbf{L} \cdot \mathbf{e}_3), \qquad L_{\bar{y}} = (\mathbf{L} \cdot \mathbf{e}_2{}^{\mathrm{I}}), \qquad \mathbf{r} = \mathbf{e}^{\mathrm{II}}\bar{\bar{\mathbf{r}}}.$$

(3) Lastly, a rotation by an angle γ about the new $\mathbf{e}_3{}^{\mathrm{II}}$ axis leads to the final position of the basis, which is determined by $\check{\mathbf{e}}_1$, $\check{\mathbf{e}}_2$, $\check{\mathbf{e}}_3$. The operator is given by

$$e^{-i\gamma L_{\check{z}}} = e^{-i\beta L_{\bar{y}}} e^{-i\gamma L_{\bar{z}}} e^{i\beta L_{\bar{y}}} \tag{182c}$$

where

$$\check{\mathbf{e}}_3 = \mathbf{e}_3{}^{\mathrm{II}}, \qquad \check{z} = \bar{\bar{z}}, \qquad L_{\check{z}} = (\mathbf{L} \cdot \check{\mathbf{e}}_3), \qquad \mathbf{r} = \mathbf{er} = \check{\mathbf{e}}\check{\mathbf{r}}.$$

These facts may be expressed in another way by the following statement:

(a) The final $\check{\mathbf{e}}_3$ axis has in the original reference system the azimuthal angle α and the polar angle β; the third operation is a rotation by the angle γ about this $\check{\mathbf{e}}_3$ axis.

(b) The original $\mathbf{e}_3$ axis has in the final reference system the azimuthal angle $\pi - \gamma$ and the polar angle $|\beta|$.

The Eulerian angles, defined by Eqs. (182a)–(182c) within the ranges

$$0 \leq \alpha \leq 2\pi, \qquad 0 \leq \beta \leq \pi, \qquad 0 \leq \gamma \leq 2\pi \tag{182d}$$

characterize completely a given rotation R, which may be denoted by

$$R = [\alpha, \beta, \gamma]. \tag{182e}$$

Wigner (1959) chooses the notation $\{\gamma\beta\alpha\}$ for this rotation, if the angles are defined as discussed above.

An operator Ω transforms into the operator $\Omega' = P_{\mathscr{R}} \Omega P_{\mathscr{R}}^{-1}$ under a unitary transformation which is governed by $P_{\mathscr{R}}$. Therefore, each of the three exponential operators, which generates one of the three successive Eulerian rotations, is given by the corresponding operator, which is defined with respect to a previous coordinate system but unitarily transformed under the Eulerian rotation which transfers that previous reference frame into the reference system under consideration. The total operator is then

$$P_{\mathscr{R}} = e^{-i\delta(\mathbf{n}\cdot\mathbf{L})} = e^{-i\gamma L_{\check{z}}} e^{-i\beta L_{\bar{y}}} e^{-i\alpha L_z}. \tag{183}$$

It works on the wave function from right to left, i.e., the operator $e^{-i\alpha L_z}$ is applied first, etc.

The rotations generated by the three operators contained in Eq. (183) are defined with respect to "floating reference systems." Eqs. (182a)–(182c) give, however,

$$P_{\mathscr{R}} = e^{-i\alpha L_z} e^{-i\beta L_y} e^{-i\gamma L_z} \tag{184}$$

which is the well-known result that the final position $\check{\mathbf{e}}_1, \check{\mathbf{e}}_2, \check{\mathbf{e}}_3$ of the reference frame can also be obtained by carrying out the rotations (of the field) in reverse order about the fixed axes $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$, namely first through the angle γ about the $\mathbf{e}_3$ axis, then through β about $\mathbf{e}_2$, finally through α about $\mathbf{e}_3$ again. The considerations about rotations given in this section should be useful to clarify questions concerning phases, etc. They are also necessary for practical calculations and the following discussions.

D. Representation Matrices of the Rotation Group

$\mathbf{D}^{(l)}(\alpha, \beta, \gamma)$ denotes the representation matrix of the rotation $R = [\alpha, \beta, \gamma]$ in the $(2l + 1)$-dimensional irreducible representation $\mathbf{D}^{(l)}$ of the rotation group, if the $2l + 1$ complex surface spherical harmonics $|lm\rangle = Y_l^m(\theta, \varphi)$ with $-l \leq m \leq l$ form the basis for this representation. Because of Eqs. (178), (180), and (184), the elements of the matrix $\mathbf{D}^{(l)}(\alpha, \beta, \gamma)$ are given by

$$\begin{aligned} \mathbf{D}^{(l)}_{m'm}(\alpha, \beta, \gamma) &= \langle lm' | P_{\mathscr{R}} | lm \rangle \\ &= \langle lm' | e^{-i\alpha L_z} e^{-i\beta L_y} e^{-i\gamma L_z} | lm \rangle \\ &= e^{-i\alpha m'} \mathbf{d}^{(l)}_{m'm}(\beta) e^{-i\gamma m}, \end{aligned} \tag{185}$$

since for z-axis quantization, the operator L_z is diagonal with respect to the $|lm'\rangle$. The second Eulerian rotation about the $\mathbf{e}_2{}^{\mathrm{I}}$ axis has the nondiagonal representation

$$\mathbf{d}^{(l)}_{m'm}(\beta) = \langle lm' | e^{-i\beta L_y} | lm \rangle. \tag{186}$$

Of course, the component $L_z = (\mathbf{L} \cdot \mathbf{e}_3)$ of the angular momentum operator refers to a quantization with respect to the $\mathbf{e}_3$ axis, whereas the component $L_{\check{z}} = (\mathbf{L} \cdot \check{\mathbf{e}}_3)$ belongs to a quantization with respect to the $\check{\mathbf{e}}_3$ axis.

Since L_z does not commute with $P_{\mathscr{R}}$, the function $P_{\mathscr{R}}|lm\rangle$ is not an eigenfunction of L_z. Therefore, it may depend on φ even for $m = 0$ and, in general, it will be no single surface spherical harmonic in θ, φ as known from Eq. (57). However, it follows from Eqs. (155a)–(155c) that

$$L_{\check{z}} = P_{\mathscr{R}} L_z P_{\mathscr{R}}^{-1}, \qquad L_z = P_{\mathscr{R}}^{-1} L_{\check{z}} P_{\mathscr{R}}, \tag{187}$$

$$L_{\check{z}} P_{\mathscr{R}} |lm\rangle = m P_{\mathscr{R}} |lm\rangle, \qquad L_z |lm\rangle = m |lm\rangle. \tag{188}$$

Therefore, $P_{\mathscr{R}}|lm\rangle$ is an eigenfunction of $L_{\check{z}}$ to the eigenvalue m. Since this function is, of course, also an eigenfunction of $\mathbf{L}^2$ to the eigenvalue $l(l+1)$, cf. Eq. (179), $P_{\mathscr{R}}|lm\rangle$ must be a surface spherical harmonic $Y_l{}^m(\check{\theta}, \check{\varphi})$ in the spherical coordinates r, $\check{\theta}$, $\check{\varphi}$ which are defined with respect to the new reference system $\check{\mathbf{e}}_1$, $\check{\mathbf{e}}_2$, $\check{\mathbf{e}}_3$. According to Eqs. (180), (184), and (185), it follows that

$$P_{\mathscr{R}} Y_l{}^m(\theta, \varphi) = Y_l{}^m(\check{\theta}, \check{\varphi}) = \sum_{m'=-l}^{l} Y_l{}^{m'}(\theta, \varphi) \mathbf{D}^{(l)}_{m'm}(\alpha, \beta, \gamma). \tag{189}$$

It is this relationship which motivated the commonly used phrase of the surface spherical harmonics transforming among each other under rotations.

If $\mathbf{Y}_l$ denotes a row vector that contains the functions $Y_l{}^m$ in standard order, i.e.,

$$\mathbf{Y}_l = (Y_l{}^l \; Y_l^{l-1} \cdots Y_l{}^1 \; Y_l{}^0 \; Y_l^{-1} \cdots Y_l^{-l+1} \; Y_l{}^{-l}), \tag{190}$$

then Eq. (189) may be written as a matrix equation:

$$P_{\mathscr{R}} \mathbf{Y}_l(\omega) = \mathbf{Y}_l(\check{\omega}) = \mathbf{Y}_l(\omega) \mathbf{D}^{(l)}(R). \tag{191}$$

The direction of the unit vector $\boldsymbol{\rho} = \mathbf{r}/r$, expressed in spherical coordinates with respect to the original reference system $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$, is given by $\omega = (\theta, \varphi)$, which may also be written as $\omega = (\mathbf{e} \cdot \boldsymbol{\rho})$. Because of

$$f(\check{\omega}) = f(\check{\mathbf{e}} \cdot \boldsymbol{\rho}) = f(\mathscr{R}\mathbf{e} \cdot \boldsymbol{\rho}) = f(\mathbf{e} \cdot \mathscr{R}^{-1}\boldsymbol{\rho}) \tag{192}$$

again two ways of interpreting the Eqs. (189) and (191) are possible:

(a) $\omega = (\theta, \varphi)$ and $\breve{\omega} = (\breve{\theta}, \breve{\varphi})$ may be considered as specifying the same direction $\boldsymbol{\rho}$ in space but relating it to the different reference systems $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ and $\breve{\mathbf{e}}_1, \breve{\mathbf{e}}_2, \breve{\mathbf{e}}_3$, respectively; then m is an eigenvalue of $L_{\breve{z}}$, while m' is an eigenvalue of L_z. The $Y_l^{m'}(\theta, \varphi)$ are spherical harmonics in the coordinate representation referred to the original frame, the $Y_l^m(\breve{\theta}, \breve{\varphi})$ are spherical harmonics in the coordinate representation referred to the new frame.

(b) If ω characterizes the direction $\boldsymbol{\rho}$ and $\breve{\omega}$ specifies another direction $\mathcal{R}^{-1}\boldsymbol{\rho}$, naturally all m as well as m' are eigenvalues of L_z, all (new and old) functions being spherical harmonics in the coordinate representation referred to the original frame.

The unitary matrics $\mathbf{D}^{(l)}(R)$ form the $(2l + 1)$-dimensional irreducible representation of the group of all pure rotations R. Particularly,

$$P_{\mathcal{R}_2} P_{\mathcal{R}_1} = P_{\mathcal{R}_1, \mathfrak{R}} P_{\mathcal{R}_2} = P_{\mathcal{R}_1, \mathfrak{R}} P_{\mathcal{R}_2, \mathfrak{R}} \tag{193}$$

is represented by $\mathbf{D}^{(l)}(R_2)\mathbf{D}^{(l)}(R_1)$.

From what was said before it follows that the inverse rotation is given by

$$R^{-1} = [\alpha, \beta, \gamma]^{-1} = [-\gamma, -\beta, -\alpha]; \tag{194}$$

the successive rotations are carried out in reverse order and with negative rotational angles. Hence, for all R

$$(\mathbf{D}^{(l)}(R))^{-1}\mathbf{D}^{(l)}(R) = \mathbf{1} = \mathbf{D}^{(l)}(R^{-1})\mathbf{D}^{(l)}(R), \tag{195}$$

$$\mathbf{D}^{(l)}(R^{-1}) = \mathbf{D}^{(l)}(-\gamma, -\beta, -\alpha) = (\mathbf{D}^{(l)}(\alpha, \beta, \gamma))^{-1} = (\mathbf{D}^{(l)}(R))^{-1}, \tag{196}$$

and, because of the unitarity,

$$\mathbf{D}^{(l)\dagger}(R) = (\mathbf{D}^{(l)}(R))^{-1} = \mathbf{D}^{(l)}(R^{-1}). \tag{197}$$

Due to Eqs. (176) and (177), the representation matrix of a given rotation, which is generated by the rotational operator $P_{\mathcal{R}}$ of Eq. (159), is the inverse of the representation matrix of the same rotation which is generated by the operator $O_{\mathcal{R}}$.

The Eqs. (194)–(197) have consequences for the elements of the representation matrices; they establish symmetry relationships which are, because of Eq. (185), particularly important for $\mathbf{d}^{(l)}_{m',m}(\beta)$:

$$(-1)^{m'-m}\mathbf{d}^{(l)}_{m',m}(\beta) = \mathbf{d}^{(l)}_{m',m}(-\beta) = \mathbf{d}^{(l)}_{-m',-m}(\beta) = \mathbf{d}^{(l)}_{m,m'}(\beta), \tag{198}$$

$$\mathbf{d}^{(l)}_{m',m}(\beta + \pi) = (-1)^{l+m'}\mathbf{d}^{(l)}_{-m',m}(\beta), \tag{199}$$

$$\mathbf{d}^{(l)}_{m',m}(0) = \delta_{m',m}; \qquad \mathbf{D}^{(l)*}_{m',m}(R) = (-1)^{m'+m}\mathbf{D}^{(l)}_{-m',-m}(R). \tag{200}$$

There are different ways to express the $\mathbf{d}^{(l)}$ matrices. With the definitions used above, one has

$$\begin{aligned}\mathbf{d}^{(l)}_{m',m}(\beta) &= [(l+m)!(l-m)!(l+m')!(l-m')!]^{1/2}\\ &\cdot \sum_K \frac{(-1)^K}{K!}\,\frac{(-1)^{m'+m}(\cos\tfrac{1}{2}\beta)^{2l+m-m'-2K}}{(l-m'-K)!(l+m-K)!(K+m'-m)!}\\ &\cdot (\sin\tfrac{1}{2}\beta)^{m'-m+2K},\end{aligned} \tag{201}$$

where the summation index K runs over all values for which the factorials do exist, i.e., the integer K assumes all values for which the factorial arguments are greater than or equal to zero. Another expression of the same $\mathbf{d}^{(l)}_{m',m}$, being more suitable for numerical calculations, is

$$\begin{aligned}\mathbf{d}^{(l)}_{m',m}(\beta) &= c_{l,m',m}(-1)^{m'-m}\sum_K (-1)^K \binom{l+m}{K}\\ &\cdot \binom{l-m}{l-m'-K}[\cos\tfrac{1}{2}\beta]^{2l-m'+m-2K}[\sin\tfrac{1}{2}\beta]^{m'-m+2K},\end{aligned} \tag{202a}$$

with

$$\begin{aligned}c_{l,m',m} = c_{l,|m'|,|m|} &= \left[\frac{(l+m')!(l-m')!}{(l+m)!(l-m)!}\right]^{1/2}\\ &= \left[\binom{l}{|m|}\binom{l}{|m'|}^{-1}\binom{l+|m|}{|m|}^{-1}\binom{l+|m'|}{|m'|}\right]^{1/2}.\end{aligned} \tag{202b}$$

Again, the sum is over all those values of the integer K for which the factorial arguments are nonnegative:

$$\max(0, m-m') \le K \le \min(l-m', l+m). \tag{202c}$$

For numerical calculations, recursion relations of the $\mathbf{d}^{(l)}_{m',m}(\beta)$ are important; however, they will not be given here.

In the sequel, elements of the rotation matrix with one index being zero will often be needed. These special elements of the rotation matrices can be expressed by surface harmonics as follows. Multiplication of Eq. (191) from the right by $\mathbf{D}^{(l)\dagger}(R)$ yields

$$\mathbf{Y}_l(\omega) = \mathbf{Y}_l(\check{\omega})\mathbf{D}^{(l)\dagger}(R) \tag{203}$$

or

$$Y_l^m(\theta, \varphi) = \sum_{m'=-l}^{l} Y_l^{m'}(\check{\theta}, \check{\varphi})\mathbf{D}_{m,m'}^{(l)*}(\alpha, \beta, \gamma), \tag{204}$$

which corresponds to Eq. (189). One may pick two particular directions:

(1) The unit vector $\boldsymbol{\rho}$ coincides with the unit vector $\mathbf{e}_3$. Then, the vector $\boldsymbol{\rho}$ points to a point on the $\mathbf{e}_3$ axis which has the spherical coordinates $\omega = (0, \varphi)$ with respect to the reference system $\mathbf{e}$, the azimuthal angle φ is arbitrary. The same point has the spherical coordinates $\check{\omega} = (\beta, \pi - \gamma)$ with respect to the reference frame $\check{\mathbf{e}}$ [see statement (b) before Eq. (182d)]. Then, because of

$$Y_l^{m'}(0, \varphi) = \left(\frac{2l+1}{2}\frac{1}{2\pi}\right)^{1/2} \delta_{m',0}, \tag{205}$$

it follows from Eq. (189)

$$\mathbf{D}_{0,m}^{(l)*}(\alpha, \beta, \gamma) = (-1)^m\left(\frac{4\pi}{2l+1}\right)^{1/2} Y_l^m(\beta, \gamma). \tag{206}$$

(2) The unit vector $\boldsymbol{\rho}$ coincides with the vector $\check{\mathbf{e}}_3$. Now the vector $\boldsymbol{\rho}$ points to a point on the $\check{\mathbf{e}}_3$ axis which has the spherical coordinates $\omega = (\theta, \varphi) = (\beta, \alpha)$ with respect to the reference system $\mathbf{e}$. However, the same point has the spherical coordinates $\check{\omega} = (0, \check{\varphi})$ with respect to the reference system $\check{\mathbf{e}}$, $\check{\varphi}$ being arbitrary. [This is in agreement with statement (a) before Eq. (182d)]. With this choice, Eq. (204) gives

$$\mathbf{D}_{m,0}^{(l)*}(\alpha, \beta, \gamma) = \left(\frac{4\pi}{2l+1}\right)^{1/2} Y_l^m(\beta, \alpha). \tag{207}$$

Both Eqs. (206) and (207) are related to each other by the condition that the $\mathbf{D}^{(l)}$ matrices are unitary. Finally, it is clear that for some special cases Eqs. (205), (207) reduce to

$$\mathbf{D}_{m,0}^{(l)*}(\alpha, 0, \gamma) = \delta_{m,0} = \mathbf{d}_{m,0}^{(l)}(0); \tag{208}$$

$$\mathbf{D}_{0,0}^{(l)}(\alpha, \beta, \gamma) = P_l(\cos \beta). \tag{209}$$

Thereby a direct relationship between the matrix elements $\mathbf{d}^{(l)}_{m,0}(\beta)$ and the associated Legendre functions is established:

$$\mathbf{d}^{(l)}_{m,0}(\beta) = (-1)^m \mathbf{d}^{(l)}_{0,m}(\beta) = [2/(2l+1)]^{1/2} \mathscr{P}_l^m(\cos\beta). \tag{210}$$

A difficulty arises from the fact that β is an Eulerian angle which, according to the definition of an inverse rotation as given by Eq. (194), has a sense of rotation that is to be taken into account by the sign of β, whereas on the other hand the polar angle of Y_l^m is unique and positive: $\theta \geq 0$. The best way to surmount this difficulty, caused by using Eulerian angles with different signs, is provided by the definition $Y_l^m(-\theta, \varphi) = Y_l^m(\theta, \varphi + \pi)$. This is also in formal agreement with the definitions given by Eq. (45) and Eq. (54) if one puts $(1 - \zeta^2)^{m/2} = (\sin\theta)^m$. All difficulties may be avoided from the very beginning if, according to Eq. (182d), only positive angles are allowed and, if negative angles do occur, the following substitutions are applied: $-\alpha \rightarrow 2\pi - \alpha$, or $-\gamma \rightarrow 2\pi - \gamma$ and, if necessary,

$$[\alpha, -\beta, \gamma] = [\alpha + \pi, \beta, \gamma + \pi]; \tag{211}$$

with

$$\alpha, \beta, \gamma \geq 0.$$

IV. Transformation of Solid Spherical Harmonics under Translation

A. Auxiliary Relations

1. Translation Operator

The derivation of the transformation of solid spherical harmonics under translations is facilitated by discussing first the translation of general functions, and by deriving some auxiliary identities which will be needed in the sequel. The transformation of functions under translations could be discussed in just the same way as their behavior under rotations, provided that some characteristic features are observed which follow from the parallel translation of basis systems. However, because of the restricted space available, we will refrain from observing a strict analogy, especially as far as the discussion of the active and passive interpretation is concerned. Leaving the comparison with the former discussion of rotations to the reader, emphasis is placed on some other aspects of simple transformations.

The starting point for the transformation of functions is provided by Taylor's formula

$$f(x+h, y+k, z+l) = \sum_{t=0}^{\infty} \frac{1}{t!} \left[h\frac{\partial}{\partial x} + k\frac{\partial}{\partial y} + l\frac{\partial}{\partial z} \right]^{(t)} f(x, y, z) \quad (212)$$

which for rotations and a suitable choice of coordinates may be written as

$$f(\theta, \varphi \pm \alpha) = \sum_{t=0}^{\infty} (1/t!)[\pm\alpha\, \partial/\partial\varphi]^{(t)} f(\theta, \varphi) \quad (213)$$

and corresponds to Eq. (158). Equivalently one has for translations, putting $h = -x_0$, $k = -y_0$, $l = -z_0$, that

$$f(x - x_0, y - y_0, z - z_0) = (\hat{P}_\tau f)(x, y, z); \quad (214)$$

$$\hat{P}_\tau = e^{-\mathbf{r}_0\, \partial/\partial\mathbf{r}} = e^{-\mathbf{r}_0 \nabla_r} = \sum_{t=0}^{\infty} \frac{1}{t!}(-1)^t \left[x_0\frac{\partial}{\partial x} + y_0\frac{\partial}{\partial y} + z_0\frac{\partial}{\partial z} \right]^{(t)}. \quad (215)$$

This definition corresponds to that one chosen for the rotations, in as much as the operator effects a displacement of the field. The operator $\hat{P}_\tau$ causes a parallel translation of the field (i.e., the contours of the function) by $\mathbf{r}_0$, if this vector $\mathbf{r}_0$ specifies the direction and amount of displacement. In fact, the new function $(\hat{P}_\tau f)$, taken at the point $\mathbf{r}$ with coordinates x, y, z relative to the reference system $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$, has (there) the value of the original function f, taken at the point $(\mathbf{r} - \mathbf{r}_0)$ with coordinates $x - x_0$, $y - y_0$, $z - z_0$ relative to the same reference frame $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$.

If one thinks of the operator as referring to translations along the z axis, one has

$$f(x, y, z - z_0) = e^{-z_0\, \partial/\partial z} f(x, y, z) \quad (216)$$

or by formal rearrangement

$$f(x, y, z) = e^{z_0\, \partial/\partial z} f(x, y, z - z_0) \quad (217)$$

which amounts to

$$f(x, y, z) = e^{z_0\, \partial/\partial z'} f(x, y, z'). \quad (218)$$

Obviously, $e^{-z_0\, \partial/\partial z}$ is the operator which is inverse to $e^{z_0\, \partial/\partial z}$ not only in an algebraic but also in the geometrical sense, referring to a translation in opposite direction.

The following special cases, which will be needed later, may serve as examples:

The dependence of the potential of an electric point (and unit) charge on the distance r between charge and field point P is represented by the function $f(x, y, z) = 1/r$. Then, for convenience, the point charge is located in the origin O of a reference frame $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$, and the vector $\mathbf{r}$ points from O to P; the coordinates of P are x, y, z with respect to $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$. If the point charge is shifted by a small amount r_0 from O to O', this point charge has a potential $1/\rho$ at the point P, where the new distance vector $\boldsymbol{\rho}$ between point charge in O' and field point P is given by $\boldsymbol{\rho} = \mathbf{r} - \mathbf{r}_0$, assuming $r_0/r \ll 1$. As is well known, the potential $1/\rho$ at the point P, which is due to a point charge displaced by r_0 from the origin O, may be substituted by the sum of the potentials of all multipoles in the origin O. This means exactly that

$$1/\rho = e^{-\mathbf{r}_0\,\partial/\partial\mathbf{r}}(1/r) \tag{219}$$

if the operator is represented by Eq. (215). The brackets in the Taylor series can be expanded according to Eq. (116), thus producing the contributions of the multipoles as defined by Eq. (8). It turns out that this is in agreement with the Laplace expansion

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{{r_<}^k}{r_>^{k+1}} P_k(\cos\,\omega) = \frac{1}{({r_1}^2 + {r_2}^2 - 2r_1 r_2 \cos\,\omega)^{1/2}}, \tag{220}$$

$$P_l(\cos\,\omega) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_l^{m*}\left(\frac{\mathbf{r}_1}{r_1}\right) {Y_l}^m\left(\frac{\mathbf{r}_2}{r_2}\right), \tag{221}$$

where ω denotes the angle between the two unit vectors $\mathbf{r}_1/r_1$ and $\mathbf{r}_2/r_2$, which are centered at the same origin. In spherical coordinates, $\mathbf{r}_1/r_1$ is characterized by the direction (θ_1, φ_1). Furthermore, $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, and $r_<$ denotes the lesser, $r_>$ the greater of r_1 and r_2. To verify the aforementioned agreement with the Laplace expansion, one may put $\omega = \theta$ and $r_{12} = r'$ according to Fig. 9. Then it follows from Eq. (220) with Eq. (8) that

$$1/r' = e^{-c\partial/\partial z}(1/r); \qquad c/r' < 1; \qquad c/r < 1. \tag{222}$$

Obviously, c may not necessarily coincide with the z axis. With $c/r' > 1$, and the definitions illustrated in Fig. 10, one obtains

$$1/c = e^{-r'\partial/\partial q_3}(1/r); \qquad r'/c < 1, \qquad r'/r < 1. \tag{223}$$

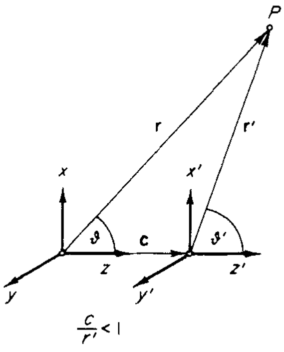


Fig. 9

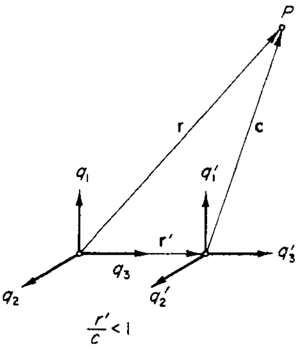


Fig. 10

This more general identity, obtained in the same way as the special formulas of this kind, has many uses. If q_3 denotes the axis which coincides with $\mathbf{r}'$, then Eq. (223) corresponds exactly to Eq. (219).

2. *Composite Derivatives of Legendre Functions*

Equation (218) shall be applied to the regular solid spherical harmonic

$$r^l P_l^m(\zeta)\cos m\varphi = f_{l,m}(r, \theta, \varphi). \tag{224}$$

For this purpose one needs the derivatives of this function given by

$$\left(\frac{\partial}{\partial z}\right)^k f_{l,m}(r, \theta, \varphi) = \frac{(l+m)!}{(l+m-k)!} f_{l-k,m}(r, \theta, \varphi) \tag{225}$$

if $k \leq l - |m|$.

The auxiliary relation of Eq. (225) follows from Eq. (36) with the help of the identities

$$\left.\begin{aligned} \xi &= x + iy = r \sin\theta\, e^{i\varphi}, \\ \eta &= x - iy = r \sin\theta\, e^{-i\varphi}, \\ \xi \cdot \eta &= x^2 + y^2 = r^2 \sin^2\theta = r^2(1 - \zeta^2), \\ z &= r\cos\theta, \qquad \zeta = \cos\theta; \\ \tfrac{1}{2}(\xi^m + \eta^m) &= (\xi\eta)^{m/2} \cos m\varphi \\ &= r^m(1 - \zeta^2)^{m/2} \cos m\varphi; \\ \frac{\partial}{\partial\xi} = \frac{1}{2}\left(\frac{\partial}{\partial x} + \frac{1}{i}\frac{\partial}{\partial y}\right)&, \qquad \frac{\partial}{\partial\eta} = \frac{1}{2}\left(\frac{\partial}{\partial x} - \frac{1}{i}\frac{\partial}{\partial y}\right). \end{aligned}\right\} \tag{226}$$

By means of these expressions one obtains from Eq. (36) the identity

$$r^l P_l^m(\zeta)\cos m\varphi = (-1)^m \frac{(l+m)!}{2^m(l-m)!m!}\frac{1}{2}(\xi^m+\eta^m)$$
$$\cdot\left[z^{l-m} - \frac{(l-m)(l-m-1)}{2\cdot(2m+2)} z^{l-m-2}\xi\eta + \frac{(l-m)\cdots(l-m-3)}{2\cdot 4\cdot(2m+2)(2m+4)} z^{l-m-4}(\xi\eta)^2 - + \cdots\right] \tag{227}$$

from which Eq. (225) immediately follows.

The following relationships, which may also be deduced from the foregoing, will prove useful later. For $m > 0$, two operators shall be defined by

$$\begin{aligned}\Omega_{m,+} &= (\partial/\partial\xi)^m + (\partial/\partial\eta)^m\\ \Omega_{m,-} &= [(\partial/\partial\xi)^m - (\partial/\partial\eta)^m]i.\end{aligned} \tag{228}$$

Then, because of

$$\frac{P_{l-m}(\zeta)}{r^{l-m+1}} = \frac{(-1)^{l-m}}{(l-m)!}\left(\frac{\partial}{\partial z}\right)^{l-m}\frac{1}{r} \tag{229}$$

the following relationship holds (if $l \geq m \geq 0$)

$$\Omega_{m,\pm}\left(\frac{P_{l-m}(\zeta)}{r^{l-m+1}}\right) = \frac{1}{2^{m-1}}\left(\frac{P_l^m(\zeta)}{r^{l+1}}\right)\cdot\begin{cases}\cos m\varphi\\ \sin m\varphi\end{cases} \tag{230}$$

as well as (if $l - m \geq m \geq 0$)

$$\Omega_{m,\pm}(r^l P_l(\zeta)) = \frac{1}{2^{m-1}}(r^{l-m}P_{l-m}^m(\zeta))\begin{cases}\cos m\varphi\\ \sin m\varphi\end{cases}. \tag{231}$$

The factor $\cos m\varphi$ applies for + index, the factor $\sin m\varphi$ applies for − index. Finally one has, according to Eq. (225), the relationship

$$\Omega_{m,\pm}\left(\frac{\partial}{\partial z}\right)^k(r^l P_l(\zeta)) = \frac{1}{2^{m-1}}\frac{l!}{(l-k)!}(r^{l-m-k}P_{l-m-k}^m(\zeta))\cdot\begin{cases}\cos m\varphi\\ \sin m\varphi\end{cases} \tag{232}$$

where $l - m - k \geq m \geq 0$.

B. Translation Along z Axis

1. Regular Harmonics

Equation (218) may be applied to the regular solid spherical harmonics. If the occurring derivatives are expressed by means of Eq. (225), one obtains

$$f_{l,m}(r,\theta,\varphi) = \sum_{k=0}^{l-|m|} \frac{z_0^{\,k}}{k!}\,\frac{(l+m)!}{(l+m-k)!}\, f_{l-k,m}(r',\theta',\varphi) \tag{233}$$

or

$$\left(\frac{r}{z_0}\right)^{l} P_l^{\,m}(\cos\theta) = \sum_{K=|m|}^{l} \binom{l+m}{K+m}\left(\frac{r'}{z_0}\right)^{K} P_K^{\,m}(\cos\theta'). \tag{234}$$

This is the desired formula which describes the translation of regular solid spherical harmonics (see Fig. 9, putting $c = z_0$). This relationship holds for small z_0, as has been proved so far. However, since the expansion given in Eq. (234) is finite and, therefore, the remainder vanishes, it should hold for all values of z_0. Hobson (1931) was the first to derive this important relationship. However, his derivation is much more cumbersome than the one given here. With the help of Eqs. (85)–(87) one shows that Eq. (234) holds for all m; hence, it may also be written for $m = |m|$.

For the purpose of a uniform notation, the result of Eq. (234) may be expressed as

$$\left(\frac{r_A}{R}\right)^{l} P_l^{\,m}(\cos\bar\theta_A) = \sum_{\lambda=|m|}^{l} \binom{l+m}{\lambda+m}\left(\frac{r_B}{R}\right)^{\lambda} P_\lambda^{\,m}(\cos\bar\theta_B). \tag{235}$$

Using the definition given by Eq. (131) and putting $\bar\varphi_A = \bar\varphi_B = \varphi$, as it is required by the problem considered here (see Fig. 11), one finally obtains

$$\mathcal{Y}_l^{\,m}\!\left(\frac{\mathbf{r}_A}{R}\right) = \sum_{\lambda=|m|}^{l} \binom{l+m}{\lambda+m}\mathcal{Y}_\lambda^{\,m}\!\left(\frac{\mathbf{r}_B}{R}\right)\frac{N_l^{\,m}}{N_\lambda^{\,m}}; \tag{236}$$

the normalization constants are those of Eq. (59).

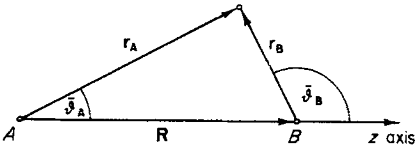


Fig. 11

2. *Irregular Harmonics*

Now the translation of an irregular solid spherical harmonic along the *z* axis from the original center *A* to a new center *B* will be considered. Such an operation produces infinite series expansions as the irregular harmonics contain negative powers of the length of the local vector. Since the expansion terms exhibit a similar dependence on the local vector, the location of the field point *P* is important for convergence properties. *P* may be a distance *r* apart from center *A* and a distance *r'* apart from center *B*, both centers *A* and *B* being separated by a distance *c*. Then, two cases are to be distinguished: In the first place the point *P* may be located outside a sphere of radius $\overline{AB}$ with center *B* (see Fig. 12a). Then, the distance of point *P* from center *B* is greater than the distance $\overline{AB}$ over which the function is translated. In the second place, the point *P* may be located inside the aforementioned sphere (see Fig. 12b). Then, the distance of point *P* from center *B* is smaller than the displacement of the function from *A* to *B*.

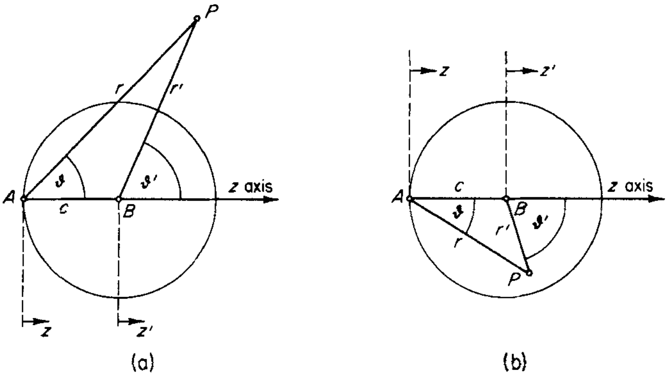


Fig. 12

a. Distance of P greater than displacement. If $c/r' < 1$, Taylor's expansion of $1/r$ is given by

$$\frac{1}{r} = \sum_{k=0}^{\infty} \frac{c^k}{k!} \left(\frac{\partial}{\partial z'}\right)^k \frac{1}{r'}; \qquad (237)$$

see Eq. (218) and Figs. 9 and 12a. Considering that $x = x'$, $y = y'$, $z = z' + c$, the application of the operator $\Omega_{m,+}(\partial/\partial z)^{l-m}$ with respect to either the unprimed or the primed coordinates yields the relation

$$\Omega_{m,+}\left(\frac{\partial}{\partial z}\right)^{l-m}\frac{1}{r}=\sum_{k=0}^{\infty}\frac{c^k}{k!}\Omega'_{m,+}\left(\frac{\partial}{\partial z'}\right)^{l-m+k}\frac{1}{r'} \tag{238}$$

or by virtue of Eqs. (229) and (230)

$$\frac{P_l^m(\zeta)}{r^{l+1}}=\sum_{k=0}^{\infty}\frac{c^k}{k!}(-1)^k\frac{(l-m+k)!}{(l-m)!}\frac{P_{l+k}^m(\zeta')}{r'^{l+k+1}}. \tag{239}$$

Since $r' = r_>$ and $c = r_<$, it is expedient to write this for later purposes as

$$\frac{P_l^m(\cos\theta)}{r^{l+1}}=\sum_{k=0}^{\infty}(-1)^k\binom{l+k-m}{l-m}\frac{r_<{}^k}{r_>^{l+k+1}}P_{l+k}^m(\cos\theta_>) \tag{240}$$

if $\theta_>$ denotes the angle between $\mathbf{r}_>$ and the z axis.

Since the derivation of the last identity was based upon the use of the operator $\Omega_{m,+}$, it has been shown so far that this formula holds for non-negative m. With the help of Eq. (64), which relates P_l^m to P_l^{-m}, it can be proved that Eq. (240) holds for all m.

b. Distance of P smaller than displacement. If $r'/c < 1$, one can expand in an analogous manner

$$\frac{1}{r}=\sum_{k=0}^{\infty}\frac{(r')^k}{k!}\left(\frac{\partial}{\partial q_3'}\right)^k\frac{1}{c} \tag{241}$$

where $c = (q_1{}^2 + q_2{}^2 + q_3'^2)^{1/2}$ (see Fig. 10). This may be written as

$$\frac{1}{r}=\sum_{k=0}^{\infty}(-1)^k\frac{(r')^k}{c^{k+1}}P_k(\cos\theta') \tag{242}$$

with $r = [x^2 + y^2 + (z' + c)^2]^{1/2}$ (see Fig. 12b). Due to

$$\left(\frac{\partial}{\partial z}\right)^l\frac{1}{r}=\left(\frac{\partial}{\partial z'}\right)^l\frac{1}{r}=\left(\frac{\partial}{\partial c}\right)^l\frac{1}{[x^2+y^2+(z'+c)^2]^{1/2}}, \tag{243}$$

considering that $z = z' + c$, one has

$$\left(\frac{\partial}{\partial z}\right)^l\frac{1}{r}=\left(\frac{\partial}{\partial c}\right)^l\sum_{k=0}^{\infty}(-1)^k\frac{(r')^k}{c^{k+1}}P_k(\cos\theta'), \tag{244}$$

and according to Eq. (8), if l is replaced by $l - m$, one finally obtains

$$\frac{P_{l-m}(\cos\theta)}{r^{l-m+1}} = \sum_{k=0}^{\infty}(-1)^k\binom{l-m+k}{k}\cdot\frac{(r')^k}{c^{l-m+k+1}}P_k(\cos\theta'). \tag{245}$$

The application of the operator $\Omega_{m,+}$ produces the "solid" associated Legendre functions from the corresponding simple ones. Hence, with the substitution $k - m = K$, one obtains

$$\frac{P_l^m(\cos\theta)}{r^{l+1}} = \sum_{K=|m|}^{\infty}(-1)^{K+m}\binom{l+K}{m+K}\frac{(r')^K}{c^{l+K+1}}P_K^m(\cos\theta'). \tag{246}$$

Because of $r' = r_<$ and $c = r_>$, with $\theta' = \theta_<$ being the angle between $\mathbf{r}_<$ and the z axis, there follows

$$\frac{P_l^m(\cos\theta)}{r^{l+1}} = \sum_{K=|m|}^{\infty}(-1)^{K+m}\binom{l+K}{l-m}\frac{r_<^K}{r_>^{l+K+1}}P_K^m(\cos\theta_<). \tag{247}$$

Although derived for positive m, this identity holds for all values of m. This may be shown by following the arguments of the previous paragaph.

c. General formula. The expansion of $r^{-l-1}P_l^m(\cos\theta)$, which is centered at A, into functions which are centered at B, has been given for the following two cases:

Either one has $c/r' < 1$ with the point P outside the sphere of radius $c = \overline{AB}$ about center B, then the expansion is given by Eq. (240); or one has $r'/c < 1$ with the point P inside that sphere, then the expansion is given by Eq. (247). Because of

$$P_\lambda^\kappa(1) = P_\lambda^\kappa(\cos 0) = \delta_{\kappa,0}, \qquad P_\lambda(1) = 1, \tag{248}$$

both identities can be combined into one formula as follows (see Fig. 11)

$$\frac{P_l^m(\cos\bar\theta_A)}{r_A^{l+1}} = \sum_{\lambda=0}^{\infty}\frac{r_<^\lambda}{r_>^{l+\lambda+1}}\sum_{\mu=-\lambda+m}^{\lambda+m}(-1)^{\lambda+m+\mu} \cdot\binom{l+\lambda-\mu}{l-m}P_{l+\lambda}^{\mu}(\cos\bar\theta_>)\cdot P_\lambda^{m-\mu}(\cos\bar\theta_<) \tag{249}$$

where

$$\left.\begin{array}{l} r_> = \text{the larger of} \\ r_< = \text{the smaller of} \end{array}\right\} R,\ r_B; \qquad \begin{array}{l} \bar\theta_> = \text{polar angle of } \mathbf{r}_>, \\ \bar\theta_< = \text{polar angle of } \mathbf{r}_<. \end{array} \tag{250}$$

C. General Translation

1. Formulation of Translation

In this section the translation of solid spherical harmonics from center A to center B shall be considered without the restriction, observed so far, that B lies on the z axis of a coordinate system centered in A. Now, two orthogonal, "parallel shifted" coordinate systems will be considered; one of them, spanned by the three orthogonal unit vectors $\mathbf{e}_1{}^A$, $\mathbf{e}_2{}^A$, $\mathbf{e}_3{}^A$, may have its origin at A. The other reference frame, which is obtained from the first one by translating it along an arbitrary direction and leaving all corresponding axes parallel to each other, has the unit vectors $\mathbf{e}_1{}^B$, $\mathbf{e}_2{}^B$, $\mathbf{e}_3{}^B$, centered at B. The point B has the spherical coordinates $(R, \theta_{AR}, \varphi_{AR})$ with respect to the reference system $\mathbf{e}_1{}^A$, $\mathbf{e}_2{}^A$, $\mathbf{e}_3{}^A$, if the distance $\overline{AB}$ is denoted by R. It is most helpful that the "lined-up" position of the atomic coordinate systems (which is illustrated in Fig. 14) can be obtained from their "parallel, shifted" position (shown in Fig. 13) by the following rotation, which is simultaneously applied to both reference systems $\mathbf{e}^A$ and $\mathbf{e}^B$:

Utilizing Eulerian angles, the rotation is carried out in three steps which may be described for the frame $\mathbf{e}^A$, although each coordinate system is rotated in the same manner about its origin, which is fixed, leaving the rotated $\mathbf{e}_i{}^A$ parallel to the rotated $\mathbf{e}_i{}^B$ $(i = 1, 2, 3)$ (see Fig. 15).

(1) The original frame is rotated by φ_{AR} about the $\mathbf{e}_3$ axis. This leads to: $\mathbf{e}_1{}^A \to \mathbf{e}_1^{A'}$ ($\mathbf{e}_1^{A'}$ falls into plane E which also contains $\mathbf{e}_3{}^A$, $\mathbf{e}_3{}^B$, $\mathbf{R}$.)

$$\mathbf{e}_2{}^A \to \mathbf{e}_2^{A'};$$
$$\mathbf{e}_3{}^A = \mathbf{e}_3^{A'} \text{ (remains unchanged).}$$

(2) The new frame is rotated by θ_{AR} about the $\mathbf{e}_2^{A'}$ axis. Then

$\mathbf{e}_1^{A'} \to \mathbf{e}_1^{A''}$ ($\mathbf{e}_1^{A''}$ is pointing down within plane E),
$\mathbf{e}_2^{A'} = \mathbf{e}_2^{A''}$ (unchanged),
$\mathbf{e}_3^{A'} \to \mathbf{e}_3^{A''}$ ($\mathbf{e}_2^{A''}$ coincides with $\mathbf{R}$).

(3) The new frame is rotated by π about the $\mathbf{e}_3^{A''}$ axis (i.e., about $\mathbf{R}$). Thereby

$\mathbf{e}_1^{A''} \to \bar{\mathbf{e}}_1{}^A$ ($\bar{\mathbf{e}}_1{}^A$ points upward within plane E),
$\mathbf{e}_2^{A''} \to \bar{\mathbf{e}}_2{}^A = -\mathbf{e}_2^{A''}$,
$\mathbf{e}_3^{A''} = \bar{\mathbf{e}}_3{}^A$ (in $\mathbf{R}$).

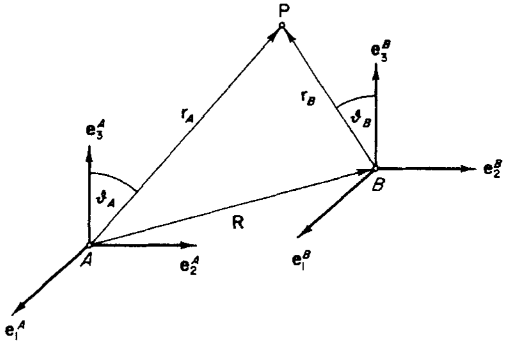


Fig. 13

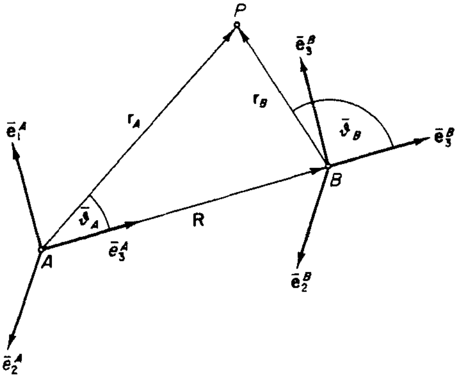


Fig. 14

This rotation, which is—according to Eq. (182e)—denoted by $\Omega = [\varphi_{AR}, \theta_{AR}, \pi]$, transforms the "parallel, shifted" position of the two coordinate systems into their "lined-up" position. Of course, the inverse rotation $\Omega^{-1} = [-\pi, -\theta_{AR}, -\varphi_{AR}]$ will cause the transformation of the "lined-up" positions into the "shifted" ones.

A field point P has the $\begin{Bmatrix}\text{spherical}\\ \text{Cartesian}\end{Bmatrix}$coordinates

$$\begin{Bmatrix}(r_A, \theta_A, \varphi_A)\\ (x_A, y_A, z_A)\end{Bmatrix} \tag{251a}$$

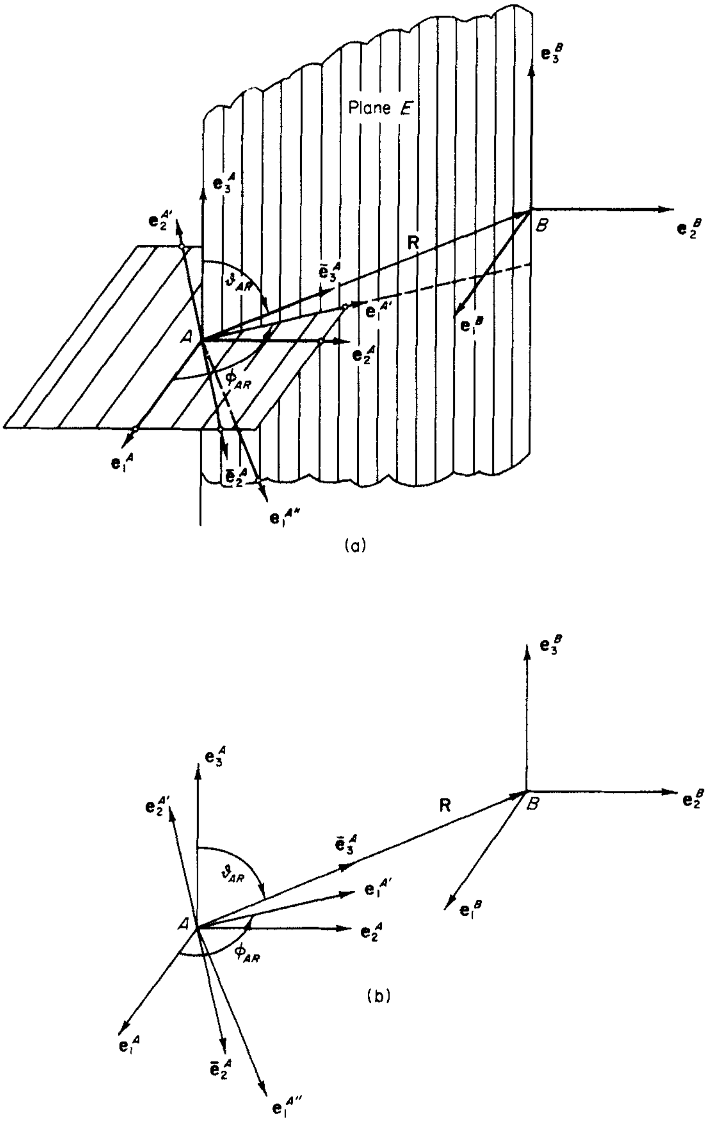

Plane E
e_3^B
e_3^A
$e_2^{A'}$
R
B
e_2^B
$\bar{e}_3^A$
ϑ_{AR}
$e_1^{A'}$
e_1^B
A
e_2^A
ϕ_{AR}
e_1^A
$\bar{e}_2^A$
$e_1^{A''}$
(a)
e_3^B
e_3^A
$e_2^{A'}$
R
B
e_2^B
$\bar{e}_3^A$
ϑ_{AR}
$e_1^{A'}$
e_1^B
A
e_2^A
ϕ_{AR}
(b)
e_1^A
$\bar{e}_2^A$
$e_1^{A''}$

Fig. 15

with respect to the reference system $\mathbf{e}_1{}^A$, $\mathbf{e}_2{}^A$, $\mathbf{e}_3{}^A$, however,

$$\begin{Bmatrix} (r_A, \bar{\theta}_A, \bar{\varphi}_A) \\ (\bar{x}_A, \bar{y}_A, \bar{z}_A) \end{Bmatrix} \tag{251b}$$

with respect to the reference system $\bar{\mathbf{e}}_1{}^A$, $\bar{\mathbf{e}}_2{}^A$, $\bar{\mathbf{e}}_3{}^A$; the local vector is $\overrightarrow{AP} = \mathbf{r}_A$. The same field point P has the corresponding coordinates, carrying the index B, with respect to the reference frame with its origin at B. Then the local vector is $\overrightarrow{BP} = \mathbf{r}_B$. It is convenient to introduce the vectors

$$\boldsymbol{\rho}_A = \mathbf{r}_A/R, \qquad \boldsymbol{\rho}_B = \mathbf{r}_B/R, \tag{252}$$

and the following abbreviations for the sets of spherical coordinates which characterize these vectors:

$$\begin{aligned} a &= (\rho_A, \theta_A, \varphi_A), & b &= (\rho_B, \theta_B, \varphi_B), \\ \bar{a} &= (\rho_A, \bar{\theta}_A, \bar{\varphi}_A), & \bar{b} &= (\rho_B, \bar{\theta}_B, \bar{\varphi}_B). \end{aligned} \tag{253}$$

In the sequel we will proceed from formulas for the translation of spherical harmonics from A to B which are derived for the case that the atomic coordinate systems having origins at A and B are in a "lined-up" position. By rotations of these reference systems we search for generalizations of these formulas to the case that the atomic coordinate systems at the points A and B are in a "parallel, shifted" position.

2. *Regular Harmonics*

According to Eq. (236), one has for the "lined-up" position

$$\mathcal{Y}_l{}^m(\bar{a}) = \sum_{\lambda=|m|}^{l} A^m_{l,\lambda}\, \mathcal{Y}_\lambda{}^m(\bar{b}); \tag{254}$$

$$\begin{aligned} A^m_{l,\lambda} = A^{|m|}_{l,\lambda} &= \binom{l+m}{\lambda+m} N_l{}^m / N_\lambda{}^m \\ &= \frac{1}{(l-\lambda)!}\left[\frac{2l+1}{2\lambda+1}\cdot\frac{(l+m)!\,(l-m)!}{(\lambda+m)!\,(\lambda-m)!}\right]^{1/2}. \end{aligned} \tag{255}$$

With the rotation $\Omega = [\varphi_{AR}, \theta_{AR}, \pi]$, which was defined in Section IV,C,1, one obtains

$$\mathcal{Y}_l{}^m(a) = \sum_{\nu=-l}^{l} \mathcal{Y}_l{}^\nu(\bar{a})\, \mathbf{D}^{(l)*}_{m\nu}(\Omega), \tag{256}$$

$$\mathcal{Y}_\lambda{}^\nu(\bar{b}) = \sum_{\mu=-\lambda}^{\lambda} \mathcal{Y}_\lambda{}^\mu(b)\, \mathbf{D}^{(\lambda)}_{\mu\nu}(\Omega) \tag{257}$$

by virtue of Eqs. (204) and (189). If Eq. (254) is inserted into Eq. (256), it follows, observing Eq. (257), that

$$\mathcal{Y}_l^m(a) = \sum_{\lambda=0}^{l} \sum_{\mu=-\lambda}^{\lambda} \mathcal{Y}_\lambda^\mu(b) C_{l,\lambda}^{m,\mu}(\theta_{AR}, \varphi_{AR}) \tag{258}$$

with

$$\sum_{\nu=-l}^{l} \sum_{\lambda=|\nu|}^{l} = \sum_{\lambda=0}^{l} \sum_{\nu=-\lambda}^{\lambda}, \tag{259}$$

$$C_{l,\lambda}^{m,\mu}(\theta_{AR}, \varphi_{AR}) = \sum_{\nu=-\lambda}^{\lambda} A_{l,\lambda}^{\nu} \mathbf{D}_{m\nu}^{(l)*}(\Omega) \mathbf{D}_{\mu\nu}^{(\lambda)}(\Omega). \tag{260}$$

Using Wigner's 3-*j* symbols, the coupling of the rotation matrices yields (Rose, 1957; Edmonds, 1957)

$$\mathbf{D}_{m\nu}^{(l)*}(\Omega) \mathbf{D}_{\mu\nu}^{(\lambda)}(\Omega) = (-1)^{m-\nu}(4\pi)^{1/2} \cdot \sum_L (2L+1)^{1/2} \cdot \begin{pmatrix} l & \lambda & L \\ -m & \mu & m-\mu \end{pmatrix} \begin{pmatrix} l & \lambda & L \\ -\nu & \nu & 0 \end{pmatrix} Y_L^{m-\mu}(\theta_{AR}, \varphi_{AR}). \tag{261}$$

The sum is over all values of the integer L for which

$$\max(|l-\lambda|, |m-\mu|) \leq L \leq l + \lambda. \tag{262}$$

In this connection, the special element of the rotation matrix as defined by Eq. (207) proved useful:

$$\mathbf{D}_{m-\mu,0}^{(L)*}(\Omega) = [4\pi/(2L+1)]^{1/2} Y_L^{m-\mu}(\theta_{AR}, \varphi_{AR}). \tag{263}$$

Furthermore,

$$C_{l,\lambda}^{m,\mu} = \sum_L (-1)^m \begin{pmatrix} l & \lambda & L \\ -m & \mu & m-\mu \end{pmatrix} Y_L^{m-\mu}(\theta_{AR}, \varphi_{AR}) B_{l,\lambda}^L \tag{264}$$

with

$$B_{l,\lambda}^L = [4\pi(2L+1)]^{1/2} \sum_{\nu=-\lambda}^{\lambda} (-1)^\nu \begin{pmatrix} l & \lambda & L \\ -\nu & \nu & 0 \end{pmatrix} A_{l,\lambda}^{\nu}. \tag{265}$$

Because of $A_{l,\lambda}^{|\nu|} = A_{l,\lambda}^{\nu}$ and

$$\begin{pmatrix} l & \lambda & L \\ -\nu & \nu & 0 \end{pmatrix} = (-1)^{l+\lambda+L} \begin{pmatrix} l & \lambda & L \\ \nu & -\nu & 0 \end{pmatrix}, \tag{266}$$

one has $B_{l,\lambda}^{L} = 0$ if $(l + \lambda + L)$ is odd. Another simplification is possible with the help of the following special 3-j symbol (Edmonds, 1957):

$$\begin{pmatrix} j_1 & j_2 & j_1 + j_2 \\ m_1 & m_2 & -(m_1 + m_2) \end{pmatrix} = (-1)^{j_1 + j_2 + m_1 + m_2} \cdot \left[\frac{(2j_1)!(2j_2)!(j_1 + j_2 + m_1 + m_2)!(j_1 + j_2 - m_1 - m_2)!}{(2j_1 + 2j_2 + 1)!(j_1 + m_1)!(j_1 - m_1)!(j_2 + m_2)!(j_2 - m_2)!} \right]^{1/2} . \tag{267}$$

With $j_1 = l - \lambda$, $j_2 = \lambda$, $m_1 = 0$, $m_2 = \nu$, one obtains

$$A_{l,\lambda}^{\nu} = (-1)^{l+\nu} \left[\frac{2l+1}{2\lambda+1} \frac{(2l+1)!}{(2l-2\lambda)!(2\lambda)!} \right]^{1/2} \begin{pmatrix} l & \lambda & l-\lambda \\ -\nu & \nu & 0 \end{pmatrix} . \tag{268}$$

By virtue of the orthogonality relation (Edmonds, 1957)

$$\begin{aligned} \sum_{\nu=-\lambda}^{\lambda} \begin{pmatrix} l & \lambda & L \\ -\nu & \nu & 0 \end{pmatrix} \begin{pmatrix} l & \lambda & l-\lambda \\ -\nu & \nu & 0 \end{pmatrix} &= \frac{1}{2L+1} \delta_{L,l-\lambda} \\ &= \sum_{\substack{\mu=-l \\ (l \geq \lambda)}}^{l} \sum_{\nu=-\lambda}^{\lambda} \begin{pmatrix} l & \lambda & L \\ \mu & \nu & 0 \end{pmatrix} \begin{pmatrix} l & \lambda & l-\lambda \\ \mu & \nu & 0 \end{pmatrix} \\ &\quad \times \delta_{\mu+\nu,0} \end{aligned} \tag{269}$$

the terms $B_{l,\lambda}^{L}$ are substantially simplified; because they contain Kronecker's δ they reduce the sum of Eq. (264) to a single term. This term may be written in a particularly simple form if again Eq. (267) is applied, observing

$$\begin{pmatrix} j_1 & j_2 & j_1 + j_2 \\ m_1 & m_2 & -m_1 - m_2 \end{pmatrix} = \begin{pmatrix} l-\lambda & \lambda & l \\ m-\mu & \mu & -m \end{pmatrix} = \begin{pmatrix} l & \lambda & l-\lambda \\ -m & \mu & m-\mu \end{pmatrix} . \tag{270}$$

Then, one may put the coefficients in Eq. (258) equal to

$$C_{l,\lambda}^{m,\mu}(\theta_{AR}, \varphi_{AR}) = Q_{l,\lambda}^{m,\mu} Y_{l-\lambda}^{m-\mu}(\theta_{AR}, \varphi_{AR}) \tag{271}$$

with

$$Q_{l,\lambda}^{m,\mu} = \begin{pmatrix} l+m \\ \lambda+\mu \end{pmatrix} \frac{N_l^m}{N_\lambda^\mu} \frac{(2\pi)^{1/2}}{N_{l-\lambda}^{m-\mu}} . \tag{272}$$

According to Eq. (270), the $C_{l,\lambda}^{m,\mu}$ vanish if the condition

$$l - \lambda \geqq |m - \mu| , \tag{273}$$

which is also imposed on the summations of Eq. (258), is not fulfilled.

The desired solution is given by Eq. (258) together with Eqs. (271)–(273). This result describes the translation of a regular solid spherical harmonic from a center A to another center B if parallel and shifted atomic coordinate systems are attached to A and B .

Further simplifications of the formulas will be considered in the sequel. Here it may be noted that, of course, the new formulas encompass the special cases which were discussed above and from which they were developed. As a check, one may consider the case that R goes to zero. Then, because of the factor $R^{l-\lambda}$, which enters Eq. (258) due to the definitions of Eqs. (252) and (253), the terms of the right-hand side of Eq. (258) vanish except if the summation index λ is equal to l and, due to Eq. (273), μ is equal to m. This yields $\mathscr{Y}_l^m(\mathbf{r}_A) = \mathscr{Y}_l^m(\mathbf{r}_B)$, hence $A = B$.

3. *Irregular Harmonics*

The formulas of the irregular harmonics are to be derived in the same manner as those of the regular harmonics. In Section IV,B,2 the transformation properties of irregular harmonics under translations along the z axis were considered. Now these functions will be subject to rotations as discussed above, in order to generalize the identities obtained for the special case of z-axis translation.

a. Distance of P greater than displacement. With the definitions given by Eqs. (132) and (253), and with $\overline{AB} = R$, $\mathbf{r}_< = \mathbf{R}$, $\mathbf{r}_> = \mathbf{r}_B$, $\mathbf{r} = \mathbf{r}_A$, Eq. (240) becomes

$$\mathscr{Z}_l^m(\bar{a}) = \sum_{\lambda=0}^{\infty} (-1)^\lambda H_{l,\lambda}^m \, \mathscr{Z}_{l+\lambda}^m(\bar{b}); \tag{274}$$

$$H_{l,\lambda}^m = \binom{l+\lambda-m}{l-m} \frac{N_l^m}{N_{l+\lambda}^m}. \tag{275}$$

Since the $\mathscr{Z}_l^m$ transform under rotations just like the $\mathscr{Y}_l^m$, one obtains, making use of Eqs. (256) and (257),

$$\mathscr{Z}_l^m(a) = \sum_{\lambda=0}^{\infty} \sum_{\kappa=-(l+\lambda)}^{l+\lambda} \mathscr{Z}_{l+\lambda}^\kappa(b) E_{l,\lambda}^{m,\kappa}(\theta_{AR}, \varphi_{AR}); \tag{276}$$

$$E_{i,\lambda}^{m,\kappa}(\theta_{AR}, \varphi_{AR}) = \sum_{\nu=-l}^{l} (-1)^\lambda H_{l,\lambda}^\nu \, \mathbf{D}_{m\nu}^{(l)*}(\Omega) \mathbf{D}_{\kappa\nu}^{(l+\lambda)}(\Omega). \tag{277}$$

The coupling of the rotation matrices yields

$$\mathbf{D}^{(l)*}_{m\nu}(\Omega)\mathbf{D}^{(l+\lambda)}_{\kappa\nu}(\Omega) = (-1)^{m-\nu}(4\pi)^{1/2}\sum_{L}(2L+1)^{1/2}$$

$$\cdot\begin{pmatrix} l & l+\lambda & L \\ -m & \kappa & m-\kappa \end{pmatrix}\begin{pmatrix} l & l+\lambda & L \\ -\nu & \nu & 0 \end{pmatrix}$$

$$\cdot Y_L^{m-\kappa}(\theta_{AR}, \varphi_{AR}); \tag{278}$$

$$\max(\lambda, |m-\kappa|) \le L \le 2l+\lambda; \qquad \lambda \ge 0. \tag{279}$$

With the help of Eq. (267), one obtains

$$H^{\nu}_{l,\lambda} = (-1)^{l+\lambda+\nu}\left[\frac{2l+1}{2(l+\lambda)+1}\,\frac{(2l+2\lambda+1)!}{(2l)!(2\lambda)!}\right]^{1/2}\begin{pmatrix} l & \lambda & l+\lambda \\ -\nu & 0 & \nu \end{pmatrix}. \tag{280}$$

By virtue of the orthogonality relations of the 3-j symbols, the summation over ν contributes again a Kronecker symbol $\delta_{L,\lambda}$ in Eq. (277). If then the single 3-j symbol $\left(\begin{smallmatrix} l & l+\lambda & \lambda \\ -m & \kappa & m-\kappa \end{smallmatrix}\right)$, which is left in the sum of all terms with the summation index L, is expressed by factorials according to Eq. (267), one obtains a simpler $E^{m,\kappa}_{l,\lambda}(\theta_{AR}, \varphi_{AR})$ which is nonvanishing only if

$$\lambda \ge |m-\kappa|. \tag{281}$$

This means, however, that

$$\sum_{\substack{\lambda=0 \\ (\lambda\ge|m-\kappa|)}}^{\infty}\;\sum_{\kappa=-(l+\lambda)}^{l+\lambda} = \sum_{\lambda=0}^{\infty}\;\sum_{\kappa=-\lambda+m}^{\lambda+m}. \tag{282}$$

The desired result is then

$$\mathscr{X}_l^m(\mathbf{r}_A) = \sum_{\lambda=0}^{\infty}\;\sum_{\kappa=-\lambda+m}^{\lambda+m}\mathscr{X}^{\kappa}_{l+\lambda}(\mathbf{r}_B)\mathscr{Y}_{\lambda}^{m-\kappa}(\mathbf{R})$$

$$\cdot(-1)^{m+\lambda+\kappa}\binom{l+\lambda-\kappa}{l-m}\frac{(2\pi)^{1/2}N_l^m}{N_{\lambda}^{m-\kappa}N^{\kappa}_{l+\lambda}}. \tag{283}$$

b. Distance of P smaller than displacement. Now one has $\overline{AB} = R$, $\mathbf{r}_< = \mathbf{r}_B$, $\mathbf{r}_> = \mathbf{R}$, $\mathbf{r} = \mathbf{r}_A$; Eq. (247) becomes

$$\mathscr{X}_l^m(\bar{a}) = \sum_{\lambda=|m|}^{\infty}(-1)^{\lambda+m}K^m_{l,\lambda}\mathscr{Y}_{\lambda}^m(\bar{b}); \tag{284}$$

$$K^m_{l,\lambda} = \binom{l+\lambda}{l-m}\frac{N_l^m}{N_{\lambda}^m}. \tag{285}$$

Applying relationships which correspond to those of Eqs. (256) and (257), one arrives at the result

$$\mathscr{X}_l^m(a) = \sum_{\nu=-l}^{l} \sum_{\lambda=|\nu|}^{\infty} (-1)^{\lambda+\nu} K_{l,\lambda}^{\nu} \sum_{\kappa=-\lambda}^{\lambda} \mathscr{Y}_{\lambda}^{\kappa}(b) \mathbf{D}_{m\nu}^{(l)*}(\Omega) \mathbf{D}_{\kappa\nu}^{(\lambda)}(\Omega). \tag{286}$$

The relevant relationship for the product of two matrix elements of the rotation matrices is given by Eq. (278) if, there, λ is replaced by $\lambda - l$; the summation limits are now

$$\max(|l-\lambda|, |m-\kappa|) \leq L \leq l + \lambda. \tag{287}$$

With

$$\sum_{\nu=-l}^{l} \sum_{\lambda=|\nu|}^{\infty} = \sum_{\lambda=0}^{\infty} \sum_{\nu=\max(-l,-\lambda)}^{\min(l,\lambda)} \tag{288}$$

and

$$K_{l,\lambda}^{\nu} = (-1)^{l+\lambda} \left[\frac{2l+1}{2\lambda+1} \frac{(2l+2\lambda+1)!}{(2l)!(2\lambda)!} \right]^{1/2} \begin{pmatrix} l & \lambda & l+\lambda \\ -\nu & \nu & 0 \end{pmatrix}, \tag{289}$$

the orthogonality relations of the 3-j symbols reduce the sum of all ν terms to a Kronecker symbol $\delta_{L,\,l+\lambda}$, which in its turn reduces the sum of all L terms also to a single term. The remaining special 3-j symbol can again be expressed by factorials according to Eq. (267). Finally one obtains the result:

$$\mathscr{X}_l^m(\mathbf{r}_A) = \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \mathscr{Y}_{\lambda}^{-\mu}(\mathbf{r}_B) \mathscr{X}_{l+\lambda}^{m+\mu}(\mathbf{R}) \cdot (-1)^{\lambda+\mu} \binom{l+\lambda-(m+\mu)}{l-m} \frac{(2\pi)^{1/2} N_l^m}{N_{\lambda}^{-\mu} N_{l+\lambda}^{m+\mu}}. \tag{290}$$

c. General formula. The two cases to be distinguished were determined by the following definitions, the sphere with radius $\overline{AB} = R$ being centered at B:

field point P "outside" sphere: $\mathbf{r}_> = \mathbf{r}_B$, $\mathbf{r}_< = \mathbf{R}$,
field point P "inside" sphere: $\mathbf{r}_> = \mathbf{R}$, $\mathbf{r}_< = \mathbf{r}_B$.

Both cases may be described by *one* formula if in Eq. (283) the following substitution is made: $\kappa - m = \mu$. Then, the general formula is given by

$$\mathscr{X}_l^m(\mathbf{r}_A) = \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \mathscr{Y}_{\lambda}^{-\mu}(\mathbf{r}_<) \mathscr{X}_{l+\lambda}^{m+\mu}(\mathbf{r}_>) \cdot (-1)^{\lambda+\mu} \binom{l+\lambda-(m+\mu)}{l-m} \frac{(2\pi)^{1/2} N_l^m}{N_{\lambda}^{-\mu} N_{l+\lambda}^{m+\mu}}. \tag{291}$$

Obviously,

$$\mathbf{r}_A = \mathbf{R} + \mathbf{r}_B = \mathbf{r}_> + \mathbf{r}_< . \tag{292}$$

This formula describes the translation of an irregular solid spherical harmonic from a center A to a new center B, the translation vector $\mathbf{R}$ ($\mathbf{R} = \overrightarrow{AB}$) being arbitrary. The vector $\mathbf{R}$ connects the origins A and B of two "parallel and shifted" coordinate systems. For the "lined-up" position of these coordinate systems with common z axes, Eq. (291) reduces to Eq. (249) which deals with this special case.

D. Addition Theorems

1. Symmetrization of Translation Identities

According to Eqs. (258), (271)–273), and Eqs. (252) and (253), an arbitrary translation of regular solid spherical harmonics is accomplished by

$$\mathcal{Y}_l^m(a) = \sum_{\substack{\lambda=0 \\ (l-\lambda \geq |m-\mu|)}}^{l} \sum_{\mu=-\lambda}^{\lambda} \mathcal{Y}_\lambda^\mu(b) Y_{l-\lambda}^{m-\mu}(\theta_{AR}, \varphi_{AR}) Q_{l,\lambda}^{m,\mu}; \tag{293}$$

$$Q_{l,\lambda}^{m,\mu} = \binom{l+m}{\lambda+\mu} \frac{N_l^m}{N_\lambda^\mu} \frac{(2\pi)^{1/2}}{N_{l-\lambda}^{m-\mu}}. \tag{294}$$

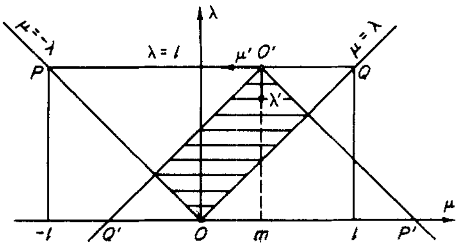
With the help of

$$\lambda' = l - \lambda, \qquad \mu' = m - \mu, \tag{295}$$

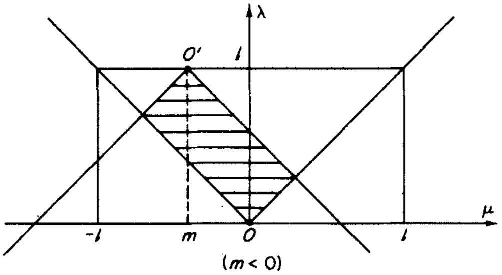
the summation, which is to be carried out in Eq. (293), allows the simple illustration given in Figs. 16a and 16b. In each diagram of this type the running summation indices λ and μ are assigned to axes of an orthogonal coordinate system such that each point within a certain region represents a term of the sum if the boundaries of this region are determined by the summation limits. Now, without the restriction

$$l - \lambda \geq |m - \mu|, \qquad \lambda' \geq |\mu'|, \tag{296}$$

the summation of Eq. (293) would require to sum over all those points in the λ, μ plane which are located on and within the right triangle OPQ of Fig. 16a, which is encompassed by the straight lines $\lambda = l$, $\mu = \lambda$, and $\mu = -\lambda$. The transformation given by Eq. (295) corresponds to a change of the reference systems of the summation indices: The new system with axes λ', μ' has its origin O' somewhere on the straight line $\lambda = l$ such that O' has the coordinates $\lambda = l$ and $\mu = m$ with respect to the old λ, μ system.



(m > 0)
(a)



(m < 0)
(b)

Fig. 16

The coordinates of a point may be denoted in the usual manner by a bracket in such a way that, for instance, the position of O' referred to the λ, μ system is characterized by (l, m). Different positions of O' on the straight line $\lambda = l$ belong to different values of m. All points with $\lambda' \geq |\mu'|$ are located in the triangle $O'P'Q'$ which is congruent with the triangle OPQ. Hence, all points in the λ, μ plane over which one has to sum according to Eq. (293) are located within the shaded area of Fig. 16a or 16b, respectively, where the two triangles OPQ and $O'P'Q'$ overlap. This region of overlap is a rectangle whose location is unambiguously determined by the position of its corner points O and O'. In the λ, μ plane the point O has the coordinates $(0, 0)$, whereas the point O' has the coordinates (l, m). If however one thinks of the coordinates as referring to the λ', μ' frame, then O is characterized by (l, m), but O' is specified by $(0, 0)$. Hence, the summation limits to be observed in Eq. (293) can unambiguously be written as

$$\sum_{(\lambda,\mu)=(0,0)}^{(l,m)} = \sum_{(\lambda,\mu)} = \sum_{\lambda=0}^{l} \sum_{\mu=\max(-\lambda,\, \lambda-l+m)}^{\mu=\min(\lambda,\, -\lambda+l+m)} . \tag{297}$$

Thereby, Eq. (293) can be expressed in a compact form as follows

$$\mathcal{Y}_l^m(\mathbf{r}_A) = \sum_{(\lambda,\mu)=(0,0)}^{(l,m)} \mathcal{Y}_\lambda^\mu(\mathbf{r}_B)\mathcal{Y}_{l-\lambda}^{m-\mu}(\mathbf{R})Q_{l,\lambda}^{m,\mu}. \tag{298}$$

As the derivation showed, this relationship holds *for arbitrarily separated, but parallel coordinate systems with origins A and B,* which are connected by the arbitrary vector $\mathbf{R}$; cf. Fig. 17.

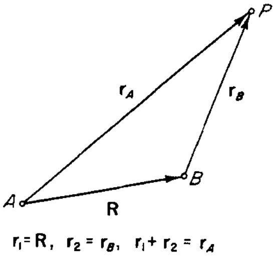


Fig. 17

The new notation has not only formal advantages by providing a simpler way of writing the expressions, but moreover it enables us to recognize the symmetry properties of the new relationships.

If one substitutes

$$\mathbf{r}_A = \mathbf{R} + \mathbf{r}_B = \mathbf{r}_B + \mathbf{R} \tag{299}$$

in Eq. (298), it becomes clear that the arguments $\mathbf{R}$ and $\mathbf{r}_B$ of the harmonics should be exchangable, since such an exchange has no effect on the left-hand side of Eq. (298), and thus must have no effect on its right-hand side either. This indeed is true since, because of

$$Q_{l,\lambda}^{m,\mu} = Q_{l,l-\lambda}^{m,m-\mu} = Q_{l,\lambda'}^{m,\mu'}, \tag{300}$$

$$\sum_{(\lambda,\mu)} = \sum_{(\lambda',\mu')}, \tag{301}$$

Eq. (298) reads

$$\mathcal{Y}_l^m(\mathbf{r}_A) = \sum_{(\lambda',\mu')=(0,0)}^{(l,m)} \mathcal{Y}_{l-\lambda'}^{m-\mu'}(\mathbf{r}_B)\mathcal{Y}_{\lambda'}^{\mu'}(\mathbf{R})Q_{l,\lambda'}^{m,\mu'}. \tag{302}$$

This, however, corresponds to an exchange of $\mathbf{R}$ with $\mathbf{r}_B$ in Eq. (298), if in Eq. (302) the new summation indices are again denoted by their unprimed counterparts, utilizing the fact that the notation of summation indices may always be subject to change. The symmetry of Eq. (299) is related to the symmetry of Figs. 16a,b. It is obvious that one obtains the most general form of the identity given by Eq. (298) if one writes

$$\mathcal{Y}_l^m(\mathbf{r}_1 + \mathbf{r}_2) = \sum_{(\lambda,\mu)} \mathcal{Y}_{l-\lambda}^{m-\mu}(\mathbf{r}_1)\mathcal{Y}_\lambda^\mu(\mathbf{r}_2)Q_{l,\lambda}^{m,\mu}. \tag{303}$$

This emphasizes the fact that it is immaterial for this relationship where the vectors are centered. In fact, one may think of the vectors $\mathbf{r}_1$, $\mathbf{r}_2$, and $(\mathbf{r}_1 + \mathbf{r}_2)$ as being centered at the same origin; then, $(\mathbf{r}_1 + \mathbf{r}_2)$ is the main diagonal of the parallelogramm spanned by $\mathbf{r}_1$ and $\mathbf{r}_2$, having its vertex in the origin. Besides the special symmetry that the relations are invariant under an operation which exchanges $\mathbf{r}_1$ and $\mathbf{r}_2$, there is an additional symmetry which is based on the way the vectors are connected. For instance, an inversion, which takes any vector $\mathbf{r}$ into $-\mathbf{r}$, does not change the relationships either, since the change of parity is compensated by the same factor

$$(-1)^l = (-1)^{l-\lambda}(-1)^\lambda \tag{304}$$

on both sides of the equation.

For the irregular solid spherical harmonics, the general relationship has already been given by Eq. (291) together with Eq. (292). Since the two vectors occurring in the arguments of this identity are to be distinguished by their lengths, the formulas given by Eqs. (291) and (292) do not exhibit a symmetry like the identities of the regular harmonics, as discussed above. Instead, the argument of the regular harmonic $\mathcal{Y}_\lambda^{-\mu}$, which is one factor of each term of the expansion given by Eq. (291), is always defined by the vector $\mathbf{r}_<$, whereas the argument of the other factor, being an irregular harmonic $\mathcal{Z}_{l+\lambda}^{m+\mu}$, is always given by $\mathbf{r}_>$ in order to guarantee the convergence of the expansion; then, higher terms $r_<^\lambda/r_>^{l+\lambda+1}$ go asymptotically to zero.

2. *Factorless Addition Theorems for Modified Harmonics*

The identities given by Eqs. (293) and (303) can be simplified further. This simplification will prove important in the sequel. Defining

$$W_l^m = [\tfrac{1}{2}(2l+1)(l-m)!(l+m)!]^{1/2}(2\pi)^{-1/2} \tag{305}$$

one has

$$\mathcal{Y}_l^m(\mathbf{r}_1 + \mathbf{r}_2) = \sum_{(\lambda,\mu)} \mathcal{Y}_{l-\lambda}^{m-\mu}(\mathbf{r}_1)\mathcal{Y}_\lambda^\mu(\mathbf{r}_2)\frac{W_l^m}{W_{l-\lambda}^{m-\mu}W_\lambda^\mu}. \tag{306}$$

This expression suggests the introduction of modified regular solid spherical harmonics of the type

$$\hat{\mathscr{Y}}_l^m(\mathbf{r}) = \frac{1}{W_l^m} \mathscr{Y}_l^m(\mathbf{r})$$

$$= r^l Y_l^m(\theta, \varphi) \left[\frac{2l+1}{4\pi} (l-m)!(l+m)! \right]^{-1/2}. \tag{307}$$

With the help of these functions Eq. (303) becomes simply

$$\hat{\mathscr{Y}}_l^m(\mathbf{r}_1 + \mathbf{r}_2) = \sum_{(\lambda,\mu)=(0,0)}^{(l,m)} \hat{\mathscr{Y}}_{l-\lambda}^{m-\mu}(\mathbf{r}_1) \hat{\mathscr{Y}}_\lambda^\mu(\mathbf{r}_2) \tag{308}$$

in which no explicit numerical factors occur (Steinborn, 1969).

For the relationships of the irregular harmonics, an analogous simplification can be obtained if the following modified irregular solid spherical harmonics are defined:

$$\hat{\mathscr{Z}}_l^m(\mathbf{r}) = \frac{1}{r^{l+1}} Y_l^m(\theta, \varphi) \left[\frac{4\pi}{2l+1} (l-m)!(l+m)! \right]^{1/2}. \tag{309}$$

The numerical factor, which has been absorbed by the newly defined function, may be expressed by W_l^m of Eq. (305). Then

$$\hat{\mathscr{Z}}_l^m(\mathbf{r}) = \frac{1}{r^{l+1}} Y_l^m(\theta, \varphi) \frac{4\pi}{2l+1} W_l^m. \tag{310}$$

Thereby all expansion coefficients disappear, replacing the identity of Eq. (291) by the "factorless" expansion

$$\hat{\mathscr{Z}}_l^m(\mathbf{r}_> + \mathbf{r}_<) = \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} (-1)^{\lambda+\mu} \hat{\mathscr{Y}}_\lambda^{-\mu}(\mathbf{r}_<) \hat{\mathscr{Z}}_{l+\lambda}^{m+\mu}(\mathbf{r}_>); \qquad |\mathbf{r}_<| < |\mathbf{r}_>|. \tag{311}$$

E. Relation to Previous Work

The first relation of the kind discussed here was derived by Hobson (1931) who explained the translation of solid harmonics along the z axis. A generalization of Hobson's formulas was given by Rose (1958) while investigating the electrostatic interaction of two charge distributions. He discovered a relationship that implied an arbitrary translation of a regular solid spherical harmonic and can be expressed as follow:

$$\mathscr{Y}_l^m(\mathbf{r}_A) = (-1)^{l+m} \sum_\lambda \sum_\mu \mathscr{Y}_\lambda^\mu(\mathbf{r}_B) \mathscr{Y}_{l-\lambda}^{m-\mu}(\mathbf{R})$$

$$\cdot \begin{pmatrix} l & \lambda & l-\lambda \\ -m & \mu & m-\mu \end{pmatrix} \left[\frac{4\pi(2l+1)(2l+1)!}{[2(l-\lambda)+1]!(2\lambda+1)!} \right]^{1/2}. \tag{312}$$

Similar relations for translations of regular as well as irregular solid harmonics were given by Sack (1964), Chiu (1964), and Dahl and Barnett (1965). Sack obtained his relationships while investigating related differential equations and, recently (1972), presented another interesting approach, based on a new generating function for spherical harmonics. Chiu (1964) applied the theory of irreducible tensors, making heavy use of Clebsch–Gordon coefficients. He also noted that Rose's expansion is essentially of one-center character and considered the case of $\mathbf{r}_A$ being a sum of three vectors leading to bipolar expansions of solid harmonics. Dahl and Barnett (1965) started from specialized formulas and verified generalized formulas by induction.

In the context of quantum–chemical calculations some workers have developed formulas for the displacement of entire atomic orbitals (Löwdin, 1956; Harris and Michels, 1965, where further references can be found). Occasional attempts to use expansions of solid harmonics for the evaluation of molecular integrals may be noted (Pitzer *et al.*, 1962; Geller, 1963).

The methods employed by some of the aforementioned investigators are ingenious and achieve important results in an elegant manner. Many of the earlier identities are however not sufficiently simplified nor adapted for practical use, containing awkward factors, sums over vanishing terms, etc. The scope, consistency, and physical concepts of the present approach have led us into the subject via more elementary and straightforward derivations. The reported formulas contain previous results as special cases.

The final simplicity of the given two-center results furthermore leads to previously unnoticed generalizations, pertaining to solid harmonics on *arbitrary* numbers of centers. Such *multicenter* expansions are of general usefulness. We shall discuss in particular quantum chemical applications.

F. Polypolar Expansions

1. *Regular Harmonics*

Coordinate systems at arbitrary centers are assumed to have parallel x-, parallel y-, and parallel z-axes, respectively, This allows various interpretations and applications of the formulas, since an argument vector may be shifted if its length and direction in space remain unchanged, its origin being arbitrary.

Falling back upon the modified solid spherical harmonics defined by Eq. (307), the relationship of Eq. (308) can be written as

$$\mathcal{Y}_l^m(\mathbf{r}_1+\mathbf{r}_2) = \sum_{\lambda_1,\mu_1}\sum_{\lambda_2,\mu_2} \mathcal{Y}_{\lambda_1}^{\mu_1}(\mathbf{r}_1)\mathcal{Y}_{\lambda_2}^{\mu_2}(\mathbf{r}_2) \tag{313}$$

where the sums are over the values of the indices λ_i and μ_i $(i = 1, 2)$ which are determined by

$$\begin{gathered} 0 \le \lambda_i \le l, \qquad -\lambda_i \le \mu_i \le \lambda_i, \qquad i = 1, 2; \\ l = \lambda_1 + \lambda_2, \qquad m = \mu_1 + \mu_2. \end{gathered} \tag{314}$$

This permits a generalization as far as the number of argument vectors is concerned. It follows immediately that the following relationship holds for any number n of argument vectors involved

$$\mathcal{Y}_L^M(\mathbf{r}_1+\mathbf{r}_2+\cdots+\mathbf{r}_n) = \sum_{l_1 m_1}\sum_{l_2 m_2}\sum_{l_3 m_3}\cdots\sum_{l_n m_n} \mathcal{Y}_{l_1}^{m_1}(\mathbf{r}_1)\mathcal{Y}_{l_2}^{m_2}(\mathbf{r}_2)\cdots\mathcal{Y}_{l_n}^{m_n}(\mathbf{r}_n) \tag{315}$$

where the indices run over the ranges defined by

$$0 \le l_i \le L, \qquad -l_i \le m_i \le l_i, \qquad i = 1, 2, 3, \ldots, n, \tag{316}$$

and are furthermore restricted by the conditions

$$L = \sum_{i=1}^{n} l_i, \qquad M = \sum_{i=1}^{n} m_i. \tag{317}$$

This shows how to expand a regular solid spherical harmonic whose argument consists of a sum of n arbitrary local vectors. To illustrate this general result, some interpretations and possible applications may be noted.

So far we used to interpret Eq. (313), which represents the case $n = 2$ of Eq. (315), as a translation of a regular solid harmonic from a center A to another center B. In particular if this relationship is to be applied in quantum-mechanical calculations, A and B may denote two atomic centers and P may denote the position of an electron, if the vectors $\mathbf{r}_1$, $\mathbf{r}_2$, and $(\mathbf{r}_1 + \mathbf{r}_2)$ are defined as illustrated in Fig. 17.

An alternative interpretation of Eq. (313) and Fig. 17 would be, however, to consider A still as an atomic center but B and P as the positions of two different electrons, so that $\overrightarrow{PB} = \mathbf{r}_{12}$ is the interelectronic vector. In this case, Eq. (313) yields the one-center or monopolar expansion of $\mathcal{Y}_l^m(\mathbf{r}_{12})$.

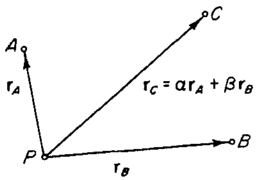
Another important conclusion may be drawn from Eq. (313) as follows.

One may give to the vectors $\mathbf{r}_1$, $\mathbf{r}_2$, $(\mathbf{r}_1 + \mathbf{r}_2)$ the meanings illustrated in Fig. 18, where A, B, C are three atomic centers and P the position of an electron, with the constraint that P lies in the plane determined by A, B, C. Within this limitation, one can always write

$$(\overrightarrow{CP}) = \alpha(\overrightarrow{AP}) + \beta(\overrightarrow{BP}) \tag{318}$$

whence

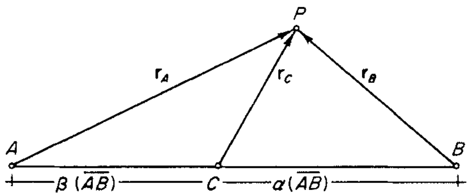
$$\mathbf{r}_C = \alpha\mathbf{r}_A + \beta\mathbf{r}_B . \tag{319}$$



$r_1 = \alpha r_A$, $r_2 = \beta r_B$, $r_1 + r_2 = r_C$

Fig. 18

Therefore, the definitions of $\mathbf{r}_1$, $\mathbf{r}_2$, and $(\mathbf{r}_1 + \mathbf{r}_2)$ chosen in Fig. 18 turn Eq. (313) into a formula expressing the splitting of a regular solid spherical harmonic on center C into regular solid harmonics on centers A and B. It may be noted that the distances between the centers do not enter the equation. A case of particular interest is that when the center C lies on the straight line connecting A and B as shown in Fig. 19. In this case, the electronic position P can be chosen completely arbitrarily, since there is always a plane containing A, B, C, and P. Furthermore, under these conditions α and β are given by



$r_1 = \alpha r_A$, $r_2 = \beta r_B$, $r_1 + r_2 = r_C$, $\alpha + \beta = 1$

Fig. 19

$$\alpha = \overline{BC}/\overline{AB}, \qquad \beta = \overline{AC}/\overline{AB}, \qquad \alpha + \beta = 1, \tag{320}$$

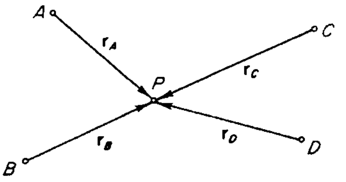
as may be taken from Fig. 19. One obviously has the following simple vector relationships:

$$\begin{aligned}\mathbf{r}_C &= \alpha(\overrightarrow{AB}) + \mathbf{r}_B = -\beta(\overrightarrow{AB}) + \mathbf{r}_A \\ &= \alpha\mathbf{r}_A + \beta\mathbf{r}_B; \qquad \alpha + \beta = 1.\end{aligned} \tag{321}$$

For the case $n = 3$, Eq. (315) takes the form

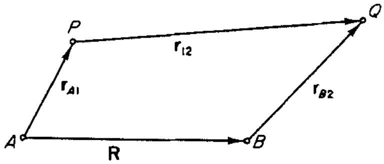
$$\hat{\mathscr{Y}}_L{}^M(\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3) = \sum_{l_1 m_1} \sum_{l_2 m_2} \hat{\mathscr{Y}}_{l_1}^{m_1}(\mathbf{r}_1)\hat{\mathscr{Y}}_{l_2}^{m_2}(\mathbf{r}_2)\hat{\mathscr{Y}}_{L-l_1-l_2}^{M-m_1-m_2}(\mathbf{r}_3). \tag{322}$$

Two possible geometric interpretations are illustrated in Figs. 20 and 21.



$r_1 = \alpha r_A$, $r_2 = \beta r_B$, $r_3 = \gamma r_C$, $r_1 + r_2 + r_3 = r_D$

Fig. 20



$r_1 = -r_{A1}$, $r_2 = r_{B2}$, $r_3 = R$, $r_1 + r_2 + r_3 = r_{12}$

Fig. 21

In Fig. 20, the points A, B, C, D are four arbitrary atomic centers and P is the arbitrary position of an electron. For the general position of the vectors it is always possible to expand

$$(\overrightarrow{DP}) = \alpha(\overrightarrow{AP}) + \beta(\overrightarrow{BP}) + \gamma(\overrightarrow{CP}), \tag{323}$$

$$\mathbf{r}_D = \alpha\mathbf{r}_A + \beta\mathbf{r}_B + \gamma\mathbf{r}_C. \tag{324}$$

With the definitions

$$\mathbf{r}_1 = \alpha\mathbf{r}_A, \qquad \mathbf{r}_2 = \beta\mathbf{r}_B, \qquad \mathbf{r}_3 = \gamma\mathbf{r}_C, \qquad \mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3 = \mathbf{r}_D, \tag{325}$$

which correspond to Fig. 20, Eq. (322) yields, therefore, an identity for splitting a regular solid spherical harmonic on center D into similar harmonics on the arbitrary centers A, B, C. Such a splitting is, therefore, always possible and, moreover, the vectors between the four centers enter the formula in no way.

On the other hand, in Fig. 21, the points A and B are atomic positions and the points P and Q are the positions of two different electrons. The interelectronic vector $\mathbf{r}_{12}$ can then be expressed as

$$\mathbf{r}_{12} = \mathbf{R}_{AB} + \mathbf{r}_{B2} - \mathbf{r}_{A1}. \tag{326}$$

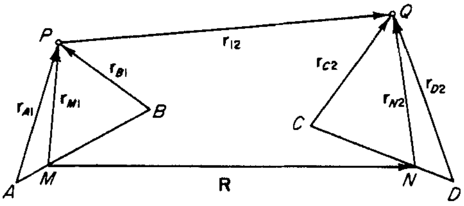
With the identification

$$\mathbf{r}_1 = -\mathbf{r}_{A1}, \qquad \mathbf{r}_2 = \mathbf{r}_{B2}, \qquad \mathbf{r}_3 = \mathbf{R}_{AB}, \qquad \mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3 = \mathbf{r}_{12}, \tag{327}$$

Eq. (322) yields the bipolar expansion of $\mathscr{Y}_L^M(\mathbf{r}_{12})$.

Another application of quantum-mechanical interest is possible for the case $n = 5$. As illustrated in Fig. 22, the points A, B, C, D are four atomic positions, M is a point on the line $\overline{AB}$, just as N is a point on the line $\overline{CD}$, P is the position of the first electron, and Q is the position of the second electron, P and Q both being arbitrary. Under these conditions, one can write (see Fig. 22)

$$\begin{aligned} \mathbf{r}_{12} &= \mathbf{R}_{MN} + \mathbf{r}_{N2} - \mathbf{r}_{M1}, \\ \mathbf{r}_{M1} &= \alpha\mathbf{r}_{A1} + \beta\mathbf{r}_{B1}, \qquad \mathbf{r}_{N2} = \gamma\mathbf{r}_{C2} + \delta\mathbf{r}_{D2}, \\ \alpha + \beta &= 1, \qquad\qquad\qquad \gamma + \delta = 1, \end{aligned} \tag{328}$$



$r_{M1} = \alpha r_{A1} + \beta r_{B1}$ $\qquad$ $r_{N2} = \gamma r_{C2} + \delta r_{D2}$

$r_1 = -\alpha r_{A1},\ r_2 = -\beta r_{B1},\ r_3 = \gamma r_{C2},\ r_4 = \delta r_{D2},\ r_5 = R$

Fig. 22

with $\overline{BM} = \alpha(\overline{AB})$, $\overline{AM} = \beta(\overline{AB})$, and $\overline{CN} = \delta(\overline{CD})$, $\overline{DN} = \gamma(\overline{CD})$. Putting

$$\begin{aligned} \mathbf{r}_1 &= -\alpha\mathbf{r}_{A1}, \qquad \mathbf{r}_2 = -\beta\mathbf{r}_{B1} \\ \mathbf{r}_3 &= \gamma\mathbf{r}_{C2}, \qquad \mathbf{r}_4 = \delta\mathbf{r}_{D2}, \qquad \mathbf{r}_5 = \mathbf{R}, \end{aligned} \tag{329}$$

the interelectronic vector becomes

$$\begin{aligned} \mathbf{r}_{12} &= \mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3 + \mathbf{r}_4 + \mathbf{r}_5 \\ &= -\alpha\mathbf{r}_{A1} - \beta\mathbf{r}_{B1} + \gamma\mathbf{r}_{C2} + \delta\mathbf{r}_{D2} + \mathbf{R}. \end{aligned} \tag{330}$$

Inserting this sum on the left-hand side of Eq. (315), observing $n = 5$, will yield a quadrupolar expansion of $\mathscr{Y}_L^M(\mathbf{r}_{12})$. Moreover, in this expansion the choices of the points M and N on the $\overline{AB}$ and $\overline{CD}$ axes are arbitrary, yielding various possible values of α, β, γ, δ, and $\mathbf{R}$.

Finally, it may be noted that application of Eq. (315) to n vectors satisfying the condition

$$\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3 + \cdots + \mathbf{r}_n = 0 \tag{331}$$

yields the relation

$$\sum_{l_1 m_1} \sum_{l_2 m_2} \cdots \sum_{l_n m_n} \mathscr{Y}_{l_1}^{m_1}(\mathbf{r}_1) \mathscr{Y}_{l_2}^{m_2}(\mathbf{r}_2) \cdots \mathscr{Y}_{l_n}^{m_n}(\mathbf{r}_n) = \delta_{0,L} \tag{332}$$

where the summations are subject to the constraints

$$\sum_{i=1}^{n} l_i = L, \qquad 0 \le l_i \le L, \tag{333a}$$

$$\sum_{i=1}^{n} m_i = M, \qquad -l_i \le m_i \le l_i, \tag{333b}$$

with L and M being arbitrary constants satisfying the relationships

$$L \ge 0, \qquad -L \le M \le L. \tag{333c}$$

2. *Irregular Harmonics*

It has been shown above that the following "factorless expansion" of modified irregular solid spherical harmonics exists:

$$\mathscr{Z}_l^m(\mathbf{r}_> + \mathbf{r}_<) = \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} (-1)^{\lambda+\mu} \mathscr{Y}_\lambda^{-\mu}(\mathbf{r}_<) \mathscr{Z}_{l+\lambda}^{m+\mu}(\mathbf{r}_>). \tag{334}$$

This identity involves modified regular and irregular solid harmonics as defined by Eqs. (307) and (309), respectively. Each term of the infinite series expansion defined by the right-hand side of Eq. (334) contains a modified regular harmonic and a modified irregular harmonic multiplied together. Of course, in a relationship of this kind, the arguments of the regular solid harmonics must be given by $\mathbf{r}_<$ whereas the arguments of the irregular solid hamonics of the expansion must be given by $\mathbf{r}_>$ in order to achieve convergence; here $\mathbf{r}_<$ is the lesser and $\mathbf{r}_>$ is the greater of the two arbitrary vectors whose sum defines the argument of the original modified irregular solid harmonic which is expanded. Hence

$$|\mathbf{r}_<| < |\mathbf{r}_>|. \tag{335}$$

There are several possible extensions of Eq. (334) to a sum of $(n + 1)$ vectors $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_{n+1}$, depending upon the relative positions of these vectors. First, it is always possible to arrange any $(n + 1)$ arbitrary vectors in an order such that

$$|\mathbf{r}_i| \le |\mathbf{r}_{i+1} + \mathbf{r}_{i+2} + \cdots + \mathbf{r}_{n+1}|, \qquad i = 1, 2, \ldots, n. \tag{336}$$

Suppose this ordering is adopted for the $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{n+1}$, then the following generalization of Eq. (334) will hold

$$\begin{aligned}\mathscr{I}_L^M(\mathbf{r}_1+\mathbf{r}_2+\cdots+\mathbf{r}_{n+1}) = \sum_{l_1 m_1}\sum_{l_2 m_2}\cdots\sum_{l_n m_n}(-1)^{l_1+m_1+l_2+m_2+\cdots+l_n+m_n}\\ \cdot\mathscr{Y}_{l_1}^{-m_1}(\mathbf{r}_1)\mathscr{Y}_{l_2}^{-m_2}(\mathbf{r}_2)\cdots\mathscr{Y}_{l_n}^{-m_n}(\mathbf{r}_n)\\ \cdot\mathscr{I}_{L+l_1+l_2+\cdots+l_n}^{M+m_1+m_2+\cdots+m_n}(\mathbf{r}_{n+1})\end{aligned} \tag{337}$$

where the indices run over ranges defined by

$$0 \le l_i < \infty, \qquad -l_i \le m_i \le l_i, \qquad i = 1, 2, \ldots, n. \tag{338}$$

In certain specific cases it may, however, be possible to form partial sums $\mathbf{s}_1, \mathbf{s}_2, \mathbf{s}_3, \ldots, \mathbf{s}_{N+1}, (N < n)$,

$$\begin{aligned}\mathbf{s}_1 &= \mathbf{r}_1 + \mathbf{r}_2 + \cdots + \mathbf{r}_{n_1}\\ \mathbf{s}_2 &= \mathbf{r}_{n_1+1} + \mathbf{r}_{n_1+2} + \cdots + \mathbf{r}_{n_2}\\ \mathbf{s}_3 &= \mathbf{r}_{n_2+1} + \mathbf{r}_{n_2+2} + \cdots + \mathbf{r}_{n_3}\\ &\vdots\\ \mathbf{s}_{N+1} &= \mathbf{r}_{n+1}\end{aligned} \tag{339}$$

in such a way that

$$\mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 + \cdots + \mathbf{s}_{N+1} = \mathbf{r}_1 + \mathbf{r}_2 + \cdots \mathbf{r}_{n+1} \tag{340}$$

and

$$|\mathbf{s}_k| < |\mathbf{s}_{k+1} + \mathbf{s}_{k+2} + \cdots + \mathbf{s}_{N+1}|, \qquad k = 1, 2, \ldots, \mathrm{N}. \tag{341}$$

In such a case the following relation will be valid

$$\begin{aligned}\mathscr{I}_L^M(\mathbf{r}_1+\mathbf{r}_2+\cdots+\mathbf{r}_{n+1}) = \sum_{l_1 m_1}\sum_{l_2 m_2}\cdots\sum_{l_N m_N}(-1)^{l_1+m_1+l_2+m_2+\cdots+l_N+m_N}\\ \cdot\mathscr{Y}_{l_1}^{-m_1}(\mathbf{s}_1)\mathscr{Y}_{l_2}^{-m_2}(\mathbf{s}_2)\cdots\mathscr{Y}_{l_N}^{-m_N}(\mathbf{s}_N)\\ \cdot\mathscr{I}_{L+l_1+l_2+\cdots+l_N}^{M+m_1+m_2+\cdots+m_N}(\mathbf{r}_{n+1})\end{aligned} \tag{342}$$

where the indices run over the ranges defined by

$$0 \le l_k < \infty, \qquad -l_k \le m_k \le l_k, \qquad k = 1, 2, \ldots, N. \tag{343}$$

In Eq. (342) the identity of Eq. (315) can then be used to further decompose the regular harmonics $\mathscr{Y}_{l_k}^{-m_k}(\mathbf{s}_k)$, thereby yielding an expansion which appears simpler than that of Eq. (337) in as much as $(n - N)$ of the n summations are finite. Thus, the more vectors $\mathbf{r}_i$ can be combined into the partial sums $\mathbf{s}_k$, the fewer infinite summations will occur. It should be noted however that appropriate interchanges of summations will in fact transform Eq. (342) back into Eq. (337).

The various special cases and geometric interpretations discussed for the regular solid harmonics apply equally to expansions of the irregular solid harmonics. In particular the following important cases may be mentioned:

Taking the case illustrated in Fig. 17, and interpreting $\overrightarrow{PB}$ as the interelectronic vector $\mathbf{r}_{12}$, one obtains from Eq. (334)

$$\mathscr{Z}_L{}^M(\mathbf{r}_{12}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \mathscr{Y}_l^{m*}(\mathbf{r}_<)\mathscr{Z}_{L+l}^{M+m}(\mathbf{r}_>) \tag{344}$$

if

$$\mathbf{r}_{12} = \mathbf{r}_> - \mathbf{r}_< . \tag{345}$$

Here the following properties of spherical harmonics $\mathscr{Y}_l{}^m(\mathbf{r})$, which have the parity $(-1)^l$, have been used:

$$\mathscr{Y}_l{}^m(\mathbf{r}) = r^l Y_l{}^m(\theta, \varphi) = r^l Y_l{}^m(\mathbf{r}/r), \tag{346a}$$

$$\begin{aligned} \mathscr{Y}_l{}^m(-\mathbf{r}) &= r^l Y_l{}^m(\pi - \theta, \varphi + \pi) = r^l Y_l{}^m(-\mathbf{r}/r) \\ &= (-1)^l \mathscr{Y}_l{}^m(\mathbf{r}), \end{aligned} \tag{346b}$$

$$\mathscr{Y}_l{}^{m*}(\mathbf{r}) = (-1)^m \mathscr{Y}_l{}^{-m}(\mathbf{r}). \tag{347}$$

For $L = M = 0$, Eq. (344) yields the familiar Laplace expansion of r_{12}^{-1}.

On the other hand, a new form of the bipolar expansion can be obtained as follows. Application of the definitions embodied in Fig. 21 and Eqs. (326) and (327) yields the bipolar expansion for $\mathscr{Z}_L{}^M(\mathbf{r}_{12})$, viz.

$$\mathscr{Z}_L{}^M(\mathbf{r}_{12}) = \sum_{l_1 m_1} \sum_{l_2 m_2} (-1)^{l_1+m_1+l_2+m_2} \mathscr{Y}_{l_1}^{-m_1}(\mathbf{r}_1) \mathscr{Y}_{l_2}^{-m_2}(\mathbf{r}_2) \mathscr{Z}_{L+l_1+l_2}^{M+m_1+m_2}(\mathbf{r}_3) \tag{348}$$

where $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$ are chosen from $\mathbf{R}$, $\mathbf{r}_{B2}$, $-\mathbf{r}_{A1}$ in such a way that

$$|\mathbf{r}_1| < |\mathbf{r}_2 + \mathbf{r}_3|, \tag{349a}$$

$$|\mathbf{r}_2| < |\mathbf{r}_3|. \tag{349b}$$

It is obvious that

$$\mathbf{r}_{12} = \mathbf{R} + \mathbf{r}_{B2} - \mathbf{r}_{A1} = \mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3 . \tag{350}$$

This form of the bipolar expansion looks simpler than previously given forms as far as the factor $\mathscr{Z}_{L+l_1+l_2}^{M+m_1+m_2}(\mathbf{r}_3)$ is concerned. (See, for instance, Ruedenberg, 1967. Further references are given there.) Especially the "range conditions" of Eqs. (349a,b) differ significantly from those considered in previous discussions, in as much as Eq. (349a) involves the length of the vector $(\mathbf{r}_2 + \mathbf{r}_3)$. These range conditions, which govern the convergence properties, deserve investigation. For example, in order to insure *absolute* convergence it may be necessary to demand that the length of the vector representing the argument of the *irregular* solid spherical harmonic in each term of the series be greater than the sum of the lengths of the vectors representing the arguments of the *regular* solid spherical harmonics in the series, thus imposing stricter conditions than Eqs. (336), (341), (349). In addition to this fact pointed out by Sack (1972), explicit relationships between the new and previously known bipolar expansions deserve exploration.

A special case of the aforementioned bipolar expansion is that for the inverse of the interelectronic distance. From Eq. (348), again by putting $L = M = 0$, we obtain for the interelectronic repulsion the bipolar expansion

$$1/r_{12} = (4\pi)^{-1/2} \sum_{l_1 m_1} \sum_{l_2 m_2} (-1)^{l_1+m_1+l_2+m_2} \mathscr{Y}_{l_1}^{-m_1}(\mathbf{r}_1) \mathscr{Y}_{l_2}^{-m_2}(\mathbf{r}_2) \mathscr{Z}_{l_1+l_2}^{m_1+m_2}(\mathbf{r}_3). \tag{351}$$

In conclusion it may be emphasized again that in the foregoing derivations *any* vector $\mathbf{r}$ with Cartesian coordinates x, y, z is related to its spherical coordinates r, θ, φ by the standard definitions

$$\begin{aligned} x &= r \sin\theta \cos\varphi, \\ y &= r \sin\theta \sin\varphi, \\ z &= r \cos\theta. \end{aligned} \tag{352}$$

Equation (352) has been assumed throughout to express the relationship between $\mathbf{r}$ and r, θ, φ for *all* occurring vectors. This implies that the coordinate systems required at various points in space must be chosen such that they differ from each other by parallel displacements only; they may not be rotated against each other. The various possible applications of the formulas derived under these assumptions illustrate the advantages that are connected with the use of parallel atomic coordinate systems as stated at the beginning.

Appendix: List of Some Notations

I. Coordinates

Cartesian coordinates: x, y, z or x_i, $i = 1, 2, 3$, cf. Eq. (136).

Spherical coordinates: r, θ, φ in Eq. (10), Fig. 2; $a = (\rho_A, \theta_A, \varphi_A)$ with respect to reference frame centered on A. Radius vector $\boldsymbol{\rho}_A = \mathbf{r}_A/R$ in Eqs. (252) and (253). Direction $\omega = (\theta, \varphi)$ in Eqs. (204)–(207).

Elliptical coordinates: ξ, η, φ in Eq. (226).

2. Angles

Polar angle θ, azimuthal angle φ in Eq. (10). *Eulerian* angles α, β, γ in Eqs. (182a)–(182c).

3. Rotations

Rotations are characterized by *Eulerian* angles α, β, γ according to definition of Eqs. (182a)–(182c) and then specified by $R = [\alpha, \beta, \gamma]$ in Eq. (182e) or Ω in Eqs. (251)–(257).

4. Vectors

Local vectors characterizing the position of a field point: $\mathbf{r}$ or $\mathbf{x}$ in Eq. (136). A position vector centered at A may be denoted by $\mathbf{r}_A$ as in Figs. 13, 14, 17. This means only its components will be referred to the coordinate system with origin A. A vector centered at A and pointing to electron i is given by $\mathbf{r}_{Ai}$, see Fig. 21. Vectors specifying a *distance AB* are usually denoted by $\mathbf{R}$, cf. Fig. 17.

Basis vectors $\mathbf{e}_i$ $(i = 1, 2, 3)$, Eq. (136), are denoted by $\mathbf{e}_i{}^A$ or $\mathbf{e}_i{}^B$ if different reference systems are to be distinguished; in Section III,B the vectors $\mathbf{e}_i{}^B$ characterize a body-fixed frame, but $\mathbf{e}_i{}^A$ specify a non-body-fixed frame. However, in Section IV the $\mathbf{e}_i{}^A$ are the basis vectors of the frame centered at A, the $\mathbf{e}_i{}^B$ those of the atomic coordinate system centered at B.

Momentum vector $\mathbf{p}$ and *angular momentum* vector $\mathbf{L}$ are defined as usual by Eq. (38); for $\mathbf{L}^2$ see "operators."

5. Matrices

Row matrices contain covariant sets: $\mathbf{e}$ contains three basis vectors, Eq. (137). $\mathbf{Y}_l$ contains $2l + 1$ surface harmonics in standard order, Eq. (190).

Column matrices contain contravariant sets: $\mathbf{x}$ collects three components x_i as well as does $\mathbf{r}$, Eq. (137).

Square matrices come in two kinds:

Orthogonal matrices of rotations in coordinate space: $\mathbf{R}$ in Eqs. (140)–(151), $\mathbf{S}$ and $\mathbf{T}$ in Eqs. (153)–(157).

Unitary matrices of rotations in the function space of spherical harmonics: $\mathbf{D}^{(l)}(\alpha, \beta, \gamma)$ in Eqs. (185)–(191): $\mathbf{d}^{(l)}(\beta)$ in Eqs. (186) and (198)–(202).

6. Operators

Differential operators:

$\partial/\partial\mathbf{r} = \nabla_r$ in Eq. (38), $\Delta = (\partial/\partial\mathbf{r})^2$ in Eqs. (11), (12). Angular momentum operators L_x, L_y, L_z in Eq. (39), $\mathbf{L}^2$ in Eq. (12), shift operators L_+ and L_- in Eqs. (46) and (49). Operators of the kind $\Omega_{m,+}$ and $\Omega_{m,-}$ contain partial derivatives with respect to elliptical coordinates ξ, η; Eq. (228).

Rotation operators come in two kinds:

$\mathcal{R}$ as well as $\mathcal{S}$, $\mathcal{T}$, and $\mathcal{A}$ of Section III,A effect rotations of vectors in coordinate space.

$P_{\mathcal{R}}$ and $O_{\mathcal{R}}$ of Section III,B effect rotations of functions.

7. Functions

Symbols for *simple* functions: f or g. It is $\zeta = r\cos\theta$, Eq. (14). Functions transformed under rotations are denoted by $(P_{\mathcal{R}} f)$ or $(O_{\mathcal{R}} f)$, respectively; see Section III,B.

Special functions:

Legendre polynomials: $P_l(\zeta)$, Section II,A,1. Legendre associated functions: $P_l^m(\zeta)$, Section II,A,2; the normalized ones are $\mathcal{P}_l^m(\zeta)$, see Eqs. (34) and (35).

Spherical harmonics:

Surface spherical harmonics $Y_l^m(\theta, \varphi)$, Section II,B; Regular solid spherical harmonics $\mathcal{Y}_l^m(\mathbf{r})$, Eq. (131); Irregular solid spherical harmonics $\mathcal{Z}_l^m(\mathbf{r})$, Eq. (132).

Their respective modified definitions are denoted by $\mathscr{Y}_l^m(\mathbf{r})$ and $\mathscr{Z}_l^m(\mathbf{r})$, Eqs. (309) and (310).

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Molecular Integrals between Real and between Complex Atomic Orbitals

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I. Introduction

In the common method of choosing linear combinations of atomic orbitals (LCAO's) to construct molecular orbitals (MO's), a given molecular orbital φ_i may be written as

$$\varphi_i = \sum_{p=1}^{A} \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^{l} \chi_{n,l,m}(p) C_{p,i}^{n,l,m}. \tag{1}$$

Here $p = 1, 2, \ldots, A$ numbers the A atomic nuclei in the molecule. At each nucleus p, different atomic orbitals $\chi_{n,l,m}(p)$ are centered which may

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be Slater-type orbitals specified by the quantum numbers n, l, m. We may then write

$$\begin{aligned} \chi_{n,l,m}(p) &= f_n(r_p)\, Y_l^m(\theta_p, \varphi_p), \\ f_n(r_p) &= (2\zeta)^{n+1/2}[(2n)!]^{-1/2} r_p^{n-1} e^{-\zeta r_p}; \end{aligned} \tag{2}$$

r_p, θ_p, φ_p are spherical coordinates of an electron with respect to center p. $f_n(r_p)$ is a real function depending only on the radial distance r_p of the electron from origin p. Of course, one has for all n which are greater than some upper limit n_0

$$C_{p,i}^{n,l,m} = 0 \qquad \text{for} \quad n > n_0, \tag{3}$$

so that the expansion Eq. (1) in fact is limited to a finite number of atomic orbitals (AO's). This treatment is easily generalized to an extended basis set.

The $Y_l^m(\theta_p, \varphi_p)$ are spherical surface harmonics which in Condon–Shortley phases are given by

$$Y_l^m(\theta, \varphi) = (-1)^m \left[\frac{2l+1}{2} \frac{(l-m)!}{(l+m)!}\right]^{1/2} P_l^m(\cos\theta) \frac{e^{im\varphi}}{(2\pi)^{1/2}} \tag{4}$$

with the associated Legendre functions

$$P_l^m(\zeta) = (1-\zeta^2)^{m/2} \left(\frac{d}{d\zeta}\right)^{l+m} \frac{1}{2^l l!} (\zeta^2 - 1)^l, \qquad \zeta = \cos\theta. \tag{5}$$

They obey the condition (see Condon and Shortley, 1953)

$$Y_l^{m*}(\theta, \varphi) = (-1)^m Y_l^{-m}(\theta, \varphi), \qquad Y_l^0(\theta, \varphi) \text{ real}. \tag{6}$$

The atomic orbitals χ are then complex.

It is often of great advantage to work with complex AO's instead of real ones. The investigation of difficult molecular integrals, for instance, often necessitates a shift of AO's from one center to another, or to consider rotations of AO's in addition to their translations. These procedures are more easily done with complex AO's than with real ones, since for real AO's one has always to consider separately the different cases of m greater than, equal to, or less than zero. All formulas then break into at least three different formulas, whereas the use of complex atomic orbitals allows a more compact and flexible way of writing and doing the calculations.

The use of complex AO's, however, will in general lead to complex integrals over the interaction operator and four complex atomic orbitals. In the LCAO–MO approximation, the real molecular integrals for the electron interaction energy are then given in terms of these complex integrals. Obviously, the common restriction that the molecular orbitals φ_i should be real imposes restrictions on the evaluation of the (real) electron interaction integrals over MO's in terms of (complex) interaction integrals over AO's. These restrictions will be considered and the evaluation formulas derived in the following section.

There are, however, different possibilities to contract products of four complex quantities such that the sum of the resulting terms is real. Therefore, according to their practical use, the following ways will be discussed: Whereas in the first place, as mentioned above, electron interaction energy integrals between real MO's will be expressed by real and imaginary parts of complex integrals between complex AO's, in the second place a comparison is made of these results with the results of the usual expression of integrals between real MO's by integrals between real AO's. In the third place, integrals between real MO's are represented by integrals between real and imaginary parts of complex charge distributions. Finally, the equivalent procedures for overlap integrals are discussed.

II. Integrals between Real MO's Represented by Integrals between Complex AO's

A. General Formula

The electron interaction energy integrals between MO's are given by

$$[\varphi_a\varphi_b|\varphi_c\varphi_d] = \int d\mathbf{r}_1 \int d\mathbf{r}_2\, \varphi_a(1)\varphi_b(1)\frac{1}{r_{12}}\varphi_c(2)\varphi_d(2). \tag{7}$$

With the LCAO expression of the MO's given in Eq. (1), this becomes

$$[\varphi_a\varphi_b|\varphi_c\varphi_d] = \sum_{p,K,k}\ \sum_{q,L,l}\ \sum_{r,M,m}\ \sum_{s,N,n} [\varphi_a{}^p\varphi_b{}^q|\varphi_c{}^r\varphi_d{}^s] \tag{8}$$

with the abbreviations

$$\varphi_a{}^p = \sum_{\kappa=-k}^{k} \chi_{K,k,\kappa}(p)\mathbb{C}_{p,a}^{K,k,\kappa}, \qquad \varphi_b{}^q = \sum_{\lambda=-l}^{l} \chi_{L,l,\lambda}(q)\mathbb{C}_{q,b}^{L,l,\lambda}, \tag{9}$$

etc. To distinguish between the four sets (n, l, m) of the effective principal quantum number n, the angular momentum quantum number l, and the magnetic quantum number m of the AO functions given in Eq. (2), we introduce the sets

$$(K, k, \kappa), \qquad (L, l, \lambda), \qquad (M, m, \mu), \qquad (N, n, \nu). \tag{10}$$

These four sets will appear in the following expressions. Then, capital letters refer to principal quantum numbers, lowercase letters stand for angular momentum quantum numbers, whereas greek letters represent magnetic quantum numbers in these sets.

Due to our definitions, in the following formulas the index a, which specifies a certain MO, the index p, which specifies a center, and the set (K, k, κ) actually will always appear together. In this sense, the indices

$$a, p, (K, k, \kappa), \qquad b, q, (L, l, \lambda), \qquad c, r, (M, m, \mu), \qquad d, s, (N, n, \nu) \tag{11}$$

belong together, and if the original definitions are kept in mind, some of these indices may be dropped for convenience. Thus, Eq. (9) may be rewritten as

$$\begin{aligned} \varphi^p &= \sum_{\kappa=-k}^{k} \chi_k{}^\kappa \mathbb{C}_k{}^\kappa, & \varphi^q &= \sum_{\lambda=-l}^{l} \chi_l{}^\lambda \mathbb{C}_l{}^\lambda, \\ \varphi^r &= \sum_{\mu=-m}^{m} \chi_m{}^\mu \mathbb{C}_m{}^\mu, & \varphi^s &= \sum_{\nu=-n}^{n} \chi_n{}^\nu \mathbb{C}_n{}^\nu. \end{aligned} \tag{12}$$

In examples we will always refer to the functions with the b, q, (L, l, λ) set of indices.

According to Eq. (8) it is sufficient to consider the integral

$$[\varphi_a{}^p \varphi_b{}^q \,|\, \varphi_c{}^r \varphi_d{}^s]. \tag{13}$$

Obviously, the functions $\varphi_i{}^j$ with $(i, j) = (a, p)$, (b, q), (c, r), (d, s) have to be real in order to get the φ_i in Eq. (1) real. One has, therefore, the condition

$$\chi_{L,l,-\lambda}(q)\mathbb{C}_{q,b}^{L,l,-\lambda} = [\chi_{L,l,\lambda}(q)\mathbb{C}_{q,b}^{L,l,\lambda}]^*, \qquad \chi_{L,l,0}(q)\mathbb{C}_{q,b}^{L,l,0} = \text{real}, \tag{14}$$

which one may write as

$$\chi_l{}^{-\lambda}\mathbb{C}_l{}^{-\lambda} = [\chi_l{}^\lambda \mathbb{C}_l{}^\lambda]^*, \qquad \chi_l{}^0 \mathbb{C}_l{}^0 = \text{real}, \tag{15}$$

or even as

$$\chi^{-\lambda}\mathbb{C}^{-\lambda} = [\chi^\lambda \mathbb{C}^\lambda]^*, \qquad \chi^0 \mathbb{C}^0 = \text{real}. \tag{16}$$

Since $\chi_l{}^\lambda$ transforms under a complex conjugation like $Y_l{}^\lambda$, i. e.,

$$\chi_l{}^{\lambda *} = (-1)^\lambda \chi_l{}^{-\lambda}, \qquad \chi_l{}^0 = \text{real}, \tag{17}$$

the same holds true for $\mathbb{C}_l{}^\lambda$:

$$\mathbb{C}_l^{\lambda *} = (-1)^\lambda \mathbb{C}_l{}^{-\lambda}, \qquad \mathbb{C}_l{}^0 = \text{real}. \tag{18}$$

To facilitate the expression of the subsequent formulas in a compact way we introduce a special notation for complex quantities which have the same behavior under complex conjugation as the Y_l^m, namely like Eqs. (6), (17), (18). We define

$$\chi_l^\lambda = \langle\lambda\rangle^\lambda[z_l^{|\lambda|} + \zeta_\lambda z_l^{-|\lambda|} i], \qquad i \equiv (-1)^{1/2}, \tag{19}$$

where the $z_l^{\pm|\lambda|}$ are real. Hence, the real part of χ_l^λ is given by

$$\operatorname{Re} \chi_l^\lambda = \langle\lambda\rangle^\lambda z_l^{|\lambda|}, \tag{20}$$

whereas the imaginary part is given by

$$\operatorname{Im} \chi_l^\lambda = \langle\lambda\rangle^\lambda \zeta_\lambda z^{-|\lambda|}. \tag{21}$$

Here, $\langle\lambda\rangle$ stands for the sign of λ, and the following abbreviations are adopted:

$$\langle\lambda\rangle = \begin{cases} 1 & \text{if } \lambda \geq 0, \\ -1 & \text{if } \lambda < 0, \end{cases} \tag{22}$$

$$\zeta_\lambda = \langle\lambda\rangle - \delta_{\lambda,0} = \begin{cases} 1 & \text{if } \lambda > 0, \\ 0 & \text{if } \lambda = 0, \\ -1 & \text{if } \lambda < 0, \end{cases} \tag{23}$$

$$\delta_{\lambda,0} = \begin{cases} 1 & \text{if } \lambda = 0, \\ 0 & \text{if } \lambda \neq 0, \end{cases} \tag{24}$$

$$1 - \delta_{\lambda,0} = (\zeta_\lambda)^2 = \begin{cases} 0 & \text{if } \lambda = 0, \\ 1 & \text{if } \lambda \neq 0, \end{cases} \tag{25}$$

which have the properties

$$\zeta_{-\lambda} = -\zeta_\lambda, \tag{26}$$

$$\langle -\lambda\rangle = (2\delta_{\lambda,0} - 1)\langle\lambda\rangle = \begin{cases} -\langle\lambda\rangle & \text{if } \lambda \neq 0, \\ \langle\lambda\rangle & \text{if } \lambda = 0, \end{cases} \tag{27}$$

$$\langle -\lambda\rangle^{-\lambda} = (-\langle\lambda\rangle)^\lambda. \tag{28}$$

In this notation, apart from the sign, the real part of the complex quantity χ_l^λ is given by $z_l^{|\lambda|}$ and the imaginary part by $z_l^{-|\lambda|}$; thus the sign of the upper index α attached to the quantity z, which characterizes χ, indicates whether z_l^α belongs to the real part (if $\alpha \geq 0$) or to the imaginary part (if $\alpha < 0$) of the quantity χ_l^λ. The same shorthand notation is adopted for z as for χ, suppressing unimportant indices. In the same way we define

$$\mathbb{C}_l^\lambda = \langle\lambda\rangle^\lambda[x_l^{|\lambda|} + \zeta_\lambda x_l^{-|\lambda|} i], \qquad i \equiv (-1)^{1/2}. \tag{29}$$

With Eqs. (22)–(28), χ_l^{λ} defined by Eq. (19) has the property of Eq. (17), and $\mathbb{C}_l^{\lambda}$ defined by Eq. (29) has the property of Eq. (18). For the integral Eq. (13) one gets then, due to Eqs. (12) and with the definition Eq. (7),

$$[\varphi^p\varphi^q|\varphi^r\varphi^s] = \sum_{\kappa=-k}^{k}\sum_{\lambda=-l}^{l}\sum_{\mu=-m}^{m}\sum_{\nu=-n}^{n} \mathbb{C}_k{}^{\kappa}\mathbb{C}_l{}^{\lambda}\mathbb{C}_m{}^{\mu}\mathbb{C}_n{}^{\nu}[\chi_k{}^{\kappa}\chi_l{}^{\lambda}|\chi_m{}^{\mu}\chi_n{}^{\nu}]. \tag{30}$$

The complex quantity given by the product of four $\mathbb{C}$ factors may be split into real and imaginary parts:

$$\mathbb{C}^{\kappa}\mathbb{C}^{\lambda}\mathbb{C}^{\mu}\mathbb{C}^{\nu} = D_1^{\kappa\lambda\mu\nu} + iD_{-1}^{\kappa\lambda\mu\nu}, \tag{31}$$

while the integral over the atomic orbitals may be split in a similar manner:

$$[\chi^{\kappa}\chi^{\lambda}|\chi^{\mu}\chi^{\nu}] = Z_1^{\kappa\lambda\mu\nu} + iZ_{-1}^{\kappa\lambda\mu\nu}. \tag{32}$$

Here we have dropped the indices k, l, m, n, as well. The $D_{\pm 1}, Z_{\pm 1}$ are real. Since $[\varphi^p\varphi^q|\varphi^r\varphi^s]$ is also real, one has

$$[\varphi^p\varphi^q|\varphi^r\varphi^s] = W_{1,1} - W_{-1,-1} + (W_{1,-1} + W_{-1,1})i \tag{33}$$

with

$$W_{i,j} = \sum_{\kappa=-k}^{k}\sum_{\lambda=-l}^{l}\sum_{\mu=-m}^{m}\sum_{\nu=-n}^{n} D_i^{\kappa\lambda\mu\nu}Z_j^{\kappa\lambda\mu\nu}, \qquad i,j = \pm 1. \tag{34}$$

Obviously, $(W_{1,-1} + W_{-1,1})$ must vanish.

B. The Expression $W_{1,1} - W_{-1,-1}$

The $D_{\pm 1}^{\kappa\lambda\mu\nu}$ as well as the $Z_{\pm 1}^{\kappa\lambda\mu\nu}$ may be evaluated by means of Eqs. (29) and (19), respectively. Multiplication gives

$$\begin{aligned} D_1^{\kappa\lambda\mu\nu} = {} & \langle\kappa\rangle^{\kappa}\langle\lambda\rangle^{\lambda}\langle\mu\rangle^{\mu}\langle\nu\rangle^{\nu} \\ & \cdot [x^{|\kappa|}x^{|\lambda|}x^{|\mu|}x^{|\nu|} + \zeta_\kappa\zeta_\lambda\zeta_\mu\zeta_\nu x^{-|\kappa|}x^{-|\lambda|}x^{-|\mu|}x^{-|\nu|} \\ & \quad - \zeta_\kappa\zeta_\lambda x^{-|\kappa|}x^{-|\lambda|}x^{|\mu|}x^{|\nu|} - \zeta_\mu\zeta_\nu x^{|\kappa|}x^{|\lambda|}x^{-|\mu|}x^{-|\nu|} \\ & \quad - \zeta_\kappa\zeta_\mu x^{-|\kappa|}x^{|\lambda|}x^{-|\mu|}x^{|\nu|} - \zeta_\lambda\zeta_\nu x^{|\kappa|}x^{-|\lambda|}x^{|\mu|}x^{-|\nu|} \\ & \quad - \zeta_\kappa\zeta_\nu x^{-|\kappa|}x^{|\lambda|}x^{|\mu|}x^{-|\nu|} - \zeta_\lambda\zeta_\mu x^{|\kappa|}x^{-|\lambda|}x^{-|\mu|}x^{|\nu|}] \end{aligned} \tag{35}$$

and

$$\begin{aligned} D_{-1}^{\kappa\lambda\mu\nu} = {} & \langle\kappa\rangle^{\kappa}\langle\lambda\rangle^{\lambda}\langle\mu\rangle^{\mu}\langle\nu\rangle^{\nu} \\ & \cdot [\zeta_\kappa x^{-|\kappa|}x^{|\lambda|}x^{|\mu|}x^{|\nu|} - \zeta_\lambda\zeta_\mu\zeta_\nu x^{|\kappa|}x^{-|\lambda|}x^{-|\mu|}x^{-|\nu|} \\ & \quad + \zeta_\lambda x^{|\kappa|}x^{-|\lambda|}x^{|\mu|}x^{|\nu|} - \zeta_\kappa\zeta_\mu\zeta_\nu x^{-|\kappa|}x^{|\lambda|}x^{-|\mu|}x^{-|\nu|} \\ & \quad + \zeta_\mu x^{|\kappa|}x^{|\lambda|}x^{-|\mu|}x^{|\nu|} - \zeta_\kappa\zeta_\lambda\zeta_\nu x^{-|\kappa|}x^{-|\lambda|}x^{|\mu|}x^{-|\nu|} \\ & \quad + \zeta_\nu x^{|\kappa|}x^{|\lambda|}x^{|\mu|}x^{-|\nu|} - \zeta_\kappa\zeta_\lambda\zeta_\mu x^{-|\kappa|}x^{-|\lambda|}x^{-|\mu|}x^{|\nu|}]. \end{aligned} \tag{36}$$

This may be written in terms of sums in the following way:

$$D_{\omega}^{\kappa\lambda\mu\nu} = \sum_{\kappa''=\pm|\kappa|}^{*} \sum_{\lambda''=\pm|\lambda|}^{*} \sum_{\mu''=\pm|\mu|}^{*} \sum_{\nu''=\pm|\nu|}^{*} \{\beta_{\omega}^{\Pi''}(\sigma'')\gamma_{\kappa}^{\kappa''}\gamma_{\lambda}^{\lambda''}\gamma_{\mu}^{\mu''}\gamma_{\nu}^{\nu''}\}x^{\kappa''}x^{\lambda''}x^{\mu''}x^{\nu''}. \tag{37}$$

The asterisk at the summation signs indicates to take only one term in the sum in case the summation index becomes equal to zero, i.e.,

$$\sum_{m_p''=\pm|m_p|}^{*} f(m_p'') = \begin{cases} f(|m_p|) + f(-|m_p|) & \text{if } m_p \neq 0, \\ f(0) & \text{if } m_p = 0. \end{cases} \tag{38}$$

The quantity in brackets in Eq. (37) is either equal to zero or ± 1, since we use

$$\omega = +1, -1; \tag{39}$$

$$\Pi'' = \langle\kappa''\rangle\langle\lambda''\rangle\langle\mu''\rangle\langle\nu''\rangle, \tag{40}$$

$$\sigma'' = \langle\kappa''\rangle + \langle\lambda''\rangle + \langle\mu''\rangle + \langle\nu''\rangle. \tag{41}$$

Since, due to Eq. (22),

$$\langle\kappa''\rangle = \pm 1, \qquad \langle\lambda''\rangle = \pm 1, \qquad \langle\mu''\rangle = \pm 1, \qquad \langle\nu''\rangle = \pm 1, \tag{42}$$

σ'' is restricted to the only possible values

$$\sigma'' = -4, -2, 0, 2, 4; \tag{43}$$

Π'' is then determined by σ'' in such a way that one may express the allowed values by

$$\Pi'' = \cos[(\pi/2)\sigma''] = \pm 1, \qquad \pi/2 = \text{arc } 90^0. \tag{44}$$

Furthermore, β and γ are defined as

$$\beta_{\omega}^{\Pi''}(\sigma'') = \sin[(\sigma'' - 1 - \omega)(\pi/4)], \qquad \pi/4 = \text{arc } 45^{\circ}; \tag{45}$$

$$\gamma_{\lambda}^{\lambda''} = \langle\lambda\rangle^{\lambda}\,\varepsilon_{\lambda}^{\lambda''} = \pm 1, \qquad \gamma_0^0 = 1; \tag{46}$$

here

$$\begin{aligned} \varepsilon_{\lambda}^{\lambda''} &= \max(\langle\lambda\rangle, \langle\lambda''\rangle) \\ &= (\langle\lambda\rangle)^{(1-\langle\lambda''\rangle)/2} \\ &= \begin{cases} 1 & \text{if } \langle\lambda''\rangle = 1 \\ \langle\lambda\rangle & \text{if } \langle\lambda''\rangle = -1 \end{cases} \end{aligned} \tag{47}$$

defines the matrix $\varepsilon_{\lambda}^{\lambda''} = \varepsilon_{\lambda''}^{\lambda}$,

$$\begin{array}{c|cc} \langle\lambda\rangle \diagdown \langle\lambda''\rangle & 1 & -1 \\ \hline 1 & 1 & 1 \\ -1 & 1 & -1 \end{array} \tag{48}$$

The upper index Π'' in $\beta_\omega^{\Pi''}(\sigma'')$ is superfluous. It is convenient, however, to indicate by this index the fact that $\beta_\omega^{\Pi''}(\sigma'')$ is proportional to a Kronecker delta $\delta_{\Pi'',\omega}$ because of

$$\beta_\omega^{\Pi''}(\sigma'') = \sin[(\sigma'' - 1 - \omega)(\pi/4)] = h(\sigma'')\omega\delta_{\Pi'',\omega}, \tag{49}$$

with

$$\omega\delta_{\Pi'',\omega} = \sin[(\omega + \Pi'')(\pi/4)], \tag{50}$$

where the factor $h(\sigma'') = \pm 1$ is given by the values of σ'' alone:

$$\begin{aligned} h(\sigma'') &= -\sin[(1 + \Pi'' + \sigma'')(\pi/4)] \\ &= -\sin[(1 + \sigma'' + \cos[(\pi/2)\sigma''])(\pi/4)]. \end{aligned} \tag{51}$$

Now, the $Z_\omega^{\kappa\lambda\mu\nu}$ may be expressed in the same way as the $D_\omega^{\kappa\lambda\mu\nu}$:

$$Z_\omega^{\kappa\lambda\mu\nu} = \sum^*_{\kappa'''=\pm|\kappa|} \sum^*_{\lambda'''=\pm|\lambda|} \sum^*_{\mu'''=\pm|\mu|} \sum^*_{\nu'''=\pm|\nu|} \cdot \{\beta_\omega^{\Pi'''}(\sigma''') \cdot \gamma_\kappa^{\kappa'''}\gamma_\lambda^{\lambda'''}\gamma_\mu^{\mu'''}\gamma_\nu^{\nu'''}\}[z^{\kappa'''}z^{\lambda'''}|z^{\mu'''}z^{\nu'''}]. \tag{52}$$

The definition Eq. (29) which satisfies Eq. (18) provides an easy way of determining which of the products of the type $x^{\kappa''}x^{\lambda''}x^{\mu''}x^{\nu''}$ in Eq. (37) belong to the real part $D_1^{\kappa\lambda\mu\nu}$, and which belong to the imaginary part $D_{-1}^{\kappa\lambda\mu\nu}$ of $\mathbb{C}^\kappa\mathbb{C}^\lambda\mathbb{C}^\mu\mathbb{C}^\nu$ given in Eq. (31). In general, if κ, λ, μ, ν are unequal to zero, there are 16 products of the type $x^{\kappa''}x^{\lambda''}x^{\mu''}x^{\nu''}$ of which eight belong to the real part, eight to the imaginary part of $\mathbb{C}^\kappa\mathbb{C}^\lambda\mathbb{C}^\mu\mathbb{C}^\nu$.

The integral $[\varphi^p\varphi^q|\varphi^r\varphi^s]$ in Eq. (33) may now be expressed by means of Eqs. (37) and (52). Before doing so, we notice that

$$\sum_{\lambda=-l}^{l} \sum^*_{\lambda''=\pm|\lambda|} = \sum_{\lambda''=-l}^{l} \sum^*_{\lambda=\pm|\lambda''|} = \sum_{\lambda''=-l}^{l} \sum^*_{\lambda=\pm\lambda''} \tag{53}$$

since the summation is carried out over the points of the two diagonals of an origin-centered square whose sides are parallel to the orthogonal λ, λ'' axes of a coordinate system, if those sides cut the λ, λ'' axes at $+l$ or $-l$, respectively (see Fig. 1). If we apply this change of summation and rename the summation indices according to

λ (new) instead of λ'' (old)

λ' (new) instead of λ (old)

we get

$$[\varphi^p\varphi^q|\varphi^r\varphi^s] = \sum_{\kappa=-k}^{k} \sum_{\lambda=-l}^{l} \sum_{\mu=-m}^{m} \sum_{\nu=-n}^{n} x^\kappa x^\lambda x^\mu x^\nu T^{\kappa\lambda\mu\nu} \tag{54}$$

with

$$T^{\kappa\lambda\mu\nu} = \sum^{*}_{\kappa'=\pm|\kappa|} \sum^{*}_{\lambda'=\pm|\lambda|} \sum^{*}_{\mu'=\pm|\mu|} \sum^{*}_{\nu'=\pm|\nu|} \gamma^{\kappa}_{\kappa'} \gamma^{\lambda}_{\lambda'} \gamma^{\mu}_{\mu'} \gamma^{\nu}_{\nu'}$$
$$\cdot (\beta^{\Pi}_{1}(\sigma) Z_{1}^{\kappa'\lambda'\mu'\nu'} - \beta^{\Pi}_{-1}(\sigma) Z_{-1}^{\kappa'\lambda'\mu'\nu'}) \tag{55}$$

where, according to Eq. (46),

$$\gamma^{\lambda}_{\lambda'} = \delta_{\langle\lambda'\rangle,1} + (-1)^{\lambda'}\langle\lambda\rangle\delta_{\langle\lambda'\rangle,-1} = (\langle\lambda'\rangle)^{\lambda'} \cdot (\langle\lambda'\rangle)^{(1-\langle\lambda\rangle)/2}. \tag{56}$$

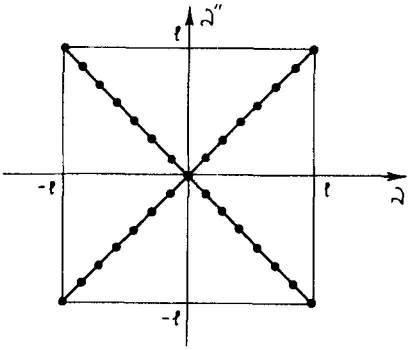

Fig. 1. Summation terms characterized by points in the space of the summation indices λ and λ''.

The coefficients $\beta^{\Pi}_{\pm 1}(\sigma)$ determine for which combination of the $\kappa\lambda\mu\nu$ indices the real part Z_1 or the imaginary part Z_{-1} of the integral over the atomic orbitals, $[\chi^{\kappa}\chi^{\lambda}|\chi^{\mu}\chi^{\nu}]$ of Eq. (32), enters the expression Eq. (55). For the only possible combinations of

$$\Pi = \langle\kappa\rangle\,\langle\lambda\rangle\,\langle\mu\rangle\,\langle\nu\rangle \tag{57}$$

$$\sigma = \langle\kappa\rangle + \langle\lambda\rangle + \langle\mu\rangle + \langle\nu\rangle \tag{58}$$

these values $\beta^{\Pi}_{\omega}(\sigma)$, $\omega = +1, -1$, are tabulated in Table I. All values, however, may be comprised in compact form by

$$\beta^{\Pi}_{\omega}(\sigma) = \sin[(\sigma - 1 - \omega)(\pi/4)], \qquad \pi/4 = \text{arc } 45^{\circ}. \tag{59}$$

In Eq. (54) it was taken for granted that the expression $(W_{1,-1} + W_{-1,1})$ of Eq. (33) vanishes. This will be verified in the next section.

TABLE I

Π	σ	$\beta_1^\Pi(\sigma)$	$\beta_{-1}^\Pi(\sigma)$
1	± 4	1	0
	0	-1	0
-1	$+2$	0	1
	-2	0	-1

C. The Expression $W_{1,-1} + W_{-1,1}$

Although the relation

$$W_{1,-1} + W_{-1,1} = 0 \tag{60}$$

with $W_{i,j}$, $i, j = \pm 1$, defined by Eq. (34), has to be fulfilled a priori due to our definition of the orbitals φ^P as real, it may be seen that Eq. (60) is consistent with the results of Eqs. (37) and (52). In fact, it is already obvious from Eqs. (35), (36), and the equivalent expressions for Z_ω, that even

$$W_{1,-1} = W_{-1,1} = 0 \tag{61}$$

holds true since all appearing products of the kind

$$x^{\kappa''} x^{\lambda''} x^{\mu''} x^{\nu''} \, [z^{\kappa'''} z^{\lambda'''} \,|\, z^{\mu'''} z^{\nu'''}] \tag{62}$$

which are contained in the expression behind the summation signs of Eq. (34), have an odd number of ζ factors, thus leading to a zero contribution to $W_{\omega,-\omega}$.

In general, if κ, λ, μ, $\nu \neq 0$, there are 64 products of the type Eq. (62) contained in $D_\omega^{\kappa\lambda\mu\nu} Z_{-\omega}^{\kappa\lambda\mu\nu}$. If $D_\omega^{\kappa\lambda\mu\nu}$ is expressed by Eq. (37), $Z_{-\omega}^{\kappa\lambda\mu\nu}$ by Eq. (52), it is

$$\begin{aligned} D_1^{\kappa\lambda\mu\nu} Z_{-1}^{\kappa\lambda\mu\nu} = & \sum_{\kappa''=\pm|\kappa|}^{*} \sum_{\lambda''=\pm|\lambda|}^{*} \sum_{\mu''=\pm|\mu|}^{*} \sum_{\nu''=\pm|\nu|}^{*} \\ & \cdot \sum_{\kappa'''=\pm|\kappa|}^{*} \sum_{\lambda'''=\pm|\lambda|}^{*} \sum_{\mu'''=\pm|\mu|}^{*} \sum_{\nu'''=\pm|\nu|}^{*} \beta_1^{\Pi''}(\sigma'') \cdot \beta_{-1}^{\Pi'''}(\sigma''') \\ & \cdot (\varepsilon_\kappa^{\kappa''} \varepsilon_\kappa^{\kappa'''} \varepsilon_\lambda^{\lambda''} \varepsilon_\lambda^{\lambda'''} \varepsilon_\mu^{\mu''} \varepsilon_\mu^{\mu'''} \varepsilon_\nu^{\nu''} \varepsilon_\nu^{\nu'''}) \\ & \cdot x^{\kappa''} x^{\lambda''} x^{\mu''} x^{\nu''} [z^{\kappa'''} z^{\lambda'''} \,|\, z^{\mu'''} z^{\nu'''}]. \end{aligned} \tag{63}$$

If one asks for $D_1^{-\kappa-\lambda-\mu-\nu} \, Z_{-1}^{-\kappa-\lambda-\mu-\nu}$, one has to replace the bracket with the eight ε factors in the above expression by

$$\varepsilon_{-\kappa}^{\kappa''} \varepsilon_{-\kappa}^{\kappa'''} \varepsilon_{-\lambda}^{\lambda''} \varepsilon_{-\lambda}^{\lambda'''} \varepsilon_{-\mu}^{\mu''} \varepsilon_{-\mu}^{\mu'''} \varepsilon_{-\nu}^{\nu''} \varepsilon_{-\nu}^{\nu'''} = (\varepsilon_\kappa^{\kappa''} \varepsilon_\kappa^{\kappa'''} \varepsilon_\lambda^{\lambda''} \varepsilon_\lambda^{\lambda'''} \varepsilon_\mu^{\mu''} \varepsilon_\mu^{\mu'''} \varepsilon_\nu^{\nu''} \varepsilon_\nu^{\nu'''}) Q, \tag{64}$$

where Q stands for

$$Q = Q_{\kappa}^{\kappa'', \kappa'''} Q_{\lambda}^{\lambda'', \lambda'''} Q_{\mu}^{\mu'', \mu'''} Q_{\nu}^{\nu'', \nu'''} \tag{65}$$

with

$$\begin{aligned} Q_{\kappa}^{\kappa'', \kappa'''} &= (2\delta_{\kappa, 0} - 1)^{1 - (\langle \kappa'' \rangle + \langle \kappa''' \rangle)/2} \\ Q_{\lambda}^{\lambda'', \lambda'''} &= (2\delta_{\lambda, 0} - 1)^{1 - (\langle \lambda'' \rangle + \langle \lambda''' \rangle)/2} \end{aligned} \tag{66}$$

and so forth. Here, Eqs. (27) and (47) have been used. The product of the two β functions in Eq. (63) does not vanish only if (see Table I)

$$\Pi''\Pi''' = -1, \quad \sigma'' + \sigma''' = 6, 2, -2, -6 \qquad \text{for} \quad \beta_1^{\Pi''}(\sigma'')\beta_{-1}^{\Pi'''}(\sigma''') \neq 0, \tag{67}$$

because of

$$\sigma'' = \pm 4, 0, \qquad \sigma''' = \pm 2, \qquad \tfrac{1}{2}(\sigma'' + \sigma''') = 3, 1, -1, -3 = \text{odd}. \tag{68}$$

For $\kappa = \lambda = \mu = \nu = 0$ one has $Q = 1$ and $\varepsilon_0^0 = 1$; then

$$\begin{aligned} &\kappa = \kappa'' = \kappa''' = 0, \qquad &&\lambda = \lambda'' = \lambda''' = 0, \qquad &&\mu = \mu'' = \mu''' = 0, \\ &\nu = \nu'' = \nu''' = 0, \qquad &&\sigma = \sigma'' = \sigma''' = 4, \qquad &&\Pi''\,\Pi''' = +1; \end{aligned}$$

due to Eq. (67), $D_1^{0000}\, Z_{-1}^{0000}$ will vanish for this case [see Eq. (63)]. Now considering the case that the number of vanishing indices in the set of four indices κ, λ, μ, ν is t with $0 \leq t \leq 3$, one has

$$Q = (-1)^{4 - t - [(\sigma'' + \sigma''')/2 - t]} = (-1)^{-(\sigma'' + \sigma''')/2} = -1. \tag{69}$$

For instance, if all κ, λ, μ, ν are unequal to zero, i.e. $t = 0$, it is

$$Q = (-1)^{4 - \text{odd}} = -1; \tag{70}$$

if, for example, $\lambda = 0$, but κ, μ, $\nu \neq 0$, it is ($t = 1$)

$$Q = (-1)^{3 - [(\sigma'' + \sigma''')/2 - 1]} = (-1)^{4 - \text{odd}} = -1 \tag{71}$$

because of

$$\tfrac{1}{2}(\langle \lambda'' \rangle + \langle \lambda''' \rangle) = \tfrac{1}{2}(\langle 0 \rangle + \langle 0 \rangle) = 1. \tag{72}$$

Therefore, since the case that all κ, λ, μ, ν vanish ($t = 4$) does not appear as mentioned earlier, one has for all cases

$$Q = -1; \tag{73}$$

hence, with $\omega = +1$ or -1,

$$D_{\omega}^{\kappa\lambda\mu\nu} Z_{-\omega}^{\kappa\lambda\mu\nu} = -D_{\omega}^{-\kappa-\lambda-\mu-\nu} Z_{-\omega}^{-\kappa-\lambda-\mu-\nu}. \tag{74}$$

However, Eq. (34) may be written as

$$\begin{aligned} W_{\omega,-\omega} &= \sum_{-\kappa=-k}^{k} \sum_{-\lambda=-l}^{l} \sum_{-\mu=-m}^{m} \sum_{-\nu=-n}^{n} D_{\omega}^{-\kappa-\lambda-\mu-\nu} Z_{-\omega}^{-\kappa-\lambda-\mu-\nu}, \\ &= \sum_{\kappa=-k}^{k} \sum_{\lambda=-l}^{l} \sum_{\mu=-m}^{m} \sum_{\nu=-n}^{n} D_{\omega}^{-\kappa-\lambda-\mu-\nu} Z_{-\omega}^{-\kappa-\lambda-\mu-\nu}, \\ &= (-1) \sum_{\kappa=-k}^{k} \sum_{\lambda=-l}^{l} \sum_{\mu=-m}^{m} \sum_{\nu=-n}^{n} D_{\omega}^{\kappa\lambda\mu\nu} Z_{-\omega}^{\kappa\lambda\mu\nu}, \end{aligned} \tag{75}$$

which means

$$W_{\omega,-\omega} = -W_{\omega,-\omega}, \tag{76}$$

from which indeed follows

$$W_{\omega,-\omega} = 0. \tag{77}$$

Therefore it has been shown that the way of writing our formulas is in agreement with the fact that the integral $[\varphi^p\varphi^q|\varphi^r\varphi^s]$ given in Eq. (33) is indeed real. Hence, if the integrals over real MO's given in Eq. (7) are expressed by integrals over complex AO's, see Eqs. (8), (9), the integrals $[\varphi^p\varphi^q|\varphi^r\varphi^s]$ are given by Eq. (54) with Eqs. (55), (56), (59), and (52).

D. Simplification of $T^{\kappa\lambda\mu\nu}$

The formulas given in Eqs. (54), (55) enable us, together with Eq. (7), to find the electron interaction energy integral over real MO's in terms of the real and imaginary parts of the complex integrals over complex AO's. Some useful variations of those formulas will be considered in this section.

There is a simplification possible in the expression $T^{\kappa\lambda\mu\nu}$ which is important for numerical calculations, because one of the four summations may be avoided and taken into account by a common factor 2, halving the number of terms of the quantity $T^{\kappa\lambda\mu\nu}$.

For future convenience, $T^{\kappa\lambda\mu\nu}$ given in Eq. (55) will be written as

$$T^{\kappa\lambda\mu\nu} = T_{1}^{\kappa\lambda\mu\nu} + T_{-1}^{\kappa\lambda\mu\nu}. \tag{78}$$

Note that there is no imaginary unit *i* in the second term of Eq. (78) since $T^{\kappa\lambda\mu\nu}$ is real. Then, for $\omega = +1, -1$,

$$T_{\omega}^{\kappa\lambda\mu\nu} = (\omega\beta_{\omega}^{\Pi}(\sigma)) \sum_{\kappa'=\pm|\kappa|}^{*} \sum_{\lambda'=\pm|\lambda|}^{*} \sum_{\mu'=\pm|\mu|}^{*} \sum_{\nu'=\pm|\nu|}^{*} \gamma_{\kappa'}^{\kappa} \gamma_{\lambda'}^{\lambda} \gamma_{\mu'}^{\mu} \gamma_{\nu'}^{\nu} Z_{\omega}^{\kappa'\lambda'\mu'\nu'}, \tag{79}$$

where [see Eq. (32)]

$$Z_1^{\kappa\lambda\mu\nu} = \mathrm{Re}[\chi^\kappa\chi^\lambda|\chi^\mu\chi^\nu], \qquad Z_{-1}^{\kappa\lambda\mu\nu} = \mathrm{Im}[\chi^\kappa\chi^\lambda|\chi^\mu\chi^\nu], \tag{80}$$

which may be written as

$$Z_\omega^{\kappa\lambda\mu\nu} = O_\omega[\chi^\kappa\chi^\lambda|\chi^\mu\chi^\nu], \qquad \omega = +1, -1, \tag{81}$$

if one defines the new symbols

$$O_1 = \mathrm{Re}, \qquad O_{-1} = \mathrm{Im}. \tag{82}$$

Then, Eq. (79) becomes

$$T_\omega^{\kappa\lambda\mu\nu} = (\omega\beta_\omega^\Pi(\sigma))O_\omega \cdot \left[\left(\sum_{\kappa'=\pm|\kappa|}^{*} \gamma_{\kappa'}^{\kappa}\chi^{\kappa'}\right)\cdot\left(\sum_{\lambda'=\pm|\lambda|}^{*} \gamma_{\lambda'}^{\lambda}\chi^{\lambda'}\right)\middle|\left(\sum_{\mu'=\pm|\mu|}^{*} \gamma_{\mu'}^{\mu}\chi^{\mu'}\right)\left(\sum_{\nu'=\pm|\nu|}^{*} \gamma_{\nu'}^{\nu}\chi^{\nu'}\right)\right]. \tag{83}$$

Note that the bracket containing the expression which follows the symbol O_ω specifies an integral. Due to Eqs. (17) and (56), it is

$$\sum_{\lambda'=\pm|\lambda|}^{*} \gamma_{\lambda'}^{\lambda}\chi^{\lambda'} = \chi^{|\lambda|} + \zeta_\lambda\chi^{|\lambda|*}. \tag{84}$$

Therefore, Eq. (83) may also be written as

$$T_\omega^{\kappa\lambda\mu\nu} = \omega\beta_\omega^\Pi(\sigma)O_\omega \cdot [(\chi^{|\kappa|} + \zeta_\kappa\chi^{|\kappa|*})(\chi^{|\lambda|} + \zeta_\lambda\chi^{|\lambda|*})|(\chi^{|\mu|} + \zeta_\mu\chi^{|\mu|*})(\chi^{|\nu|} + \zeta_\nu\chi^{|\nu|*})]. \tag{85}$$

Doing the multiplication, the integral may be split into a sum of sixteen integrals. For these integrals another abbreviation should be used, for instance

$$\begin{aligned} [\chi^{|\kappa|}\chi^{|\lambda|}|\chi^{|\mu|}\chi^{|\nu|}] &= (\kappa\lambda|\mu\nu), \\ [\chi^{|\kappa|}\chi^{|\lambda|*}|\chi^{|\mu|}\chi^{|\nu|}] &= (\kappa\bar{\lambda}|\mu\nu). \end{aligned} \tag{86}$$

Note that the indices κ, λ, μ, ν, which are contained in the parentheses, correspond to the absolute values of the indices of the AO's in square brackets. Now, since

$$(\kappa\bar{\lambda}|\mu\nu) = (\bar{\kappa}\lambda|\bar{\mu}\bar{\nu})^*, \tag{87}$$

one has

$$
\begin{aligned}
&[(\chi^{|\kappa|}+\zeta_\kappa\chi^{|\kappa|*})(\chi^{|\lambda|}+\zeta_\lambda\chi^{|\lambda|*})|(\chi^{|\mu|}+\zeta_\mu\chi^{|\mu|*})(\chi^{|\nu|}+\zeta_\nu\chi^{|\nu|*})]\\
&\quad=\{(\kappa\lambda|\mu\nu)+\zeta_\kappa\zeta_\lambda\zeta_\mu\zeta_\nu(\kappa\lambda|\mu\nu)^*\\
&\qquad+\zeta_\kappa\zeta_\lambda(\bar\kappa\bar\lambda|\mu\nu)+\zeta_\mu\zeta_\nu(\bar\kappa\bar\lambda|\mu\nu)^*\\
&\qquad+\zeta_\kappa\zeta_\mu(\bar\kappa\lambda|\bar\mu\nu)+\zeta_\lambda\zeta_\nu(\bar\kappa\lambda|\bar\mu\nu)^*\\
&\qquad+\zeta_\kappa\zeta_\nu(\bar\kappa\lambda|\mu\bar\nu)+\zeta_\lambda\zeta_\mu(\bar\kappa\lambda|\mu\bar\nu)^*\\
&\qquad+\zeta_\kappa(\bar\kappa\lambda|\mu\nu)+\zeta_\lambda\zeta_\mu\zeta_\nu(\bar\kappa\lambda|\mu\nu)^*\\
&\qquad+\zeta_\lambda(\kappa\bar\lambda|\mu\nu)+\zeta_\kappa\zeta_\mu\zeta_\nu(\kappa\bar\lambda|\mu\nu)^*\\
&\qquad+\zeta_\mu(\kappa\lambda|\bar\mu\nu)+\zeta_\kappa\zeta_\lambda\zeta_\nu(\kappa\lambda|\bar\mu\nu)^*\\
&\qquad+\zeta_\nu(\kappa\lambda|\mu\bar\nu)+\zeta_\kappa\zeta_\lambda\zeta_\mu(\kappa\lambda|\mu\bar\nu)^*\}.
\end{aligned}
\tag{88}
$$

For any complex quantity w, i.e.,

$$
w=u+iv,\qquad w^*=u-iv,\qquad u,\,v\ \text{real},\qquad i=(-1)^{1/2},
\tag{89}
$$

is

$$
\begin{aligned}
w+w^*&=2u=2\,\mathrm{Re}(w)=2O_1\,w,\\
w-w^*&=2iv=2i\mathrm{Im}(w)=2iO_{-1}\,w;
\end{aligned}
\tag{90}
$$

hence

$$
\begin{aligned}
\mathrm{Re}(w+w^*)&=O_1(w+w^*)=2O_1\,w,\\
\mathrm{Im}(w-w^*)&=O_{-1}(w-w^*)=2O_{-1}\,w.
\end{aligned}
\tag{91}
$$

These simple relations become important since they furnish the wanted factor two. Due to the $\beta_\omega^\Pi(\sigma)$ factor in $T_\omega^{\kappa\lambda\mu\nu}$, the 16 ζ products in Eq. (88) are not independent from each other. Considering the case that all κ, λ, μ, ν are unequal to zero, one has

$$
\begin{aligned}
\zeta_\kappa&=\langle\kappa\rangle,\quad \kappa\neq0; &\qquad \zeta_\lambda&=\langle\lambda\rangle,\quad \lambda\neq0;\\
\zeta_\mu&=\langle\mu\rangle,\quad \mu\neq0; &\qquad \zeta_\nu&=\langle\nu\rangle,\quad \nu\neq0.
\end{aligned}
\tag{92}
$$

Then, the $\beta_\omega^\Pi(\sigma)$ factor enforces that

$$
\begin{aligned}
\Pi\equiv\langle\kappa\rangle\langle\lambda\rangle\langle\mu\rangle\langle\nu\rangle=1\qquad&\text{for}\quad\omega=1,\\
\langle\kappa\rangle\langle\lambda\rangle=\langle\mu\rangle\langle\nu\rangle&,\\
\langle\kappa\rangle=\langle\lambda\rangle\langle\mu\rangle\langle\nu\rangle&,
\end{aligned}
\tag{93}
$$

or

$$\begin{aligned} \Pi \equiv \langle\kappa\rangle\langle\lambda\rangle\langle\mu\rangle\langle\nu\rangle &= -1 \qquad \text{for} \quad \omega = -1, \\ \langle\kappa\rangle\langle\lambda\rangle &= -\langle\mu\rangle\langle\nu\rangle, \\ \langle\kappa\rangle &= -\langle\lambda\rangle\langle\mu\rangle\langle\nu\rangle, \end{aligned} \tag{94}$$

respectively.

Because of Eq. (91) it is enough, therefore, to keep only the eight terms in Eq. (88) that contain round brackets, i.e., integrals, without asterisks and to multiply the whole expression by a factor 2. Instead, one may also choose the remaining eight integrals by picking the ones which contain the AO to one special index, for instance κ, without asterisk, i.e., that contain $\chi^{|\kappa|}$ but not $\chi^{|\kappa|^*}$. Then, one may write

$$\begin{aligned} T_\omega^{\kappa\lambda\mu\nu} = 2\omega\beta_\omega^\Pi(\sigma)O_\omega[\chi^{|\kappa|}(\chi^{|\lambda|} + \langle\lambda\rangle\chi^{|\lambda|^*})\,|\,(\chi^{|\mu|} + \langle\mu\rangle\chi^{|\mu|^*}) \\ (\chi^{|\nu|} + \langle\nu\rangle\chi^{|\nu|^*})] \qquad \text{for}\ \kappa, \lambda, \mu, \nu \neq 0, \end{aligned} \tag{95}$$

which amounts to

$$T_\omega^{\kappa\lambda\mu\nu} = 2\omega\beta_\omega^\Pi(\sigma) \sum_{\lambda' = \pm|\lambda|}^{*} \sum_{\mu' = \pm|\mu|}^{*} \sum_{\nu' = \pm|\nu|}^{*} \gamma_{\lambda'}^{\lambda} \gamma_{\mu'}^{\mu} \gamma_{\nu'}^{\nu} Z_\omega^{|\kappa|\lambda'\mu'\nu'}. \tag{96}$$

This is equal to Eq. (79) if there $\gamma_{\kappa'}^{\kappa}$ is replaced by $2\delta_{\kappa', |\kappa|}$.

In addition to the case discussed above that all indices $\kappa, \lambda, \mu, \nu$ are unequal to zero, there are cases of one or more indices being zero. There are four cases that anyone of those indices is equal to zero, the other ones different from zero. There are six cases that any two of them are equal to zero, the remaining two different from zero. There are four cases of three indices being zero, only one being different from zero, and finally there is the case that all indices $\kappa, \lambda, \mu, \nu$ are equal to zero.

If $\kappa = \lambda = \mu = \nu = 0$ only one term survives in Eq. (88). However, for all other cases one may see from Eq. (88) that always two terms match in the way described above so that one is able to keep only half the number of terms and to multiply the whole expression by a factor 2. The selection rule which terms to keep and which to discard while correcting the effect by introducing the factor 2, may be formulated as follows:

(a) If $\kappa = \lambda = \mu = \nu = 0$, $T_\omega^{\kappa\lambda\mu\nu}$ in Eq. (79) reduces to one term

$$T_{+1}^{\kappa\lambda\mu\nu} = [\chi_k{}^0\chi_l{}^0\,|\,\chi_m{}^0\chi_n{}^0], \qquad T_{-1}^{\kappa\lambda\mu\nu} = 0. \tag{97}$$

(b) If not all four indices $\kappa, \lambda, \mu, \nu$ vanish, any nonvanishing index, for instance λ, may be picked and the expression may be written for only one value of the corresponding sum over λ', for instance $\lambda' = +|\lambda|$, multiplied by a factor 2. This is the same as leaving all four sums in Eq. (79) unchanged and replacing one γ with nonvanishing indices, for instance $\gamma_{\lambda'}^{\lambda}$, by $2\delta_{\lambda',|\lambda|}$. That one is able to pick any nonvanishing index is due to the fact that all four indices appear symmetrically in the formula.

Instead of picking an arbitrary nonvanishing index, with regard to electronic computing one may check in the sequence κ, λ, μ, ν and pick the first nonvanishing index in this series as the one for which the γ is replaced by 2 times the Kronecker delta. This is done by the factor

$$\begin{aligned}\delta_{\kappa'\lambda'\mu'\nu'}^{\kappa\lambda\mu\nu} \equiv 2\{&(1-\delta_{\kappa,0})\delta_{\kappa',|\kappa|} + \delta_{\kappa,0}(1-\delta_{\lambda,0})\delta_{\lambda',|\lambda|} \\ &+ \delta_{\kappa,0}\,\delta_{\lambda,0}(1-\delta_{\mu,0})\delta_{\mu',|\mu|} + \delta_{\kappa,0}\,\delta_{\lambda,0}\,\delta_{\mu,0}(1-\delta_{\nu,0})\delta_{\nu',|\nu|} \\ &+ \tfrac{1}{2}\delta_{\kappa,0}\,\delta_{\lambda,0}\,\delta_{\mu,0}\,\delta_{\nu,0}\}\end{aligned} \tag{98}$$

if one writes

$$T_{\omega}^{\kappa\lambda\mu\nu} = (\omega\beta_{\omega}^{\Pi}(\sigma)) \sum_{\kappa'=\pm|\kappa|}^{*} \sum_{\lambda'=\pm|\lambda|}^{*} \sum_{\mu'=\pm|\mu|}^{*} \sum_{\nu'=\pm|\nu|}^{*} \Delta_{\kappa'\lambda'\mu'\nu'}^{\kappa\lambda\mu\nu} Z_{\omega}^{\kappa'\lambda'\mu'\nu'} \tag{99}$$

with

$$\Delta_{\kappa'\lambda'\mu'\nu'}^{\kappa\lambda\mu\nu} = \gamma_{\kappa'}^{\kappa}\,\gamma_{\lambda'}^{\lambda}\,\gamma_{\mu'}^{\mu}\,\gamma_{\nu'}^{\nu}\,\delta_{\kappa'\lambda'\mu'\nu'}^{\kappa\lambda\mu\nu} \tag{100}$$

or

$$\begin{aligned}\Delta_{\kappa'\lambda'\mu'\nu'}^{\kappa\lambda\mu\nu} = 2\{&(1-\delta_{\kappa,0})\delta_{\kappa',|\kappa|}\gamma_{\lambda'}^{\lambda}\gamma_{\mu'}^{\mu}\gamma_{\nu'}^{\nu} + \delta_{\kappa,0}(1-\delta_{\lambda,0})\delta_{\lambda',|\lambda|}\gamma_{\mu'}^{\mu}\gamma_{\nu'}^{\nu} \\ &+ \delta_{\kappa,0}\,\delta_{\lambda,0}(1-\delta_{\mu,0})\delta_{\mu',|\mu|}\gamma_{\nu'}^{\nu} + \delta_{\kappa,0}\,\delta_{\lambda,0}\,\delta_{\mu,0}(1-\delta_{\nu,0})\,\delta_{\nu',|\nu|} \\ &+ \tfrac{1}{2}\delta_{\kappa,0}\,\delta_{\lambda,0}\,\delta_{\mu,0}\,\delta_{\nu,0}\}.\end{aligned} \tag{101}$$

III. Integrals between Real MO's Represented by Integrals between Real AO's

A. Real and Complex AO's

Since the molecular orbitals (MO's) of Eq. (1) or the functions defined by Eq. (9) are real, they are often expressed by real atomic orbitals

$$\rho_{L,l}^{\lambda}(q) = f_L(r_q)\,\mathcal{Y}_l^{\lambda}(\theta_q, \varphi_q) \tag{102}$$

instead of complex atomic orbitals

$$\chi_{L,l}^{\lambda}(q) = f_L(r_q)\;Y_l^{\lambda}(\theta_q, \varphi_q) \tag{103}$$

which were introduced by Eq. (2) and used so far. The $\mathcal{Y}_l^{\lambda}$ designate real spherical harmonics to be defined in the sequel, whereas the Y_l^{λ} are the complex spherical surface harmonics. If the AO's are assumed to be real, then not only the linear combinations Eq. (9) are real, but from the very beginning each term of the linear combination is also real. As far as the expression of integrals between MO's by integrals between AO's is concerned, this way of using only real quantities throughout seems more logical. However, for the mathematical calculation of many-center integrals it is often more practical to use complex atomic orbitals. For instance, if it is necessary to rotate atomic orbitals and to translate them to different centers, these operations are more easily done for complex orbitals. Therefore, in the treatment given in the preceding section the assumption of Eq. (14) was made that the linear combinations of Eq. (9) become real because to each complex term another term matches which is the complex conjugate of the first one, thus canceling the imaginary parts. Now it is desirable to compare the results of this procedure with the expressions which are obtained if only real quantities are used. This will be done in this section.

In Condon–Shortley phases the complex spherical surface harmonics are defined by [see Eqs. (4)–(6)]

$$Y_l^\lambda(\theta, \varphi) = (-1)^\lambda N_l^\lambda P_l^\lambda(\cos\theta)\, e^{i\lambda\varphi}/(2\pi)^{1/2} \tag{104}$$

with the unnormalized associated Legendre functions

$$P_l^\lambda(\zeta) = (1-\zeta^2)^{\lambda/2}\left(\frac{d}{d\zeta}\right)^{l+\lambda} \frac{1}{2^l l!}(\zeta^2-1)^l, \qquad \zeta = \cos\theta, \tag{105}$$

N_l^λ is the normalization constant

$$N_l^\lambda = \left[\frac{2l+1}{2}\frac{(l-\lambda)!}{(l+\lambda)!}\right]^{1/2}. \tag{106}$$

One has, of course,

$$-l \leq \lambda \leq +l. \tag{107}$$

For purposes of comparison, one may note that the following also holds

$$Y_l^\lambda(\theta, \varphi) = \hat{\varepsilon}_\lambda N_l^{|\lambda|} P_l^{|\lambda|}(\cos\theta)\, e^{i\lambda\varphi}/(2\pi)^{1/2} \tag{108}$$

where

$$\hat{\varepsilon}_\lambda = \begin{cases} (-1)^\lambda & \text{if } \lambda \geq 0 \\ 1 & \text{if } \lambda < 0. \end{cases} \tag{109}$$

The so defined spherical surface harmonics obey the relation

$$Y_l^{\lambda *}(\theta, \varphi) = (-1)^\lambda Y_l^{-\lambda}(\theta, \varphi); \qquad Y_l^0(\theta) = \text{real}. \tag{110}$$

One may write

$$Y_l^\lambda(\theta, \varphi) = R_l^\lambda(\theta, \varphi) + i\, I_l^\lambda(\theta, \varphi); \qquad I_l^0 = 0; \tag{111}$$

then R_l^λ is the real, I_l^λ the imaginary part of the complex Y_l^λ. Equation (111) leads to

$$R_l^\lambda = (-1)^\lambda R_l^{-\lambda}, \qquad I_l^\lambda = -(-1)^\lambda I_l^{-\lambda}, \qquad I_l^0 = 0. \tag{112}$$

To be in agreement with our former way of writing complex quantities and with the behavior under complex conjugation, which is specified by Eq. (110), we may also write

$$Y_l^\lambda = \langle\lambda\rangle^\lambda [y_l^{|\lambda|} + \zeta_\lambda\, y_l^{-|\lambda|} i]; \tag{113}$$

then

$$R_l^\lambda = \langle\lambda\rangle^\lambda y_l^{|\lambda|}, \qquad I_l^\lambda = \langle\lambda\rangle^\lambda \zeta_\lambda\, y_l^{-|\lambda|}. \tag{114}$$

With the normalized associated Legendre functions

$$\mathscr{P}_l^\lambda(\zeta) = (-1)^\lambda N_l^\lambda P_l^\lambda(\zeta) = \hat{\varepsilon}_\lambda\, N_l^{|\lambda|} P_l^{|\lambda|}(\zeta), \qquad \zeta = \cos\theta, \tag{115}$$

which are normalized according to

$$\int_{-1}^{1} d\zeta\, \mathscr{P}_l^\lambda(\zeta)\, \mathscr{P}_{l'}^\lambda(\zeta) = \delta_{ll'} \tag{116}$$

so that the spherical surface harmonics

$$Y_l^\lambda(\theta, \varphi) = \mathscr{P}_l^\lambda(\cos\theta)\, e^{i\lambda\varphi}/(2\pi)^{1/2} \tag{117}$$

are normalized like

$$\int d\Omega\; Y_l^{\lambda *}(\theta, \varphi) Y_{l'}^{\lambda'}(\theta, \varphi) = \delta_{ll'}\delta_{\lambda\lambda'} \tag{118}$$

with

$$\int d\Omega = \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta = \int_0^{2\pi} d\varphi \int_{-1}^{1} d\zeta, \tag{119}$$

one has from Eqs. (104), (108), (111)

$$R_l^\lambda = \mathscr{P}_l^\lambda(\cos\theta)[\cos\lambda\varphi]/(2\pi)^{1/2}, \tag{120}$$

$$I_l^\lambda = \mathscr{P}_l^\lambda(\cos\theta)[\sin\lambda\varphi]/(2\pi)^{1/2}. \tag{121}$$

In agreement with Eqs. (105), (106), (115), it is due to Eqs. (110), (117) that

$$\mathscr{P}_l^{-\lambda}(\cos\theta) = (-1)^\lambda\, \mathscr{P}_l^\lambda(\cos\theta). \tag{122}$$

With these auxiliary formulas, the real spherical surface harmonics $\mathscr{Y}_l^{\lambda}$ can be related to the complex spherical surface harmonics Y_l^{λ} as follows (see also O-Ohata and Ruedenberg, 1966):

$$\begin{aligned} \mathscr{Y}_l^{\lambda} &= 2^{1/2}(-1)^{\lambda}R_l^{\lambda} = [Y_l^{-\lambda} + (-1)^{\lambda}Y_l^{\lambda}]/2^{1/2} && \text{if} \quad \lambda > 0, \\ \mathscr{Y}_l^{0} &= R_l^{0} = Y_l^{0} && \text{if} \quad \lambda = 0, \\ \mathscr{Y}_l^{\lambda} &= 2^{1/2}(-1)^{\lambda}I_l^{|\lambda|} = [Y_l^{\lambda} - (-1)^{\lambda}Y_l^{-\lambda}]i/2^{1/2} && \text{if} \quad \lambda < 0. \end{aligned} \tag{123}$$

This may be written as

$$\mathscr{Y}_l^{\lambda} = (2 - \delta_{\lambda,0})^{1/2}(-1)^{\lambda}[R_l^{\lambda}\delta_{\langle\lambda\rangle,1} + I_l^{|\lambda|}\delta_{\langle\lambda\rangle,-1}] \tag{124}$$

or, using the operator $O_{\langle\lambda\rangle}$ defined by Eq. (82),

$$\mathscr{Y}_l^{\lambda} = (2 - \delta_{\lambda,0})^{1/2}(-1)^{\lambda}O_{\langle\lambda\rangle}\, Y_l^{|\lambda|}. \tag{125}$$

Furthermore, Eq. (113) gives

$$y_l^{\lambda} = O_{\langle\lambda\rangle}\, Y_l^{|\lambda|}. \tag{126}$$

This finally yields the simple expression

$$\mathscr{Y}_l^{\lambda} = (2 - \delta_{\lambda,0})^{1/2}\,(-1)^{\lambda}y_l^{\lambda} \tag{127}$$

for the real spherical harmonics. It has the advantage that it holds for all values of λ, i.e., for $\lambda \gtreqless 0$. Sometimes one uses the definition

$$\mathscr{Y}_l^{\lambda} = \hat{\varepsilon}_{\lambda}\,\mathscr{P}_l^{\lambda}(\cos\theta)[(1 + \delta_{\lambda,0})\pi]^{-1/2} \begin{cases} \cos\lambda\varphi & \text{for} \quad \lambda \geq 0 \\ \sin|\lambda|\varphi & \text{for} \quad \lambda < 0 \end{cases} \tag{128}$$

which is also in accordance with the formulas given in the foregoing.

For the normalization product one has

$$\begin{aligned} Y_l^{\lambda *}Y_l^{\lambda} &= [(\mathscr{Y}_l^{|\lambda|})^2 + (\mathscr{Y}_l^{-|\lambda|})^2]/(2 - \delta_{\lambda,0}) \\ &= [\mathscr{P}_l^{|\lambda|}(\cos\theta)]^2/2\pi. \end{aligned} \tag{129}$$

Since now the connection between real and complex atomic orbitals is discussed, the electron interaction integral between real MO's may be represented by integrals between real AO's or by integrals between complex AO's as well. In the next section the formulas for the representation by integrals between real AO's will be derived and compared with those for the representation by integrals between complex AO's which were derived in the foregoing section.

B. General Formula

With complex atomic orbitals χ given in Eq. (103), the functions defined by Eq. (12), namely

$$\varphi_b{}^q = \sum_{\lambda=-l}^{l} \chi_{L,l}^{\lambda}(q)\mathbb{C}_{q,b}^{L,l,\lambda}, \tag{130}$$

may be expressed as follows; see also Eqs. (2) and (9)–(12). Due to Eqs. (19), (29), we have

$$\mathbb{C}^{\lambda}\chi^{\lambda} = [x^{|\lambda|}z^{|\lambda|} - (\zeta_\lambda)^2 x^{-|\lambda|}z^{-|\lambda|}] + i\zeta_\lambda[x^{-|\lambda|}z^{|\lambda|} + x^{|\lambda|}z^{-|\lambda|}]. \tag{131}$$

Then, with Eq. (25),

$$\begin{aligned}
\varphi^q &= \sum_{\lambda=-l}^{l} \mathbb{C}^{\lambda}\chi^{\lambda} = \sum_{\lambda=-l}^{l} [x^{|\lambda|}z^{|\lambda|} - (\zeta_\lambda)^2 x^{-|\lambda|}z^{-|\lambda|}],\\
&= x^0 z^0 + 2\sum_{\lambda=1}^{l} [x^{|\lambda|}z^{|\lambda|} - x^{-|\lambda|}z^{-|\lambda|}],\\
&= x^0 z^0 + 2\sum_{\lambda=1}^{l} [x^{\lambda}z^{\lambda} - x^{-\lambda}z^{-\lambda}],\\
&= \sum_{\lambda=-l}^{l} (2 - \delta_{\lambda,0})\langle\lambda\rangle x^{\lambda}z^{\lambda},
\end{aligned} \tag{132}$$

where we made use of

$$\sum_{\lambda=-l}^{l} \zeta_\lambda[x^{-|\lambda|}z^{|\lambda|} + x^{|\lambda|}z^{-|\lambda|}] = \sum_{\lambda=1}^{l} (\zeta_\lambda + \zeta_{-\lambda})[x^{-\lambda}z^{\lambda} + x^{\lambda}z^{-\lambda}] = 0, \tag{133}$$

which holds true since φ^q is real.

With real atomic orbitals ρ as defined by Eq. (102), the same functions defined by Eq. (12) are now given by

$$\varphi_b{}^q = \sum_{\lambda=-l}^{l} \rho_{L,l}^{\lambda}(q) d_{q,b}^{L,l,\lambda} \tag{134}$$

with real coefficients $d_{q,b}^{L,l,\lambda}$. In short-hand notation one has

$$\varphi^q = \sum_{\lambda=-l}^{l} \rho^{\lambda}(q)\, d^{\lambda}. \tag{135}$$

With Eqs. (2), (10)–(12), (19), and (113), it is

$$f_L\, y_l^{\pm|\lambda|} = z^{\pm|\lambda|}, \qquad f_L\, y^{\lambda} = z^{\lambda}. \tag{136}$$

Thus, one has for Eq. (134), introducing Eq. (127),

$$\varphi^q = \sum_{\lambda=-l}^{l} (2 - \delta_{\lambda,0})^{1/2}(-1)^\lambda z^\lambda d^\lambda. \tag{137}$$

Since this holds for arbitrary (real) values of d and z, comparison of Eq. (132) with Eq. (137) gives

$$x^\lambda = (-1)^\lambda d^\lambda/[\langle\lambda\rangle (2 - \delta_{\lambda,0})^{1/2}]. \tag{138}$$

This gives the connection of both ways of writing the MO linear combination of atomic orbitals, i.e., either with complex or with real AO's. With Eq. (134) one gets now for the integral, instead of Eqs. (30), (54), (99),

$$[\varphi^p\varphi^q|\varphi^r\varphi^s] = \sum_{\kappa=-k}^{k} \sum_{\lambda=-l}^{l} \sum_{\mu=-m}^{m} \sum_{\nu=-n}^{n} d^\kappa d^\lambda d^\mu d^\nu U^{\kappa\lambda\mu\nu} \tag{139}$$

where, similar to Eq. (78),

$$U^{\kappa\lambda\mu\nu} = U_1^{\kappa\lambda\mu\nu} + U_{-1}^{\kappa\lambda\mu\nu} \tag{140}$$

and corresponding to Eq. (99), $\omega = +1, -1$,

$$U_\omega^{\kappa\lambda\mu\nu} = \beta_\omega^\Pi(\sigma)\left\{\frac{(-1)^\kappa}{(2-\delta_{\kappa,0})^{1/2}} \frac{(-1)^\lambda}{(2-\delta_{\lambda,0})^{1/2}} \frac{(-1)^\mu}{(2-\delta_{\mu,0})^{1/2}} \frac{(-1)^\nu}{(2-\delta_{\nu,0})^{1/2}}\right\}$$
$$\cdot \sum^*_{\kappa'=\pm|\kappa|} \sum^*_{\lambda'=\pm|\lambda|} \sum^*_{\mu'=\pm|\mu|} \sum^*_{\nu'=\pm|\nu|} \Delta^{\kappa\lambda\mu\nu}_{\kappa'\lambda'\mu'\nu'} Z_\omega^{\kappa'\lambda'\mu'\nu'}. \tag{141}$$

In addition to the curled bracket factor, this $U_\omega^{\kappa\lambda\mu\nu}$ differs from $T_\omega^{\kappa\lambda\mu\nu}$ by a missing factor ω which is canceled by the $\langle\kappa\rangle\langle\lambda\rangle\langle\mu\rangle\langle\nu\rangle$ product.

On the other hand, comparison of Eq. (135) with Eq. (139) gives

$$U^{\kappa\lambda\mu\nu} = [\rho^\kappa\rho^\lambda|\rho^\mu\rho^\nu]. \tag{142}$$

Then, the integral of Eq. (139) is very easily obtained as a sum of integrals between real AO's.

The real φ^q may consist of only one real AO. Then, one may assume, for instance, that d^λ is equal to a nonvanishing constant only for a special value $\lambda = \bar\lambda$. If this is the case for all four functions, one would have, for example,

$$\begin{aligned} d^\kappa &= d^{\bar\kappa}\,\delta_{\kappa,\bar\kappa}, & d^\lambda &= d^{\bar\lambda}\,\delta_{\lambda,\bar\lambda}, \\ d^\mu &= d^{\bar\mu}\,\delta_{\mu,\bar\mu}, & d^\nu &= d^{\bar\nu}\,\delta_{\nu,\bar\nu}. \end{aligned} \tag{143}$$

With

$$\bar\kappa > 0, \qquad \bar\lambda > 0, \qquad \bar\mu > 0, \qquad \bar\nu > 0, \tag{144}$$

this leads to

$$U^{\bar{\kappa}\bar{\lambda}\bar{\mu}\bar{\nu}} = [\rho^{\bar{\kappa}}\rho^{\bar{\lambda}} | \rho^{\bar{\mu}}\rho^{\bar{\nu}}] \tag{145}$$

and

$$U^{\bar{\kappa}\bar{\lambda}\bar{\mu}\bar{\nu}} = U_{1}^{\bar{\kappa}\bar{\lambda}\bar{\mu}\bar{\nu}}, \qquad U_{-1}^{\bar{\kappa}\bar{\lambda}\bar{\mu}\bar{\nu}} = 0. \tag{146}$$

IV. Integrals between Real MO's Represented by Integrals between Real and Imaginary Parts of Complex Charge Distributions

General Formula

In the foregoing, the decomposition of the electron-electron interaction energy integral between real MO's into sums of real and imaginary parts of complex integrals between complex AO's was considered in Section II. The results are given in Eq. (54) with Eq. (55) or with Eqs. (78)–(80). In Section III this expression was compared with the formulas obtained if real AO's are used from the beginning. Hence, in that procedure, the basic elements of the calculation are the AO's which have to be stored in the computer in order to be available for necessary calculations at any time. As pointed out by Ruedenberg (1951, 1964) it is most important and helpful to use charge density distributions instead of atomic orbitals as the basic quantities of the calculation, since then the number of terms to be stored and of computational operations is highly reduced, and only then calculations of large molecules are becoming practical or even possible. Following this pattern, the necessary integrals can be calculated by using repeatedly the charge densities.

If complex AO's are considered, it is therefore important to know the electron–electron interaction integral between real MO's in terms of integrals between real and imaginary parts of complex charge density distributions, i.e., of products of two complex AO's. Therefore, the expressions obtained in the foregoing will be specified to this case in this section.

Since the expansion of the electron–electron interaction integral according to Eq. (54) remains unchanged in the new procedure, it is sufficient to discuss the alterations of the quantity $T^{\kappa\lambda\mu\nu}$ under the new point of view.

The $T^{\kappa\lambda\mu\nu}$ given in Eqs. (55) and (78)–(80) may be brought into a different form by noticing that due to Table I and Eq. (44) the quantity Π is uniquely defined by σ which can assume only certain values, namely

$$\sigma = 4, 2, 0, -2, -4; \tag{147}$$

$$\Pi = \Pi(\sigma) = \cos(\pi\sigma/2) = \pm 1. \tag{148}$$

Since $\omega^2 = 1$, Eq. (49) yields

$$\omega\beta_{\omega}^{\Pi}(\sigma) = h(\sigma)\delta_{\Pi,\omega} \tag{149}$$

with

$$h(\sigma) = 2^{1/2}\sin[(\sigma + 5)(\pi/4)] = \begin{cases} 1 & \text{for} \quad \sigma = \pm 4, -2; \\ -1 & \text{for} \quad \sigma = 2, 0. \end{cases} \tag{150}$$

This relation is in accordance with Eq. (51). Now, instead of

$$T^{\kappa\lambda\mu\nu} = T_1^{\kappa\lambda\mu\nu} + T_{-1}^{\kappa\lambda\mu\nu} \tag{151}$$

one has

$$T^{\kappa\lambda\mu\nu} = T^{\kappa\lambda\mu\nu}(\sigma) \tag{152}$$

since

$$\delta_{\Pi,1} + \delta_{\Pi,-1} = 1 \qquad \text{for} \quad \Pi = \pm 1, \tag{153}$$

which transforms Eq. (78) into

$$T^{\kappa\lambda\mu\nu} = h(\sigma) \sum_{\kappa' = \pm|\kappa|}^{*} \sum_{\lambda' = \pm|\lambda|}^{*} \sum_{\mu' = \pm|\mu|}^{*} \sum_{\nu' = \pm|\nu|}^{*} \Gamma_{\kappa'\lambda'\mu'\nu'}^{\kappa\lambda\mu\nu} Z_{\Pi}^{\kappa'\lambda'\mu'\nu'}, \tag{154}$$

where the abbreviation

$$\Gamma_{\kappa'\lambda'\mu'\nu'}^{\kappa\lambda\mu\nu} = \gamma_{\kappa'}^{\kappa}\gamma_{\lambda'}^{\lambda}\gamma_{\mu'}^{\mu}\gamma_{\nu'}^{\nu} \tag{155}$$

is used and, due to Eqs. (80)–(82),

$$Z_{\Pi}^{\kappa'\lambda'\mu'\nu'} = O_{\Pi} Z^{\kappa'\lambda'\mu'\nu'}. \tag{156}$$

In order to split this expression into sums of integrals between real and imaginary parts of complex charge distributions, i.e., products of two complex AO's, the formulas of Eqs. (85)–(88) are advantageous. Obviously, one has to divide the following quantity into the desired terms:

$$\begin{aligned} h(\sigma) \cdot T^{\kappa\lambda\mu\nu} &= O_{\Pi}\left\{ \sum_{\kappa' = \pm|\kappa|}^{*} \sum_{\lambda' = \pm|\lambda|}^{*} \sum_{\mu' = \pm|\mu|}^{*} \sum_{\nu' = \pm|\nu|}^{*} \Gamma_{\kappa'\lambda'\mu'\nu'}^{\kappa\lambda\mu\nu} Z^{\kappa'\lambda'\mu'\nu'} \right\} \\ &= O_{\Pi}[(\chi^{|\kappa|} + \zeta_{\kappa}\chi^{|\kappa|*})(\chi^{|\lambda|} + \zeta_{\lambda}\chi^{|\lambda|*})| \\ &\qquad \times (\chi^{|\mu|} + \zeta_{\mu}\chi^{|\mu|*})(\chi^{|\nu|} + \zeta_{\nu}\chi^{|\nu|*})] \end{aligned} \tag{157}$$

The last bracket specifies an integral as usual.

Consider the case $\kappa \neq 0$, $\lambda \neq 0$, $\mu \neq 0$, $\nu \neq 0$; then $\zeta_\kappa = \langle\kappa\rangle$, $\zeta_\lambda = \langle\lambda\rangle$, $\zeta_\mu = \langle\mu\rangle$, $\zeta_\nu = \langle\nu\rangle$. Hence,

$$\begin{aligned} h(\sigma)\, T^{\kappa\lambda\mu\nu} = 2O_\Pi\{(\kappa\lambda|\mu\nu) &+ \langle\kappa\rangle\langle\lambda\rangle(\bar{\kappa}\bar{\lambda}|\mu\nu) \\ &+ \langle\kappa\rangle\langle\mu\rangle(\bar{\kappa}\lambda|\bar{\mu}\nu) + \langle\kappa\rangle\langle\nu\rangle(\bar{\kappa}\lambda|\mu\bar{\nu}) \\ &+ \langle\kappa\rangle(\bar{\kappa}\lambda|\mu\nu) + \langle\lambda\rangle(\kappa\bar{\lambda}|\mu\nu) \\ &+ \langle\mu\rangle(\kappa\lambda|\bar{\mu}\nu) + \langle\nu\rangle(\kappa\lambda|\mu\bar{\nu})\}. \qquad (158) \end{aligned}$$

Obviously, one can proceed only if the signs of the products $\langle\kappa\rangle\langle\lambda\rangle$ and $\langle\mu\rangle\langle\nu\rangle$ are also known. This distinguishes four cases A, B, C, D which are specified in Table II. For later purposes the values of $\langle s\rangle$, namely the signs of the quantity

$$s = \langle\kappa\rangle\langle\lambda\rangle + \langle\mu\rangle\langle\nu\rangle \qquad (159)$$

for the four cases A, B, C, D are also listed.

TABLE II

Case	$\langle\kappa\rangle\langle\lambda\rangle$	$\langle\mu\rangle\langle\nu\rangle$	Π	σ	$\langle s\rangle$
A	1	1	1	$\pm4, 0$	1
B	-1	-1	1	0	-1
C	1	-1	-1	±2	1
D	-1	1	-1	±2	1

In Table III, in addition to the case (No. 1) that all four indices κ, λ, μ, ν are unequal to zero, there are the following cases possible: There are four cases (Nos. 21, 22, 23, 24) that one of the four indices is equal to, whereas the remaining three are different from, zero. There are six cases (Nos. 31–36) that two of the four indices are equal to, the other two are unequal to zero. There are four possible cases (No. 41–44) that three indices vanish, but one index is unequal to zero. Finally, there is one case (No. 5) that all four indices are equal to zero.

This defines sixteen possible cases. To each of these cases belong in general four different cases A, B, C, D, so that one finally has to distinguish $16 \times 4 = 64$ different cases. However, the division of the four indices κ, λ, μ, ν into groups of two, i.e., κ, λ and μ, ν, excludes some cases. Due to Table III where the cases No. 1–5 are listed, the following cases do not occur: The possibilities B and D are excluded for the cases No. 31, 41, 43,

TABLE III

Case	κ	λ	μ	ν
1	$\neq 0$	$\neq 0$	$\neq 0$	$\neq 0$
21	0	$\neq 0$	$\neq 0$	$\neq 0$
22	$\neq 0$	0	$\neq 0$	$\neq 0$
23	$\neq 0$	$\neq 0$	0	$\neq 0$
24	$\neq 0$	$\neq 0$	$\neq 0$	0
31	0	0	$\neq 0$	$\neq 0$
32	$\neq 0$	0	0	$\neq 0$
33	$\neq 0$	$\neq 0$	0	0
34	0	$\neq 0$	0	$\neq 0$
35	$\neq 0$	0	$\neq 0$	0
36	0	$\neq 0$	$\neq 0$	0
41	0	0	0	$\neq 0$
42	$\neq 0$	0	0	0
43	0	0	$\neq 0$	0
44	0	$\neq 0$	0	0
5	0	0	0	0

and 5, whereas the cases B and C are excluded for the cases No. 33, 42, 44, and 5. If these fifteen not existing combinations are subtracted, there remain 64 – 15 = 49 possible cases, each of them resulting in a different expression of $T^{\kappa\lambda\mu\nu}$.

It turns out that it is possible to express $T^{\kappa\lambda\mu\nu}$ for all cases by one formula which is symmetrical with respect to the pairs of indices κ, λ and μ, ν, if the following definitions are used:

$$O^{(1)} = O_{\langle\kappa\rangle\langle\lambda\rangle} = \begin{cases} \mathrm{Re} & \text{for } \langle\kappa\rangle\langle\lambda\rangle = 1, \\ \mathrm{Im} & \text{for } \langle\kappa\rangle\langle\lambda\rangle = -1; \end{cases} \tag{160}$$

$$O^{(2)} = O_{\langle\mu\rangle\langle\nu\rangle} = \begin{cases} \mathrm{Re} & \text{for } \langle\mu\rangle\langle\nu\rangle = 1, \\ \mathrm{Im} & \text{for } \langle\mu\rangle\langle\nu\rangle = -1; \end{cases} \tag{161}$$

$$\xi^{(1)} = \xi_{\kappa,\lambda} = \begin{cases} 1 & \text{if } \kappa \neq 0, \lambda \neq 0, \\ 0 & \text{otherwise;} \end{cases} \tag{162}$$

$$\xi^{(2)} = \xi_{\mu,\nu} = \begin{cases} 1 & \text{if } \mu \neq 0, \nu \neq 0, \\ 0 & \text{otherwise;} \end{cases} \tag{163}$$

$$\eta^{(1)} = \eta(|\kappa| + |\lambda|) = \begin{cases} 1 & \text{if } |\kappa| + |\lambda| = 0, \\ 2 & \text{if } |\kappa| + |\lambda| \neq 0; \end{cases} \tag{164}$$

$$\eta^{(2)} = \eta(|\mu| + |\nu|) = \begin{cases} 1 & \text{if } |\mu| + |\nu| = 0, \\ 2 & \text{if } |\mu| + |\nu| \neq 0. \end{cases} \tag{165}$$

σ is defined by Eqs. (22), (58), (147); s is defined by Eq. (159) with $\langle s\rangle =$ sign (s) given in Table II; $h(\sigma)$ is determined by Eq. (150) with $h(\sigma)\, h(\sigma) = 1$. Then, Eq. (158) becomes

$$\begin{aligned} T^{\kappa\lambda\mu\nu} = h(\sigma)\langle s\rangle\, \eta^{(1)}\, \eta^{(2)}\{&(O^{(1)}(\chi^{|\kappa|}\chi^{|\lambda|})\,|\,O^{(2)}(\chi^{|\mu|}\chi^{|\nu|})) \\ &+ \langle\kappa\rangle\xi^{(1)}\langle\mu\rangle\xi^{(2)}(O^{(1)}(\chi^{|\kappa|*}\chi^{|\lambda|})\,|\,O^{(2)}(\chi^{|\mu|*}\chi^{|\nu|})) \\ &+ \langle\kappa\rangle\xi^{(1)}(O^{(1)}(\chi^{|\kappa|*}\chi^{|\lambda|})\,|\,O^{(2)}(\chi^{|\mu|}\chi^{|\nu|})) \\ &+ \langle\mu\rangle\xi^{(2)}(O^{(1)}(\chi^{|\kappa|}\chi^{|\lambda|})\,|\,O^{(2)}(\chi^{|\mu|*}\chi^{|\nu|}))\}. \end{aligned} \tag{166}$$

This may be written in an even more compact form as follows. $Q^{(1)}$ and $Q^{(2)}$ may be defined by

$$\begin{aligned} Q^{(1)}\, O^{(1)}(\chi^{|\kappa|}\chi^{|\lambda|}) &= \langle\kappa\rangle\xi^{(1)}O^{(1)}(\chi^{|\kappa|*}\,\chi^{|\lambda|}) \\ &= \langle\kappa\rangle(1-\delta_{\kappa,0})(1-\delta_{\lambda,0})\, O^{(1)}(\chi^{|\kappa|*}\,\chi^{|\lambda|}), \end{aligned} \tag{167}$$

$$\begin{aligned} Q^{(2)}O^{(2)}(\chi^{|\mu)}\chi^{|\nu|}) &= \langle\mu\rangle\xi^{(2)}O^{(2)}(\chi^{|\mu|*}\,\chi^{|\nu|}) \\ &= \langle\mu\rangle(1-\delta_{\mu,0})(1-\delta_{\nu,0})\, O^{(2)}(\chi^{|\mu|*}\,\chi^{|\nu|}). \end{aligned} \tag{168}$$

Hence, $O^{(1)}$ and $Q^{(1)}$ operate only on $\chi^{|\kappa|}\chi^{|\lambda|}$ but not on $\chi^{|\mu|}\chi^{|\nu|}$. Equivalently, $O^{(2)}$ operates only on $\chi^{|\mu|}\chi^{|\nu|}$ but not on $\chi^{|\kappa|}\chi^{|\lambda|}$, and $Q^{(2)}$ operates only on $O^{(2)}(\chi^{|\mu|}\chi^{|\nu|})$ but not on $O^{(1)}(\chi^{|\kappa|}\chi^{|\lambda|})$. Then, one can write

$$\begin{aligned} T^{\kappa\lambda\mu\nu} = h(\sigma)\langle\langle\kappa\rangle\langle\lambda\rangle + \langle\mu\rangle\langle\nu\rangle\rangle\, \eta(|\kappa| + |\lambda|)\, \eta(|\mu| + |\nu|) \\ \cdot((1 + Q^{(1)})O^{(1)}(\chi^{|\kappa|}\chi^{|\lambda|})\,|\,(1 + Q^{(2)})O^{(2)}(\chi^{|\mu|}\chi^{|\nu|})). \end{aligned} \tag{169}$$

If this is introduced into Eq. (54), the integrals between real MO's are expressed by integrals between real and imaginary parts of complex charge distributions.

V. Overlap Integrals between Real MO's

A. Representation by Overlap Integrals between Complex AO's

Since the operators of the Hamiltonian used in the MO theory are real, the only difficulty due to the use of complex atomic orbitals is caused by their products in the integrals which lead to real and complex contributions and have to be rearranged in such a manner that the integrals between MO's become real. This procedure was described above with respect to the product of four orbitals, because electron–electron interaction integrals between products of two functions were discussed.

A special case is the overlap integral where the integral between two functions instead of two products of two functions is considered, i.e., for real MO's

$$[\varphi_a | \varphi_c] = \int d\mathbf{r}_1 \, \varphi_a(1) \, \varphi_c(1). \tag{170}$$

In this section, the procedures discussed in the foregoing should be specified to this simpler case which may also serve as an example. Since the simplification of the formulas given for the general case is straightforward, the new expressions can elucidate the procedure and summarize the former discussions. With Eqs. (9)–(12) and Eqs. (19), (29), it is, according to Eq. (30),

$$[\varphi^p | \varphi^r] = \sum_{\kappa=-k}^{k} \sum_{\mu=-m}^{m} \mathbb{C}_k{}^{\kappa} \mathbb{C}_m{}^{\mu} [\chi_k{}^{\kappa} | \chi_m{}^{\mu}]. \tag{171}$$

Again, one may write

$$\mathbb{C}_k{}^{\kappa} \mathbb{C}_m{}^{\mu} = D_1^{\kappa\mu} + i D_{-1}^{\kappa\mu}, \tag{172}$$

$$[\chi_k{}^{\kappa} | \chi_m{}^{\mu}] = Z_1^{\kappa\mu} + i Z_{-1}^{\kappa\mu}. \tag{173}$$

Here, $D_{\pm 1}^{\kappa\mu}$ and $Z_{\pm 1}^{\kappa\mu}$ with two upper indices are used which will not be confused with the different quantities of Eqs. (31), (32) with four upper indices. Since the integral of Eq. (171) is real, one has also

$$[\varphi^p | \varphi^r] = \sum_{\kappa=-k}^{k} \sum_{\mu=-m}^{m} \{D_1^{\kappa\mu} Z_1^{\kappa\mu} - D_{-1}^{\kappa\mu} Z_{-1}^{\kappa\mu}\}, \tag{174}$$

$$0 = \sum_{\kappa=-k}^{k} \sum_{\mu=-m}^{m} \{D_1^{\kappa\mu} Z_{-1}^{\kappa\mu} + D_{-1}^{\kappa\mu} Z_1^{\kappa\mu}\}. \tag{175}$$

Furthermore

$$D_1^{\kappa\mu} = \langle\kappa\rangle^{\kappa} \langle\mu\rangle^{\mu} \{x_k^{|\kappa|} x_m^{|\mu|} - \zeta_\kappa \zeta_\mu x_k^{-|\kappa|} x_m^{-|\mu|}\}, \tag{176}$$

$$D_{-1}^{\kappa\mu} = \langle\kappa\rangle^{\kappa} \langle\mu\rangle^{\mu} \{\zeta_\kappa x_k^{-|\kappa|} x_m^{|\mu|} + \zeta_\mu x_k^{|\kappa|} x_m^{-|\mu|}\}. \tag{177}$$

These relations may be obtained from Eqs. (35), (36) with $\lambda = \nu = 0$ and $x_l{}^0 = x_n{}^0 = 1$, and may be written as

$$D_\omega^{\kappa\mu} = \sum_{\kappa''=\pm|\kappa|}^{*} \sum_{\mu''=\pm|\mu|}^{*} \varepsilon_{\kappa''}^{\mu''} \delta_{\Pi'',\omega} \gamma_\kappa^{\kappa''} \gamma_\mu^{\mu''} x_k^{\kappa''} x_m^{\mu''} \tag{178}$$

with $\omega = +1, -1$, and the definitions of Eqs. (46)–(48). If besides Π'' also σ'' and $\beta_\omega^{\Pi''}(\sigma'')$ are used according to Eqs. (41), (45), one has to observe that $\langle\lambda'' = 0\rangle = \langle\nu'' = 0\rangle = 1$ have to be kept in Eq. (41) and the other expressions; then, $D_\omega^{\kappa\mu}$ of Eq. (178) follows also from Eq. (37) immediately, since then

$$\beta_\omega^{\Pi''}(\sigma'') = \varepsilon_{\kappa''}^{\mu''} \delta_{\Pi'',\omega} \tag{179}$$

holds for

$$\sigma'' = \langle\kappa''\rangle + \langle\mu''\rangle + 2, \qquad \Pi'' = \langle\kappa''\rangle\langle\mu''\rangle \cdot 1 \cdot 1, \tag{180}$$

where $\varepsilon_{\kappa''}^{\mu''}$ is defined by Eq. (47) and $\delta_{\Pi'',\omega}$ is the Kronecker delta. With $z_l{}^0 = z_n{}^0 = 1$ one has from Eq. (52)

$$Z_\omega^{\kappa\mu} = \sum_{\kappa'''=\pm|\kappa|}^{*} \sum_{\mu'''=\pm|\mu|}^{*} \varepsilon_{\kappa'''}^{\mu'''} \delta_{\Pi''',\omega} \gamma_\kappa^{\kappa'''} \gamma_\mu^{\mu'''} [z^{\kappa'''} | z^{\mu'''}]. \tag{181}$$

If Eq. (178) is introduced into Eq. (174), the interchange of summation signs as used in Eq. (53) leads to

$$[\varphi^p | \varphi^r] = \sum_{\kappa=-k}^{k} \sum_{\mu=-m}^{m} x^\kappa x^\mu T^{\kappa\mu} \tag{182}$$

where

$$T^{\kappa\mu} = \varepsilon_\kappa^\mu \sum_{\kappa'=\pm|\kappa|}^{*} \sum_{\mu'=\pm|\mu|}^{*} \gamma_{\kappa'}^{\kappa} \gamma_{\mu'}^{\mu} (\delta_{\Pi,1} Z_1^{\kappa'\mu'} - \delta_{\Pi,-1} Z_{-1}^{\kappa'\mu'}). \tag{183}$$

With

$$\begin{aligned} \Pi &= \langle\kappa\rangle\langle 0\rangle\langle\mu\rangle\langle 0\rangle = \langle\kappa\rangle\langle\mu\rangle \\ \sigma &= \langle\kappa\rangle + \langle 0\rangle + \langle\mu\rangle + \langle 0\rangle = \langle\kappa\rangle + \langle\mu\rangle + 2 \end{aligned} \tag{184}$$

is

$$\begin{aligned} \langle\kappa\rangle\langle\mu\rangle\varepsilon_\kappa^\mu &= \langle\kappa\rangle\delta_{\langle\mu\rangle,1} + \langle\mu\rangle\delta_{\langle\mu\rangle,-1} \\ &= h(\langle\kappa\rangle + \langle\mu\rangle + 2), \end{aligned} \tag{185}$$

where $h(\langle\kappa\rangle + \langle\mu\rangle + 2) = h(\sigma)$ is given by Eq. (150). Then follows in accordance with Eqs. (149)–(154)

$$T^{\kappa\mu} = h(\langle\kappa\rangle + \langle\mu\rangle + 2) \sum_{\kappa'=\pm|\kappa|}^{*} \sum_{\mu'=\pm|\mu|}^{*} \gamma_{\kappa'}^{\kappa} \gamma_{\mu'}^{\mu} Z_\Pi^{\kappa'\mu'} \tag{186}$$

or

$$\begin{aligned} T^{\kappa\mu} &= h(\langle\kappa\rangle + \langle\mu\rangle + 2)\, O_\Pi[(\chi^{|\kappa|} + \zeta_\kappa \chi^{|\kappa|*}) | (\chi^{|\mu|} + \zeta_\mu \chi^{|\mu|*})] \\ &= h(\langle\kappa\rangle + \langle\mu\rangle + 2)\, O_\Pi\{[\chi^{|\kappa|} | \chi^{|\mu|}] + \zeta_\kappa \zeta_\mu [\chi^{|\kappa|*} | \chi^{|\mu|*}] \\ &\quad + \zeta_\kappa [\chi^{|\kappa|*} | \chi^{|\mu|}] + \zeta_\mu [\chi^{|\kappa|} | \chi^{|\mu|*}]\}. \end{aligned} \tag{187}$$

In order to compare this with former results, one has to put

$$\lambda = \nu = 0, \qquad \langle\lambda\rangle = \langle\nu\rangle = 1. \tag{188}$$

Then only the nine cases

35: A,B,C,D; 42: A,D; 43: A,C; 5: A

of Table III are possible. If for these cases all expressions are calculated, the results allow two comparisons. In the first place, the operators $O_1 = \mathrm{Re}$ and $O_{-1} = \mathrm{Im}$ may be drawn into the integrals; then one can check that for all cases the compact way of writing $T^{\kappa\mu}$ according to Eqs. (166), (169) holds true:

$$T^{\kappa\mu} = h(\langle\kappa\rangle + \langle\mu\rangle + 2)\,\langle\langle\kappa\rangle + \langle\mu\rangle\rangle\,\eta^{(1)}\,\eta^{(2)}[O^{(1)}\chi^{|\kappa|}\,|\,O^{(2)}\chi^{|\mu|}]. \tag{189}$$

This, however, corresponds to expressing the results derived in Section II by the results derived in Section IV. As discussed there, the integrals between real MO's may be represented by sums of real and imaginary parts of complex integrals between complex AO's [this way of doing the calculation corresponds to the expression Eq. (187) of the present discussion of overlap integrals] *or* the integrals between real MO's may be represented by sums of integrals between real and imaginary parts of the complex functions which are products of two AO's, i.e., charge density distributions, if electron–electron interaction integrals are concerned, or single AO's in the case of overlap integrals which is considered here. This procedure leads to Eq. (189).

In the second place, the relationships of the formulas written in either real or complex AO's become obvious if the simple overlap integral is considered, as will be shown in the next section.

B. Representation by Overlap Integrals between Real AO's

Because of Eq. (188), now holds

$$O^{(1)} = O_{\langle\kappa\rangle}, \qquad O^{(2)} = O_{\langle\mu\rangle}. \tag{190}$$

Therefore, by use of Eqs. (102), (103), (125), the expression Eq. (189) may be written as

$$T^{\kappa\mu} = h(\langle\kappa\rangle + \langle\mu\rangle + 2)\,\langle\langle\kappa\rangle + \langle\mu\rangle\rangle\eta^{(1)}\eta^{(2)} \times \frac{(-1)^{\kappa}}{(2-\delta_{\kappa,0})^{1/2}}\,\frac{(-1)^{\mu}}{(2-\delta_{\mu,0})^{1/2}}\,[\rho^{\kappa}\,|\,\rho^{\mu}], \tag{191}$$

where ρ^{κ} and ρ^{μ} specify real AO's. Since

$$h(\langle\kappa\rangle + \langle\mu\rangle + 2)\,\langle\langle\kappa\rangle + \langle\mu\rangle\rangle = \langle\kappa\rangle\langle\mu\rangle, \tag{192}$$

and also due to Eq. (188)

$$\eta^{(1)} = 2 - \delta_{\kappa,0}, \qquad \eta^{(2)} = 2 - \delta_{\mu,0}, \tag{193}$$

one finally has

$$T^{\kappa\mu} = (-1)^{\kappa}\langle\kappa\rangle(2-\delta_{\kappa,0})^{1/2}(-1)^{\mu}\langle\mu\rangle(2-\delta_{\mu,0})^{1/2}[\rho^{\kappa}\,|\,\rho^{\mu}]. \tag{194}$$

Therefore, if x^κ and x^μ are replaced by d^κ and d^μ according to Eq. (138), then Eq. (182) becomes indeed

$$[\varphi^p|\varphi^r] = \sum_{\kappa=-k}^{k} \sum_{\mu=-m}^{m} d^\kappa d^\mu [\rho^\kappa|\rho^\mu], \tag{195}$$

corresponding to Eqs. (139) and (142).

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The Symmetric Groups and Calculation of Energies of *n*-Electron Systems in Pure Spin States

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I. Introduction

The discovery by Heisenberg (1926) of the exchange phenomenon involving identical particles in quantum mechanical systems answered several problems in the old quantum theory and started the investigations of the properties of permutations as constants of the motion, the properties of the symmetric groups, and the ways in which exchange and spin interact. Dirac (1928) exploited the duality (see, for example, Murnaghan, 1938) between the irreducible representation of symmetric groups on the one hand and continuous unitary groups on the other to develop the vector model. Van Vleck (1932) made further developments in the vector model, removing some of the original restrictions, and Serber (1934) investigated the use of some particular types of irreducible representations of S_n in the exchange problem. Wigner (1931) gave a thorough discussion of applications of group theoretic methods to discussions of atomic spectra. Weyl (1930) and others during this same period developed the spin–valence procedure based upon the theory of the symmetric groups. By this time Slater (1929) had introduced the determinantal function now bearing his name, and using it he and many others made applications to many problems of atomic spectra with great success.

Examination of formulas and equations cast in the symmetric group formalism reveals the presence of sums over in general all $n!$ permutations of this group. For a system of any size this is a distressingly large number, and in spite of the fact that these sums are usually easily handled in formal discussions, such equations appear to have a limited usefulness in numerical computation—at least if used directly. It would seem that this fact has contributed significantly to the popularity of the Slater determinant as a computational device, since in spite of the fact that the basic definition of an $n \times n$ determinant involves $n!$ terms, the many mathematical properties enable one to evaluate a determinant numerically with an amount of labor roughly proportional to n^3. Thus, among its other useful properties, the Slater determinant may be considered a device for circumventing a direct sum over the symmetric groups.

Yamanouchi (1936) returned to the symmetric group representation formalism and derived a particular irreducible representation based on the spin branching diagram. This representation proved to be the same as Young's *orthogonal* representation (see, for example, Rutherford, 1948), and Kotani *et al.* (1955) has made further developments in the theory for uses in molecular calculations.

More recently Matsen (1964) and his co-workers have developed a spin-free formalism which is based on the observation that for a spin-free Hamiltonian the spin functions are essentially determined by symmetry and the dynamical problem of obtaining the energy may be confined to the spatial part of the wave function. Matsen's proposal is to solve the spatial problem first in a spin-free context and then proceed to include the more subtle effects of spin, if needed, by the application of perturbation theory.

Still more recently Goddard (1967) and his co-workers have utilized Yamanouchi's representation to give a factorization of the antisymmetrizer for applications to calculations of essentially a DODS type.

The present author (Gallup, 1968a) has also examined the DODS problem and some other aspects of the theory in an essentially spin-free way with the use of certain Young operators.

It is the purpose of this chapter to reexamine certain aspects of the theory of symmetric group representations and algebras, however, always with an eye to the applications of these in numerical computations of the spin-free portion of the problem. Löwdin (1967) and Löwdin and Goscinski (1970) have recently given reviews which examine some of these subjects.

II. Representations of S_n, Young Operators, and the Variational Problem

A. Characteristic Units

If a complete set of irreducible representation matrices for S_n is available, one can use these to construct a matric basis (see, for example, Littlewood, 1950; Löwdin, 1967) for the group algebra

$$e^{\alpha}_{ij} = (f_\alpha/n!)\sum_{\pi} D^{\alpha}(\pi^{-1})_{ji}\,\pi, \tag{1}$$

(note the convention used here for the subscripts on e and D) where f_α is the dimension of D^α. The matric basis satisfies the multiplication rules

$$e^{\alpha}_{ij}\,e^{\beta}_{kl} = \delta_{\alpha\beta}\,\delta_{jk}\,e^{\alpha}_{il}. \tag{2}$$

Any element of the group algebra, x, may be written as $\sum x(\pi)\pi$ and we shall use the notation [ ] to indicate the coefficient of the identity permutation in the contained algebraic element. Thus

$$[x] = x(I), \tag{3}$$

and one of the most important properties of this quantity is

$$[xy] = [yx]. \tag{4}$$

If instead of the irreducible representation matrices, we had been provided with an irreducible matric basis, the matrices can be obtained using (3)

$$\begin{aligned} D^{\alpha}_{ij}(\pi) &= (n!/f_\alpha)[e^{\alpha}_{ji}\,\pi],\\ \pi &= \sum_{\alpha ij} D^{\alpha}(\pi)_{ij}\,e^{\alpha}_{ij}. \end{aligned} \tag{5}$$

This is a most important result, since as it will be seen the theory of Young tableaux provides us with quantities of this type directly rather than representation matrices. We shall return to this later.

The several analyses of the spin-free problem given recently show that for a spin-free Hamiltonian one need not use the entire antisymmetric, space-spin function to obtain the energy. The energy is provided by the spatial part alone and one has

$$E_i^\alpha = \frac{\langle\varphi|H|e_{ii}^\alpha\varphi\rangle}{\langle\varphi|e_{ii}^\alpha\varphi\rangle}; \qquad e_{ii}^\alpha\varphi \neq 0, \tag{6}$$

as a calculation of the energy. The irreducible representation α is determined by the spin state of interest. In (6) φ is a trial spatial function and E_i^α depends upon i and α, in general. It should be emphasized that this simple form for (6) is obtained only if the matric basis satisfies the conditions

$$(e_{ij}^\alpha)^\dagger = e_{ji}^\alpha, \tag{7}$$

hence e_{ii}^α is Hermitian, and (7) with (5) implies that D^α is a unitary representation.

If we have chosen a specific form for φ, such as the product of orbitals, there is an optimal characteristic unit $\mathscr{E}^\alpha$ determined by this choice. Thus, defining $\mathscr{E}^\alpha$ as

$$\mathscr{E}^\alpha = \sum_{ij} a_i{}^* a_j e_{ij}^\alpha; \qquad \sum_i |a_i|^2 = 1, \tag{8}$$

$$(\mathscr{E}^\alpha)^2 = \mathscr{E}^\alpha, \tag{9}$$

and (7) becomes

$$E^\alpha(a) = \frac{\langle\varphi|H\mathscr{E}^\alpha|\varphi\rangle}{\langle\varphi|\mathscr{E}^\alpha\varphi\rangle}. \tag{10}$$

The problem of minimizing $E^\alpha(a)$ with respect to a_i gives one the familiar matrix eigenvalue problem:

$$\begin{gathered}(\mathbf{H}^\alpha - E\mathbf{S}^\alpha)\mathbf{a} = 0,\\ H_{ij}^\alpha = \langle\varphi|He_{ij}^\alpha|\varphi\rangle,\\ S_{ij}^\alpha = \langle\varphi|e_{ij}^\alpha|\varphi\rangle.\end{gathered} \tag{11}$$

Byers-Brown (1966) has shown that the eigenvalues of (11) depend only on the character of the representation α (see also Löwdin, 1967; Gallup, 1968a). However, if one is also interested in obtaining the eigenvectors it is in effect necessary to know the e_{ij}^α also. This is, of course, a severe problem for the symmetric groups. However, it appears possible to make considerable progress in solving this problem.

B. Young Operators and Sandwich Representation

The symmetric groups, being non-abelian, have many multidimensional irreducible representations, and as is well known, such representations are far from unique. Thus any representation $D(\pi)$, $\pi \in S_n$, may be subjected to a similarity transformation,

$$\bar{D}(\pi) = A^{-1} D(\pi) A, \tag{12}$$

to get an equivalent one. It may be, however, that for computational purposes one particular representation has advantages over all others among the infinity of possibilities, and in this sense there may be a preferred one. Of course, one must take care that the final results do not depend on this choice. Since a really clear-cut criterion of computational ease is seldom available, a choice may be somewhat subjective, but the run time of a reasonably efficient computer program may always be used.

In the problem of solving (11) it is necessary to have expressions for the e_{ij}^{α} and Yamanouchi's work may be used. However, in his analyses of the properties of the symmetric groups, Young introduced the concept of tableaux and defined two operators P^{α}, the row symmetrizer of the tableau and N^{α}, the column antisymmetrizer of the tableau α. In this article we shall normalize P^{α} and N^{α} so that they are idempotent

$$(P^{\alpha})^2 = P^{\alpha}, \tag{13}$$

$$(N^{\alpha})^2 = N^{\alpha}. \tag{14}$$

The result which is of principal interest to us is that

$$\begin{aligned} \theta' N^{\alpha} P^{\alpha} &= e_{11}^{\alpha}, \\ 1/\theta' &= (n!/f^{\alpha})[P^{\alpha} N^{\alpha}], \end{aligned} \tag{15}$$

where we have chosen to write (15) for the 1,1 characteristic unit. The quantity $\theta' P^{\alpha} N^{\alpha} = (\theta' N^{\alpha} P^{\alpha})^{\dagger}$ would also work. As was pointed out above, it is much more convenient to have e_{ii}^{α} Hermitian, and two other expressions which satisfy this criterion are

$$\theta N^{\alpha} P^{\alpha} N^{\alpha} = e_{11}^{\alpha} = (e_{11}^{\alpha})^{\dagger}, \tag{16}$$

$$\theta' P^{\alpha} N^{\alpha} P^{\alpha} = e_{11}^{\alpha'} = (e_{11}^{\alpha'})^{\dagger}. \tag{17}$$

It was apparently this author (Gallup, 1969) who first observed that $\theta N^{\alpha} P^{\alpha} N^{\alpha}$ is considerably simpler to handle computationally for two-column tableaux than is $\theta' P^{\alpha} N^{\alpha} P^{\alpha}$ and gave an explicit subgroup-coset factorization (Gallup, 1968b). Corresponding to (16) and a partition $[2^k, 1^{n-2k}]$ we have

$$\theta N^\alpha P^\alpha N^\alpha = \theta_N N^\alpha X^\alpha, \tag{18}$$

$$X^\alpha = \sum_{l=0}^{k} \binom{n-k}{l}^{-1} B_l, \tag{19}$$

where B_l is the sum of all coset generators of N^α in the $(1^{n-2l}, 2^l)$ class of S_n. More recently Klein and Junker (1971) have given the corresponding expression for $\theta' P^\alpha N^\alpha P^\alpha$. Matsen (1966) and his co-workers have shown that the coefficients of the permutations in this are the same as the "Pauling numbers" introduced by Pauling (1933) in discussions of the valence bond method. Apparently by analogy, these workers have called the coefficients in (19) Pauling numbers, also. However, the inverse binomial coefficients in $\theta N^\alpha P^\alpha N^\alpha$ are just a special case (Gallup, 1969) of the "Sanibel coefficients" (Löwdin, 1956; Pauncz, 1967) introduced in connection with spin-projected Slater determinants. It appears to be necessary to await the results of general usage to decide between these terminologies.

We shall investigate some of the properties of $\theta N^\alpha P^\alpha N^\alpha$ in this section and return to $\theta' P^\alpha N^\alpha P^\alpha$ later. Also, for convenience in this section, we shall denote $\theta N^\alpha P^\alpha N^\alpha$ as e^α.

We now consider all elements of the group algebra of the form $e^\alpha x$. These form a *right invariant algebra* or a right *ideal*, and the theory of standard tableaux provides a *basis* for this invariant algebra. Thus we have $T_1^\alpha \ldots T_f^\alpha$ standard tableau in their customary "last number order" and also permutations $\pi_1^\alpha(=I), \ldots, \pi_f^\alpha$ such that

$$\pi_j^\alpha T_1^\alpha = T_j^\alpha. \tag{20}$$

The central result of the theory is that $e^\alpha \pi_1^\alpha \ldots e^\alpha \pi_f^\alpha$ constitute a complete basis for all elements of the form $e^\alpha x$. It is evident that the set $(\pi_j^\alpha)^{-1} e^\alpha = (e^\alpha \pi_j^\alpha)^\dagger$ is also linearly independent and that these constitute a basis for a *left* invariant algebra. We may define the quantities

$$m_{ij}^\alpha = (\pi_i^\alpha)^{-1} e^\alpha \pi_j^\alpha, \tag{21}$$

and these constitute a basis for the entire αth irreducible representation. The m_{ij}^α satisfy an equation analogous to (3)

$$m_{ij}^\alpha m_{kl}^\beta = (n!/f_\alpha)\, \delta_{\alpha\beta} [\pi_j^\alpha (\pi_k^\alpha)^{-1} e^\alpha] m_{il}^\alpha, \tag{22}$$

where we have used the fact that e^α is primitive. The quantities $[\pi_j^\alpha(\pi_i^\alpha)^{-1}e^\alpha]$ define a set of $f_\alpha \times f_\alpha$ real Hermitian, nonsingular matrices, one for each irreducible representation. We define this as

$$(M^\alpha)_{ij}^{-1} = (n!/f_\alpha)[\pi_i^\alpha(\pi_j^\alpha)^{-1}e^\alpha] = (n!/f_\alpha)[m_{ji}^\alpha], \tag{23}$$

and the inverse matrix is given for later convenience. The m_{ij}^α constitute a basis which we call a t basis (tableau basis) for the entire algebra, and hence

$$\pi = \sum_{\alpha ij} \gamma^\alpha(\pi)_{ij} m_{ij}^\alpha. \tag{24}$$

The constants $\gamma^\alpha(\pi)_{ij}$ are easily seen to be

$$f_\alpha \gamma^\alpha(\pi)_{ij} = n! \sum_{kl} [\pi m_{kl}^\alpha] M_{il}^\alpha M_{kj}^\alpha, \tag{25}$$

and when π is set equal to I, we get

$$I = \sum_{\alpha ij} M_{ij}^\alpha m_{ij}^\alpha. \tag{26}$$

It has been seen that a matric basis such as the e_{ij}^α can be used to determine the matrices of the irreducible representations using (6). Our t basis also defines a set of matrices through an analogous relation,

$$C^\alpha(\pi)_{ij} = (n!/f_\alpha)[\pi m_{ji}^\alpha]. \tag{27}$$

With this definition (24) may be rewritten as

$$\pi = \sum_{\alpha ijkl} C^\alpha(\pi)_{lk} M_{il}^\alpha M_{kj}^\alpha m_{ij}^\alpha. \tag{28}$$

The matrices defined by (27) do not constitute a representation in the normal sense, and we investigate the relationship between $C(\rho\sigma)$ and $C(\rho)$ and $C(\sigma)$. Using (27) and (28) it is seen that

$$\begin{aligned} C^\alpha(\rho\sigma)_{pq} &= (n!/f_\alpha)[\rho\sigma m_{qp}^\alpha] \\ &= (n!/f_\alpha)\sum_{ijkl} M_{il}^\alpha C^\alpha(\rho)_{lk} M_{kj}^\alpha [m_{ij}^\alpha \sigma m_{qp}^\alpha] \\ &= \sum_{jk} C^\alpha(\rho)_{pk} M_{kj}^\alpha C^\alpha(\sigma)_{jq}. \end{aligned} \tag{29}$$

In matrix language this reads

$$\mathbf{C}^\alpha(\rho)\mathbf{M}^\alpha\mathbf{C}^\alpha(\sigma) = \mathbf{C}^\alpha(\rho\sigma). \tag{30}$$

An alternate proof of this has been given (Gallup, 1972a). Matrices functions over a group which satisfy an equation like (30) have been called "sandwich representations" by mathematicians, and we shall retain this picturesque terminology. It may be observed that

$$\mathbf{M}^\alpha = \mathbf{C}^\alpha(I)^{-1}, \tag{31}$$

and that the matrices $\mathbf{M}^\alpha\mathbf{C}^\alpha(\pi)$ and also $\mathbf{C}^\alpha(\pi)\mathbf{M}^\alpha$ are members of ordinary representations, which are, of course, normally not unitary.

The elements of irreducible representation matrices satisfy several important theorems, of which the most important is certainly the orthogonality theorem. These sandwich representations are also irreducible in the same sense and satisfy an analogous equation, viz.,

$$\sum_\pi C^\alpha(\pi)_{ij} C^\beta(\pi^{-1})_{kl} = (n!/f_\alpha)\, \delta_{\alpha\beta} (M^\alpha)^{-1}_{il} (M^\alpha)^{-1}_{jk}. \tag{32}$$

Some other easily derived results are

$$(M^\alpha)^{-1}_{ii} = 1, \qquad i = 1, 2, \ldots, f_\alpha, \tag{33}$$

$$C^\alpha(\pi)_{ij} = C^\alpha(\pi^{-1})_{ji}, \tag{34}$$

$$\begin{aligned} \pi m^\alpha_{ij} &= \sum_{kl} M^\alpha_{lk} C^\alpha(\pi)_{ki} m^\alpha_{lj} \\ &= \sum_{kl} C^\alpha(\pi^{-1})_{ik} M^\alpha_{kl} m^\alpha_{lj}. \end{aligned} \tag{35}$$

The equations we have given for the t bases and sandwich representations all presuppose the coefficients of e^α to be real, as is the case when $e^\alpha = \theta N^\alpha P^\alpha N^\alpha$. Should an e^α be used which has complex coefficients but still $e^\alpha = (e^\alpha)^\dagger$, several of the preceding equations require the insertion of a complex conjugation symbol in places.

Using the t basis we have an alternative expression for $\mathscr{E}^\alpha$,

$$\begin{aligned} &\mathscr{E}^\alpha = \sum_{ij} a_i{}^* a_j m^\alpha_{ij}, \qquad \sum_{ij} a_i{}^* a_j (M^\alpha)^{-1}_{ij} = 1, \\ &(\mathscr{E}^\alpha)^2 = \mathscr{E}^\alpha, \end{aligned} \tag{36}$$

and (36) with (11) yields a variational problem with the same eigenvalues as obtained before. The Hamiltonian and overlap matrices are, of course, obtained in a different representation, hence

$$\mathbf{H}^\alpha_{ij} = \langle \varphi | H m^\alpha_{ij} | \varphi \rangle, \tag{37}$$

$$\mathbf{S}^\alpha_{ij} = \langle \varphi | m^\alpha_{ij} | \varphi \rangle. \tag{38}$$

Again the generalization to more than one configuration is obvious, but we take this up later.

There is one significant difference between the procedure using the matric basis and the procedure using the t basis which involves the computational problem. In order to calculate $\mathbf{H}^\alpha$ (and also $\mathbf{S}^\alpha$) in the matric basis representation one must deal with $\sim f_\alpha{}^2/2$ different operators e^α_{ij}, $i \leq j$ in which the detailed structure is quite different, and this appears to be $\sim f_\alpha{}^2/2$ different problems. However, using the t basis we have a different situation, viz.,

$$\mathbf{H}^\alpha_{ij} = \langle \varphi | H m^\alpha_{ij} | \varphi \rangle = \langle \pi_i{}^\alpha \varphi | H e^\alpha | \pi_j{}^\alpha \varphi \rangle, \tag{39}$$

and from this we see that the different elements of the matrices involve the use of functions differing by only a permutation, and the difficult part of the expression, e^α, is always the same. The same considerations apply to $\mathbf{S}^\alpha$, of course. Klein *et al.* (1971) have also remarked upon this situation.

Examination of (27) shows that

$$m^\alpha_{ij} = (f_\alpha/n!) \sum_\pi C^\alpha(\pi^{-1})_{ji}\pi = (f_\alpha/n!) \sum_\pi C^\alpha(\pi^{-1})_{11}(\pi^\alpha_i)^{-1}\pi\pi_j{}^\alpha, \tag{40}$$

and the coefficients in the m^α_{ij} are always the same set of numbers. The only difference between different m^α_{ij} is that the coefficients are permuted with respect to the permutations. Using (40) and (39) we obtain

$$\mathbf{H}^\alpha_{ij} = \sum_\pi C^\alpha(\pi^{-1})_{11} \langle \pi_i{}^\alpha \varphi | H\pi | \pi_j{}^\alpha \varphi \rangle, \tag{41}$$

and this equation displays the difficulties before us quite clearly, and if we can learn to deal in an indirect fashion with the $n!$ terms in an expression like $\langle \psi | He^\alpha | \varphi \rangle$ for arbitrary ψ and φ, we have apparatus for greatly simplifying the calculation of $\mathbf{H}^\alpha$ and $\mathbf{S}^\alpha$. We shall defer the examination of this question to a later section.

C. Symmetry Adaptation with the t Basis

If we have an arbitrary function of the spatial coordinates of particles, φ, a symmetry-adapted function $m^\alpha_{ij}\varphi$ may be constructed and used in a variational calculation,

$$E^\alpha_{ij} = \frac{\langle m^\alpha_{ij}\varphi | H | m^\alpha_{ij}\varphi \rangle}{\langle m^\alpha_{ij}\varphi | m^\alpha_{ij}\varphi \rangle}; \qquad m^\alpha_{ij}\varphi \neq 0. \tag{42}$$

Using (22) we get

$$E^\alpha_{ij} = \frac{(M^\alpha)^{-1}_{ii}}{(M^\alpha)^{-1}_{ii}} \frac{\langle \varphi | H | m^\alpha_{jj}\varphi \rangle}{\langle \varphi | m^\alpha_{jj}\varphi \rangle}, \tag{43}$$

and it is seen that E^{α}_{ij} is degenerate with respect to i, as is the case when the matric basis is used for symmetry adaptation.

If the function φ is sufficiently arbitrary the functions $\pi\varphi$, $\pi \in S_n$ will all be linearly independent and of necessity the symmetry-adapted functions $m^{\alpha}_{ij}\varphi$ are all also linearly independent. That is, a relation

$$\sum_{\alpha ij} a^{\alpha}_{ij} m^{\alpha}_{ij} \varphi = 0, \tag{44}$$

implies all $a^{\alpha}_{ij} = 0$. Now, there may be occasions where one wishes to relinquish the requirement that the $\pi\varphi$ are all linearly independent. This is particularly true if φ is to be expressed as a CI expansion based upon a complete set of one-particle functions, since a complete set of configurations must contain members with multiple occupancy. These will satisfy a relation

$$\pi\varphi = \varphi, \qquad \pi \neq I, \tag{45}$$

for at least some $\pi \in S_n$. A function satisfying (45) will show linear dependence among the symmetry-adapted functions $m^{\alpha}_{ij}\varphi$ also.

If we examine the overlap matrix of our variation problem (38) for this case, it is seen to be singular and possess a null space spanned by all independent vectors satisfying

$$\mathbf{S}^{\alpha}\mathbf{C}^{\alpha} = 0, \qquad |\mathbf{C}^{\alpha}| \neq 0. \tag{46}$$

$\mathbf{H}^{\alpha}$ possesses the same null space, of course, and for practical calculations it is necessary to eliminate the null space before solving

$$(\mathbf{H}^{\alpha} - E\mathbf{S}^{\alpha})\mathbf{C}^{\alpha} = 0.$$

The t basis constructed from $m^{\alpha}_{11} = \theta N^{\alpha} P^{\alpha} N^{\alpha}$ provides a very simple solution to this problem. The product function

$$\varphi = x_1(1)x_2(2)\cdots x_n(n), \tag{47}$$

where the x_i are the orbitals used, may be symbolized as a tableau, and if the product is arranged so that doubly occupied orbitals occur in the same row of the tableau and all such pairs are listed first, $\mathbf{S}^{\alpha}$ and $\mathbf{H}^{\alpha}$ are presented in blocked form (Gallup, 1972a). Thus

$$\mathbf{S}^{\alpha} = \left\{\begin{array}{c|c} \mathbf{S}^{\alpha}_{11} & 0 \\ \hline 0 & 0 \end{array}\right\}, \qquad |\mathbf{S}^{\alpha}_{11}| \neq 0, \tag{48}$$

and the elimination of the null space is trivial. $\mathbf{H}^{\alpha}$ has the same block structure, of course. Löwdin and Goscinski (1970) have discussed this problem more generally in terms of the supersecular equation.

D. CI Representations of φ

It is well known, of course, that a complete basis for an n-particle tensor space may be constructed from products of one-particle orbitals taken from a complete set, and that this is the idea underlying CI representations of wave functions. We therefore consider a set of ordered configurations,

$$\varphi(\hat{k}) = x_{k_1}(1) \cdots x_{k_n}(n), \tag{49}$$

where the k_i are arranged to give tableaux of the pattern described in the last section, and just one tableau of this type is used for each $\hat{k}$. When these functions are symmetry-adapted, one obtains

$$\varphi^\alpha(\hat{k})_{ij} = m^\alpha_{ij}\, \varphi(\hat{k}). \tag{50}$$

Some of the $\varphi^\alpha(\hat{k})_{ij}$ are identically zero, but we need all of those which are not, and ψ^α_{il}, defined as

$$\psi^\alpha_{il} = \sum_{\hat{k}j} C_{\hat{k}jl}\, \varphi^\alpha(\hat{k})_{ij} \tag{51}$$

is, for the correct $C_{\hat{k}jl}$ an exact solution to the spin-free Schrödinger equation

$$H\psi^\alpha_{il} = E_l^\alpha \psi^\alpha_{il}. \tag{52}$$

In (51) the sum over j includes only those $\varphi^\alpha(\hat{k})_{ij} \neq 0$, and it is seen that E_l^α in (52) is degenerate with respect to i. Because of this degeneracy, in (51) and (52) we may choose $i = 1$ and

$$\psi^\alpha_{1l} = e^\alpha \sum_{\hat{k}i} C_{\hat{k}jl}\, \pi_j{}^\alpha \varphi(\hat{k}). \tag{53}$$

In (53) the $\pi_j{}^\alpha \varphi(\hat{k})$ are equivalent to the use of φ belonging to different standard tableau to get an independent set of functions, a procedure discussed by Matsen (1964).

E. A Determinantal Expression for $e^\alpha \varphi$

We have seen how the t basis with $m^\alpha_{11} = \theta N^\alpha P^\alpha N^\alpha$ provides a simple solution to the null-space problem in $\mathbf{S}^\alpha$ if the φ products are constructed correctly. We now consider possible simplifications which may be used for (37) and which will allow us to evaluate $\mathbf{H}^\alpha$ and $\mathbf{S}^\alpha$ without a direct sum over S_n.

It was suggested in the Introduction that one of the reasons for the popularity of Slater determinants is just that they provide such an indirect summation over $\mathbf{S}_n$. As far as this author is aware, there is no mathematical construct other than a determinant which provides so efficient a way of dealing with such sums, and it appears that a determinantal representation of $e^{\alpha}\varphi$ might be the most fruitful. Such a representation for φ which are orbital products is indeed possible (Gallup, 1972b), with the result that

$$\theta N^{\alpha}P^{\alpha}N^{\alpha}\varphi = [(n-k+1)f_{\alpha}/n!]\int_0^1 (t-1)^k t^{n-2k}\Delta(\varphi, q)\,dt. \tag{54}$$

In (54) $\Delta(\varphi, q)$ is the determinant of a matrix $\Delta(\varphi, q)$ constructed as follows: We define the quantities $\omega_{ij}(q)$ as

$$\begin{aligned} \omega_{ij}(q) &= q, \qquad i, j \leq n-k; \\ &= 1, \qquad \text{otherwise}. \end{aligned} \tag{55}$$

We have taken φ as the product of a set of spatial orbitals $x_1, \ldots, x_n$ and the elements of $\Delta(\varphi, q)$ are

$$\Delta(\varphi, q)_{ij} = \omega_{ij}(q)x_j(i), \tag{56}$$

and before the integration in (54) is performed q is set equal to $t/(t-1)$. Thus (54) provides an expression of the type we have been looking for in that the sum over S_n is contained indirectly in the determinant.

A careful examination of (54) also shows that the integrand is a polynomial in t of degree $n-k$; a numerical quadrature formula may be used to obtain the integral precisely. Therefore

$$e^{\alpha}\varphi = \sum_{i=1}^{N} A_i\Delta(\varphi, q_i), \tag{57}$$

and we have represented $e^{\alpha}\varphi$ as a linear combination of a small number of determinants of the form $\Delta(\varphi, q_i)$. The coefficients are

$$A_i = (f_{\alpha}/n!)(n-k+1)(t_i-1)^k t_i^{n-2k} C_i^N, \tag{58}$$

where t_i and C_i^N are the quadrature points and coefficients, respectively. N may be chosen to be the minimum value necessary to give the integral precisely and hence is $(n-k+1)/2$ or $(n-k+2)/2$, whichever is an integer. In this case the values of A_i and t_i are unique.

F. Matrix Elements of $\mathbf{S}^{\alpha}$ and $\mathbf{H}^{\alpha}$

An adaptation of the formulas given by Löwdin (1955) for Slater determinants is now available for evaluating $\mathbf{S}^{\alpha}$ and $\mathbf{H}^{\alpha}$. Thus, if we have two product functions

$$\begin{aligned} \varphi_x &= x_1(1)\cdots x_n(n) = \pi_j{}^{\alpha}\varphi(\hat{k}), \\ \varphi_\eta &= \eta_1(1)\cdots \eta_n(n) = \pi_i{}^{\alpha}\varphi(\hat{k}'), \end{aligned} \tag{59}$$

the $\mathbf{S}^\alpha$ matrix element is

$$\mathbf{S}^\alpha(\hat{k}'\hat{k})_{ij} = \sum_{l=1}^{N} A_l \Delta(S_{\eta x}, q_l), \tag{60}$$

where

$$\begin{aligned} (S_{\eta x})_{ij} &= \langle \eta_i | x_j \rangle, \\ \Delta(S_{\eta x}, q) &= |\omega_{ij}(q)(S_{\eta x})_{ij}|, \end{aligned} \tag{61}$$

and the result is a sum of a small number of determinants constructed from $S_{\eta x}$.

For the standard quantum chemical Hamiltonian

$$H = \sum_i f_i + \sum_{i<j} g_{ij}, \tag{62}$$

we obtain

$$\begin{aligned} \mathbf{H}^\alpha(\hat{k}', \hat{k})_{ij} &= \sum_{st} B_{st} \langle \eta_s | f | x_t \rangle \\ &+ \sum_{\substack{s<u \\ t<v}} [C_{st,uv} \langle \eta_s \eta_u | g | x_t x_v \rangle - D_{st,uv} \langle \eta_s \eta_u | g | x_v x_t \rangle], \end{aligned} \tag{63}$$

$$B_{st} = \sum_l A_l \omega_{st}(q_l) \Delta^{st}(S_{\eta x}, q_l) \tag{64}$$

$$C_{su,tv} = \sum_l A_l \omega_{st}(q_l) \omega_{uv}(q_l)\, \Delta^{su,tv}(S_{\eta x}, q_l), \tag{65}$$

$$D_{su,tv} = \sum_l A_l \omega_{sv}(q_l) \omega_{ut}(q_l)\, \Delta^{su,tv}(S_{\eta x}, q_l). \tag{66}$$

In (64), (65), and (66) Δ^{st} and $\Delta^{su,tv}$ are the single and double cofactors of the *st* element and *su–tv* pair, respectively, in the determinant.

For actual computations the cofactors in (64), (65), and (66) may be expressed in terms of elements $S_{\eta x}^{-1}$ more simply, and in case $S_{\eta x}$ is singular quite accurately, in terms of $(S_{\eta x} + \varepsilon)^{-1}$, where ε is a small matrix arranged so that $S_{\eta x} + \varepsilon$ is nonsingular. This is necessary in some cases only, since if $S_{\eta x}$ is singular and of rank $\leq (n - 3)$ the corresponding elements of $\mathbf{S}^\alpha$ and $\mathbf{H}^\alpha$ are both zero. For further details the reader is referred to another article (Gallup, 1972b).

G. Representations of $\theta' P^\alpha N^\alpha P^\alpha \varphi$

As was mentioned above, Young's theory also provides the primitive, Hermitian idempotent, $\theta' P^\alpha N^\alpha P^\alpha$, from which another t basis may be constructed. The question as to whether there is a representation, determinantal or otherwise, of $\theta' P^\alpha N^\alpha P^\alpha$ of comparable simplicity to (54) or (57) is open. It may be mentioned that if $n = 3$, doublet or $n = 4$, singlet, the determinant in (54) may be replaced by the permanent, $\overset{+}{|}\ \overset{+}{|}$, and $\theta' P^\alpha N^\alpha P^\alpha$ is obtained, because in these cases the representations of S_n are self-conjugate. Whether or not such expressions involving the permanent can be generalized appears unimportant, since the permanent has almost none of the useful mathematical properties of a determinant and does not provide an efficient way of dealing with sums over S_n.

An alternative is to express $\theta' P^\alpha N^\alpha P^\alpha$ in terms of the $N^\alpha P^\alpha N^\alpha$ t basis. Let us define

$$p^\alpha_{11} = \theta' P^\alpha N^\alpha P^\alpha = (p^\alpha_{11})^2, \tag{67}$$

and

$$p^\alpha_{ij} = (\pi_i^\alpha)^{-1} p^\alpha_{11} \pi_j^\alpha. \tag{68}$$

The whole theory of these elements and the corresponding sandwich representations may be carried through as was done for the m^α_{ij}. Thus

$$p^\alpha_{ij} p^\beta_{kl} = \delta_{\alpha\beta} (P^\alpha)^{-1}_{jk} p^\alpha_{il}, \tag{69}$$

where P^α is the matrix analogous to M^α for the m^α_{ij}. The completeness of the m^α_{ij} in the αth subalgebra allows us to write

$$p^\alpha_{ij} = \sum_{kl} d^\alpha_{ij,kl} m^\alpha_{kl}, \tag{70}$$

and an easy calculation gives

$$d^\alpha_{ij,kl} = (n!/f_\alpha) \sum_{pq} M^\alpha_{lp} [p^\alpha_{ij} m^\alpha_{pq}] M^\alpha_{qk}. \tag{71}$$

Computationally, (71) is not very simple, and it appears that representing the p^α_{ij} in terms of determinants in this way is not very fruitful.

III. Mathematical Properties of $\theta N^\alpha P^\alpha N^\alpha \varphi$

In this section some of the mathematical properties of $\theta N^\alpha P^\alpha N^\alpha \varphi$ and its determinantal form (54) will be investigated. As we shall see, this expression has much the same convenience of use as has the Slater determinant. As before we consider those tableaux for which $\alpha = [2^k, 1^{n-2k}]$, and in the following we reserve k for this purpose.

A. Effects of Double Occupancy

When the product function φ contains particular orbitals more than once, (54) may be simplified. Consideration of (56) shows that Δ may be written in block form

$$\Delta(\varphi, q) = \left\{\begin{array}{c|c} A & B \\ \hline C & qD \end{array}\right\}, \tag{72}$$

where the block D is $k \times k$. It should be recalled that in Δ we use the particle numbers as row labels and the function indices as column labels. If now in our tableau, the first p rows have paired functions inserted, $p \leq k$, we further refine the blocks of Δ and have

$$\Delta(\varphi, q) = \left\{\begin{array}{c|c|c|c} A_1 & A_2 & B_1 & B_2 \\ \hline C_1 & C_2 & qD_1 & qD_2 \end{array}\right\}, \tag{73}$$

where A_1 is $(n - k) \times p$, etc. Because of our double-occupancy assumption it is seen that $A_1 = B_1$ and $C_1 = D_1$ and when $|\Delta|$ is formed it is seen that it may be written

$$\Delta(\varphi, q) = (q - 1)^p \left|\begin{array}{c|c|c|c} A_1 & A_2 & 0 & B_2 \\ \hline 0 & C_2 & D_1 & qD_2 \end{array}\right|. \tag{74}$$

When (74) is inserted into (54) we get

$$\theta N^\alpha P^\alpha N^\alpha \varphi = \left(\frac{f_\alpha}{n!}\right)(n - k + 1) \int_0^1 (t - 1)^{k-p} t^{n-2k} \left|\begin{array}{c|c|c|c} A_1 & A_2 & 0 & B_2 \\ \hline 0 & C_2 & D_1 & qD_2 \end{array}\right| dt. \tag{75}$$

The degree of the integrand has been reduced and fewer terms are required in (57).

If $p = k$, the maximum pairing allowed, B_2 and D_2 are not present and (75) becomes just one term

$$\theta N^\alpha P^\alpha N^\alpha \varphi = \frac{f_\alpha (n - k + 1)}{n!\,(n - 2k + 1)} \left|\begin{array}{c|c|c} A_1 & A_2 & 0 \\ \hline 0 & C_2 & D_1 \end{array}\right|. \tag{76}$$

The null space of (46) is of dimensionality $f_\alpha - 1$ in this case and $\mathbf{H}^\alpha$ and $\mathbf{S}^\alpha$ are 1×1 matrices and the variational problem reduces to

$$E^\alpha = \frac{\langle \varphi \,|\, H N^\alpha P^\alpha N^\alpha \,|\, \varphi \rangle}{\langle \varphi \,|\, N^\alpha P^\alpha N^\alpha \varphi \rangle}, \tag{77}$$

and if the orbitals in φ are optimized to give a minimum in E^α, we have the restricted Hartree–Fock problem.

If in addition to $p = k$, we have $k = n/2$ also, A_2 and C_2 are not present in (76). In this case

$$\theta N^\alpha P^\alpha N^\alpha \varphi = \frac{(n+2)f_\alpha}{2n!} |A_1||D_1|, \tag{78}$$

and except for a trivial normalization we have the type of double determinantal function originally introduced by Hartree (1928) to handle the Pauli exclusion principle.

B. Linear Transformations of the Orbitals

A well-known but nonetheless remarkable theorem of determinants states that

$$|AB| = |A||B|, \tag{79}$$

where A and B are square matrices of the same order. This is a special case of the more general theorem concerning any element of a matric basis e_{ij}^α. We shall examine this problem for a matric basis, a t basis, and then for $\theta N^\alpha P^\alpha N^\alpha$ specifically.

We shall first define a few quantities. Consider a square matrix, $A = \{a_{ij}\}$, $i, j = 1, 2, \ldots, n$. Let $\hat{p} = \{p_i\}$, $i = 1, \ldots, n$ be a set of n integers taken from the set $1, \ldots, n$. We assume that $p_1 \le p_2 \le \cdots \le p_n$ and $\hat{p}$ represents an ordered configuration. Using A and two, in general different, configurations, $\hat{p}$ and $\hat{q}$, we construct the product,

$$A_{\hat{p}\hat{q}} = \prod_{i=1}^{n} a_{p_i q_i}, \tag{80}$$

where the subscripts $\hat{p}$ and $\hat{q}$ are associated with the row and column labels of A, respectively.

We now allow a permutation π to operate on $A_{\hat{p}\hat{q}}$ by permuting the subscripts on the $\hat{p}$ or $\hat{q}$. There are two possibilities to be distinguished, and we write $\pi_c A_{\hat{p}\hat{q}}$ if the column labels are to be permuted and $\pi_r A_{\hat{p}\hat{q}}$ if it is to be the row labels. A most important property of these quantities is

$$\pi_c A_{\hat{p}\hat{q}} = \pi_r^{-1} A_{\hat{p}\hat{q}}, \tag{81}$$

because of the commutation of ordinary multiplication. Any element, $x = \sum x(\pi)\pi$, of the symmetric group algebra may operate on $A_{\hat{p}\hat{q}}$ and again we use a subscript r or c to denote row or column permutations, respectively. Therefore,

$$\begin{aligned} x_{\mathrm{c}} A_{\hat{p}\hat{q}} &= \sum x(\pi)\pi_{\mathrm{c}} A_{\hat{p}\hat{q}}, \\ x_{\mathrm{r}} A_{\hat{p}\hat{q}} &= \sum x(\pi)\pi_{\mathrm{r}} A_{\hat{p}\hat{q}}. \end{aligned} \tag{82}$$

We note that in all of these expressions the r or c subscript does not modify the quantity to which it is appended, but denotes the mode of operation. Now, choosing an element of a matric basis, e^{α}_{ij} we may form the quantities $e^{\alpha}_{\mathrm{c}ij} A_{\hat{p}\hat{q}}$ or $e^{\alpha}_{\mathrm{r}ij} A_{\hat{p}\hat{q}}$. These are connected by the relation,

$$e^{\alpha}_{\mathrm{c}ij} A_{\hat{p}\hat{q}} = e^{\alpha}_{\mathrm{r}ji} A_{\hat{p}\hat{q}}. \tag{83}$$

It will be observed that if $\hat{p} = \hat{q} = \{1, 2, \ldots, n\}$, $\alpha = [1^n]$, $f_\alpha = 1$, and

$$e^{\alpha}_{\mathrm{r}11} A_{\hat{p}\hat{p}} = \frac{1}{n!} \, |A| = e^{\alpha}_{\mathrm{c}11} A_{\hat{p}\hat{p}}. \tag{84}$$

Again if $\hat{p} = \hat{q} = \{1, 2, \ldots, n\}$ and we sum over the f_α, diagonal e^{α}_{ii}, we obtain the αth immanent of the matrix A (Littlewood 1950).

We may now proceed to discuss the situation of primary interest, viz., the discovery of the relations for e^{α}_{ij} in general analogous to (79), when A is the product of two other matrices. Therefore, we let $A = BC$, where B is $n \times m$ and C is $m \times n$, and in general, $m \neq n$. Writing $A_{\hat{p}\hat{q}}$ in terms of the elements of B and C we have

$$\begin{aligned} A_{\hat{p}\hat{q}} &= \sum_{i_1 i_2 \cdots i_n} B_{p_1 i_1} C_{i_1 q_1} \cdots B_{p_n i_n} C_{i_n q_n}, \\ &= \sum_{\hat{u}} \frac{1}{[\hat{u}]} \sum_{\pi} (\pi_{\mathrm{r}}^{-1} B_{\hat{p}\hat{u}})(\pi_{\mathrm{r}} C_{\hat{u}\hat{q}}). \end{aligned} \tag{85}$$

The $\hat{u}$ are configurations from the numbers $\{1, 2, \ldots, m\}$. In $\hat{u}$ 1 occurs μ_1 times, 2, μ_2 times, etc., and the symbol $[\hat{u}]$ is defined as

$$[\hat{u}] = \mu_1! \, \mu_2! \cdots \mu_m! \tag{86}$$

Using (5) and (85) we have

$$A_{\hat{p}\hat{q}} = n! \sum_{\hat{u}} \frac{1}{[\hat{u}]} \sum_{\alpha ij} \frac{1}{f_\alpha} (e^{\alpha}_{\mathrm{r}ij} B_{\hat{p}\hat{u}})(e^{\alpha}_{\mathrm{r}ji} C_{\hat{u}\hat{q}}). \tag{87}$$

We now apply e^{α}_{ij} (row) to both sides of (87) and get

$$e^{\alpha}_{\mathrm{r}ij} A_{\hat{p}\hat{q}} = \frac{n!}{f_\alpha} \sum_{\hat{u}} \frac{1}{[\hat{u}]} \sum_{l} (e^{\alpha}_{\mathrm{r}il} B_{\hat{p}\hat{u}})(e^{\alpha}_{\mathrm{r}lj} C_{\hat{u}\hat{q}}). \tag{88}$$

This is the generalization of (79) which we need, and it is easily seen that (88) reduces to (79) when $\alpha = [1^n]$, $m = n$, and $\hat{p} = \hat{u} = \hat{q} = \{1, 2, \ldots, n\}$. Using (83), seven other versions of (88) are possible.

The steps we have carried out in arriving at (88) are easily repeated for a t basis, with the result that

$$m^{\alpha}_{\mathrm{r}ij} A_{\hat{p}\hat{q}} = \frac{n!}{f_{\alpha}} \sum_{\hat{u}} \frac{1}{[\hat{u}]} \sum_{lm} (m^{\alpha}_{\mathrm{r}il} B_{\hat{p}\hat{u}}) M^{\alpha}_{lm} (m^{\alpha}_{\mathrm{r}mj} C_{\hat{u}\hat{q}}), \tag{89}$$

and since $\theta N^{\alpha} P^{\alpha} N^{\alpha} = m^{\alpha}_{11}$, we have specifically

$$(\theta N^{\alpha} P^{\alpha} N^{\alpha})_{\mathrm{r}} A_{\hat{p}\hat{q}} = \frac{n!}{f_{\alpha}} \sum_{\hat{u}} \frac{1}{[\hat{u}]} \sum_{ij} (m^{\alpha}_{\mathrm{r}1i} B_{\hat{p}\hat{u}}) M^{\alpha}_{ij} (m^{\alpha}_{\mathrm{r}j1} C_{\hat{u}\hat{q}}). \tag{90}$$

We now consider the application of (90) to the case where we subject a set of orbitals $x_1, x_2, \ldots, x_m$ to a linear transformation to get the set $\xi_1, \xi_2, \ldots, \xi_m$,

$$x_i = \sum_j \xi_j P_{ji}.$$

Thus we take for the matrix, X

$$X = \{x_{q_j}(i)\}, \qquad i, j = 1, 2, \ldots, n, \tag{91}$$

and $\theta N^{\alpha} P^{\alpha} N^{\alpha} X_{\hat{p}\hat{q}}$ is a symmetry-adapted function based on the orbital product $x_{q_1}(1) \cdots x_{q_n}(n)$. It is observed that the only $\hat{p}$ in which we are interested is $\{1, 2, \ldots, n\}$. The other orbitals, ξ_i, are formed in a matrix Ξ,

$$\Xi = \{\xi_{u_j}(i)\} \tag{92}$$

and hence

$$(\theta N^{\alpha} P^{\alpha} N^{\alpha})_{\mathrm{r}} X_{\hat{p}\hat{q}} = \sum_{\hat{u}i} C_{\hat{u}i\hat{q}} (m^{\alpha}_{\mathrm{r}1i} \Xi_{\hat{p}\hat{u}}), \tag{93}$$

$$C_{\hat{u}i\hat{q}} = \frac{n!}{f_{\alpha}[\hat{u}]} \sum_j M^{\alpha}_{ij} (m^{\alpha}_{\mathrm{r}j1} P_{\hat{u}\hat{q}}). \tag{94}$$

If the ξ_i are arranged to be orthonormal (93) provides a relation for expressing symmetry-adapted functions of nonorthogonal orbitals in terms of such functions of orthonormal orbitals. The integral form of $\theta N^{\alpha} P^{\alpha} N^{\alpha}$ may also be used to evaluate the $C_{\bar{u}l\hat{q}}$, thus

$$\begin{aligned} m^{\alpha}_{\mathrm{r}j1} P_{\hat{u}\hat{q}} &= (\pi^{\alpha}_{\mathrm{r}j})^{-1} m^{\alpha}_{11} P_{\hat{u}\hat{q}} = m^{\alpha}_{\mathrm{r}11} \pi^{\alpha}_{\mathrm{c}j} P_{\hat{u}\hat{q}}, \\ &= (f_{\alpha} | n!)(n - k + 1) \int_0^1 (t-1)^k t^{n-2k} \, \Delta(\pi^{\alpha}_{\mathrm{c}j} P_{\hat{u}\hat{q}}, q) \, dt, \end{aligned} \tag{95}$$

and when substituted into (94) we obtain $C_{\hat{a}i\hat{q}}$. It is also possible to use (93) as a device for evaluating the matrix elements of $\mathbf{H}^\alpha$ and $\mathbf{S}^\alpha$ since the orthogonality of the ξ_i will simplify summations over S_n, also. McWeeny (1954) has considered such procedures, but such a method does not appear as simple as direct use of (60) and (63).

C. Adaptation to Spatial Symmetry

For many systems the spin-free Hamiltonian exhibits symmetry in three-dimensional space as well as the exchange symmetry of identical particles. The adaptation of trial functions to the group of spatial symmetry, G_s, is also very convenient, and we may apply the results of the last section to this problem, also.

We assume that the orbitals form a basis for a (in general) reducible representation of G_s, with the general element R,

$$Rx_i = \sum_j x_j\, D(R)_{ji} \tag{96}$$

and using (90)

$$R[\theta N^\alpha P^\alpha N^\alpha X_{p\hat{q}}] = \frac{n!}{f_\alpha} \sum_{\hat{a}} \frac{1}{[\hat{a}]} \sum_{ij} (m^\alpha_{r1i} X_{p\hat{a}}) M^\alpha_{ij} [m^\alpha_{rj1}\, D(R)_{\hat{a}\hat{q}}]. \tag{97}$$

The matric basis for G_s is

$$R^\gamma_{ij} = \frac{f_\gamma}{g} \sum_R D^\gamma(R^{-1})_{ji} R \tag{98}$$

and therefore,

$$R^\gamma_{st}\, m^\alpha_{r11}\, X_{p\hat{q}} = \sum_{\hat{a}i} (m^\gamma_{r1i} X_{p\hat{a}}) F^\gamma_{i\hat{a}\hat{q}st}, \tag{99}$$

$$F^\gamma_{i\hat{a}\hat{q}st} = \frac{f_\gamma n!}{f_\alpha g[\hat{a}]} \sum_{jR} M^\alpha_{ij}\, D^\gamma(R^{-1})_{ts} (m^\alpha_{r1j}\, D(R)_{\hat{a}\hat{q}}), \tag{100}$$

and all the symmetry-adapted functions contained in $m^\alpha_{r11} X_{p\hat{q}}$ may be generated this way. As before, the quantities $m^\alpha_{r1j}\, D(R)_{\hat{a}\hat{q}}$ may be evaluated using (95).

If $X_{p\hat{q}}$ is arranged such that the paired orbitals are closed under operations of G_s, it is easily seen that this portion of the determinant $m^\alpha_{11}\varphi$ is invariant to $R \in G_s$. The orbitals involved can be said to be in a closed shell whether or not the portion of $D(R)$ corresponding is in completely reduced form.

The character of the representation provided by the symmetry-adapted functions $R^{\gamma}_{st} m^{\alpha}_{rij} X_{pq}$ has been discussed by Kotani (1964) and Goscinski and Öhrn (1968). An alternative procedure has been given by the author (Gallup, 1966).

If the system with which we are dealing is a single atom, G_s is O_3 the three-dimensional orthogonal group, and in this case symmetry adaptation is more conveniently done with elements of the Lie algebra. The procedure used here gives directly only Russell–Saunders type states, since the use of m^{α}_{ij} gives functions for which S is a good quantum number. Most of the details of such a procedure are very similar to those which have been used for years with Slater determinants (Condon and Shortley, 1935). There is, however, one point of difference and we may illustrate with the doublet case of three equivalent d electrons outside a closed shell.

Because of the closed shell, only that portion of the function involving the d orbitals is affected by the operators and we may symbolize the various functions as

$$\begin{pmatrix} m_{l_1} & m_{l_2} \\ m_{l_3} & \end{pmatrix}$$

which is the last two rows of the tableau. We write all the possible combinations of three m_l values and get a table as follows:

$$M_L = 5; \qquad \begin{pmatrix} 2 & 2 \\ 1 & \end{pmatrix}$$

$$M_L = 4; \qquad \begin{pmatrix} 2 & 1 \\ 1 & \end{pmatrix}\begin{pmatrix} 2 & 2 \\ 0 & \end{pmatrix}$$

$$M_L = 3; \qquad \begin{pmatrix} 2 & 1 \\ 0 & \end{pmatrix}\begin{pmatrix} 2 & 0 \\ 1 & \end{pmatrix}\begin{pmatrix} 2 & 2 \\ -1 & \end{pmatrix}$$

$$M_L = 2; \qquad \begin{pmatrix} 2 & 0 \\ 0 & \end{pmatrix}\begin{pmatrix} 1 & 1 \\ 0 & \end{pmatrix}\begin{pmatrix} 2 & 2 \\ -2 & \end{pmatrix}\begin{pmatrix} 2 & 1 \\ -1 & \end{pmatrix}\begin{pmatrix} 2 & -1 \\ 1 & \end{pmatrix}$$

$$M_L = 1; \qquad \begin{pmatrix} 1 & 0 \\ 0 & \end{pmatrix}\begin{pmatrix} 1 & 1 \\ -1 & \end{pmatrix}\begin{pmatrix} 2 & 0 \\ -1 & \end{pmatrix}\begin{pmatrix} 2 & -1 \\ 0 & \end{pmatrix}\begin{pmatrix} 2 & -2 \\ 1 & \end{pmatrix}\begin{pmatrix} 2 & 1 \\ -2 & \end{pmatrix}$$

$$M_L = 0; \qquad \begin{pmatrix} 1 & -1 \\ 0 & \end{pmatrix}\begin{pmatrix} 1 & 0 \\ -1 & \end{pmatrix}\begin{pmatrix} 2 & -2 \\ 0 & \end{pmatrix}\begin{pmatrix} 2 & 0 \\ -2 & \end{pmatrix}\begin{pmatrix} 2 & -1 \\ -1 & \end{pmatrix}$$

$$\begin{pmatrix} 1 & 1 \\ -2 & \end{pmatrix}$$

$$M_L = -1; \quad \begin{pmatrix} 0 & 0 \\ -1 & \end{pmatrix}\begin{pmatrix} 1 & -1 \\ -1 & \end{pmatrix}\begin{pmatrix} 1 & 0 \\ -2 & \end{pmatrix}\begin{pmatrix} 0 & 1 \\ -2 & \end{pmatrix}\begin{pmatrix} 2 & -2 \\ -1 & \end{pmatrix}$$

$$\begin{pmatrix} 2 & -1 \\ -2 & \end{pmatrix}$$

$$M_L = -2; \quad \begin{pmatrix} 0 & 0 \\ -2 & \end{pmatrix}\begin{pmatrix} 0 & -1 \\ -1 & \end{pmatrix}\begin{pmatrix} 2 & -2 \\ -2 & \end{pmatrix}\begin{pmatrix} 1 & -2 \\ -1 & \end{pmatrix}\begin{pmatrix} 1 & -1 \\ -2 & \end{pmatrix}$$

$$M_L = -3; \quad \begin{pmatrix} 0 & -1 \\ -2 & \end{pmatrix}\begin{pmatrix} 0 & -2 \\ -1 & \end{pmatrix}\begin{pmatrix} 1 & -2 \\ -2 & \end{pmatrix}$$

$$M_L = -4; \quad \begin{pmatrix} -1 & -1 \\ -2 & \end{pmatrix}\begin{pmatrix} 0 & -2 \\ -2 & \end{pmatrix}$$

$$M_L = -5; \quad \begin{pmatrix} -1 & -2 \\ -2 & \end{pmatrix}.$$

The Russell–Saunders states occurring can be read off of this table immediately, and are ^2H, ^2G, ^2F, two different ^2D, and a ^2P, which is recognized as the familiar result for this case.

In order to obtain the correct linear combinations to be eigenfunctions of L^2, we may apply the orbital angular momentum raising operator, L, to a general linear combination of the functions in a single row for which $M_L \geq 0$ and set the result to zero,

$$L\sum_i (a_i y_i) = 0. \tag{101}$$

When (101) is solved for the a_i we obtain a function Y such that

$$L^2 Y = M_L(M_L + 1)Y, \qquad M_L \geq 0, \tag{102}$$

and hence is an eigenfunction of L^2. Applying these ideas to the $M_L = 2$ row we have

$$0 = L\left[a\begin{pmatrix} 2 & 0 \\ 0 & \end{pmatrix} + b\begin{pmatrix} 1 & 1 \\ 0 & \end{pmatrix} + c\begin{pmatrix} 2 & 2 \\ -2 & \end{pmatrix} + d\begin{pmatrix} 2 & 1 \\ -1 & \end{pmatrix} + e\begin{pmatrix} 2 & -1 \\ 1 & \end{pmatrix}\right],$$

$$= \sqrt{6}\,a\left[\begin{pmatrix} 2 & 1 \\ 0 & \end{pmatrix} + \begin{pmatrix} 2 & 0 \\ 1 & \end{pmatrix}\right] + 2b\left[\begin{pmatrix} 1 & 2 \\ 0 & \end{pmatrix} + \begin{pmatrix} 2 & 1 \\ 0 & \end{pmatrix}\right] + 2c\begin{pmatrix} 2 & 2 \\ -1 & \end{pmatrix}$$

$$+ d\left[\sqrt{6}\begin{pmatrix} 2 & 1 \\ 0 & \end{pmatrix} + 2\begin{pmatrix} 2 & 2 \\ -1 & \end{pmatrix}\right] + \sqrt{6}\,e\begin{pmatrix} 2 & 0 \\ 1 & \end{pmatrix}.$$

The coefficient of b contains the only difficulty and we must express $\left(\begin{smallmatrix}1&2\\0&\end{smallmatrix}\right)$ in terms of $\left(\begin{smallmatrix}2&1\\0&\end{smallmatrix}\right)$ and $\left(\begin{smallmatrix}2&0\\1&\end{smallmatrix}\right)$. This case is reasonably simple and using (35) we have

$$\begin{pmatrix}1 & 2\\ 0 & \end{pmatrix} = \begin{pmatrix}2 & 1\\ 0 & \end{pmatrix} + \begin{pmatrix}2 & 0\\ 1 & \end{pmatrix},$$

which results in the system of equations

$$\begin{aligned} \sqrt{6}a + 4b + \sqrt{6}d &= 0,\\ \sqrt{6}a + 2b + \sqrt{6}e &= 0,\\ 2c + 2d \quad &= 0. \end{aligned}$$

The number of equations here is, of course, the number of functions in the $M_L = 3$ row. The solution space is two-dimensional and is spanned by the vectors

$$(abcde)_1 = (4, -\sqrt{6}, 0, 0, -2),$$

and

$$(abcde)_2 = (2, -\sqrt{6}, -2, 2, 0),$$

which give the two independent ${}^2D$ functions. Matsen (1966) has given a discussion of the case of equivalent p electrons.

IV. Symmetry Adaptation of Spin Functions

The Dirac identity,

$$S^2 = n(4 - n)/3 + C(1^{n-2}2), \tag{103}$$

where $C(1^{n-2}2)$ is the sum of all permutations in the $(1^{n-2}2)$ class, i.e., all binary permutations, gives the connection between the Casamir operator for the representations of $SU(2)$ and the representation of S_n supported by spin functions. For any group a symmetry-adapted function will be an eigenfunction of the class operators from the group. As is well known, only those representations corresponding to tableaux possessing no more than two rows are supported by spin functions. These are the tableaux conjugate to the one- or two-column tableaux used for spatial functions, and it is very convenient to use the conjugate t-basis elements for these tableaux. Thus we have

$$m_{ij}^{\alpha} = \theta(\pi_i^{\alpha})^{-1} P^{\alpha} N^{\alpha} P^{\alpha} \pi_j^{\alpha}, \tag{104}$$

where it should be observed that $M^{\alpha} = M^{\bar{\alpha}}$, and that $\pi_i^{\alpha} = \pi_i^{\bar{\alpha}}$. If $\alpha = [n-k, k]$, then

$$S^2 m_{ij}^{\alpha} = (\tfrac{1}{2}n - k)(\tfrac{1}{2}n - k + 1)m_{ij}^{\alpha}, \tag{105}$$

which gives the connection between k and the total spin quantum number, $S = \frac{1}{2}n - k$.

A basis in spin space is the set of product functions $\alpha_1 \cdots \beta_n = \zeta$, which are eigenfunctions of S_z,

$$S_z \zeta = M_s \zeta, \tag{106}$$

and (106) provides a separation of spin-space into orthogonal subspaces, one for each $M_s = \frac{1}{2}n, \ldots, -\frac{1}{2}n$. The dimensionality of each subspace is

$$N_{M_s} = \binom{n}{\frac{1}{2}n - M_s} \tag{107}$$

and (106) becomes

$$S_z \zeta_i = M_s \zeta_i; \qquad i = 1, 2, \ldots, N_{M_s}. \tag{108}$$

The symmetry-adapted functions are $m_{ij}^{\alpha} \zeta_l$ and these are identically zero if $|M_s| > \frac{1}{2}n - k$.

We examine the principal case $M_s = \frac{1}{2}n - k$, and it is observed that for each ζ_l there is a permutation ρ_l such that

$$\zeta_l = \rho_l \zeta_1, \tag{109}$$

where ζ_1 is chosen such that

$$P^{\alpha} \zeta_1 = \zeta_1. \tag{110}$$

Thus the symmetry-adapted functions may be written

$$m_{ij}^{\alpha} \zeta_l = \theta (\pi_i^{\alpha})^{-1} P^{\alpha} N^{\alpha} P^{\alpha} \pi_j^{\alpha} \rho_l P^{\alpha} \zeta_1. \tag{111}$$

Now, one of the principal results of Young's theory is that

$$P^{\alpha} = x^{\alpha} + \sum_{\beta} x^{\beta}, \tag{112}$$

where x^{β} is an element, necessarily idempotent, of the βth subalgebra, β ranges over those tableaux earlier than α in the standard sequence only, and in particular, x^{α} is primitive in α. Therefore,

$$x^{\alpha} = \theta P^{\alpha} N^{\alpha} P^{\alpha}, \tag{113}$$

$$P^{\alpha} = \theta P^{\alpha} N^{\alpha} P^{\alpha} + \sum_{\beta} x^{\beta}. \tag{114}$$

It is seen that

$$\begin{aligned} m^\alpha_{ij}\rho_l P^\alpha &= (f_\alpha/n!)C^\alpha(\rho_l^{-1}\pi_j^{\alpha-1})_{11}\, m^\alpha_{i1}, \\ &= d^\alpha_{jl}\, m^\alpha_{i1}, \end{aligned} \tag{115}$$

and using (111) we get

$$m^\alpha_{ij}\zeta_l = d^\alpha_{jl}\, m^\alpha_{i1}\,\zeta_1 \tag{116}$$

and the only dependence of $m^\alpha_{ij}\zeta_l$ upon either j or l is in a numerical constant which disappears in the normalization. This phenomenon is termed a lack of "vertical splitting" by Löwdin and Goscinski (1970), and as we shall see this is what allows us to have a unique spin-free problem for a spin-free Hamiltonian.

If we take the conjugate of (18) it is seen that

$$\theta P^\alpha N^\alpha P^\alpha = \theta' P^\alpha \sum_l (-1)^l \binom{n-k}{l}^{-1} B_l, \tag{117}$$

and we have a formula corresponding to (54)

$$m^\alpha_{11}\zeta_1 = (f_\alpha/n!)(n-k+1)\int_0^1 (t-1)^k t^{n-2k}\,\Pi(\zeta_1, q)\,dt, \tag{118}$$

where $\Pi(\zeta_1, q)$ is the *permanent*

$$\Pi(\zeta_1, q) = \overset{+}{\left|\begin{matrix} \bar\alpha_1 & \bar\beta_1 \\ \bar\alpha_2 & q\bar\beta_2 \end{matrix}\right|}{}^{\!+}, \tag{119}$$

and $\bar\alpha_1$ is $(n-k) \times (n-k)$, etc. It is also easily shown that

$$\frac{f_\alpha (n-k+1)^{3/2}}{n!\,(n-2k+1)^{1/2}}\int_0^1 (t-1)^k t^{n-2k}\,\Pi(\zeta_1, q)\,dt$$

is normalized. The other M_s values may be obtained with the spin-lowering operator, $S_x - iS_y$.

V. The Complete Antisymmetric Space-Spin Wave Function

The previous sections have given a discussion of the construction of symmetry-adapted space functions for the calculation of the energy of a spin-free Hamiltonian. In order to carry out the procedure suggested by Matsen, we must now include the spin in our wave function. In recent times Matsen (1964) and Löwdin and Goscinski (1970) have emphasized that there is a unique space-spin function corresponding to the symmetry-adapted space functions we have constructed. Nevertheless, there appears to be some confusion on this point and the argument will be repeated here. The most crucial point of the theory is very easily demonstrated with our t basis and we shall use this language.

A. Uniqueness of Space-Spin Function

The previous theory has provided us with an f_α-fold set of linearly independent, symmetry-adapted functions, ${\varphi_i}^\alpha$; $i = 1, \ldots, f_\alpha$. These satisfy the relations

$$\begin{aligned} m^\alpha_{ii}\,{\varphi_i}^\alpha &= {\varphi_i}^\alpha, \\ m^\alpha_{jk}\,{\varphi_i}^\beta &= \delta_{\alpha\beta}(M^\alpha)^{-1}_{ki}\,{\varphi_j}^\alpha. \end{aligned} \tag{120}$$

Because of the energy degeneracy with respect to i in ${\varphi_i}^\alpha$, the function $\varphi^\alpha(a)$,

$$\varphi^\alpha(a) = \sum_i a_i\,{\varphi_i}^\alpha, \tag{121}$$

is the most general spatial function of this energy. In a similar manner we may construct the most general spin function

$$\zeta(b) = \sum_l b_l\,\zeta_l, \tag{122}$$

and using (108)

$$S_z\,\zeta(b) = M_s\,\zeta(b). \tag{123}$$

An antisymmetric space-spin function may be obtained as

$$\psi = \mathscr{A}\varphi^\alpha(a)\zeta(b), \tag{124}$$

where $\mathscr{A}$ is the antisymmetrizer. The properties of ψ are most easily studied by writing the antisymmetrizer in the form

$$\mathscr{A} = \frac{1}{n!}\sum_\pi \varepsilon_\pi\,\pi_r\,\pi_s \tag{125}$$

where π_r and π_s are the same permutation but are to be applied to φ^α and ζ, respectively. The antisymmetrizer has been studied before by rewriting (125) in terms of a matric basis. We, however, use the t basis and obtain with the aid of (28)

$$\mathscr{A} = \sum_{\beta ijkl} \frac{1}{f_\beta}\,M^\beta_{ij}\,M^\beta_{kl}(m^\beta_{ik})_r(m^{\bar{\beta}}_{jl})_s, \tag{126}$$

and hence, (124) becomes

$$\psi = \sum_{\beta ijkl} \frac{1}{f_\beta}\,M^\beta_{ij}\,M^\beta_{kl}[m^\beta_{ik}\,\varphi^\alpha(a)][m^{\bar{\beta}}_{jl}\,\zeta(b)]. \tag{127}$$

Now from (120) and (121) we have

$$m_{ik}^{\beta}\varphi^{\alpha}(a) = \delta_{\alpha\beta}\sum_{p} a_p (M^{\alpha})_{kp}^{-1}\varphi_i{}^{\alpha}, \tag{128}$$

and from (115),

$$m_{jl}^{\bar{\alpha}}\zeta(b) = \sum_{p} b_p\, d_{lp}^{\bar{\alpha}}\, m_{j1}^{\bar{\alpha}}\, \zeta_1, \tag{129}$$

and finally

$$\psi = \left\{\sum_{lp} a_l b_p d_{lp}^{\bar{\alpha}}\right\} \frac{1}{f_\alpha}\sum_{ij} M_{ij}^{\alpha}\varphi_i{}^{\alpha}(m_{j1}^{\bar{\alpha}}\zeta_1). \tag{130}$$

Except for an unimportant constant, ψ is unique.

B. Operators Containing Spin

The consequences of this result are important. We now consider a Hamiltonian which contains terms dependent upon spin operators

$$H(\lambda) = H_{\mathrm{sf}} + \lambda H_s, \tag{131}$$

where we have written the spin terms as a perturbation, and H_{sf} is our former spin-free Hamiltonian. The Schrödinger equation for (131)

$$H(\lambda)\psi(\lambda) = E(\lambda)\psi(\lambda) \tag{132}$$

possesses solutions for small values of λ, at least, and we examine

$$\psi(0) = \lim_{\lambda \to 0} \psi(\lambda), \tag{133}$$

and see that $\psi(\lambda)$ has a unique limit, except for possible modifications in spatial symmetry due to H_s. An alternative statement of this phenomenon is as follows: When we wish to compute matrix elements of an operator such as H_s, these are determined completely, in a dynamical sense, by the spin-free wave functions $\varphi_i{}^{\alpha}$.

We now examine the problem of calculating a matrix element of H_s, and for the moment we assume it is a one-particle operator,

$$H_s = \sum_i W_i \Omega_i, \tag{134}$$

where W_i is an operator on spatial functions and Ω_i on spin functions. If we have two space-spin functions $\psi_\mu{}^{\alpha}$ and $\psi_\nu{}^{\beta}$ the matrix element is

$$\langle \alpha\mu | H_s | \beta\nu \rangle = K\langle \varphi_{1\mu}^{\alpha} | Z^{\alpha\beta} | \varphi_{1\nu}^{\beta} \rangle, \tag{135}$$

where $1/K = f_\alpha f_\beta[\langle\alpha\mu|\alpha\mu\rangle\langle\beta\nu|\beta\nu\rangle]^{1/2}$. Equation (135) contains a transformed operator, $Z^{\alpha\beta}$,

$$Z^{\alpha\beta} = \sum_{ij} W_i \, Q_{ij}^{\alpha\beta}(\pi_j{}^\beta)^{-1}, \tag{136}$$

where the $Q_{ij}^{\alpha\beta}$ are a set of numbers determined purely from group theoretic considerations and the nature of the spin operator Ω,

$$Q_{ij}^{\alpha\beta} = \sum_{rst} M_{rs}^{\alpha}[M^\beta C^\beta(\pi_r{}^\beta \pi_s^{\alpha-1})M^\beta]_{jt}\langle\zeta_{1\mu}^{\bar{\alpha}}|\Omega_{\bar{i}_{rs}}\pi_t^{\beta-1}|\zeta_{1\nu}^{\bar{\beta}}\rangle. \tag{137}$$

The index $\bar{i}_{rs}$ on Ω is related to i by the equation

$$\Omega_{\bar{i}_{rs}} = \pi_s{}^\alpha \pi_r^{\alpha-1}\Omega_i \pi_r{}^\alpha \pi_s^{\alpha-1}. \tag{138}$$

The relations defining the operator $Z^{\alpha\beta}$ are not very simple but the $Q_{ij}^{\alpha\beta}$ need to be calculated only once for each $\alpha\beta$ pair.

The generalization of these results to operators containing two-particle operators and higher is simple and will not be discussed here, but it is evident that operators similar in nature to $Z^{\alpha\beta}$ will be obtained. The problem of calculating matrix elements of operators containing spin reduces to the determination of the $Q_{ij}^{\alpha\beta}$ type quantities and thereafter, the spin-free wave functions are all that are needed.

A somewhat different approach to the calculation of matrix elements of spin-dependent operators has recently been given by the author (Gallup, 1970).

VI. Conclusion

In this chapter we have reexamined some of the problems of doing quantum mechanical calculations of electronic structures of atoms and molecules for a spin-free Hamiltonian. Specifically, a t basis based upon the Young operator $\theta N^\alpha P^\alpha N^\alpha$ has been used. The determinantal form of this operator provides a solution to the problem that was discussed in the Introduction of summing over all $n!$ permutations in such expressions. Whether other even more efficient solutions are possible must be decided by future developments.

Another problem upon which we have not touched is related to the fact that for large systems

$$f_\alpha = \frac{n-2k+1}{n+1}\binom{n+1}{k}$$

is not a small number. Hence the question arises: Do we need all $f_\alpha{}^2 m_{ij}^\alpha$ in our calculations, even when $m_{ij}^\alpha \varphi \neq 0$? This appears to be very difficult to answer. As long as all elements of the group algebra are used, their representation does not effect the final results. If, however, some are to be eliminated on a more or less arbitrary basis, the situation is quite different. Indeed, the basis of selection appears to need to include knowledge of the particular system (Heikes and Gallup, 1970), and hence such considerations will need to be handled with great delicacy. We shall say no more about this except to observe that in some cases, a solution to this problem and a solution to the summation problem may be somewhat mutually exclusive, as is seen by a consideration of the rather arbitrary nature of the operator $\mathscr{E}^\alpha$ of (9). This appears at best to be a somewhat gloomy conclusion.

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Scattered-Wave Theory of the Chemical Bond*

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I. Introduction

Currently there is much interest in developing quantitative descriptions of the chemical bonding of large molecules and complex solids, e.g., polyatomic molecules in the gaseous phase, in crystalline environments, or in aqueous solution; "molecular" crystals with many atoms per unit cell; impurities and defects in an otherwise perfect crystal; disordered and amorphous materials; biological macromolecules; and polymers. It is evident that if we are to apply quantum chemistry effectively to such systems, within the range of available computer facilities and at the present level of research funding, we must look for practical and accurate new computational methods.

Traditional *ab initio* Hartree–Fock self-consistent-field methods, based

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on representing molecular orbitals as linear combinations of atomic orbitals (SCF–LCAO methods) (Slater, 1963), are difficult and costly in computer time to implement on many-electron polyatomic systems, because of the necessity of having to adopt large basis sets and having to compute many multicenter integrals or equivalent Hartree–Fock matrix elements. Simpler approximate and semiempirical LCAO-type molecular-orbital methods, such as those based on the "complete neglect of differential overlap" (CNDO methods) (Pople and Beveridge, 1970) depend on various approximations to multicenter integrals or parametization of matrix elements. Such methods have been found to be quite useful for the semiquantitative description of both small and large molecules containing atoms of low atomic number. However, they do not seem to be well suited for the treatment of molecules and crystals containing atoms of higher atomic number (e.g., transition and rare earth elements). Conventional band theory (Slater, 1965a) is likewise difficult to apply to crystals with more than a few atoms per unit cell, and it is dependent on the assumption of lattice periodicity and on the use of a reciprocal-space representation. Traditional theories of the "deep-level" electronic states associated with certain types of impurities in crystals (e.g., transition metal impurities in semiconductors) require, in principle, the knowledge of a complete set of one-electron wave functions for the otherwise perfect host lattice (Koster and Slater, 1954).

Following a suggestion made originally by Slater (1965b), we have developed (Johnson, 1966, 1967, 1968, 1971, 1972; Johnson and Smith, 1970a,b, 1971a,b,c; Smith and Johnson, 1969) a new theoretical approach to calculating, from first principles, the electronic structures of polyatomic molecules and solids. This technique avoids many of the aforementioned difficulties associated with more conventional methods of quantum chemistry and crystal band theory. It leads to an accurate description of the chemical bonding of molecules and solids of considerable stereochemical complexity without undue computational effort or cost.

The method is based, first of all, on the division of matter into component polyatomic clusters. Each cluster, which may be an entire polyatomic molecule, part of a macromolecule, or a polyatomic complex in an ordered or disordered solid, is geometrically partitioned into contiguous *atomic*, *interatomic*, and *extramolecular* regions. The one-electron Schrödinger equation is numerically integrated within each region in the partial-wave representation for spherically averaged and volume-averaged potentials which include the Xα statistical approximation (Slater *et al.*, 1969a,b; Slater and Wood, 1971; Slater, 1971, 1972; Slater and Johnson, 1972) to exchange correlation. [It is recommended that the reader consult the recent review article by Slater (1972) in *Advances in Quantum Chemistry*, Vol. 6, for a detailed description of the Xα method.] The wave functions and their first derivatives are joined continuously throughout the various regions of the cluster via multiple-scattered-wave theory somewhat similar to that developed originally by Korringa (1947). The effects of a particular environment on the cluster are described by boundary conditions, e.g., in the case of a symmetric polyatomic molecule the matching of the solutions of Schrödinger's equation in the extramolecular region to those within the cluster at an artificial spherical boundary surrounding the molecule. This procedure leads to a set of rapidly convergent secular equations which are solved numerically for the molecular-orbital energies and wave functions. The matrix elements of these equations are simple to evaluate in comparison with those characteristic of *ab initio* LCAO methods. In particular, there are no multicenter integrals. This entire numerical procedure is repeated, using the wavefunctions obtained at each iteration to generate a charge density and new potential, until self-consistency is attained.

The SCF-Xα scattered-wave technique uses only a small fraction of the computer time required by *ab initio* Hartree–Fock LCAO methods. Furthermore, it will be shown that this technique yields molecular orbitals which are in significantly better quantitative agreement with experiment than do either *ab initio* or semiempirical LCAO methods. For example, in conjunction with the "transition-state" theory of optical excitations (Slater, 1971, 1972; Slater and Johnson, 1972), the scattered-wave model leads to an accurate description of the optical properties of molecules and crystals, including the effects of orbital relaxation. The method is practicable, moreover, on molecules and crystals where *ab initio* LCAO methods are too difficult and costly to implement. The total energy as a function of stereochemical geometry can also be determined by the scattered-wave approach, using the Xα statistical total Hamiltonian (Slater and Wood, 1971; Slater, 1971, 1972; Slater and Johnson, 1972) as the starting point. For the electronic structure of an ordered complex crystal, i.e., one with several or more atoms per unit cell (e.g., a "molecular crystal"), one can assume the periodic cell to be the unit polyatomic cluster. The boundary condition on the cluster orbitals is then just the Bloch condition, and the theoretical model reduces exactly to band theory (Johnson and Smith, 1971a). Because it is possible to adopt different boundary conditions and practical to handle reasonably large clusters of atoms, the theoretical formalism can be extended easily to a variety of problems in the electronic structure of complex crystals. For example, since the cluster model is not dependent on the assumption of long-range order, problems such as the bonding of impurities and defects in crystals and the electronic structures of disordered or amorphous materials are readily within the scope of the theory.

II. The SCF–Xα Scattered-Wave Method

The SCF–Xα scattered-wave formalism is most clearly illustrated for the case of a symmetric cluster of atoms. Consider, for example, the two-dimensional representation of a four-atom "molecule" shown schematically in Fig. 1. The space of the cluster is geometrically partitioned into three fundamental types of regions:

I. *Atomic*: The regions within nonoverlapping spheres centered on the constituent atoms
II. *Interatomic*: The region between the "inner" atomic spheres and an "outer" sphere surrounding the entire molecule
III. *Extramolecular*: The region exterior to the "outer" sphere

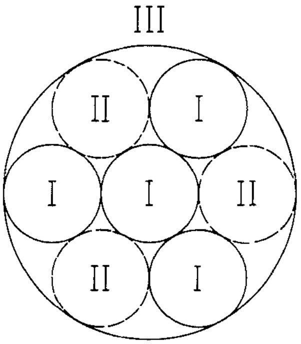

Fig. 1 Division of a molecular cluster into (I) atomic, (II) interatomic, and (III) extramolecular spherical regions.

In addition to the atomic spheres I, we have the option of introducing spherical regions within the interatomic region II, illustrated in Fig. 1 by the broken circles. Most generally, the atomic, outer, and interatomic sphere radii are chosen so as to minimize the volume between the spheres. However other physical considerations, such as empirical atomic or ionic radii, can also influence the initial choice of sphere sizes.

We shall be concerned with solving the one-electron Schrödinger equation (written in Rydberg units)

$$[-\nabla^2 + V(\mathbf{r})]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{II.1}$$

in each of the regions I, II, and III for a local potential energy function

$$V(\mathbf{r}) = V_C(\mathbf{r}) + V_{X\alpha}(\mathbf{r}), \tag{II.2}$$

which includes, in addition to the usual Coulomb contribution $V_C(\mathbf{r})$, the Xα statistical approximation (Slater *et al.*, 1969a,b; Slater and Wood, 1971; Slater, 1971, 1972; Slater and Johnson, 1972)

$$V_{X\alpha}(\mathbf{r}) = -6\alpha[(3/8\pi)\rho(\mathbf{r})]^{1/3} \tag{II.3}$$

to exchange correlation. The latter is a function only of the local electronic charge density $\rho(\mathbf{r})$ and of the scaling parameter α. To start the SCF scattered-wave calculation, we expand the potential energy at an arbitrary point $\mathbf{r}$ of the molecule as a superposition

$$V(\mathbf{r}) = \sum_j V^j(|\mathbf{r} - \mathbf{R}_j|) \tag{II.4}$$

of free-atom or free-ion SCF–Xα potentials centered at positions $\mathbf{R}_j$. The latter potentials and their associated electronic charge densities can be generated by a computer program of the type developed originally by Herman and Skillman (1963), but modified to permit the use of different Xα exchange-correlation scaling parameters. These parameters can be optimized for each atom by the first-principles scheme suggested by Slater (1972, Slater and Wood, 1971), namely matching the statistical total energy of the atom or ion to the Hartree–Fock total energy. Schwarz (1972) has recently calculated Xα parameters for the atoms hydrogen through niobium, matching the statistical total energies to the Hartree–Fock values determined by Mann (1967). These parameters are then used for generating the superposed-atom potential (II.4) in the various atomic regions I of the molecular cluster.

For the four-atom molecule illustrated in Fig. 1, we let the atomic index j in expression (II.4) range over the values $j = 1, 2, 3, 4$. In this case the position of the central atom (e.g., $\mathbf{R}_1$) coincides with $\mathbf{R}_0$ the position of the center of the outer spherical boundary. The potential energy is represented inside each atomic region I by expanding the superposition (II.4) in a series of spherical harmonics

$$V_I(\mathbf{r}) = \sum_L V_L(r)Y_L(\mathbf{r}), \tag{II.5}$$

where $L = (l, m)$ is the angular-momentum index, applying the elegant spherical-harmonic expansion theorems described by Löwdin (1956) to evaluate the radial components $V_L(r)$. The next approximation consists of using only the first (spherically symmetric) term $L = (0, 0)$ of the expansion (II.5) as the initial model potential in each atomic region I, retaining the higher order terms $L \neq (0, 0)$ as a perturbation. This is equivalent to the so-called "muffin-tin" approximation for the potential, which has been successfully used in the augmented-plane-wave (APW) (Slater, 1937; 1965a) and Korringa–Kohn–Rostoker (KKR) (Korringa, 1947; Kohn and Rostoker, 1954) methods of crystal band theory. The potential can also be spherically averaged inside nonoverlapping spheres within the interatomic region II (see Fig. 1), using weighted averages of the Xα exchange-correlation scaling parameters for the neighboring atomic regions. For many applications, however, it is necessary only to carry out an average of the potential over the interatomic volume Ω_{II}, resulting in a constant interatomic potential energy

$$\bar{V}_{\text{II}} = \frac{1}{\Omega_{\text{II}}} \int_{\Omega\text{II}} V(\mathbf{r})\, d\mathbf{r}. \tag{II.6}$$

Finally in the extramolecular region III, we can perform a spherical average of the potential with respect to the center of the molecule.

It is important to emphasize that the first term of the expansion (II.5) in a particular atomic region I includes not only the contribution of the atom located there, but also the spherically averaged contribution of all the other atomic potentials to that region. Thus the effects of overlapping potentials are included to first order. This is also true for regions II and III. As we shall demonstrate in later sections of this paper, this theoretical model yields accurate molecular-orbital energies and wave functions for symmetric polyatomic molecules, such as the one illustrated in Fig. 1, and for polyatomic clusters in symmetric crystalline environments without including higher nonspherical components of the potential (II.5). For less symmetric complex polyatomic molecules, the model can serve as an excellent first approximation, which is superior to other available theoretical techniques and for which the accuracy can be systematically improved via perturbation theory.

The partitioning of the space of the molecule into local regions of spherically averaged and volume-averaged potential energy allows one to introduce a rapidly convergent, composite partial-wave representation of the molecular-orbital wave functions. Within each spherical atomic region I of radius b_j we expand the wave functions in the single-center form

$$\psi_{\mathrm{I}}{}^j(\mathbf{r}) = \sum_L C_L{}^j R_l{}^j(E; r) Y_L(\mathbf{r}), \qquad 0 < r \le b_j, \tag{II.7}$$

where the quantities $C_L{}^j$ are partial-wave coefficients (to be determined) and $Y_L(\mathbf{r})$ are real spherical harmonics. The functions $R_l{}^j(E; r)$ are solutions of the radial Schrödinger equation

$$\left[-\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{l(l+1)}{r^2} + V^j(r) - E\right] R_l{}^j(E; r) = 0 \tag{II.8}$$

for the spherically averaged potential $V^j(r)$. The radial functions must be finite at the origin $r = 0$ of each atomic sphere. The solutions are generated by outward numerical integration of Eq. (II.8) for each trial energy parameter E and partial-wave component l. If we include spherically averaged regions of potential energy in the interatomic space II, then the solutions of Schrödinger's equation in these regions will also be of the form (II.7).

In the extramolecular region the orbitals are expanded with respect to the center of the cluster in the representation

$$\psi_{\mathrm{III}}(\mathbf{r}) = \sum_L C_L{}^0 R_l{}^0(E; r) Y_L(\mathbf{r}), \qquad b_0 \le r < \infty, \tag{II.9}$$

where b_0 is the radius of the outer sphere (see Fig. 1). The functions $R_l{}^0(E; r)$ are solutions of a radial Schrödinger equation similar to (II.8) for the spherical average of the potential in the extramolecular region. For localized molecular orbitals, these radial functions must decay exponentially at large distances from the molecule. The solutions are generated by inward numerical integration of the radial equation for trial values of E and l.

For the intersphere region of volume-averaged potential energy (II.6), Schrödinger's equation reduces to the ordinary wave equation

$$(\nabla^2 + E - \bar{V}_{\mathrm{II}})\psi_{\mathrm{II}}(\mathbf{r}) = 0. \tag{II.10}$$

The exact solutions of (II.10) for the energy range $E < \bar{V}_{\mathrm{II}}$ can be written in the multicenter partial-wave representation

$$\psi_{\mathrm{II}}(\mathbf{r}) = \sum_j \sum_L A_L{}^j k_l^{(1)}(\kappa r_j) Y_L(\mathbf{r}_j) + \sum_L A_L{}^0 i_l(\kappa r_0) Y_L(\mathbf{r}_0), \tag{II.11}$$

where

$$i_l(x) = i^{-l} j_l(ix) \tag{II.12}$$

is a modified spherical Bessel function:

$$k_l^{(1)}(x) = -i^{-l} h_l^{(1)}(ix) \tag{II.13}$$

is a modified spherical Hankel function of the first kind;

$$\kappa = (\overline{V}_{\text{II}} - E)^{1/2} \tag{II.14}$$

is the "wave propagation constant"; and

$$\mathbf{r}_j = \mathbf{r} - \mathbf{R}_j. \tag{II.15}$$

For the energy range $E > \overline{V}_{\text{II}}$ the proper solutions of (II.10) are

$$\psi_{\text{II}}(\mathbf{r}) = \sum_j \sum_L A_L{}^j n_l(\kappa r_j) Y_L(\mathbf{r}_j) + \sum_L A_L{}^0 j_l(\kappa r_0) Y_L(\mathbf{r}_0) \tag{II.16}$$

in which

$$\kappa = (E - \overline{V}_{\text{II}})^{1/2}, \tag{II.17}$$

and where n_l and j_l are ordinary spherical Neumann and Bessel functions, respectively.

We may interpret the first term of each of the expressions (II.11) and (II.16) as "outgoing" spherical waves which have been scattered by the regions of spherically averaged potential energy centered at positions $\mathbf{R}_j$. The second term may be interpreted as an "incoming" spherical wave directed toward the center of the molecule, which has been scattered by the extramolecular region of spherically averaged potential energy. We see that the argument of the spherical Hankel function in expression (II.13) is imaginary. Thus for bound molecular orbitals in the energy range $E < \overline{V}_{\text{II}}$ we are not dealing with progressive waves in the usual sense of scattering theory, but rather functions which decay more or less exponentially away from the atomic regions. The appearance of the spherical Neumann function with real argument in expression (II.16) suggests "standing waves" in the intersphere region for the energy range $E > \overline{V}_{\text{II}}$.

It is also possible to fix one's attention on a particular atom j in the molecule and write the intersphere wave function entirely with respect to that atom as the sum of an "incident wave"

$$\psi_{\text{II}}^i(\mathbf{r}) = \sum_L B_L{}^j i_l(\kappa r_j) Y_L(\mathbf{r}_j), \qquad E < \overline{V}_{\text{II}}, \tag{II.18}$$

$$\psi_{\text{II}}^i(\mathbf{r}) = \sum_L B_L{}^j j_l(\kappa r_j) Y_L(\mathbf{r}_j), \qquad E > \overline{V}_{\text{II}}, \tag{II.19}$$

and a "scattered wave"

$$\psi_{\text{II}}^{s}(\mathbf{r}) = \sum_{L} A_L{}^{j} k_l^{(1)}(\kappa r_j) Y_L(\mathbf{r}_j), \qquad E < \bar{V}_{\text{II}}, \tag{II.20}$$

$$\psi_{\text{II}}^{s}(\mathbf{r}) = \sum_{L} A_L{}^{j} n_l(\kappa r_j) Y_L(\mathbf{r}_j), \qquad E > \bar{V}_{\text{II}}. \tag{II.21}$$

We can then identify the wave function written in the form

$$\psi_{\text{II}}(\mathbf{r}) = \psi_{\text{II}}^{i}(\mathbf{r}) + \psi_{\text{II}}^{s}(\mathbf{r}) \tag{II.22}$$

with expressions (II.11) and (II.16), respectively. This effectively allows us to relate the wave "incident" on atom j [expressions (II.18) and (II.19)] to the waves "scattered" by all the other atoms and interatomic spherical potentials $j' \neq j$ of the molecule and to the wave "scattered" by the extramolecular potential [Eq. (II.11) and (II.16)]. Thus it is possible to express the coefficients $B_L{}^{j}$ in terms of the coefficients $A_L{}^{j}$ and $A_L{}^{0}$.

To implement this procedure we make use of the following expansion theorems:

$$k_l^{(1)}(\kappa|\mathbf{r}_2 - \mathbf{r}_1|) Y_L(\mathbf{r}_2 - \mathbf{r}_1) = 4\pi \sum_{L'} (-1)^{l+l'} \sum_{L''} I_{L''}(L; L') k_{l''}^{(1)}(\kappa r_1) Y_{L''}(\mathbf{r}_1) \times i_{l'}(\kappa r_2) Y_{L'}(\mathbf{r}_2), \qquad r_1 > r_2; \tag{II.23}$$

$$k_l^{(1)}(\kappa|\mathbf{r}_2 - \mathbf{r}_1|) Y_L(\mathbf{r}_2 - \mathbf{r}_1) = 4\pi \sum_{L'} (-1)^{l+l'} \sum_{L''} I_{L''}(L; L') i_{l''}(\kappa r_1) Y_{L''}(\mathbf{r}_1) \times k_{l'}^{(1)}(\kappa r_2) Y_{L'}(\mathbf{r}_2), \qquad r_1 < r_2; \tag{II.24}$$

$$i_l(\kappa|\mathbf{r}_2 - \mathbf{r}_1|) Y_L(\mathbf{r}_2 - \mathbf{r}_1) = 4\pi \sum_{L'} (-1)^{l+l'} \sum_{L''} I_{L''}(L; L') i_{l''}(\kappa r_1) Y_{L''}(\mathbf{r}_1) \times i_{l'}(\kappa r_2) Y_{L'}(\mathbf{r}_2); \tag{II.25}$$

$$n_l(\kappa|\mathbf{r}_2 - \mathbf{r}_1|) Y_L(\mathbf{r}_2 - \mathbf{r}_1) = 4\pi \sum_{L'} i^{l'-l} \sum_{L''} i^{-l''} I_{L''}(L; L') n_{l''}(\kappa r_1) Y_{L''}(\mathbf{r}_1) \times j_{l'}(\kappa r_2) Y_{L'}(\mathbf{r}_2), \qquad r_1 > r_2; \tag{II.26}$$

$$n_l(\kappa|\mathbf{r}_2 - \mathbf{r}_1|) Y_L(\mathbf{r}_2 - \mathbf{r}_1) = 4\pi \sum_{L'} i^{l'-l} \sum_{L''} i^{-l''} I_{L''}(L; L') j_{l''}(\kappa r_1) Y_{L''}(\mathbf{r}_1) \times n_{l'}(\kappa r_2) Y_{L'}(\mathbf{r}_2), \qquad r_1 < r_2; \tag{II.27}$$

$$j_l(\kappa|\mathbf{r}_2 - \mathbf{r}_1|) Y_L(\mathbf{r}_2 - \mathbf{r}_1) = 4\pi \sum_{L'} i^{l'-l} \sum_{L''} i^{-l''} I_{L''}(L; L') j_{l''}(\kappa r_1) Y_{L''}(\mathbf{r}_1) \times j_{l'}(\kappa r_2) Y_{L'}(\mathbf{r}_2). \tag{II.28}$$

The integrals

$$I_{L''}(L; L') = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \, Y_{L''}(\theta, \phi) Y_L(\theta, \phi) Y_{L'}(\theta, \phi) \tag{II.29}$$

over triple products of real spherical harmonics occur in these expressions. They are nonzero only for the following conditions on the angular momentum indices:

$$|l - l'| \leq l'' \leq l + l' \tag{II.30}$$

$$l'' + l + l' = \text{even integer.} \tag{II.31}$$

A detailed proof of the above expansion theorems is given in the Appendix.

Substitution of these expansions into expressions (II.11) and (II.16) and comparison of the resulting equations with expressions (II.18) through (II.22) leads to the set of equations (one for each value of the indices j and L)

$$B_L{}^j = \sum_{j'} \sum_{L'} G_{LL'}^{jj'}(E) A_{L'}^{j'} + \sum_{L'} S_{LL'}^{j0}(E) A_{L'}^{0}, \tag{II.32}$$

in which we define the quantities

$$G_{LL'}^{jj'}(E) = (1 - \delta_{jj'}) 4\pi(-1)^{l+l'} \sum_{L''} I_{L''}(L; L') \times k_{l''}^{(1)}(\kappa R_{jj'}) Y_{L''}(\mathbf{R}_{jj'}), \qquad E < \bar{V}_{\text{II}}; \tag{II.33}$$

$$G_{LL'}^{jj'}(E) = (1 - \delta_{jj'}) 4\pi i^{l-l'} \sum_{L''} i^{-l''} I_{L''}(L; L') \times n_{l''}(\kappa R_{jj'}) Y_{L''}(\mathbf{R}_{jj'}), \qquad E > \bar{V}_{\text{II}}; \tag{II.34}$$

$$S_{LL'}^{j0}(E) = 4\pi(-1)^{l+l'} \sum_{L''} I_{L''}(L; L') \times i_{l''}(\kappa R_{j0}) Y_{L''}(\mathbf{R}_{j0}), \qquad E < \bar{V}_{\text{II}}; \tag{II.35}$$

$$S_{LL'}^{j0}(E) = 4\pi i^{l-l'} \sum_{L''} i^{-l''} I_{L''}(L; L') \times j_{l''}(\kappa R_{j0}) Y_{L''}(\mathbf{R}_{j0}), \qquad E > \bar{V}_{\text{II}}. \tag{II.36}$$

In the above expressions, the vectors

$$\mathbf{R}_{jj'} = \mathbf{R}_{j'} - \mathbf{R}_j \tag{II.37}$$

connect the centers of any two atomic or interatomic regions of spherically averaged potential. The vectors

$$\mathbf{R}_{j0} = \mathbf{R}_0 - \mathbf{R}_j \tag{II.38}$$

locate each such region with respect to the defined center of the molecule.

If we fix our attention on the outer spherical boundary (see Fig. 1) then, in place of expressions (II.18) and (II.19), we can write for the proper "incident-wave" intersphere wave function

$$\psi_{\text{II}}^{i}(\mathbf{r}) = \sum_{L} B_L{}^0 k_L^{(1)}(\kappa r_0)\, Y_L(\mathbf{r}_0), \qquad E < \overline{V}_{\text{II}}; \tag{II.39}$$

$$\psi_{\text{II}}^{i}(\mathbf{r}) = \sum_{L} B_L{}^0 n_L(\kappa r_0)\, Y_L(\mathbf{r}_0), \qquad E > \overline{V}_{\text{II}}. \tag{II.40}$$

For the "scattered-wave" solution we have, in place of expressions (II.20) and (II.21),

$$\psi_{\text{II}}^{s}(\mathbf{r}) = \sum_{L} A_L{}^0 i_l(\kappa r_0) Y_L(\mathbf{r}_0), \qquad E < \overline{V}_{\text{II}}; \tag{II.41}$$

$$\psi_{\text{II}}^{s}(\mathbf{r}) = \sum_{L} A_L{}^0 j_l(\kappa r_0)\, Y_L(\mathbf{r}_0), \qquad E > \overline{V}_{\text{II}}. \tag{II.42}$$

It may be noted that (II.39) and (II.40) represent "outgoing waves" with respect to the center of the molecule. Thus they are solutions of the wave equation (II.10) which are singular at the origin $r_0 = 0$. On the other hand, (II.41) and (II.42) represent "incoming waves" with respect to the molecular center and thus must be regular solutions of the wave equation at the origin.

Comparison of the sum of expressions (II.39) and (II.41) with expression (II.11) and comparison of the sum of (II.40) and (II.42) with (II.16) permits one to write the coefficients $B_L{}^0$ in terms of the coefficients $A_L{}^j$. In other words, we can relate the wave "incident" on the interior surface of the outer spherical boundary to the waves "scattered" by all the atomic and interatomic regions of spherically averaged potential (see Fig. 1). Substituting the expansion theorems (II.23) through (II.28) into expressions (II.11) and (II.16) and comparing the latter with (II.39) through (II.42), we arrive at the set of equations (one for each value of the index L)

$$B_L{}^0 = \sum_{j'} \sum_{L'} S_{LL'}^{oj'}(E) A_{L'}^{j'}. \tag{II.43}$$

Here we again make use of the quantities (II.35) and (II.36).

We also require continuity of the wave functions and their first derivatives across each spherical boundary in the molecule. Therefore, we can equate the logarithmic derivatives of the intersphere wave function written in the form (II.22) with the logarithmic derivatives of the wave functions (II.7) and (II.9) at the various sphere radii b_j and b_0. This immediately leads to the following relations between partial-wave coefficients:

$$A_L{}^j = t_l{}^j(E) B_L{}^j \tag{II.44}$$

$$A_L{}^0 = t_l{}^0(E) B_L{}^0, \tag{II.45}$$

where we introduce the quantities

$$t_l{}^j(E) = -\frac{[i_l(\kappa b_j),\, R_l{}^j(E;\, b_j)]}{[k_l^{(1)}(\kappa b_j),\, R_l{}^j(E;\, b_j)]}, \qquad E < \bar{V}_{\text{II}}; \tag{II.46}$$

$$t_l{}^j(E) = -\frac{[j_l(\kappa b_j),\, R_l{}^j(E;\, b_j)]}{[n_l(\kappa b_j),\, R_l{}^j(E;\, b_j)]}, \qquad E > \bar{V}_{\text{II}}; \tag{II.47}$$

$$t_l{}^0(E) = -\frac{[k_l^{(1)}(\kappa b_0),\, R_l{}^0(E;\, b_0)]}{[i_l(\kappa b_0),\, R_l{}^0(E;\, b_0)]}, \qquad E < \bar{V}_{\text{II}}; \tag{II.48}$$

$$t_l{}^0(E) = -\frac{[n_l(\kappa b_0),\, R_l{}^0(E;\, b_0)]}{[j_l(\kappa b_0),\, R_l{}^0(E;\, b_0)]}, \qquad E > \bar{V}_{\text{II}}; \tag{II.49}$$

and use the Wronskian notation

$$[F(x),\, G(x)] = F(x)\frac{dG(x)}{dx} - G(x)\frac{dF(x)}{dx}. \tag{II.50}$$

With expressions (II.44) and (II.45) and the identities

$$[i_l(\kappa b),\, k_l^{(1)}(\kappa b)] = (-1)^{l+1}/\kappa b^2 \tag{II.51}$$

$$[j_l(\kappa b),\, n_l(\kappa b)] = 1/\kappa b^2 \tag{II.52}$$

the matching of the wave functions (II.22), (II.7), and (II.9) at the various spherical boundaries also leads to the following relations between partial-wave coefficients:

$$A_L{}^j = (-1)^{l+1}\kappa b_j{}^2[i_l(\kappa b_j),\, R_l{}^j(E;\, b_j)]C_L{}^j, \qquad E < \bar{V}_{\text{II}}; \tag{II.53}$$

$$A_L{}^0 = (-1)^{l+1}\kappa b_0{}^2[R_l{}^0(E;\, b_0),\, k_l^{(1)}(\kappa b_0)]C_L{}^0, \qquad E < \bar{V}_{\text{II}}; \tag{II.54}$$

$$A_L{}^j = \kappa b_j{}^2[j_l(\kappa b_j),\, R_l{}^j(E;\, b_j)]C_L{}^j, \qquad E > \bar{V}_{\text{II}}; \tag{II.55}$$

$$A_L^0 = \kappa b_0{}^2[R_l{}^0(E;\, b_0),\, n_l(\kappa b_0)]C_L{}^0, \qquad E > \bar{V}_{\text{II}}. \tag{II.56}$$

The scattering on a given site of the molecule must be compatible with the scattering between different sites. Thus we can combine expressions (II.44) and (II.45) with expressions (II.32) and (II.43), respectively, to obtain a set of compatibility relations for the partial-wave coefficients $A_L{}^j$ and $A_L{}^0$. These relations may be written in the form of the linear homogeneous equations

$$\sum_{j'}\sum_{L'}[T^{-1}(E)]_{LL'}^{jj'}A_{L'}^{j'} - \sum_{L'}S_{LL'}^{j0}(E)A_{L'}^0 = 0, \tag{II.57}$$

$$\sum_{j'}\sum_{L'}S_{LL'}^{0j'}(E)A_{L'}^{j'} - \sum_{L'}\delta_{LL'}[t_l{}^0(E)]^{-1}A_{L'}^0 = 0, \tag{II.58}$$

where we define the matrix element

$$[T^{-1}(E)]_{LL'}^{jj'} = \delta_{jj'}\delta_{LL'}[t_l^{j}(E)]^{-1} - G_{LL'}^{jj'}(E). \tag{II.59}$$

Expressions (II.57) and (II.58) constitute the secular equations of the SCF–Xα scattered-wave method. The molecular-orbital energies correspond to zeros of the determinant of the matrix

$$\begin{bmatrix} [T^{-1}(E)]_{LL'}^{jj'} & -S_{LL'}^{j0}(E) \\ S_{LL'}^{0j'}(E) & -\delta_{LL'}[t_l^{0}(E)]^{-1} \end{bmatrix}. \tag{II.60}$$

Because real spherical harmonics are used throughout and because of conditions (II.30) and (II.31), the matrix elements are real and symmetric, i.e., for $E > \overline{V}_{\text{II}}$,

$$[T^{-1}(E)]_{L'L}^{j'j} = [T^{-1}(E)]_{LL'}^{jj'} = [T^{-1}(E)]_{LL'}^{jj'*} \tag{II.61}$$

$$G_{L'L}^{j'j}(E) \quad = G_{LL'}^{jj'}(E) \quad = G_{LL'}^{jj'*}(E) \tag{II.62}$$

$$S_{L'L}^{0j}(E) \quad = S_{LL'}^{j0}(E) \quad = S_{LL'}^{j0*}(E). \tag{II.63}$$

When the index j refers to an atom at the defined center of the molecule (see Fig. 1), then the vector (II.38) is identically zero, and it can be shown from expressions (II.35) and (II.36) that

$$S_{LL'}^{j0}(E) = \delta_{LL'} \qquad (j = \text{central atom}). \tag{II.64}$$

Although the matrix elements (II.33) through (II.36) and (II.46) through (II.49) may look complicated, they are relatively straightforward to compute efficiently. This is due, in part, to the dependence of these quantities only on radial functions [e.g., $R_l^{j}(E; b_j)$ and $k_l^{(1)}(\kappa b_j)$] and their first derivatives at appropriate sphere radii b_j, and on "structure factors" [e.g., $k_l^{(1)}(\kappa R_{jj'})Y_L(\mathbf{R}_{jj'})$] which are functions of the interatomic vectors $\mathbf{R}_{jj'}$. The Noumerov method (Pratt, 1952) can be used to perform the numerical integrations of the radial Schrödinger equation (II.8) as a function of E and l. Standard computer programs are available from various sources for evaluating spherical Bessel functions and spherical harmonics. There are no integrals of the multicenter type encountered in LCAO molecular-orbital methods. The integrals (II.29) are easily computed directly or in terms of products of Clebsch–Gordon coefficients. They are closely related to the Condon–Shortley coefficients (Condon and Shortley, 1951). Computer programs for their evaluation are available from the *Quantum Chemistry Program Exchange* (QCPE), University of Indiana.

Because the energy E is a parameter occurring in all the matrix elements, the latter must be computed over a range of energies bracketing each orbital eigenvalue and the determinant of the matrix (II.60) interpolated to find the zeros. One can start with trial wave functions consisting of one or two partial waves until an increase in the size of the determinant produces no significant change in the orbital energies. We have found that two or three partial waves ($l = 0, 1, 2$) per atom are sufficient in applications to most polyatomic molecules (including those involving transition metals) to yield a convergence of the orbital energies to ± 0.001 Ry. With such rapid partial-wave convergence, the typical size of the secular array (II.60) for a given molecule is much smaller than that characteristic of LCAO methods, which depend on more slowly convergent analytic atomic-orbital basis sets.

Furthermore, the matrix (II.60) can be partially factorized by exploiting any symmetry which the molecule may possess. Instead of expanding the wave functions (II.7), (II.9), and (II.11) in ordinary spherical harmonics, we can expand them in linear combinations

$$K_{ln}^{\Gamma j}(\mathbf{r}) = \sum_{m} C_{lnm}^{\Gamma j} \, Y_{lm}(\mathbf{r}) \tag{II.65}$$

of spherical harmonics which are bases for the various irreducible representations Γ of the appropriate symmetry point group. The index n indicates that a particular value of l may occur more than once in a given irreducible representation. The coefficients $C_{lmn}^{\Gamma j}$ which may be generated by group projection operators lead to compact symmetrized versions of the matrix elements (II.33) through (II.36). In the case of a symmetrically coordinated molecule like that illustrated in Fig. 1, the symmetrized form of the matrix elements (II.33) which connect ligand atoms is

$$G_{ln;l'n'}^{\mathrm{symm}} = \sum_{j} \sum_{j'} \sum_{m} \sum_{m'} C_{lnm}^{\Gamma j} \, G_{lm;l'm'}^{jj'} \, C_{l'n'm'}^{\Gamma j'} . \tag{II.66}$$

The summations over j and j' are over equivalent ligand atoms. For a tetrahedrally coordinated molecule such as MnO_4^- (to be discussed in detail in a later section), symmetrized secular arrays of only 3 × 3, 4 × 4, and 7 × 7 dimensions are obtained for the various irreducible representations of the tetrahedral (T_d) point group, if we include partial waves up to $l_{\max} = 3$ for the manganese atom and extramolecular region and up to $l_{\max} = 1$ for each oxygen atom.

We also can use partitioning theory (Löwdin, 1964) to contract the original set of secular equations (II.57) and (II.58). This reduces the size of the matrix (II.60) and leads to a very interesting interpretation of the scattered-wave method. The contracted secular equations can be written in the form

$$\sum_{j'}\sum_{L'}\{\delta_{jj'}\delta_{LL'}[t_l^j(E)]^{-1} - W_{LL'}^{jj'}(E)\}A_{L'}^{j'} = 0, \qquad \text{(II.67)}$$

where

$$W_{LL'}^{jj'}(E) = G_{LL'}^{jj'}(E) + \sum_{L''} S_{LL''}^{j0}(E)t_{l''}^{0}(E)S_{L''L'}^{0j'}(E). \qquad \text{(II.68)}$$

The inverse of the set of equations (II.67) can be interpreted in terms of the summing, to all orders of perturbation theory, of a "T-matrix" (Messiah, 1962) in the form of a "Dyson equation" for the multiple scattering of an electron by a system of nonoverlapping spherical potentials. The fact that expression (II.67) is set equal to zero is just the condition for the occurrence of bound single-particle states (the T-matrix itself has poles at these states). The amplitude of scattering at each potential j for each partial-wave l of energy E is described by the individual "atomic T-matrix" $t_l^j(E)$ defined in expressions (II.46) and (II.47). The "propagation" of the partial waves between any two atoms j and j' is described by the matrix element $W_{LL'}^{jj'}(E)$ defined in Eq. (II.68). However, the latter is not equal solely to the "free-space" single-particle Green's function in the angular-momentum representation $G_{LL'}^{jj'}(E)$, as it would be for simple "muffin-tin" potentials. The second term on the right side of expression (II.68) effectively "renormalizes" the Green's function $G_{LL'}^{jj'}(E)$ to the original boundary condition placed on the molecular orbitals, in the case of a symmetric molecule like that shown in Fig. 1 the solution of Schrödinger's equation in the extramolecular region.

The use of an outer spherical boundary is not a stringent requirement of the scattered-wave method, and it may actually be inappropriate for a large or highly asymmetric polyatomic molecule or for certain applications to crystals. In the absence of such a boundary, the secular equations reduce to

$$\sum_{j'}\sum_{L'}[T^{-1}(E)]_{LL'}^{jj'} = \sum_{j'}\sum_{L'}\{\delta_{jj'}\delta_{LL'}[t_l^j(E)]^{-1} - G_{LL'}^{jj'}(E)\} = 0. \qquad \text{(II.69)}$$

It is particularly easy to see from the latter form of the secular equations that as the internuclear distances between the various atoms in a molecule are increased indefinitely, the present theory automatically leads to the proper separated-atom limit. The matrix elements $G_{LL'}^{jj'}(E)$ become smaller numerically as the internuclear distances $R_{jj'}$ increase [see expression (II.33)] because the modified spherical Hankel functions decrease exponentially with increasing argument. In the limit $R_{jj'} \rightarrow \infty$ where $G_{LL'}^{jj'}(E) \rightarrow$

0, the zeros of the secular determinant occur at energies for which the quantities $[t_l^j(E)]^{-1}$ are identically zero. This is just the condition for the occurrence of energy levels for the free atoms.

The generation of a set of occupied molecular-orbital energy levels and wave functions for a superposed-atom potential of the form (II.4) is the starting point for a complete self-consistent-field calculation within the framework of the Xα statistical approximation (II.3) to exchange correlation. The initial set of orbital wave functions leads to an electronic charge density which is used as the basis for generating a new potential. This potential is spherically averaged inside the various atomic and interatomic spheres and in the extramolecular region. A volume average of the potential is carried out within the intersphere region. A suitable average of this potential and the starting potential in each region serves as the input for the first iteration. A new set of orbital energies and wave functions is computed, and the entire numerical procedure is repeated until self-consistency of the potentials and charge densities is achieved.

In all of our applications of the SCF–Xα scattered-wave method to polyatomic molecules and crystals, thus far, we have found that the charge densities of the deepest "core" orbitals can be kept fixed and the final "chemically shifted" core-orbital energies recalculated in the self-consistent field of the remaining core and valence electrons, without introducing appreciable error. Nevertheless, since the SCF–Xα computational procedure is very efficient (typically a few minutes of time on an IBM 360/65 computer), the additional cost of including all core electrons in the calculation is not prohibitive.

The SCF calculations are also easily carried out in spin-unrestricted form (i.e., different orbitals for different spins), using the unrestricted version

$$V_{X\alpha}\uparrow(\mathbf{r}) = -6\alpha[(3/4\pi)\rho\uparrow(\mathbf{r})]^{1/3} \tag{II.70}$$

$$V_{X\alpha}\downarrow(\mathbf{r}) = -6\alpha[(3/4\pi)\rho\downarrow(\mathbf{r})]^{1/3} \tag{II.71}$$

of the Xα approximation to exchange correlation [cf. Eq. (II.3)] (Slater, 1971,1972; Slater and Johnson, 1972). In these expressions $\rho\uparrow(\mathbf{r})$ and $\rho\downarrow(\mathbf{r})$ represent the charge densities associated with "spin-up" and "spin-down" electrons, respectively. The spin-unrestricted version of the SCF–Xα scattered-wave method is particularly valuable for developing a quantitative understanding of the electronic structures and related properties (magnetic and optical) of "open-shell" molecules and crystals, such as transition metal complexes.

III. Applications to Polyatomic Molecules

A. The Permanganate Ion

As our first illustrative application of the formalism described in the preceding section, we consider the chemical bonding of the permanganate ion (MnO_4^-). [The results of preliminary calculations on MnO_4^- by the SCF–Xα scattered-wave method have been reported earlier (Johnson and Smith, 1971b).] The electronic structures and related properties of transition-metal complexes like MnO_4^- have been discussed by inorganic chemists for many years (Cotton and Wilkinson, 1966). MnO_4^- does not exist in the gaseous phase, but is a stable anion in crystals such as $KMnO_4$, as an "impurity" cluster in crystals like $KClO_4$, and in aqueous solution. The characteristic purple color of $KMnO_4$ is associated with a strong optical absorption peak at 2.3 eV in the complementary green part of the spectrum (Holt and Ballhausen, 1967). Permanganate crystals exhibit only a weak temperature-independent paramagnetism of the Van Vleck type (Van Vleck and Frank, 1929), suggesting a "closed-shell" ground-state electronic structure.

Several different semiempirical LCAO molecular-orbital calculations for MnO_4^- have been published (Wolfsberg and Helmholz, 1952; Ballhausen and Liehr, 1958; Fenske and Sweeney, 1964; Viste and Gray, 1964; Oleari *et al.*, 1966; Dahl and Ballhausen, 1968; Dahl and Johansen, 1968). These calculations are at considerable variance with respect to magnitudes and ordering of orbital energies. None of the calculations is in good quantitative agreement with the measured optical properties of permanganate crystals. *Ab initio* LCAO calculations, using both minimal and "better-than-minimal" basis sets and requiring many hours of computer time, have recently been reported (Hillier and Saunders, 1970b, 1971). In spite of their sophistication, e.g., the direct evaluation of all multicenter integrals and the inclusion of some configuration interaction, the latter investigations have not resulted in a more accurate description of the electronic structure of MnO_4^- than have the simpler semiempirical LCAO methods.

The similarities of the chemical, magnetic, and optical properties of the permanganate ion in various crystalline environments suggest that the neighboring cations have little effect on the chemical bonding of the MnO_4^- cluster, other than providing a stabilizing electrostatic field. For example, the unit cell of the orthorhombic $KMnO_4$ crystal can clearly be divided into four distinct tetrahedrally coordinated MnO_4^- molecules and four K^+ ions (Mooney, 1931). Thus we can focus our attention on a single

MnO_4^- molecule and partition its space into *atomic*, *interatomic*, and *extramolecular* regions inside of which we generate an initial superposed-atom potential of the form (II.4), as described in the preceding section. Schwarz (1972) has determined optimized Xα exchange-correlation scaling parameters of $\alpha = 0.712$ and $\alpha = 0.744$ for the Mn and O atoms, respectively. We then use these values in the corresponding atomic spheres of the MnO_4^- cluster. A weighted average value of $\alpha = 0.738$ (four parts O to one part Mn) is chosen for the interatomic region. We choose $\alpha = 0.744$, the value appropriate for O, in the extramolecular region. The potential energy is spherically averaged in each atomic region and in the extramolecular region. A simple volume average [see Eq. (II.6)] is carried out for the interatomic region.

During the SCF–Xα calculation for the ground state of MnO_4^-, the electronic energy levels are filled successively so as to yield a net charge of -1. By surrounding the MnO_4^- cluster with a spherical shell of charge $+1$ at the outer spherical boundary separating the extramolecular region from the atomic regions, we are able to approximate the stabilizing electrostatic field of a typical crystalline environment such as $KMnO_4$. This procedure is analogous to the one used originally by Watson (1958) in Hartree–Fock calculations on oxygen ions. We allow the "Watson sphere" to enclose and just touch the Mn and O atomic spheres, so that the former does not overlap the nearest K^+ ions and neighboring MnO_4^- molecules in the

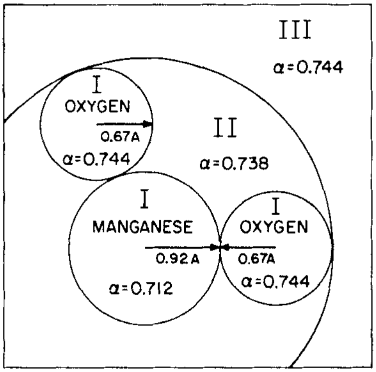

Fig. 2. Division of the MnO_4^- cluster (in an O—Mn—O plane) into (I) atomic, (II) interatomic, and (III) extramolecular regions of spherically averaged and volume-averaged potential. The Xα exchange-correlation parameters, optimized by the first-principles method suggested by Slater, are shown.

$KMnO_4$ unit cell. The Mn and O atomic spheres are assumed to be touching at respective radii where the corresponding initial potentials are equal. For the Mn–O internuclear distance we use 1.59 Å, the average value measured for a $KMnO_4$ crystal (Mooney, 1931). The various spherical regions of the MnO_4^- molecule are schematically illustrated for an O—Mn—O plane in Fig. 2, including the optimized values of the Xα exchange-correlation parameter.

Only 15 iterations were necessary to achieve an SCF convergence of the MnO_4^- orbital energies to ± 0.001 Ry. The total computation time for this procedure was only 8 minutes on an IBM 360/65 computer. This may be contrasted with the 10 hours of time (on a computer of comparable speed) required in a recent Hartree–Fock minimal-basis SCF–LCAO calculation on MnO_4^- (Hillier and Saunders, 1970b).

To investigate the observed magnetic ground state of permanganate crystals, we have carried out both spin-unrestricted and spin-restricted calculations. In constructing the superposed-atom potential used to initiate the spin-unrestricted SCF procedure, we assumed that all five Mn 3*d* electrons have their spins unpaired. The spin-unrestricted calculation converged in 15 iterations to the same non-spin-polarized "closed-shell" limit determined in the spin-restricted calculation (± 0.001 Ry). This result is consistent with the observation that permanganate crystals, e.g., $KMnO_4$, exhibit only a weak, temperature-independent paramagnetism.

Our results for the SCF ground-state orbital energies of the MnO_4^- molecule are listed in Table I, where we have labeled the levels according to the various irreducible representations of the tetrahedral (T_d) symmetry group. The deepest energies $(1a_1)^2(2a_1)^2(1t_2)^6(3a_1)^2(2t_2)^6(4a_1)^2(3t_2)^6(5a_1)^2(4t_2)^6$ are Mn $1s^2 2s^2 2p^6 3s^2 3p^6$ and O $1s^2 2s^2$ levels "chemically shifted" from the free-atom limits (determined by the SCF–Xα method) shown in the parentheses in Table I. The $(5t_2)^6(1e)^4(6a_1)^2(6t_2)^6(1t_1)^6$ levels correspond to the more delocalized valence orbitals, which are symmetry-allowed combinations of partial waves associated principally with the O 2*p* and Mn 3*d* electrons. These levels are also shown in Fig. 3, along with the first few unoccupied orbital energies $(2e)^0(7t_2)^0(8t_2)^0(7a_1)^0$, and are compared with the SCF–Xα Mn and O atomic energy levels. In Table II we have written the normalized contribution of each of the valence orbitals to the electronic charge in the various regions of the MnO_4^- cluster. The principal component partial waves of each orbital are noted in parentheses.

The $5t_2$ and $1e$ valence orbitals correspond specifically to "σ-" and "π-bonding" combinations of O 2*p*-like partial waves with Mn 3*d*-like partial waves. Visual evidence supporting this statement is presented in the

TABLE I

SCF-Xα ELECTRONIC ENERGY LEVELS (IN RYDBERGS) OF AN MnO_4^- CLUSTER IN A CRYSTALLINE ENVIRONMENT[a]

Symmetry	Energy Levels
$7a_1$	−0.006
$8t_2$	−0.020
$7t_2$	−0.350
$2e$	−0.526
- - - - - -	- - - - - -
$1t_1$	−0.682
$6t_2$	−0.761
$6a_1$	−0.775
$1e$	−0.901
$5t_2$	−0.915
$4t_2$ (O 2*s*)	−1.785 (−1.732)
$5a_1$ (O 2*s*)	−1.813 (−1.732)
$3t_2$ (Mn 3*p*)	−4.259 (−3.952)
$4a_1$ (Mn 3*s*)	−6.435 (−6.126)
$2t_2$ (O 1*s*)	−37.738 (−37.822)
$3a_1$ (O 1*s*)	−37.738 (−37.822)
$1t_2$ (Mn 2*p*)	−46.513 (−46.274)
$2a_1$ (Mn 2*s*)	−54.105 (−53.859)
$1a_1$ (Mn 1*s*)	−468.584 (−468.203)

[a] Levels below the dashed line are fully occupied in the ground state; those above the line are empty. Corresponding "free-atom" energy levels are shown in parentheses.

TABLE II

CONTRIBUTION OF EACH NORMALIZED VALENCE ORBITAL OF MnO_4^- TO A UNIT OF ELECTRONIC CHARGE IN THE VARIOUS REGIONS OF THE CLUSTER [a]

Symmetry	Mn sphere	O sphere	Interatomic Region	Extra-molecular region
$1t_1$	0.003 (3)	0.165 (1)	0.303 (1,3)	0.035 (3)
$6t_2$	0.036 (2)	0.138 (1)	0.369 (1,2)	0.041 (2)
$6a_1$	0.048 (0)	0.134 (1)	0.406 (0,1)	0.008 (0)
$1e$	0.381 (2)	0.078 (1)	0.284 (1,2)	0.022 (2)
$5t_2$	0.425 (2)	0.084 (1)	0.208 (1,2)	0.030 (2)

[a] The principal component partial-wave (angular-momentum) indices are shown in parentheses.

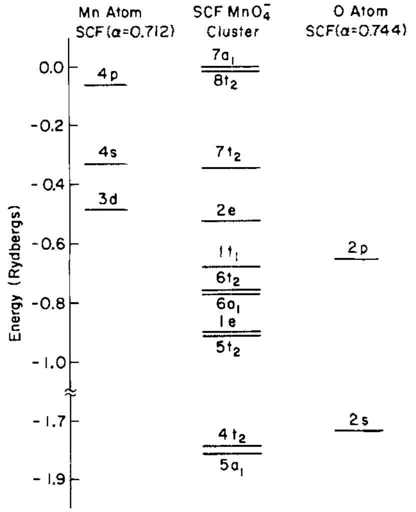

Fig. 3. SCF electronic energy levels of an MnO_4^- cluster in the stabilizing field of a crystalline environment. The energies are labeled according to the various irreducible representations of the tetrahedral (T_d) symmetry group. The highest occupied level in the ground state is $(1t_1)^6$. Also shown, for comparison, are the corresponding SCF–Xα energy levels of the free atoms.

form of computer-generated contour maps of these orbitals in Figs. 4 and 5, respectively. In Fig. 4 we show a map for one of the three orbitally degenerate normalized $5t_2$ wave functions in an O—Mn—O plane. The "σ-bonding" of O 2*p*-like partial waves with Mn 3*d*-like partial waves is clearly visible. O 2*p*–Mn 3*d* "π-bonding" is likewise apparent in Fig. 5, where we show a map for one of the two orbitally degenerate 1*e* wave functions in an O—Mn—O plane. It should be emphasized that these contour maps have not been generated from linear combinations of analytic atomic orbitals of the type traditionally used in Hartree–Fock molecular-orbital theory. They have been generated simply from the numerical partial-wave solutions of Schrödinger's equation for an SCF–Xα model potential, the wave functions and their first derivatives being joined throughout the various regions of the MnO_4^- molecule by the multiple-scattered-wave theory outlined in the preceding section. To ensure continuity of the wave functions and their first derivatives in the calculation of these contour maps, we have included symmetry-allowed partial waves up to $l_{max} = 5$ in the Mn atomic and extramolecular regions and up to $l_{max} = 2$ in the O regions.

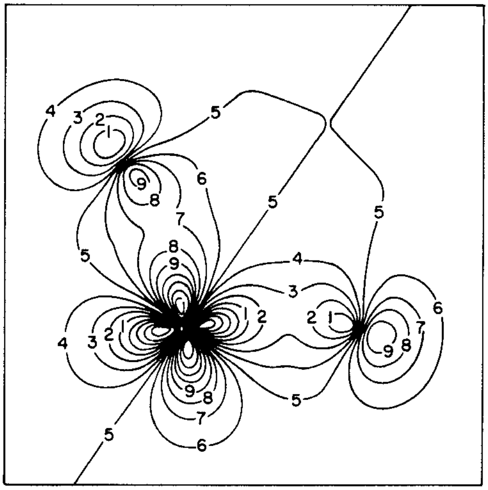

Fig. 4. Contour map of a normalized $5t_2$ "σ-bonding" orbital wave function for MnO_4^- in an O—Mn—O plane. Value of contour No. 1 = −0.2; value of contour No. 9 = +0.2; contour interval = 0.05.

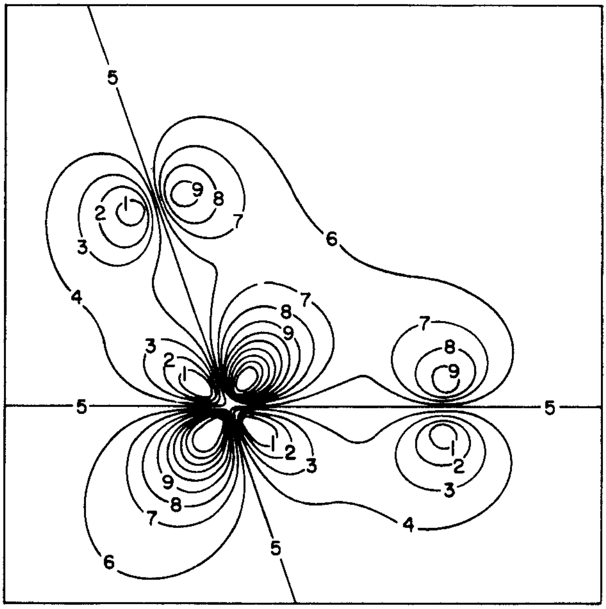

Fig. 5. Contour map of a normalized $1e$ "π-bonding" orbital wave function for MnO_4^- in an O—Mn—O plane. Value of contour No. 1 = −0.2; value of contour No. 9 = +0.2; contour interval = 0.05.

It is interesting to digress for a moment to compare the chemical bonding in MnO_4^- with that in the sulfate ion (SO_4^{2-}), which is also a tetrahedrally coordinated system. There has been a considerable amount of discussion in the literature (e.g., see Cruickshank, 1961) about the importance of 3*d* contributions to the bonding in sulfur complexes like SO_4^{2-}. In recent publications (Johnson and Smith, 1970b, 1971c) we have described the results of molecular-orbital calculations for SO_4^{2-} by the SCF scattered-wave technique. We have found that there is no significant S 3*d* contribution to the electronic structure of SO_4^{2-}, even though S $l = 2$ partial waves were automatically included in the calculations. This is quite evident in Fig. 6, where we show a contour map for the 1*e* valence orbital of SO_4^{2-} in an O—S—O plane. Comparing this figure with Fig. 5, which shows the corresponding 1*e* wave function for MnO_4^-, we see that there is no localized 3*d*-like contribution on the S atom, as there is on the Mn atom. The fact that it has been essential to include S 3*d* atomic orbitals in LCAO-type calculations on SO_4^{2-} in order to obtain meaningful results (Hillier and Saunders, 1970a), is due to the inherently slow convergence of analytic atomic-orbital basis functions. In the scattered-wave method there is no such convergence problem, because we are numerically solving Schrödinger's equation in partial waves throughout the space of the molecule for an SCF–Xα potential.

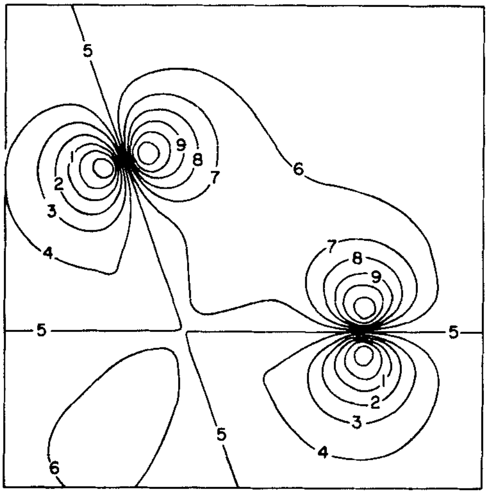

Fig. 6. Contour map of a normalized 1*e* orbital wave function for SO_4^{2-} in an O—S—O plane. Value of contour No. 1 = −0.2; value of contour No. 9 = +0.2; contour interval = 0.05.

The MnO_4^- valence orbitals $6a_1$ and $6t_2$ are associated principally with the O $2p$ electrons, although there is some hybridization with the Mn $3d$ electrons in the $6t_2$ orbital and with the Mn $4s$ electrons in the $6a_1$ orbital (see Table II). The highest occupied valence state $1t_1$ is essentially a "nonbonding" O $2p$ orbital. There is considerable delocalization of the valence orbitals into the interatomic region, as indicated in column 4 of Table II. Column 5 of this table shows that the orbitals are well localized to the MnO_4^- cluster as a whole.

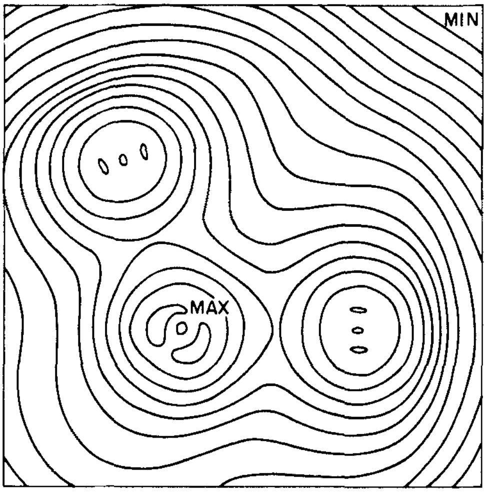

Fig. 7. Contour map of the total valence electronic charge density for MnO_4^- in an O—Mn—O plane. Value of maximum contour, 1.23. The values of succeeding contours decrease by a factor of 2 to a minimum value of 7.1×10^{-6} (in units of electrons per cubic Bohr radius).

In Fig. 7 we display a contour map of the total SCF charge density in an O—Mn—O plane for the $(5t_2)^6(1e)^4(6a_1)^2(6t_2)^6(1t_1)^6$ valence orbitals. The formation of directed "chemical bonds" is suggested in this figure. If we compare this map with a simple superposition of the valence charge densities of neutral Mn and O atoms, we find that there is relatively little net spatial transfer of charge between the atoms indicated for the ground-state electronic structure of the MnO_4^- cluster. The distribution of the total electronic charge (core electrons included) among the various regions of the cluster is shown in Table III. If we make the crude assumption that each Mn and O atom contributes one-fifth of the interatomic charge and that each O atom contributes one-fourth of the extramolecular charge,

TABLE III

TOTAL ELECTRONIC CHARGE (IN UNITS OF e) IN THE VARIOUS REGIONS OF THE MnO_4^- CLUSTER

Mn sphere:	−22.462
O sphere:	−6.276
Interatomic region:	−9.465
Exramolecular region:	−0.968

then we can estimate net effective charges of +0.64 and −0.41 for Mn and O, respectively.

The small values of these charges, relative to the extreme ionic limits of +7 and −2 expected for Mn and O, respectively, on the basis of formal valence theory, is not a surprising result. The 4*s* wave function of a Mn atom is very diffuse spatially with respect to the Mn—O internuclear distance. The maxima of the radial charge densities of the Mn 4*s* and O 2*p* wave functions practically intersect at a point along the Mn—O axis (for the observed internuclear distance) in MnO_4^-. Thus the formal transfer of Mn 4*s* electrons to O 2*p* orbitals involves very little actual spatial redistribution of charge. This fact has been stressed by Slater (1965a) for crystal and molecular bonding in general.

The first two unoccupied orbital energy levels 2*e* and $7t_2$ for the ground state of MnO_4^-, listed in Table I and illustrated in Fig. 3, are predominantly localized on the central Mn atom and correspond closely to 3*d* states. They are the "crystal-field" levels appropriate for tetrahedral geometry. Their ordering (2*e* lower than $7t_2$) and their small energy separation relative to the ordering and separation of the t_{2g} and e_g levels (t_{2g} lower than e_g) characteristic of systems with octahedral (O_h) symmetry, are consistent with the predictions of elementary crystal-field theory. The positions of these levels with respect to the fully occupied valence levels, which are not within the scope of crystal-field theory, are critical to the interpretation of the measured optical properties of permanganate crystals. The next unoccupied level $8t_2$ is associated principally with a "virtual" 4*p* orbital of Mn, and the highest level shown, $7a_1$, corresponds to a Mn 4*s* state.

The optical absorption spectrum of MnO_4^-, measured for a solid solution of $KMnO_4$ in $KClO_4$ (Holt and Ballhausen, 1967), consists of three intense bands with maxima at 2.3, 4.0, and 5.5 eV, and a "shoulder" at 3.5 eV. A complete theoretical analysis of the optical properties cannot be carried out without a quantitative treatment of orbital relaxation and configuration interaction. Nevertheless, Slater (1971, 1972) has recently shown that the difference between the Xα statistical total energies of the initial and final many-electron states of an optical transition is equal, to good approximation, to the difference between the Xα one-electron energies of orbitals whose occupation numbers are halfway between those of the initial and final states. To determine these orbitals, called "transition states," it is necessary for one to carry out a complete SCF–Xα calculation for each pair of levels involved in an optical transition, removing one-half of a unit of electronic charge from the initial orbital and adding one-half of a unit of charge to the final orbital. Because of the efficiency of our scattered-wave computer programs, this procedure is practicable for all the optical transitions of interest and requires only one or two minutes of computer time per transition state if we start with the SCF ground-state potentials. The transition-state method automatically accounts for the effects of orbital relaxation (Slater, 1971, 1972; Slater and Johnson, 1972).

The calculated energy differences between the initial and final SCF transition-state orbitals for each orbitally allowed optical transition of MnO_4^- are listed in Table IV. For comparison, we have included the energy differences between the corresponding "unrelaxed" virtual orbitals and valence orbitals for the ground-state SCF eigenvalues shown in Table I. The assigned experimental absorption energies are also included. There is close agreement between the two sets of theoretical transition energies. This result is consistent with Slater's argument that the relaxation of Xα orbitals should be relatively small in crystals for optical transitions between occupied valence-type levels and empty levels lying immediately

TABLE IV

THEORETICAL AND EXPERIMENTAL OPTICAL TRANSITION ENERGIES (IN eV) FOR MnO_4^-

Transition	Unrelaxed SCF calculation	Transition-state calculation	Experiment[a]
$1t_1 \rightarrow 2e$	2.1	2.3	2.3
$6t_2 \rightarrow 2e$	3.2	3.3	3.5
$1t_1 \rightarrow 7t_2$	4.5	4.7	4.0
$5t_2 \rightarrow 2e$	5.3	5.3	5.5

[a] See Holt and Ballhausen (1967).

above because the perturbation to the potential energy is small (Slater, 1971, 1972). This argument also explains the well-known success of band theory, using the Xα approximation for exchange correlation, in accounting for the visible and near-ultraviolet optical properties of many simple crystals, in terms of the differences between the one-electron energies of bands just below and bands just above the Fermi level. We see, however, that in the case of a complex crystal like $KMnO_4$, which has many atoms per unit cell, it is not necessary for one to carry out a complete band calculation in order to arrive at a good understanding of the optical properties. It is necessary only to calculate the detailed electronic structure of the component "molecular" clusters.

The theoretical optical transition energies listed in Table IV are in better quantitative agreement with experiment than are the results of semiempirical LCAO calculations (Wolfsberg and Helmholz, 1952; Ballhausen and Liehr, 1958; Fenske and Sweeney, 1964; Viste and Gray, 1964; Oleari *et al.*, 1966; Dahl and Ballhausen, 1968; Dahl and Johansen, 1968). They are also in better agreement with experiment than are the results of *ab initio* LCAO calculations (Hillier and Saunders, 1970b, 1971). The transition-state calculation leads to "exact" agreement of the $1t_1 \rightarrow 2e$ transition energy with the measured 2.3 eV absorption peak, although this accuracy may be fortuitous. Thus we interpret this absorption peak, and the purple color of $KMnO_4$ crystals, as due principally to electronic "charge transfer" between the fully occupied $1t_1$ nonbonding $2p$ orbital localized on the O ligands and the empty $2e$ $3d$-like orbital localized on the Mn atom (see Fig. 3).

It may be surprising to the reader that the scattered-wave method, in conjunction with Slater's Xα method and transition-state theory, can lead to a reasonably accurate description of the chemical bonding and optical properties of MnO_4^- with the expenditure of only a few minutes of computer time. In contrast, the *ab initio* calculations reported by Hillier and Saunders (1970b, 1971), using both minimal and "better-than-minimal" atomic-orbital basis sets, required many hours of computer time on a comparable machine.

B. Sulfur Hexafluoride

For our second example we consider the octahedrally coordinated molecule sulfur hexafluoride (SF_6). Like MnO_4^-, SF_6 is a system of traditional interest among theoretical chemists. Several *ab initio* Hartree–Fock SCF–LCAO calculations have been reported for this molecule (Bendazolli *et al.*, 1970; Gelius, 1970; Gelius *et al.*, 1970; Gianturco *et al.*, 1971), as well as two semiempirical LCAO calculations of the CNDO type (Santry and Segal, 1967; Siegbahn *et al.*, 1969). As in the case of MnO_4^-, the various LCAO calculations on SF_6 are not in very good agreement with each other or with experiment, differing considerably with respect to ordering and magnitudes of orbital energies. In Table V we list the orderings of the occupied valence orbitals of SF_6 obtained in the LCAO work, along with the ordering determined with the SCF–Xα scattered-wave method by J. W. D. Connolly and the author (Connolly and Johnson, 1971). The various physical parameters used in the latter calculation (chosen in the first-principles fashion described above for MnO_4^-) are

TABLE V

COMPARISON OF THEORETICAL ORDERINGS OF THE OCCUPIED VALENCE ORBITALS FOR SF_6

Type of calculation	Ordering
SCF–Xα scattered-wave	$a_{1g}\ t_{1u}\ e_g\ a_{1g}\ t_{1u}\ t_{2g}\ e_g\ t_{2u}\ t_{1u}\ t_{1g}$
Ab initio SCF–LCAO[a]	$a_{1g}\ t_{1u}\ e_g\ a_{1g}\ t_{1u}\ t_{2g}\ e_g\ t_{2u}\ t_{1u}\ t_{1g}$
Ab initio SCF–LCAO[b]	$a_{1g}\ t_{1u}\ e_g\ a_{1g}\ t_{1u}\ t_{2g}\ t_{1u}\ t_{2u}\ t_{1g}\ e_g$
Ab initio SCF–LCAO[c]	$a_{1g}\ t_{1u}\ e_g\ t_{1u}\ a_{1g}\ t_{2g}\ e_g\ t_{1u}\ t_{2u}\ t_{1g}$
CNDO–LCAO[d]	$a_{1g}\ t_{1u}\ e_g\ a_{1g}\ t_{1u}\ t_{2g}\ t_{2u}\ t_{1g}\ t_{1u}\ e_g$
CNDO–LCAO[e]	$a_{1g}\ t_{1u}\ e_g\ a_{1g}\ t_{2g}\ t_{1u}\ t_{2u}\ e_g\ t_{1g}\ t_{1u}$

[a] See Gelius *et al.* (1970; Gelius, 1970).
[b] See Bendazolli *et al.* (1970).
[c] See Gianturco *et al.* (1971).
[d] See Siegbahn *et al.* (1969).
[e] See Santry and Segal (1967).

TABLE VI

PARAMETERS USED IN THE SCF–Xα SCATTERED-WAVE CALCULATION ON SF_6

S–F internuclear distance	1.580 Å
S sphere radius	0.932 Å
F sphere radius	0.648 Å
Outer sphere radius	2.228 Å
S α-value	0.724
F α-value	0.737

listed in Table VI. We see in Table V that the ordering of orbitals obtained in the scattered-wave calculation is most consistent with that determined by Gelius *et al.* (1970; Gelius, 1970) in the most extensive and accurate *ab initio* Hartree–Fock LCAO calculation reported for SF_6 thus far. In the latter work, Clementi's IBMOL programs (Clementi and Davis, 1966) were used and an equivalent of approximately 20 hours of time on an IBM 360/65 computer was required. For comparison, our calculation of all the ground-state molecular orbitals for SF_6 by the SCF–Xα scattered-wave procedure required a total of only 3 minutes of computational time on the same type of machine.

We list our results for the occupied valence-orbital energies of SF_6 in Table VII. The energy levels are labeled according to the various irreducible representations of the octahedral (O_h) symmetry group. SF_6 is a "closed-shell" system. The three deepest levels a_{1g}, t_{1u}, and e_g correspond principally to F 2*s* orbitals, "chemically shifted" from their free-atom limits. The remaining valence orbitals are predominantly admixtures of S 3*s*-like and 3*p*-like partial waves with F 2*p*-like partial waves. The highest fully occupied level t_{1g} corresponds to a nonbonding F 2*p* orbital. As we pointed out for the sulfate ion (SO_4^{2-}), there is no significant contribution of S 3*d* orbitals to the chemical bonding of SF_6, although $l = 2$ and higher partial waves were included in the calculation.

TABLE VII

SCF–Xα ELECTRONIC ENERGY LEVELS (IN HARTREES) FOR THE OCCUPIED VALENCE ORBITALS OF SF_6

Symmetry	Ground-state energies	Transition-state energies
t_{1g}	−0.445	−0.584
t_{1u}	−0.479	−0.616
t_{2u}	−0.481	−0.619
e_g	−0.506	−0.644
t_{2g}	−0.553	−0.689
t_{1u}	−0.665	−0.803
a_{1g}	−0.844	−0.983
e_g	−1.168	−1.307
t_{1u}	−1.205	−1.343
a_{1g}	−1.305	−1.443

The first column of orbital energies shown in Table VII refers to the ground-state of SF_6. We list in the second column a set of SCF–Xα "transition-state" orbital levels which may be compared directly with the experimental ionization energies of the molecule. In the standard Hartree–Fock formulation of molecular-orbital theory, one traditionally makes use of Koopmans' theorem, which states that the ionization energy of a particular electron is approximately equal to the negative of its ground-state orbital energy. Unfortunately Koopmans' theorem ignores the significant orbital relaxation which accompanies ionization and thus is actually a rather poor approximation for most polyatomic molecules. To determine the ionization energies more accurately with the Hartree–Fock method, it is necessary to perform separate SCF calculations of the total energies of the molecule in its various ionic configurations and then to take the differences between these energies and the total energy of the molecule in its ground state. This procedure is too complicated and costly to implement on a molecule as complex as SF_6, if one uses *ab initio* SCF–LCAO methods. On the other hand, in the SCF–Xα formulation of molecular-orbital theory, the difference between the total energies of the ionic and ground states is, to very good approximation, equal to the energy of the "transition-state" orbital from which one-half a unit of electronic charge has been removed (Slater, 1971, 1972; Slaterand Johnson, 1972). The transition states automatically include the effects of orbital relaxation, and the negative values of their energies may be compared with the ionization energies. As described above, we have used an analogous procedure to interpret the optical absorption spectrum of MnO_4^-.

We have listed the SCF–Xα transition-state levels for SF_6 along with the ground-state results in Table VII. The significant differences between these two sets of energies reflect the large amount of orbital relaxation which occurs upon ionization of the molecule. In Table VIII we restate the negative values of the transition-state energies in units of electron volts and compare them with the experimental ionization energies measured for SF_6 by the method of ESCA (Siegbahn *et al.*, 1969). Also included, for comparison, are the theoretical ionization energies based on the application of Koopman's theorem to molecular-orbital energies calculated by Gelius *et al.* (1970; Gelius 1970) and Siegbahn *et al.* (1969), using the *ab initio* LCAO and CNDO methods, respectively. It is evident in Table VIII that the results obtained by the SCF–Xα scattered-wave technique, in conjunction with the transition-state procedure, are in much better agreement with experiment than are the results of the LCAO calculations.

TABLE VIII

COMPARISON OF THEORETICAL AND EXPERIMENTAL IONIZATION ENERGIES (IN eV) FOR SF_6

Symmetry	SCF–Xα transition-state energies	*Ab initio*[a] SCF–LCAO energies	CNDO[b] LCAO energies	Experimental[b] ionization energies
t_{1g}	15.9	18.2	22.4	~16
t_{1u}	16.8	19.0	21.5	17.3
t_{2u}	16.8	19.4	23.1	17.3
e_g	17.5	19.4	17.8	18.7
t_{2g}	18.8	22.2	24.2	19.9
t_{1u}	21.8	24.7	29.0	22.9
a_{1g}	26.7	29.6	30.8	27.0
e_g	35.6	45.3	43.1	39.3
t_{1u}	36.5	46.8	50.8	41.2
a_{1g}	39.3	50.4	57.0	44.2

[a] See Gelius *et al.* (1970; Gelius, 1970).
[b] See Siegbahn *et al.* (1969).

IV. Applications to Deep-Level Impurities in Semiconductors

We next consider the problem of determining the electronic structures of semiconductor impurities which lead to discrete energy levels lying deep within the band gap of the host crystal. The effective-mass theorem (Ziman 1964) is not applicable here, and conventional deep-level impurity theory (Koster and Slater, 1954) is difficult to implement because it is necessary to determine a complete set of Wannier or Bloch wave-functions for the otherwise perfect host lattice. To illustrate how the SCF–Xα scattered-wave model can be extended to this problem, we discuss the example of transition and noble metal impurities in II–VI semiconductors and their relationship to the luminescent properties of these materials. The luminescence of II–VI compounds (e.g., ZnS and CdS) has been and continues to be a very active area for scientific and technological investigation (Curie and Prener, 1967). Of particular importance to the phenomenon of luminescence in II–VI compounds is the presence of small amounts of substitutional metallic impurities (called "activators"), such as Cu, Ag, Au, and Mn. Specific impurities in specific compounds produce characteristic luminescent emission bands, e.g., the "blue" and "green" emission lines associated with Cu in ZnS.

Although some progress has been made toward developing a quantitative theory of impurity-activated luminescence, many questions remain to be answered. For example, it is believed that impurity-activated luminescence involves electronic transitions between the energy bands of the host crystal and impurity levels lying deep within the band gap (Birman, 1961). However, the exact nature of these levels and their positions with respect to the valence- and conduction-band edges are not thoroughly understood from first principles. Perhaps the most serious recent attempt to solve this problem has been that of Birman (1968), who has used semiempirical LCAO molecular-orbital theory of the Wolfsberg–Helmholz type (Wolfsberg and Helmholz, 1952) to calculate the electronic structure of a finite cluster of atoms surrounding an impurity in the II–VI lattice. We believe that Birman's cluster model is an excellent approach to the problem. The Wolfsberg–Helmholz technique, however, depends critically on several *ad hoc* parameters, even when applied to a reasonably small transition metal complex like MnO_4^-, the system for which this method was originally developed (Wolfsberg and Helmholz, 1952; Ballhausen and Liehr, 1958).

To describe how the SCF–Xα scattered-wave model (which we have shown in Section III to give accurate results for MnO_4^-) can be extended to the impurity problem, we consider a Mn atom substitutionally replacing a Zn atom in the tetrahedrally coordinated II–VI compound ZnS. Following Birman (1968) we focus attention on a 17-atom cluster MnS_4Zn_{12} consisting of a Mn atom tetrahedrally coordinated by four S atoms, each of which completes its tetrahedral bonding with three Zn atoms (see Fig. 8). For a model of the "unperturbed," impurity-free ZnS crystal, we consider a 17-atom cluster ZnS_4Zn_{12} with a Zn atom at the center. The effects of the rest of the crystal lattice are described in terms of the contribution of

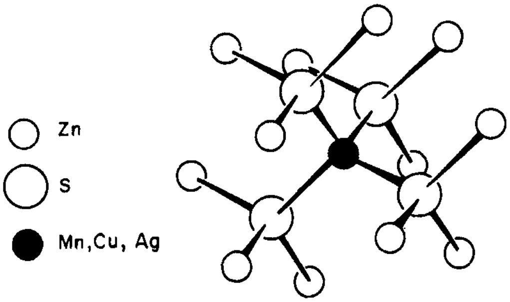

Fig. 8. Seventeen-atom cluster centered on an impurity atom (e.g., Mn, Cu, or Ag replacing Zn) in a ZnS crystal.

the crystal potential to the Xα atomic potentials within the cluster and in terms of a potential in the "extramolecular" region spherically averaged with respect to the center of the cluster. Schrödinger's equation is then solved self-consistently throughout the various regions of the cluster by the scattered-wave theory outlined earlier.

Preliminary applications of this model indicate that a ZnS_4Zn_{12} cluster is indeed large enough to yield electronic energy levels which correspond approximately to the valence and conduction bands of a ZnS crystal and which are separated by an energy gap that is a good approximation to the actual band gap. Comparison of these energies with those calculated for the MnS_4Zn_{12} cluster leads to the approximate positions of the Mn impurity levels with respect to the bands of the host crystal. The cluster energy levels (determined for a preliminary exchange-correlation parameter $\alpha = 1$) are illustrated in Fig. 9. Also shown for the same Xα parameter are the free-atom energy levels. Comparison of Fig. 9 with Fig. 3 suggests that the S 3*p* electrons play very much the same role in determining the valence bands of a ZnS crystal as do the O 2*p* electrons in determining

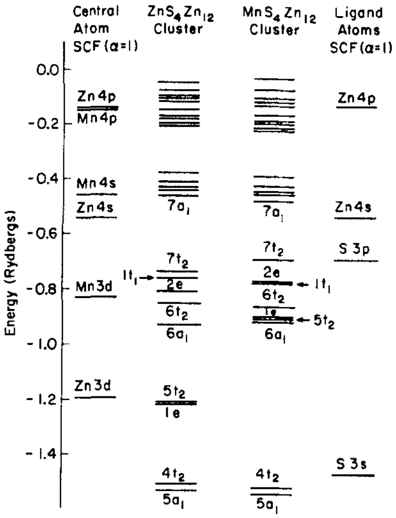

Fig. 9. Comparison of the electronic energy levels of a ZnS_4Zn_{12} cluster with those of a MnS_4Zn_{12} impurity cluster in a ZnS crystal, for an Xα exchange-correlation parameter $\alpha = 1$. Also shown are the corresponding free-atom energy levels. The levels labeled $7t_2$ and $2e$ for the MnS_4Zn_{12} cluster and their positions with respect to the "valence-band" edge (level $7t_2$) for the ZnS_4Zn_{12} cluster should be especially noted. These levels correspond to localized Mn 3*d*-like orbitals and may be compared with the $7t_2$ and $2e$ levels shown in Fig. 3 for an MnO_4^- cluster.

the valence levels of an MnO_4^- cluster in a $KMnO_4$ crystal. The conduction bands are determined principally by the 4*s* electrons and "virtual" 4*p* orbitals of the Zn atoms. The localized Mn impurity levels correspond to 3*d*-like orbitals which are completely analogous to the 2*e* and $7t_2$ levels shown in Fig. 3 for the MnO_4^- cluster, except that they are partially occupied in the ZnS crystal. On the basis of these cluster calculations and transition-state theory, we find that electronic transitions between these impurity levels and the bands of the host crystal are consistent with the observed optical absorption and luminescent emission spectra of Mn-doped ZnS. These transitions involve electronic "charge transfer" between the Mn atom and ligands, as do the principal optical transitions of MnO_4^-.

Applications of the scattered-wave method to transition metals and other defects (e.g., vacancies) in II–VI compounds are in progress. In addition to the determination of electronic energy levels in the fashion described above, contour maps of the charge densities, similar to those in Figs. 4–7, are being generated, showing for the first time the nature of the chemical bonds between the impurity and the host crystal. This work will be reported in detail in later publications.

V. Applications to Metal Bonding in Enzymes and Proteins

We consider another very interesting application of the SCF–Xα scattered-wave model which is currently under investigation, namely the chemical bonding of transition metals and other metals which are the biologically active centers of certain enzymes and proteins. Among these, the most familiar perhaps are the iron-containing hemoproteins, including hemoglobin, myoglobin, cytochrome, catalase, and peroxidase. Enzymes and proteins containing the metals cobalt (e.g., vitamin B_{12}), zinc (carboxypeptidase), copper (ceruloplasmin), and magnesium (chlorophyll) are also recognized to be biocatalysts of important metabolic processes occurring in the living cells of animals and plants.

The biological functions of these systems cover a wide spectrum, varying with the particular metal and organic ligands with which it interacts (Johnson, 1972). Nevertheless, there are gross similarities in the stereochemical geometries of the active centers of these macromolecules, e.g., approximate octahedral, tetrahedral, or square-planar coordination of a central metal atom with the organic ligands of a porphyrin-like prosthetic group or other molecular sub-unit (e.g., see Fig. 10). A quantitative theoretical analysis of the electronic structures and chemical bonding of these metals in their local molecular environments should lead to a better under-

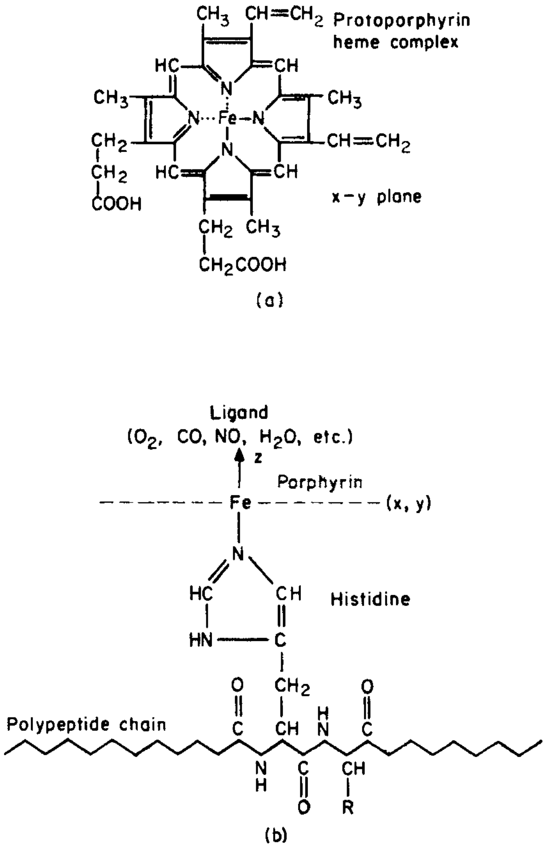

Fig. 10. (a) Protoporphyrin heme complex in hemoglobin; (b) attachment of the heme complex to the polypeptide chain of the hemoglobin protein via the amino acid histidine.

standing of the nature of their biocatalytic and transport functions. Since complex "charge-transfer" and spin-polarization effects between the metal atom and ligands are undoubtedly important in these systems, conventional ligand-field and semiempirical molecular-orbital theories are not appropriate. *Ab initio* Hartree–Fock LCAO theory is also inappropriate because of the vast computational effort which would be required to obtain a reliable description of the electronic structure.

To illustrate how the more practical SCF–Xα scattered-wave technique is applied to this problem we consider in greater detail the structure of the hemoglobin protein macromolecule (see Fig. 10), whose biological function is well known to be the transport of oxygen between the lungs and tissues. Protein molecules are long-chain polymers consisting of amino acid residues called polypeptides, each protein being characterized by a specific sequence of amino acids along the polypeptide chains. The hemoglobin molecule consists of 574 amino acids ($\sim 10{,}000$ atoms) organized into four intricately wound chains (Perutz, 1965, 1970). A prosthetic heme group is tucked into each of the four chains. The heme group itself consists of an iron ion coordinated by four nitrogen-atom ligands which are part of a planar molecule known as protoporphyrin [see Fig. 10(a)]. A fifth nitrogen ligand "below" the plane of the porphyrin attaches the heme complex to the protein chain via the amino acid histidine [see Fig. 10(b)]. The corresponding position "above" the plane of the porphyrin is of major importance to the biological function of hemoglobin, for it is here that an oxygen molecule (or other ligands such as carbon monoxide) can be attached to the iron atom for transport between the lungs and tissues. If an oxygen molecule attaches itself by only one of the oxygen atoms, then this atom together with the five nitrogen ligands are in sixfold coordination with respect to the central Fe atom (Pauling, 1964). It has also been suggested that the O_2 molecule may be joined symmetrically to the heme by both O atoms, leading to a sevenfold geometry (Griffith, 1956). From steric considerations, some conformational changes of the heme complex during deoxygenation can be expected, including a small displacement of the Fe atom out of the plane of the porphyrin (Perutz, 1970; Hoard, 1966).

Although the nature of the electronic structure of the heme complex before and after oxygenation and as a function of conformation is a more difficult problem than the nonbiological examples described earlier, it is well within the scope of the SCF–Xα cluster method. For our initial model of the heme complex we have chosen a cluster consisting of the central Fe atom, five N atoms (four in the porphyrin plane and one "below" the plane), and the ring of nearest porphyrin C atoms centered on the Fe atom (see Fig. 10). In oxyhemoglobin the position "above" the porphyrin plane is occupied, symmetrically or asymmetrically, by the O_2 molecule. In deoxyhemoglobin this position is vacant. The SCF–Xα potentials are constructed and the Schrödinger solved self-consistently for the atomic, interatomic, and extramolecular regions of the cluster in essentially the same fashion described earlier. We model the O_2 vacancy in deoxyhemoglobin in terms of "empty" diatomic regions in which only the contributions of the Xα potentials of neighboring atoms are superposed. For oxyhemoglobin the contributions of the O atomic potentials are included in these regions. Thus we can directly compare the electronic energy levels and charge densities of the heme cluster before and after oxygenation and as a function of geometry within the same theoretical framework.

A variety of experimental techniques, leading to information about the magnetic state of the heme complex, have been applied to hemoglobin and myoglobin, including magnetic susceptibility (Scheler *et al.*, 1957; Schoffa *et al.*, 1959), electron paramagnetic resonance (Bennett *et al.*, 1957), Mössbauer absorption (Lang and Marshall, 1966; Lang, 1967), and nuclear magnetic resonance (Wüthrich and Shulman, 1970). It has been established that the heme group is paramagnetic in deoxyhemoglobin and diamagnetic in oxyhemoglobin, suggesting spin pairing upon oxygenation. One can therefore carry out SCF–Xα calculations on the heme cluster in spin-unrestricted form, as we described earlier for the example of the MnO_4^- cluster. Magnetic hyperfine parameters can be calculated and contour maps of the charge and spin densities throughout the cluster can be generated for comparison with experiment. Details of this research will appear in forthcoming publications.

VI. Discussion

It is well known that the limitations of applying *ab initio* LCAO methods to complex molecules and solids are the size of the basis sets and the number of multicenter integrals or equivalent Hartree–Fock matrix elements. In the SCF–Xα scattered-wave model, which is also a first-principles technique, there is no basis-set problem because we are numerically integrating Schrödinger's equation for an Xα potential. There are no multicenter integrals, and the model is practicable in both spin-restricted and spin-unrestricted forms for polyatomic systems of considerable stereochemical complexity.

Extensive applications of the scattered-wave method to the individual areas of interest in complex molecules and solids discussed above are in progress and will be reported in greater detail in separate publications. The purpose of this chapter has been to describe the possible advantages of treating several difficult problems of current interest within one self-consistent conceptual and computational framework. The present approach requires that we specify the geometrical and atomic configurations of each polyatomic cluster. However, the efficiency with which we can perform reliable numerical calculations on real polyatomic systems as a function of configuration now makes it possible to implement some of the recently proposed cluster theories for the structures of disordered and amorphous materials (Butler and Kohn, 1971).

Thus far, our applications of the scattered-wave method to polyatomic molecules and crystals have been concerned primarily with the generation of one-electron energies and wave functions. While an SCF–Xα one-electron analysis leads to an accurate quantitative description of many chemical and physical properties (e.g., charge densities, chemical shifts, magnetic and optical properties), it is also very important to determine the total many-electron energy. A knowledge of the ground-state total energy as a function of stereochemical geometry is essential to developing a quantitative understanding of molecular and crystalline cohesive properties (e.g., the binding energy or force constants) and the nature of chemical reactions. Therefore, we have recently extended our scattered-wave computer programs to permit the calculation of total energies within the framework of the Xα statistical total Hamiltonian (Slater and Wood, 1971; Slater, 1971, 1972; Slater and Johnson, 1972). It should be noted in this connection that both the virial and Hellmann–Feynman theorems are satisfied, to a high degree of approximation, in the SCF–Xα scattered-wave formulation. Furthermore, in contrast to the Hartree–Fock method, the present technique automatically goes to the proper separated-atom limit as the internuclear distances are increased to infinity.

Because the present method leads to a rapidly convergent numerical representation of the orbital wave functions, the accuracy of the theoretical model can easily be improved via perturbation theory, when necessary. Finally, the original theoretical formalism can be extended to more general forms of superposed-atom Xα potentials (e.g., overlapping spherical potentials), by means of the generalized scattered-wave theory recently described by the author (Johnson, 1971).

Appendix

Derivation of Scattered-Wave Expansion Theorems

Let us consider first the derivation of the expansion theorem (II.28). We can write the well-known plane-wave expansion

$$\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}) = 4\pi \sum_L i^l j_l(\kappa r) Y_L(\mathbf{r}) Y_L(\boldsymbol{\kappa}), \tag{A.1}$$

using real spherical harmonics. Thus we can express the following plane wave in the two equivalent expansions

$$\exp[i\boldsymbol{\kappa}\cdot(\mathbf{r}_2-\mathbf{r}_1)] = 4\pi \sum_L i^l j_l(\kappa|\mathbf{r}_2-\mathbf{r}_1|) Y_L(\mathbf{r}_2-\mathbf{r}_1) Y_L(\boldsymbol{\kappa}) \tag{A.2}$$

and

$$\begin{aligned}\exp[i\boldsymbol{\kappa}\cdot(\mathbf{r}_2-\mathbf{r}_1)] &= \exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_2)\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r}_1)\\ &= 4\pi\sum_{L'} i^{l'}j_{l'}(\kappa r_2)Y_{L'}(\mathbf{r}_2)Y_{L'}(\boldsymbol{\kappa})\\ &\quad\times 4\pi\sum_{L''} i^{-l''}j_{l''}(\kappa r_1)Y_{L''}(\mathbf{r}_1)Y_{L''}(\boldsymbol{\kappa}).\end{aligned}\tag{A.3}$$

If we multiply both sides of Eq. (A.2) by $Y_L(\boldsymbol{\kappa})$, integrate over the solid angle

$$d\Omega(\boldsymbol{\kappa}) = \sin\theta_\kappa\, d\theta_\kappa\, d\phi_\kappa \tag{A.4}$$

and use the orthonormality of the spherical harmonics, we can write

$$\int \exp[i\boldsymbol{\kappa}\cdot(\mathbf{r}_2-\mathbf{r}_1)]Y_L(\boldsymbol{\kappa})\,d\Omega(\boldsymbol{\kappa}) = 4\pi i^l j_l(\kappa|\mathbf{r}_2-\mathbf{r}_1|)Y_L(\mathbf{r}_2-\mathbf{r}_1). \tag{A.5}$$

If we then apply the same procedure to Eq. (A.3), we find

$$\begin{aligned}\int \exp[i\boldsymbol{\kappa}\cdot(\mathbf{r}_2-\mathbf{r}_1)]Y_L(\boldsymbol{\kappa})\,d\Omega(\boldsymbol{\kappa}) &= (4\pi)^2\sum_{L'}\sum_{L''} i^{l'-l''}I_L(L';L'')\\ &\quad\times j_{l'}(\kappa r_2)j_{l''}(\kappa r_1)Y_{L'}(\mathbf{r}_2)Y_{L''}(\mathbf{r}_1),\end{aligned}\tag{A.6}$$

where we have introduced the quantities [cf. Eq. (II.29)].

$$I_L(L';L'') = \int Y_L(\boldsymbol{\kappa})Y_{L'}(\boldsymbol{\kappa})Y_{L''}(\boldsymbol{\kappa})\,d\Omega(\boldsymbol{\kappa}). \tag{A.7}$$

Setting (A.5) equal to (A.6), we can write

$$\begin{aligned}j_l(\kappa|\mathbf{r}_2-\mathbf{r}_1|)Y_L(\mathbf{r}_2-\mathbf{r}_1) &= 4\pi\sum_{L'} i^{l'-l}\sum_{L''} i^{-l''}I_L(L';L'')\\ &\quad\times j_{l'}(\kappa r_2)j_{l''}(\kappa r_1)Y_{L'}(\mathbf{r}_2)Y_{L''}(\mathbf{r}_1).\end{aligned}\tag{A.8}$$

This is the expansion theorem (II.28) if we recognize that the integral (A.7) is invariant under a permutation of indices, i.e.,

$$I_L(L';L'') = I_{L''}(L;L'). \tag{A.9}$$

A similar procedure applied to the expansion

$$\exp(-\boldsymbol{\kappa}\cdot\mathbf{r}) = 4\pi\sum_L(-1)^l i_l(\kappa r)Y_L(\mathbf{r})Y_L(\boldsymbol{\kappa}), \tag{A.10}$$

where $i_l(\kappa r)$ is the modified spherical Bessel function defined in Eq. (II.12), leads to the relation

$$i_l(\kappa|\mathbf{r}_2-\mathbf{r}_1|)Y_L(\mathbf{r}_2-\mathbf{r}_1)=4\pi\sum_{L'}(-1)^{l+l'}\sum_{L''}I_{L''}(L;L') \times i_{l'}(\kappa r_2)i_{l''}(\kappa r_1)Y_{L'}(\mathbf{r}_2)Y_{L''}(\mathbf{r}_1), \tag{A.11}$$

which is the expansion theorem (II.25).

To derive the theorem (II.23), we write the well-known spherical-wave expansion

$$\frac{1}{4\pi}\frac{\exp(i\kappa|\mathbf{r}_2-\mathbf{r}_1|)}{|\mathbf{r}_2-\mathbf{r}_1|}=i\kappa\sum_L h_l^{(1)}(\kappa r_1)j_l(\kappa r_2)\,Y_L(\mathbf{r}_1)Y_L(\mathbf{r}_2), \qquad r_1>r_2 \tag{A.12}$$

For imaginary $\kappa \to i\kappa$ this expression becomes

$$\frac{1}{4\pi}\frac{\exp(-\kappa|\mathbf{r}_2-\mathbf{r}_1|)}{|\mathbf{r}_2-\mathbf{r}_1|}=\sum_L(-1)^l k_l^{(1)}(\kappa r_1)i_l(\kappa r_2) \times Y_L(\mathbf{r}_1)Y_L(\mathbf{r}_2), \qquad r_1>r_2, \tag{A.13}$$

where we use the modified spherical Bessel and Hankel functions defined in (II.12) and (II.13), respectively. Thus, for the following spherical wave, we can write two alternative expressions.

$$\frac{1}{4\pi}\frac{\exp(-\kappa|\mathbf{r}_2-\mathbf{r}_1-\mathbf{r}_3|)}{|\mathbf{r}_2-\mathbf{r}_1-\mathbf{r}_3|}=\sum_L(-1)^l k_l^{(1)}(\kappa|\mathbf{r}_2-\mathbf{r}_1|)i_l(\kappa r_3) \times Y_L(\mathbf{r}_2-\mathbf{r}_1)Y_L(\mathbf{r}_3), \qquad |\mathbf{r}_2-\mathbf{r}_1|>r_3, \tag{A.14}$$

and

$$\frac{1}{4\pi}\frac{\exp(-\kappa|\mathbf{r}_2-\mathbf{r}_1-\mathbf{r}_3|)}{|\mathbf{r}_2-\mathbf{r}_1-\mathbf{r}_3|}=\sum_{L''}(-1)^{l''}k_{l''}^{(1)}(\kappa r_1)i_{l''}(\kappa|\mathbf{r}_2-\mathbf{r}_3|) \times Y_{L''}(\mathbf{r}_1)Y_{L''}(\mathbf{r}_2-\mathbf{r}_3), \qquad r_1>|\mathbf{r}_2-\mathbf{r}_3|. \tag{A.15}$$

From the expansion theorem (A.11) it follows that

$$i_{l''}(\kappa|\mathbf{r}_2-\mathbf{r}_3|)Y_{L''}(\mathbf{r}_2-\mathbf{r}_3)=4\pi\sum_{L'}(-1)^{l''+l'}\sum_{L}I_{L''}(L;L') \times i_{l'}(\kappa r_2)i_l(\kappa r_3)Y_{L'}(\mathbf{r}_2)Y_L(\mathbf{r}_3). \tag{A.16}$$

Substituting (A.16) into (A.15) we obtain

$$\frac{1}{4\pi}\frac{\exp(-\kappa|\mathbf{r}_2-\mathbf{r}_1-\mathbf{r}_3|)}{|\mathbf{r}_2-\mathbf{r}_1-\mathbf{r}_3|}=4\pi\sum_{L''}k_{l''}^{(1)}(\kappa r_1)Y_{L''}(\mathbf{r}_1)$$
$$\sum_{L}\sum_{L'}(-1)^{l'}I_{L''}(L;L')i_{l'}(\kappa r_2)i_l(\kappa r_3)Y_{L'}(\mathbf{r}_2)Y_L(\mathbf{r}_3),\qquad r_1>r_2;\,r_1>r_3 \tag{A.17}$$

Setting (A.17) equal to (A.14) we arrive at the identity

$$k_l^{(1)}(\kappa|\mathbf{r}_2-\mathbf{r}_1|)Y_L(\mathbf{r}_2-\mathbf{r}_1)=4\pi\sum_{L'}(-1)^{l+l'}\sum_{L''}I_{L''}(L;L')$$
$$\times\,k_{l''}^{(1)}(\kappa r_1)i_{l'}(\kappa r_2)Y_{L''}(\mathbf{r}_1)Y_{L'}(\mathbf{r}_2),\qquad r_1>r_2 \tag{A.18}$$

which is the expansion theorem (II.23). Expressions (II.24), (II.26), and (II.27) can be derived in a similar fashion.

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Projection Operators in Hartree–Fock Theory

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I. Introduction

Use of the projection operator technique in Hartree–Fock-type theories is so widespread and ubiquitous that it is beyond us to present a comprehensive review of the subject. We shall consequently only discuss some selected topics.

In the approximate treatment of many-electron systems, one often applies the variational procedure in which the wave function and accordingly the energy of the system are expressed as functionals of electron orbital functions $\{\phi_i\}$:

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$$\Phi \equiv \Phi(\{\phi_i\}), \tag{1.1}$$

$$E \equiv E(\{\phi_i\}). \tag{1.2}$$

In most cases the orthonormality conditions are imposed on $\{\phi_i\}$, namely,

$$\langle \phi_i | \phi_j \rangle = \langle \phi_j | \phi_i \rangle = \delta_{ij}. \tag{1.3}$$

These constraints may be incorporated into the variational treatment of the energy E by the use of Lagrangian multipliers. The resulting Euler equations may assume the form

$$\sum_k A_{ik} | \phi_k \rangle = \sum_j | \phi_j \rangle \theta_{ji}, \tag{1.4}$$

where the operators A_{ik} are functionals of $\{\phi_i\}$ and θ_{ji} are the Lagrangian multipliers. Equations (1.4) are of a very general form and constitute an adequate basis for a general multiconfiguration SCF theory (Huzinaga, 1969a). In the present article we shall be concerned with the case in which $A_{ik} = \delta_{ik} F_i$ and consequently Eqs. (1.4) reduce to

$$F_i | \phi_i \rangle = \sum_j | \phi_j \rangle \theta_{ji}, \tag{1.5}$$

where F_i are functionals of $\{\phi_i\}$. If the total wave function Φ and also F_i are both invariant with respect to arbitrary unitary transformation among $\{\phi_i\}$, one can eliminate the off-diagonal multipliers $\{\theta_{ji}\}$ $(j \neq i)$ immediately. This is the case for a closed-shell system, but in the open-shell case it is not generally possible to utilize allowed unitary transformations among $\{\phi_i\}$ to eliminate the nondiagonal multipliers completely. There have been various proposals to deal with this problem. Among them one of the most successful so far is the coupling operator method proposed by Roothaan (1960). Mathematically speaking, it is a simple example of projection operator techniques.

By the use of appropriate coupling operators (Huzinaga, 1969b), one may bring the Hartree–Fock equation to the following form, including general open-shell cases:

$$R | \phi_i \rangle = | \phi_i \rangle \varepsilon_i, \tag{1.6}$$

where R is a functional of the occupied orbitals $\{\phi_i\}$. In solving Eq. (1.6) self-consistently, we persue the establishment of a certain manifold, usually called the Hartree–Fock manifold, which consists of a finite set of functions to be identified as occupied orbitals. If there are N distinct occupied orbitals, the Hartree–Fock manifold is made of $\{\phi_i\}$, $i = 1, \ldots, N$. In fact, this particular function space is the only theater which has physically solid meanings. However, Eq. (1.6) as an eigenvalue equation defines a complete set of functions and the Hartree–Fock manifold spans only a small subspace of the total function space. Sometimes, people wish to use eigenfunctions outside of the Hartree–Fock manifold, which are vaguely called virtual orbitals. It appears useful to manipulate artificially the eigenvalue spectrum of the virtual orbitals in certain meaningful ways and this may be done by adding terms which are essentially projection operators to the original Hartree–Fock operator. The subject is discussed in the second section from a practical point of view and in the third section some relevant mathematical background is described at some length.

A wide class of problems in atomic and molecular physics can be reduced to finding the extremum of the functional,

$$\langle\Psi|\mathscr{H}|\Psi\rangle/\langle\Psi/\Psi\rangle, \tag{1.7}$$

where $\mathscr{H}$ is a Hermitian operator and Ψ satisfies orthonormality constraints of the form

$$\langle\Psi|\phi_c\rangle = 0 \tag{1.8}$$

for some set of functions $\{\phi_c\}$ lying within a given subspace of the total function space. The set $\{\phi_c\}$ may span only a part (core region) of the Hartree–Fock manifold and Ψ occupies the rest—or Ψ could be a certain correlation function which is one-electron orthogonal to a Hartree–Fock "sea" represented by $\{\phi_c\}$. The generalized problem of variation in a restricted subspace is not an easy subject (Löwdin, 1965). In the fourth section of the present article we shall present a restricted discussion of this subject Here again an extensive use of projection operator techniques is made.

II. The Properties of Virtual Orbitals

A. Preliminaries

In recent years, outstanding advances have been made in the design of electronic computers and this has made possible the large number of Hartree–Fock calculations that have appeared in the literature. Unfortunately, these calculations all display one rather unsatisfactory property. That is, the virtual orbital "energies" are usually positive, suggesting that they correspond to a state in the continuum.

In order to understand the origin of this defect we must return to the method used to derive the Hartree–Fock equations themselves. For simplicity we will consider the closed-shell electron case, where the energy of the system is given by

$$E = 2\sum_{i}^{N} H_i + \sum_{i \neq j}^{N} (2J_{ij} - K_{ij}) + \sum_{i}^{N} J_{ii}. \tag{2.1}$$

The variational principle may be applied to this expression, resulting in a set of self-consistent field equations,

$$F_i|\psi_i\rangle = \varepsilon_i|\psi_i\rangle, \tag{2.2}$$

where

$$F_i = -\tfrac{1}{2}\Delta - \sum_{a} (Z_a/r_a) + J_i + \sum_{i \neq j} (2J_j - K_j), \tag{2.3}$$

and J_j and K_j are the usual Coulomb and exchange operators.

However, this is not the usual procedure. It is customary to employ the relation,

$$J_{ii} - K_{ii} = 0 \tag{2.4}$$

so that the energy expression (2.1) may be rewritten as

$$E = 2\sum_{i}^{N} H_i + \sum_{ij}^{N} (2J_{ij} - K_{ij}). \tag{2.5}$$

Applying the variational principle to Eq. (2.5) we obtain the well-known Hartree–Fock equations,

$$F|\psi_i\rangle = \varepsilon_i|\psi_i\rangle, \tag{2.6}$$

where

$$F = -\tfrac{1}{2}\Delta - \sum_{a} (Z_a/r_a) + \sum_{j} (2J_j - K_j). \tag{2.7}$$

Obviously, it is more convenient to use Eqs. (2.6) rather than Eqs. (2.3) since they have only a single F operator common to all the orbitals. Further, if $|\psi_i\rangle$ is an *occupied* orbital, Eqs. (2.3) and (2.6) are equivalent due to the relation,

$$(J_i - K_i)|\psi_i\rangle = 0. \tag{2.8}$$

However, they are not equivalent for the virtual orbitals. To understand this difference between the F_i operators and the Hartree–Fock operator, F, we must consider the potentials acting on an electron in an occupied orbital, say $|\psi_i\rangle$. It will feel the influence of an operator J_j from each electron of opposite spin to itself and $(J_j - K_j)$ from each electron of the same spin. It will not, of course, be influenced by its own electronic charge, but it is just this effect that has been introduced into the F operator by using Eq. (2.4). Fortunately, Eq. (2.8) provides an "automatic" correction for the occupied orbitals.

The virtual orbitals undergo no such correction and the situation is represented by Fig. 1. The consequences are clear. If we use either F or F_i an electron in an occupied orbital feels the influence of the other $(2N - 1)$ electrons while one in a virtual orbital of F feels the full influence of $2N$ "core" electrons. On the other hand, an electron in a virtual orbital of F_i sees the core with an electron removed from the "occupied" $|\psi_i\rangle$. Thus the F_i produce virtual orbitals which correspond to the system under investigation, while F produces virtual orbitals more appropriate to the $(2N + 1)$-electron system.

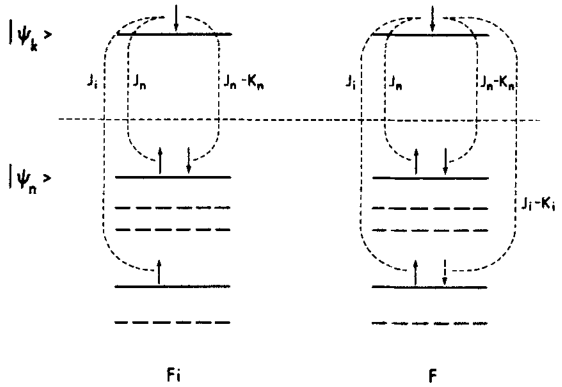

Fig. 1. Difference between F_i and F.

For many purposes, this distinction is not important, since the virtual orbitals may be of little interest. However, if they are to be used in, say, a perturbation expansion, then the effect could be significant. In such cases it would therefore seem reasonable to generate the virtual orbitals using one of the F_i operators.

This has been done successfully by Kelly (1964) in his perturbational calculations on beryllium. In his first paper (1963) he employed the Hartree–Fock operator and found that the virtual levels did not correspond to bound states. He was therefore able to use only continuum states in the perturbation expansion, and convergence was slow. In his second paper (1964), he employed F_{2s} to generate the virtual levels. When these were included in the expansion, convergence was greatly improved, but they had one very undesirable property. They were not rigorously orthogonal to the occupied $1s$ orbital. This is an obvious consequence of the fact that $|1s\rangle$ is not an eigenfunction of F_{2s}, although it is one of both F and F_{1s}.

B. The Use of Projection Operators

The work of Kelly emphasized the need for a technique which would retain the physical principles mentioned above but which would avoid the nonorthogonality problem. This may be achieved by a straightforward mathematical device first discovered by Silverstone and Yin (1968). A simplified version of their method was proposed by Huzinaga and Arnau (1970, 1971).

Suppose that we have any Hermitian operator, R, and the associated eigenvalue problem,

$$R|\phi_i\rangle = |\phi_i\rangle\varepsilon_i. \tag{2.9}$$

Let us now divide the eigenfunctions, $|\phi_i\rangle$, into "occupied" and "virtual" groups and define the operator,

$$V = (1 - P)\Omega(1 - P). \tag{2.10}$$

Here P is the projection operator,

$$P = \sum_i^{\text{occ}} |\phi_i\rangle\langle\phi_i| \tag{2.11}$$

and Ω is any arbitrary Hermitian operator.

Now if we define R' by

$$R' = R + V, \tag{2.12}$$

it is easy to see that for an occupied orbital,

$$R'|\phi_i\rangle = R|\phi_i\rangle = |\phi_i\rangle\varepsilon_i, \tag{2.13}$$

while for a virtual orbital we have

$$R'|\phi_a\rangle = (R + \Omega - P\Omega)|\phi_a\rangle = |\phi_a\rangle\varepsilon_a. \tag{2.14}$$

Of course, the ε_a and $|\phi_a\rangle$ of Eq. (2.14) are not the same virtual orbitals or energies as are obtained from (2.9) but have been modified by the presence of V. The occupied orbitals and energies, on the other hand, are unchanged but they are rigorously orthogonal to the new virtual orbitals because they are generated by a single Hermitian operator R'.

Further from Eq. (2-14) we have

$$\varepsilon_a = \langle \phi_a | R + \Omega | \phi_a \rangle, \tag{2.15}$$

which clearly indicates the relationship of the new energies to the R and Ω operators.

Obviously this technique can be used to modify the virtual orbitals of the Hartree–Fock operator and comparison of F_i and F indicates that appropriate choice of Ω would be

$$\Omega_i = -J_i + K_i. \tag{2.16}$$

Thus we obtain the modified equation,

$$[F - J_i + K_i + P(J_i - K_i)] | \psi_k \rangle = | \psi_k \rangle \varepsilon_k. \tag{2.17}$$

The virtual orbitals obtained from (2.17) will be almost, but not quite, identical to those obtained from F_i, and they will be rigorously orthogonal to all the occupied orbitals.

The virtual orbitals may be altered in an arbitrary manner since the only restriction placed on Ω is that it should be Hermitian. However, for a physically meaningful result we must select Ω with care, but even so there are many reasonable choices.

One important point must be stressed. The modified Hartree–Fock operator of Eq. (2.17) is not a straightforward addition of the F and Ω operators. Instead Ω has been guarded by the projection operator as shown in Eq. (2.10), so that there is no disturbance of the original occupied orbitals.

Another, practical, point to be mentioned is that we do not have to do any iterative SCF calculation with the modified Hartree–Fock operator. If the solution to the usual Hartree–Fock equations is known, all that is required is the construction of the modified operator and the solution of (2.17). We may simplify the matter even one step further, as will be shown later [Eq. (3.20)].

C. The Choice of Ω

The brief discussion on an appropriate form for Ω in the previous section of necessity related to the F and F_i operators of Eqs. (2.2) and (2.6). However, these refer to a closed-shell ground state which can be represented by a single Slater determinant. The virtual orbitals obtained from these also refer to a single Slater determinant with $m_s = 0$. This is unsatisfactory since such a wave function is not an eigenfunction of the S^2 operator.

If we assume that an electron has been excited from $|\psi_i\rangle$ to $|\psi_k\rangle$ and that neither is a member of a degenerate set, appropriate singlet and triplet eigenfunctions are

$$^1\Phi_{i\to k} = A\{\cdots (1/\sqrt{2})(\psi_i\alpha\psi_k\beta - \psi_i\beta\psi_k\alpha)\cdots\} \tag{2.18}$$

and

$$^3\Phi_{i\to k} = A\{\cdots \begin{bmatrix} \psi_i\alpha\psi_k\alpha \\ (1/\sqrt{2})(\psi_i\alpha\psi_k\beta + \psi_i\beta\psi_k\alpha) \\ \psi_i\beta\psi_k\beta \end{bmatrix} \cdots\}. \tag{2.19}$$

The corresponding energy expression is

$$\begin{aligned} E(^{1,3}\Phi_{i\to k}) = 2\sum_j^{\text{occ}} H_j &+ \sum_{jl}^{\text{occ}} (2J_{jl} - K_{jl}) - H_i \\ &- \sum_j^{\text{occ}} (2J_{ji} - K_{ji}) + H_k + \sum_j^{\text{occ}} (2J_{jk} - K_{jk}) \\ &- (J_{ik} - K_{ik}) \pm K_{ik}, \end{aligned} \tag{2.20}$$

where the plus and minus signs of the last term refer to the singlet and triplet, respectively. Hunt and Goddard (1969) have applied the variational principle to this expression and have obtained an "excited-state" operator suitable for the virtual orbitals

$$\begin{aligned} ^{1,3}F_i^{\text{EX}} &= -\tfrac{1}{2}\Delta - \sum_a (Z_a/r_a) + \sum_j (2J_j - K_j) - (J_i - K_i) \pm K_i \\ &= F - (J_i - K_i) \pm K_i. \end{aligned} \tag{2.21}$$

Thus a very desirable choice for Ω would be

$$^{1,3}\Omega_i = -(J_i - K_i) \pm K_i, \tag{2.22}$$

where the suffix i indicates that the potential is appropriate to a state where an electron has been excited from $|\psi_i\rangle$.

Using Eqs. (2.15) and (2.22) we obtain the new excited-state orbital energies

$$\begin{aligned} \varepsilon_k^{\text{EX}} &= \langle\psi_k|F|\psi_k\rangle - (J_{ik} - K_{ik}) \pm K_{ik} \\ &= \varepsilon'_{kk} - (J_{ik} - K_{ik}) \pm K_{ik}. \end{aligned} \tag{2.23}$$

It should be noted that the ε'_{kk} of Eq. (2.23) has the same mathematical form as the ε_k of the Hartree–Fock equations, but that these two quantities are not equal. This is because the $|\psi_k\rangle$ are slightly different for the two operators. Another consequence of this is that the ε'_{kl} are not diagonal.

According to Roothaan (1951), the energy required to excite an electron from $|\psi_j\rangle$ to $|\psi_k\rangle$ is given by

$$E({}^{1,3}\Phi_{j\to k}) - E({}^{1}\Phi_0) = \varepsilon_k - \varepsilon_j - (J_{jk} - K_{jk}) \pm K_{jk}. \tag{2.24}$$

Substituting (2.23) into (2.24) we obtain,

$$\begin{aligned} &E^{\mathrm{EX}}({}^{1,3}\Phi_{j\to k}) - E({}^{1}\Phi_0) \\ &\qquad = \varepsilon_k^{\mathrm{EX}} - \varepsilon_j - (J_{jk} - K_{jk}) \pm K_{jk} + (J_{ik} - K_{ik}) \mp K_{ik}. \end{aligned} \tag{2.25}$$

Hence, if the potential employed is appropriate to the excitation being examined (that is if $i = j$), Eq. (2.25) reduces to

$$E^{\mathrm{EX}}({}^{1,3}\Phi_{i\to k}) - E({}^{1}\Phi_0) = \varepsilon_k^{\mathrm{EX}} - \varepsilon_i. \tag{2.26}$$

Thus the new orbital energies have a very simple physical interpretation and are appropriate for use in discussions of excitation energies. This is a definite conceptual improvement since it is difficult to visualize the relationship between the excitation energies and the old orbital energies. Mulliken (1949) has called the latter "unacceptable" and has defined $\varepsilon_k - J_{ik} + K_{ik}$ as being more meaningful. This, of course, corresponds to the F_i operator and is the average of the singlet and triplet cases outlined above.

Another pleasing aspect of using ${}^{1,3}\Omega_i$ is that the excited-state virtual orbitals depend on the orbital from which the electron is excited and on the multiplicity of the state formed. Both of these are essential from a physical point of view and the extent of the effect is illustrated by the Pariser–Parr–Pople calculation on aniline given in Fig. 2.

A great number of other potentials are, of course, possible. For example, in the atomic case an average correction could be obtained by using $-1/r_a$ since this would approximately cancel out one of the $2N$ core electrons. Comparison with (2.22) shows that this would yield an averaged triplet case since $1/r_a \sim (\sum_i J_i/N)$. Similarly (2.22) could be generalized to

$$\Omega_i = aJ_i + bK_i, \tag{2.27}$$

where the constants a and b would be chosen to suit the problem at hand. As mentioned previously, $a = -b = -1$ would yield an average of the singlet and triplet cases. There is therefore a great deal of latitude in the choice of Ω and the only limitations are that they are physically reasonable

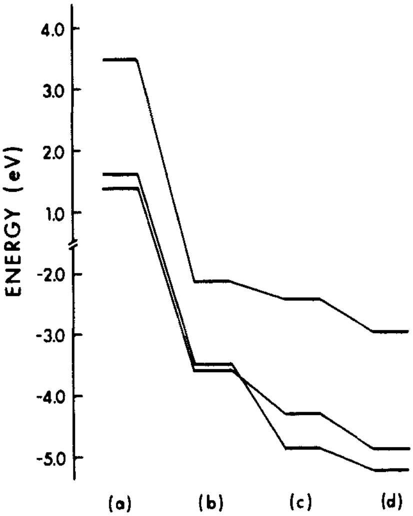

Fig. 2. The π virtual orbital energies obtained from a Pariser–Parr–Pople calculation on aniline using no modifying potential (a) and potentials appropriate for the following excitations: (b) highest occupied to a singlet state; (c) lowest occupied to a singlet state; (d) highest occupied to a triplet state.

and are suited to the level of approximation to be employed in the calculation.

D. The Expansion Method

In Roothaan's expansion method the $|\psi_i\rangle$ are expressed in terms of a finite basis set, $\{\chi_p\}$.

$$\psi_i = \sum_p c_{pi}\chi_p \, . \tag{2.28}$$

In this case the inclusion of the modifying potential follows closely that previously described. For simplicity we may assume that the $\{\chi_p\}$ and $\{c_{pi}\}$ are real and we define the matrices **D**, $\mathbf{D}_j$, and **S** by

$$D_{pq} = \sum_j^{\text{occ}} c_{pj}c_{qj} = \sum_j^{\text{occ}} D_{j,\,pq}, \tag{2.29}$$

$$S_{pq} = \langle \chi_p | \chi_q \rangle . \tag{2.30}$$

The matrix corresponding to V in Eq. (2.10) is expressed as

$$\mathbf{V} = (\mathbf{I} - \mathbf{D})\boldsymbol{\Omega}(\mathbf{I} - \mathbf{D}), \tag{2.31}$$

where

$$\Omega_{pq} = \langle \chi_p | \mathbf{\Omega} | \chi_q \rangle, \tag{2.32}$$

and **I** is the unit matrix. If we choose the **Ω** operator according to Eq. (2.27) the elements Ω_{pq} can easily be expressed in terms of two-electron integrals over the basis functions

$$\Omega_{i,\,pq} = \sum_{vw} \{a(pq|vw) + b(pw|vq)\} D_{i,\,vw}, \tag{2.33}$$

where

$$(pq|vw) = \int \chi_p(1)\chi_q(1)(1/r_{12})\chi_v(2)\chi_w(2)\, dV_{12}. \tag{2.34}$$

All the equations of the previous sections have their matrix counterparts and we obtain an "excited-state" equation, which generates both occupied and virtual orbitals,

$$\mathbf{F}_i^{\mathrm{EX}}\mathbf{C}_k^{\mathrm{EX}} = \mathbf{S}\mathbf{C}_k^{\mathrm{EX}}\varepsilon_k, \tag{2.35}$$

where

$$\mathbf{F}_i^{\mathrm{EX}} = \mathbf{F} + (\mathbf{I} - \mathbf{D})\mathbf{\Omega}_i(\mathbf{I} - \mathbf{D}), \tag{2.36}$$

and **F** is the usual Fock matrix.

In order to investigate the improvement we might expect that when using the expansion method we must consider the relationship between the old and new virtual orbitals. This can be described by the transformation

$$\mathbf{C}^{\mathrm{EX}} = \mathbf{C}\mathbf{U}, \tag{2.37}$$

where $\mathbf{C}^{\mathrm{EX}}$ is the $n \times q$ matrix with all the modified virtual orbital coefficients by columns, **C** is the corresponding matrix for the old virtual orbitals, and **U** is a $q \times q$ unitary matrix.

Let us now consider the sum of the virtual orbital energies:

$$\begin{aligned} \sum_k^{\mathrm{VIRT}} \varepsilon_k &= \mathrm{Tr}(\mathbf{C}^+\mathbf{F}\mathbf{C}) = \mathrm{Tr}(\mathbf{U}^+\mathbf{C}^+\mathbf{F}\mathbf{C}\mathbf{U}) \\ &= \sum_k^{\mathrm{VIRT}} \varepsilon'_{kk}. \end{aligned} \tag{2.38}$$

Here ε'_{kk} is defined as in Eq. (2.23). Similarly, for the exchange and Coulomb integrals we obtain

$$\sum_k^{\mathrm{VIRT}} K_{jk} = \sum_k^{\mathrm{VIRT}} K_{jk}^{\mathrm{EX}} \tag{2.39}$$

and

$$\sum_{k}^{\mathrm{VIRT}} J_{jk} = \sum_{k}^{\mathrm{VIRT}} J_{jk}^{\mathrm{EX}}. \tag{2.40}$$

Summing Eqs. (2.24) and (2.25) over all the virtual orbitals and substituting Eqs. (2.38), (2.39), and (2.40) we have

$$\sum_{k}^{\mathrm{VIRT}} E^{\mathrm{EX}}({}^{m}\Phi_{i\to k}) = \sum_{k}^{\mathrm{VIRT}} E({}^{m}\Phi_{i\to k}). \tag{2.41}$$

Thus, Eq. (2.41) shows that the energy of any given excited configuration can only be improved at the expense of at least one other. This is not necessarily a problem when a large basis can be employed, since many of the virtual orbitals generated will be of little interest. However, with a minimal basis set all the virtual orbitals are usually important and this restriction is serious.

Symmetry and orthogonality conditions also impose restrictions on minimal basis set calculations, as is clearly demonstrated by the virtual orbitals of pyridine (Fig. 3). The virtual orbital π_4 is entirely determined by the occupied π_3 and cannot undergo any modification of the expansion coefficients. However, π_5 and π_6 can mix, allowing electron density to flow towards or away from the nitrogen atom. This is particularly important for $n \to \pi$ transitions since the lone-pair electrons are located mainly

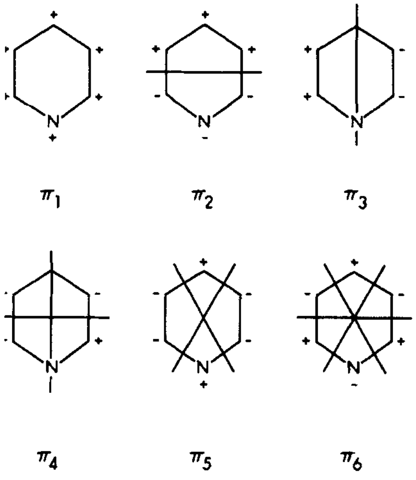

Fig. 3. The π-orbitals of pyridine.

on the nitrogen, and the use of ${}^1\Omega_n$ in a semiempirical all-valence-electron calculation resulted in the modified virtual orbitals

$$\pi_5^{\mathrm{EX}} = 0.8909\pi_5 + 0.4543\pi_6, \tag{2.42}$$

$$\pi_6^{\mathrm{EX}} = 0.4543\pi_5 - 0.8909\pi_6, \tag{2.43}$$

and an improvement in $E({}^1\Phi_{n\to 5})$ from -4199.33 eV to -4200.28 eV.

However, no overall improvement can be obtained with minimal basis sets. In fact, in some cases no modification at all is possible. Butadiene is such a case.

Further, it can easily be shown that Eq. (2.35) is entirely equivalent to a configuration interaction of the form

$${}^{1,3}\Psi_{il} = \sum_{k}^{\mathrm{VIRT}} {}^{1,3}\Phi_{i\to k}\, u_{kl}, \tag{2.44}$$

where the optimum values of the u_{kl} are the elements of the **U** matrix of Eq. (2.37). Therefore little improvement can be expected in a single excitation CI calculation, although there will be some change if double and higher excitations are included.

E. Discussion

As we have seen, when the expansion method is used with a minimal basis set, there is little room for maneuver. This is particularly true in semiempirical calculations where parameterization has already been employed to obtain the best possible result. Of course, this difficulty is not present in numerical Hartree–Fock calculations where we effectively have infinite freedom, and calculations with extended basis sets will lie between these two extremes.

Since the use of the potential (2.22) corresponds to improving the virtual orbitals by using a limited CI treatment, we may generally expect an improvement in the convergence of perturbation expansions. This is verified by the work of Kelly (1964) and the only application of the method at the time of writing is the work of Chase *el al.* (1971) on the correlation energy and auger rates in neon.

III. Mathematical Background

Suppose we have an eigenvalue equation of an Hermitian operator H,

$$H|\psi_i\rangle = \varepsilon_i|\psi_i\rangle. \tag{3.1}$$

For convenience, we divide the whole eigenspace into two subspaces, A and R:

$$\{|\psi_k\rangle\}, \qquad k \in A \qquad \text{and} \qquad \{|\psi_m\rangle\}, \qquad m \in B. \tag{3.2}$$

We also consider another eigenvalue equation,

$$(H + V)|\phi_i\rangle = \lambda_i|\phi_i\rangle, \tag{3.3}$$

where V is a projection of an arbitrary Hermitian operator Ω over one of the two subspaces, say A,

$$V = P^{+}\Omega P, \tag{3.4}$$

$$P = \sum_{k}^{A} |\psi_k\rangle\langle\psi_k|. \tag{3.5}$$

Using Eqs. (3.1), (3.4), and (3.5), we have

$$(H + V)|\psi_i\rangle = \varepsilon_i|\psi_i\rangle + \sum_{kl}^{A} \delta_{ik}|\psi_l\rangle\langle\psi_l|\Omega|\psi_k\rangle. \tag{3.6}$$

If $i \in B$,

$$(H + V)|\psi_i\rangle = \varepsilon_i|\psi_i\rangle, \tag{3.7}$$

which means

$$|\phi_i\rangle = |\psi_i\rangle, \qquad \lambda_i = \varepsilon_i \qquad \text{for } i \in B. \tag{3.8}$$

If $i \in A$,

$$(H + V)|\psi_i\rangle = \varepsilon_i|\psi_i\rangle + \sum_{l}^{A} |\psi_l\rangle\langle\psi_l|\Omega|\psi_i\rangle. \tag{3.9}$$

Suppose that A contains only one element, say k, then we have only one equation modified to be

$$(H + V)|\psi_k\rangle = (\varepsilon_k + \langle\psi_k|\Omega|\psi_k\rangle)|\psi_k\rangle,$$

which implies that all the eigenfunctions of $(H + V)$ remain the same as those of H but the particular kth eigenvalue is shifted by an amount of $\langle\psi_k|\Omega|\psi_k\rangle$. This property can be used in connection with deflation techniques in the diagonalization problem of secular equations. See, for instance, Wilkinson (1965) and Householder (1964). There is, however, an obvious possibility that the particular kth eigenvalue is shifted in such a way that it now coincides with one of other eigenvalues, say ε_m. This can be realized if

$$\langle\psi_k|\Omega|\psi_k\rangle = \varepsilon_m - \varepsilon_k. \tag{3.10}$$

Then the state m has an "accidental" degeneracy and an arbitrariness is introduced to the eigenfunctions: One may take any linear combination of $|\psi_k\rangle$ and $|\psi_m\rangle$. Furthermore, a similar but more general situation can arise even when A consists of two or more indices. In this case we may write Eq. (3.9) as

$$(H+V)|\psi_k\rangle = (\varepsilon_k + \langle\psi_k|\Omega|\psi_k\rangle)|\psi_k\rangle + \sum_{l\,(l\neq k)}^{A} |\psi_l\rangle\langle\psi_l|\Omega|\psi_k\rangle. \quad (3.11)$$

Let us first suppose that the operator Ω is diagonal with respect to the eigenstates $\{|\psi_k\rangle\}$, $k \in A$;

$$\langle\psi_l|\Omega|\psi_k\rangle = b_k\,\delta_{lk}, \quad (3.12)$$

where b_k are any real numbers. Then we have

$$V = P^{+}\Omega P = \sum_{k}^{A} b_k |\psi_k\rangle\langle\psi_k|, \quad (3.13)$$

and Eq. (3.11) may be written as

$$(H+V)|\psi_k\rangle = (\varepsilon_k + b_k)|\psi_k\rangle, \qquad k \in A. \quad (3.14)$$

The implication becomes more apparent if we consider the case where all have a common shifting parameter, say ε_m,

$$b_k = \varepsilon_m - \varepsilon_k. \quad (3.15)$$

Then the eigenvalue ε_m has now a manyfold degeneracy, and the eigenfunctions have accompanying arbitrariness. In the general case where the operator Ω is not necessarily diagonal, we define a new Hermitian matrix T by the elements

$$t_{lk} = \delta_{lk}\varepsilon_l + \langle\psi_l|\Omega|\psi_k\rangle, \qquad k, l \in A. \quad (3.16)$$

Equation (3.11) can then be written as

$$(H+V)|\psi_k\rangle = \sum_{l}^{A} t_{lk}|\psi_l\rangle. \quad (3.17)$$

In Eq. (3.3) if $i \in B$ then Eqs. (3.8) are valid. If $i \in A$, Eq. (3.17) allows us to conclude that

$$|\phi_i\rangle = \sum_{k}^{A} c_{ki}|\psi_k\rangle, \qquad i \in A. \quad (3.18)$$

Here the linear independence of $\{|\psi_k\rangle\}$ is utilized. The implication is that $\{|\phi_i\rangle\}$ $(i \in A)$ are connected with $\{|\psi_i\rangle\}$ $(i \in A)$ by a unitary matrix $\mathbf{C}$

(c_{ki}). Substituting Eq. (3.18) into Eq. (3.3) and using the linear independence of $\{|\psi_l\rangle\}$ $(l \in A)$, we are led to the relations

$$\sum_{k}^{A} t_{lk} c_{ki} = \lambda_i c_{li}. \tag{3.19}$$

In a compact matrix form Eqs. (3.19) may be written

$$\mathbf{TC} = \mathbf{C\Lambda}, \tag{3.20}$$

with the obvious definitions of matrices, **T**, **C**, and **Λ**. The practical implication is that instead of solving the eigenvalue problem (3.3) to obtain the modified eigenvalues and eigenfunctions, the problem is reduced to the construction of an Hermitian matrix **T** and the diagonalization of the secular equation (3.20).

So far, we have tacitly had the virtual orbitals in mind and identified the subspace A with the virtual orbital space. At one point, however, we have come very close to the theory of the pseudopotential. In fact, it should be easily noticed that the projection operator V in Eq. (3.13) is a generalization of the pseudopotential introduced by Phillips and Kleinman (1959).

We do not intend to present a comprehensive general theory of the pseudopotential. Instead we shall present a brief sketch of it in relation to the use of projection operators.

Let us start again with Eqs. (3.1) and (3.3), but we do *not* specify the operator V from the outset and proceed along the line of Austin *et al.* (1962). As for the partition of the eigenspace we use $\{|\psi_c\rangle\}$ and $\{|\psi_v\rangle\}$ but this core–valence partition can be quite arbitrary from the mathematical point of view.

We assume that $|\phi_i\rangle$ can be expressed as

$$|\phi_i\rangle = \sum_c \alpha_c |\psi_c\rangle + \sum_v \alpha_v |\psi_v\rangle. \tag{3.21}$$

Then, from Eq. (3.3) we have

$$\begin{aligned}(H + V - \lambda_i)|\phi_i\rangle \\ = \sum_c \alpha_c(\varepsilon_c - \lambda_i + V)|\psi_c\rangle + \sum_v \alpha_v(\varepsilon_v - \lambda_i + V)|\psi_v\rangle = 0.\end{aligned} \tag{3.22}$$

Now let us characterize the operator V by specifying its projection properties.

Case 1 (Phillips–Kleinman)

$$\begin{aligned} V|\psi_c\rangle &= b_c|\psi_c\rangle \\ V|\psi_v\rangle &= 0 \end{aligned} \tag{3.23}$$

Here b_c is a number that can be viewed as an eigenvalue and V can be expressed as

$$V = \sum_c b_c|\psi_c\rangle\langle\psi_c|. \tag{3.24}$$

Equation (3.22) becomes

$$\sum_c \alpha_c(\varepsilon_c - \lambda_i + b_c)|\psi_c\rangle + \sum_v \alpha_v(\varepsilon_v - \lambda_i)|\psi_v\rangle = 0, \tag{3.25}$$

which means

$$\alpha_c(\varepsilon_c - \lambda_i + b_c) = 0, \tag{3.26}$$

$$\alpha_v(\varepsilon_v - \lambda_i) = 0. \tag{3.27}$$

If $(\varepsilon_v - \lambda_i) \neq 0$ for all v, then all the coefficients $\{\alpha_v\}$ vanish and at best we have

$$|\phi_i\rangle = \sum_c \alpha_c|\psi_c\rangle. \tag{3.28}$$

If λ_i coincides with one of $\{\varepsilon_v'\}$, say $\varepsilon_v : (\varepsilon_v - \lambda_i) = 0$, then the particular α_v survives and we possibly have

$$|\phi_i\rangle = \sum_c \alpha_c|\psi_c\rangle + |\psi_v\rangle. \tag{3.29}$$

Now for $\{\alpha_c\}$ we have from Eq. (3.26)

$$\alpha_c(\varepsilon_c - \varepsilon_v + b_c) = 0. \tag{3.30}$$

Again, if $\varepsilon_c - \varepsilon_v + b_c \neq 0$ for all c, then all $\{\alpha_c\}$ should vanish and Eq. (3.29) gives simply $|\phi_i\rangle = |\psi_v\rangle$. Thus the necessary condition that we have Eq. (3.29) with nonvanishing $\{\alpha_c\}$ is that

$$\varepsilon_c - \varepsilon_v + b_c = 0. \tag{3.31}$$

Going back to Eq. (3.24), we have

$$V = \sum_c (\varepsilon_v - \varepsilon_c)|\psi_c\rangle\langle\psi_c|, \tag{3.32}$$

which is the Phillips–Kleinman pseudopotential.

Case 2

$$\begin{aligned} V|\psi_c\rangle &= \textstyle\sum_{c'} b_{c',c}|\psi_{c'}\rangle \\ V|\psi_v\rangle &= 0 \end{aligned} \tag{3.33}$$

The above operator V can be Hermitian and be expressed as

$$V = \textstyle\sum_{c',c} b_{c',c} \, |\psi_{c'}\rangle\langle\psi_c| . \tag{3.34}$$

It is now clear that we are talking about the operator which is mathematically the same as the one in Eq. (3.4.)

Case 3 (Austin–Heine–Sham)

$$\begin{aligned} V|\psi_c\rangle &= \textstyle\sum_{c'} b_{c',c} \, |\psi_{c'}\rangle \\ V|\psi_v\rangle &= \textstyle\sum_{c} d_{c,v} \, |\psi_c\rangle \end{aligned} \tag{3.35}$$

It is obvious that the operator V in Eqs. (3.35) cannot be Hermitian. In the projection operator form it may be written

$$V = \sum_c |\psi_c\rangle\langle F_c| . \tag{3.36}$$

Here, the F_c are completely arbitrary functions and this is the Austin–Heine–Sham pseudopotential (1962).

Case 4

$$\begin{aligned} V|\psi_c\rangle &= \textstyle\sum_{c'} b_{c',c}|\psi_{c'}\rangle + \sum_{v} e_{v,c}|\psi_v\rangle \\ V|\psi_v\rangle &= \textstyle\sum_{c} d_{c,v}|\psi_c\rangle + \sum_{v'} g_{v',v}|\psi_{v'}\rangle \end{aligned} \tag{3.37}$$

This is the most general case in which the operator V can be Hermitian with additional restrictions among the coefficients. It presents a theoretical basis for the discussion of various model potentials.

IV. Theory of Separability of Many-Electron Systems

A. Concept of Separability

The idea of separating the electrons of an atomic or molecular system into sets describing “relevant” regions (or groups) and sets describing “unimportant” regions has indeed been among chemists for some decades. Examples of such an idea and some of the terminology that has evolved from this concept include the “core” and “valence” electrons of atoms, the σ and π electrons of conjugated hydrocarbons, functional groups of organic chemistry, and “valence” and “core” regions in spatially separated interacting systems. The latter example, of course, includes the previous examples as special cases as well as a polyatomic molecule and a stage of a chemical reaction involving several systems. The case of just two interacting systems, which we shall hereafter consider,

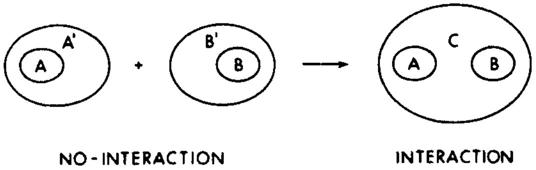

Fig. 4 Two interacting systems. Regions A and B are taken as "unimportant" and noninteracting. For R being any of the regions we let N_R be its number of electrons. The interacting system is taken to have $N = N_A + N_B + N_C$ electrons where $N_C = N_{A'} + N_{B'}$.

exemplifies the separability idea quite generally and this situation is schematically illustrated in Fig. 4.

Intuitively the meaning of "relevant" and "unimportant" regions is rather naive. With regards to our example we can say that the A and B parts are "unimportant" and are thus unaffected by the chemical behavior of the (chemically) "relevant" part C. This can be taken to mean that the states and energies of the total system are governed by the states and energies of the "relevant" part.

Our goal shall be to provide a theoretical meaning or model for the separability idea. Any such model, whose ultimate purpose should be to properly provide states and energies of the "relevant" region C, will involve a determination of an effective-Hamiltonian for the C region which somehow incorporates the effect of the A and B parts, as is the case, for example, when one uses pseudo or model potentials. We shall, however, avoid the commonly used notion of pseudopotentials and develop an effective-Hamiltonian which accounts for the A and B effects through appropriate *projection operators*. In this way, for example, we can assure that the molecular nodal characteristics of the system wave function are not disturbed. Along these lines, Szasz (1959) proceeded to develop such a model based on projection operators, and some errors in his formalism were pointed out by Weeks and Rice (1968). We used these developments together with ideas developed by McWeeny (1959) to provide a theory which leads to possible new simplifications in the treatment of complex many-electron systems.

B. Setup of a Theoretical Model

This part is founded on the works of McWeeny (1959) and Lykos and Parr (1956). Credit is also due to the early work of Fock *et al.* (1940) as well as the work of Szász (1959). Hence we shall only briefly present the ideas of these workers in a form relevant to our problem.

An antisymmetric and normalized wave function[1] of the N-electron interacting system of Fig. 4 can be expressed as

$$\Psi = \Psi_{ABC} = M\tilde{A}_p(\Phi_A \Phi_B \Phi_C), \tag{4.1}$$

where each of the "group" functions,

$$\begin{aligned}\Phi_A &= \Phi_A(1, 2, \ldots, N_A),\\ \Phi_B &= \Phi_B(N_A + 1, N_A + 2, \ldots, N_A + N_B),\\ \Phi_C &= \Phi_C(N_A + N_B + 1, \ldots, N_A + N_B + N_C)\end{aligned}$$

is antisymmetric and normalized, M is a normalization constant, and $\tilde{A}_p$ is the partial antisymmetrizer. It should be noted that each Φ_R can be a linear combination of some product-type function as mentioned by Lykos and Parr (1956),

$$\Phi_R = R_1\Phi_{R,1} + R_2\Phi_{R,2} + \cdots. \tag{4.2}$$

We shall assume that each total Ψ satisfies the *A–B–C separability condition.* This merely means that Φ_A, Φ_B, and Φ_C are strongly orthogonal, i.e., for $R \neq S \in \{A, B, C\}$,

$$\int \Phi_R{}^*(1, i, j, \ldots)\Phi_S(1, k, m, \ldots)\, d\tau_1 = 0. \tag{4.3}$$

In accordance with the partitioning of Ψ in Eq. (4.1), the spin-free electronic Hamiltonian can be written as

$$\mathscr{H} = (\mathscr{H}^A + \mathscr{H}^B + \mathscr{H}^{A,B}) + (\mathscr{H}^C + \mathscr{H}^{A,C} + \mathscr{H}^{B,C}), \tag{4.4}$$

where, for groups $R \neq S \in \{A, B, C\}$,

$$\mathscr{H}^{R,S} = \sum_{\substack{\nu \in R\\ \mu \in S}} 1/r_{\mu\nu} \tag{4.5}$$

is the electron repulsion term between the electrons in group R and group S, and

$$\mathscr{H}^R = \sum_{\mu \in R} h(\mu) + \sum_{\substack{\mu < \nu\\ \mu, \nu \in R}} 1/r_{\mu\nu}, \tag{4.6}$$

with

$$h(\mu) = -\tfrac{1}{2}\Delta_\mu + V(\mu), \tag{4.7}$$

---

[1] A wave function is taken to mean an approximate state. We assume at the outset that we have adequate wave functions.

where $V(\mu)$ is the potential energy of electron μ in the field of the nuclei of the total system. Using this form of $\mathscr{H}$, the total energy expression of the system for a state approximated by an A–B–C separable wave function becomes

$$E = \langle \Psi | \mathscr{H} | \Psi \rangle = H^{A,B} + \hat{H}^C. \tag{4.8}$$

Here $H^{A,B}$ describes the energy of the A, B "core";

$$H^{A,B} = H^A + H^B + J^{AB} - K^{AB}, \tag{4.9}$$

where, for $R \neq S \in \{A, B\}$,

$$H^R = \langle \Phi_R | \mathscr{H}^R | \Phi_R \rangle, \tag{4.10}$$

$$J^{RS} = \int (1/r_{12}) P_1{}^R(1;1) P_1{}^S(2;2)\, dV_1\, dV_2, \tag{4.11}$$

$$K^{RS} = \frac{1}{2} \int (1/r_{12}) P_1{}^R(2;1) P_1{}^S(1;2)\, dV_1\, dV_2, \tag{4.12}$$

and $P_1{}^R$, for example, is the spinless one-particle density matrix for Φ_R. $\hat{H}^C$, on the other hand, describes the energy of the "important" region C;

$$\hat{H}^C = \langle \Phi_C | \hat{\mathscr{H}}^C | \Phi_C \rangle \tag{4.13}$$

where

$$\hat{\mathscr{H}}^C = \sum_{\mu \in C} \hat{h}(\mu) + \sum_{\substack{\mu < \nu \\ \mu, \nu \in C}} 1/r_{\mu\nu} \tag{4.14}$$

and

$$\hat{h}(\mu) = h(\mu) + \mathscr{J}^A(\mu) - \mathscr{K}^A(\mu) + \mathscr{J}^B(\mu) - \mathscr{K}^B(\mu). \tag{4.15}$$

Here $\mathscr{J}^A(\mu)$ and $\mathscr{K}^A(\mu)$, for example, are appropriately defined Coulomb and exchange integral operators, respectively.

The energy expression (4.8) is a generalization of the Fock, Wesselov, and Petraschen (1940) formula. Furthermore, in the form written, it takes the "core" form of the "core"–"peel" relation of Lykos and Parr (1956). We should note that $\hat{\mathscr{H}}^C$ operates only on the C electrons and has the effect of the A, B "core" incorporated into it through $\mathscr{J}^R(\mu)$ and $\mathscr{K}^R(\mu)$, $R \in \{A, B\}$. We shall assume now that the system satisfies the *C-electron approximation*, that is, there exists a set of states which are adequately approximated by a set of wave functions $\{\Psi_{ABC}\}$ each of which is A–B–C

separable and, for the set, Φ_A and Φ_B are taken as fixed. One can equivalently say that we are neglecting the effect of the C electrons on the A and B electrons, or, more crudely, the behavior of the system is determined by the states of the C region.

C. Determination of the Optimum Φ_C

We shall hereafter assume that the system satisfies the C-electron approximation. Consequently the equation for the optimum Φ_C will serve for a set of approximate states of the system. Following Fock *et al.* (1940), let us take the further approximation that each of the "core" Φ_A and Φ_B is an antisymmetrized product of orthonormal spin-orbitals,

$$\Phi_R = \frac{1}{\sqrt{N_R!}} \det[\phi_1{}^R \phi_2{}^R \ldots \phi_{N_R}^R] \tag{4.16}$$

and

$$\langle \phi_i{}^R | \phi_j{}^R \rangle = \delta_{ij} \qquad \text{for} \quad i, j = 1, \ldots, N_R, \tag{4.17}$$

where $R \in \{A, B\}$. The strong orthogonality among Φ^A, Φ^B, and Φ^C then becomes

$$\int \Phi_C{}^*(1, i, j, \ldots) \phi_p{}^R(1) \, d\tau_1 = 0 \qquad \text{for} \quad \begin{matrix} R \in \{A, B\} \\ p = 1, \ldots, N_R \end{matrix} \tag{4.18}$$

and

$$\langle \phi_i{}^A | \phi_j{}^B \rangle = 0 \qquad \text{for} \quad \begin{matrix} i = 1, \ldots, N_A \\ j = 1, \ldots, N_B. \end{matrix} \tag{4.19}$$

Regardless of the choice of spin-orbitals $\{\phi_i{}^R\}$, $R \in \{A, B\}$, we will always have an upper bound to the total energies of the system. Assuming that we hold $\{\phi_i{}^R\}$, $R \in \{A, B\}$, fixed in some convenient and physically meaningful way, we shall derive the equation for the optimum Φ_C. This was essentially done by Weeks and Rice (1968) but their main concern was the derivation of a formal pseudopotential type equation. Our emphasis, as stated before, is different from theirs in that we rather deliberately avoid the pseudopotential–pseudo-wave-function approach.

Let us begin by defining the projection operator Q as

$$(1 - Q) = (1 - Q^A)(1 - Q^B), \tag{4.20}$$

where, for $R \in \{A, B\}$,

$$(1 - Q^R) = \prod_{\mu \in C} (1 - P_\mu{}^R) \tag{4.21}$$

and

$$P_\mu{}^R = \sum_{k=1}^{N_R} |\phi_k{}^R(\mu)\rangle\langle\phi_k{}^R(\mu)|. \tag{4.22}$$

Some properties of Q are

(*a*) $(1 - Q) = (1 - Q^B)(1 - Q^A) = \prod_{\mu\in C}(1 - P_\mu{}^A - P_\mu{}^B)$; (4.23)

(*b*) $Q^R(1 - Q) = (1 - Q)Q^R = 0 \quad \text{for} \quad R \in \{A, B\}$; (4.24)

(*c*) $Q(1 - Q) = (1 - Q)Q = 0$; (4.25)

(*d*) $|\Phi\rangle$ is strongly orthogonal to $|\Phi_A\rangle$ and $|\Phi_B\rangle$ if and only if

$$Q|\Phi\rangle = 0. \tag{4.26}$$

For a nonzero $|\Phi_C\rangle$ that satisfies Eq. (4.26), there exists a $|\Phi_C^{(0)}\rangle$ such that

$$|\Phi_C\rangle = (1 - Q)|\Phi_C^{(0)}\rangle. \tag{4.27}$$

This $|\Phi_C^{(0)}\rangle$ is free from the requirement of satisfying Eq. (4.26).

In the energy expression (4.8) let us take the "core" part $H^{A,B}$ as fixed and treat

$$\bar{H}^C = \langle\Phi_C|\mathscr{H}^C|\Phi_C\rangle = \langle\Phi_C^{(0)}|(1 - Q)\mathscr{H}^C(1 - Q)|\Phi_C^{(0)}\rangle \tag{4.28}$$

variationally with the normalization constraint

$$\langle\Phi_C|\Phi_C\rangle = \langle\Phi_C^{(0)}|(1 - Q)|\Phi_C^{(0)}\rangle = 1. \tag{4.29}$$

The resulting Euler equation reduces to

$$[(1 - Q)\mathscr{H}^C(1 - Q)]|\Phi_C^{(0)}\rangle = E_C(1 - Q)|\Phi_C^{(0)}\rangle \tag{4.30}$$

or, by using (4.27), to

$$(1 - Q)\mathscr{H}^C|\Phi_C\rangle = E_C|\Phi_C\rangle, \tag{4.31}$$

where E_C is the Lagrangian multiplier. Note that Q, $\mathscr{H}^C$, and consequently $(1 - Q)\mathscr{H}^C$ do not depend on $|\Phi_C\rangle$. Since $(1 - Q)\mathscr{H}^C$ is not Hermitian unless $[\mathscr{H}^C, Q] = 0$ and since $|\Phi_C\rangle$ must satisfy (4.26), then $(1 - Q)\mathscr{H}^C$ cannot be used to determine upper bounds to E_C variationally. However, the Hermitian operator (Huzinaga and Cantu, 1971),

$$\tilde{\mathscr{H}}^C = (1 - Q)\mathscr{H}^C - \mathscr{H}^C Q \tag{4.32}$$

possesses an energy spectrum that overlaps with set of energy values E_C from (4.30). Hence $\tilde{\mathscr{H}}^C$ is a proper Hermitian effective Hamiltonian which can be used in a straightforward variational calculation to determine upper bounds to the lowest E_C, if the term $-\mathscr{H}^C Q$ does not create eigenvalues lower than the lowest in Eq. (4.31). This condition will be met in most cases of real interest.

If we can divide $\mathscr{H}^C$ as

$$\mathscr{H}^C = \mathscr{H}_\alpha{}^C + \mathscr{H}_\beta{}^C \tag{4.33}$$

where

$$[\mathscr{H}_\alpha{}^C, Q] = 0 \qquad \text{and} \qquad [\mathscr{H}_\beta{}^C, Q] \neq 0 \tag{4.34}$$

then

$$\mathscr{H}'^C = (1 - Q)\mathscr{H}^C - \mathscr{H}_\beta{}^C Q \tag{4.35}$$

will still serve as a proper effective Hamiltonian. Szász (1959) proposed as a proper effective Hamiltonian the operator

$$\mathscr{H}_{\mathrm{SZ}}^C = \mathscr{H}^C - Q\mathscr{H}_\beta{}^C, \tag{4.36}$$

which gives the same expectation value as that of Eq. (4.35) provided Eq. (4.26) is used. However, this $\mathscr{H}_{\mathrm{SZ}}^C$ will have eigenvalues lower than the lowest E_C in Eq. (4.31). Consequently, its use will lead to the determination of wrong energy values.

$\mathscr{H}^C$ or $\mathscr{H}'^C$ of Eq. (4.32) and (4.35), respectively, is in a general form but a drawback is that Q is quite an involved nonlocal operator when the number of electrons is large. If Φ_C takes the form [see Eq. (4.2)]

$$\Phi_C = \sum_i C_i \Phi_{C,i}, \tag{4.37}$$

where each $\Phi_{C,i}$ is a Slater determinant built from a set of orthonormal spin-orbitals, then, as shown in the Appendix, $\mathscr{H}^C$ (or $\mathscr{H}'^C$) has an equivalent simplified form given by

$$\begin{aligned}\mathscr{H}^C \Leftrightarrow \mathscr{H}_{\mathrm{equiv}}^C &= \sum_{\mu \in C} [(1 - P_\mu)\hat{h}(\mu) - \hat{h}(\mu)P_\mu] \\ &+ \sum_{\substack{\nu<\mu \\ \mu,\nu \in C}} \left[(1 - P_\mu)(1 - P_\nu)\frac{1}{r_{\mu\nu}} + \frac{1}{r_{\mu\nu}}(P_\mu P_\nu - P_\mu - P_\nu)\right],\end{aligned} \tag{4.38}$$

where P_μ is equal to $P_\mu{}^A + P_\mu{}^B$ and the equivalence, $\Leftrightarrow$, means that both Hamiltonians give the same energy expression upon using Φ_C of Eq. (4.37).

D. Hartree–Fock Approximation for Φ_C

We shall consider the situation where all three, Φ_A, Φ_B, and Φ_C, are doubly occupied, closed-shell singlet functions. Each of these can then be written as

$$\Phi_R = \frac{1}{\sqrt{N_R!}} A[|\psi_1{}^R\psi_1{}^R\psi_2{}^R\psi_2{}^R \ldots \psi^R_{N_R/2}\psi^R_{N_R/2}\rangle|\alpha\beta\alpha\beta \ldots \alpha\beta\rangle] \tag{4.39}$$

with

$$\langle\psi_i{}^R|\psi_j{}^R\rangle = \delta_{ij} \qquad \text{for} \qquad i, j = 1, \ldots, N_R/2, \tag{4.40}$$

where $R \in \{A, B, C\}$, A is the antisymmetrizer, and the first and second ket after the antisymmetrizer are the spatial and spin N_R-electron kets, respectively. As before, let us hold Φ_A and Φ_B fixed and determine the optimum Φ_C, or $\{\psi_i{}^C\}$ in this case, under the strong orthogonality constraints which reduce to

$$\langle\psi_i{}^A|\psi_j{}^B\rangle = \langle\psi_i{}^A|\psi_k{}^C\rangle = \langle\psi_j{}^B|\psi_k{}^C\rangle = 0, \tag{4.41}$$

with

$$\begin{aligned} i &= 1, \ldots, N_A/2 \\ j &= 1, \ldots, N_B/2 \\ k &= 1, \ldots, N_C/2 \end{aligned}$$

The energy expression in (4.13) becomes

$$\begin{aligned} \bar{H}^C &= \langle\Phi_C|\mathscr{H}^C|\Phi_C\rangle \\ &= \sum_{i=1}^{N_C/2} \langle\psi_i{}^C|\hat{h}|\psi_i{}^C\rangle + \sum_{i,j=1}^{N_C/2} (2J^C_{ij} - K^C_{ij}), \end{aligned} \tag{4.42}$$

where [see Eq. (4.15)]

$$\hat{h} = h + \sum_{j=1}^{N_A/2} (2J_j{}^A - K_j{}^A) + \sum_{j=1}^{N_B/2} (2J_j{}^B - K_j{}^B). \tag{4.43}$$

Here the numbers J^C_{ij} and K^C_{ij} are Coulomb and exchange integrals, respectively, defined over the spatial orbitals and $J_i{}^R$ and $K_i{}^R$ are Coulomb and exchange integral operators, respectively, defined also over the spatial orbitals. Upon proceeding with our variational treatment we arrive at the Euler equation

$$F|\psi_i{}^C\rangle = \sum_{j=1}^{N_C/2} \varepsilon^C_{ij}|\psi_j{}^C\rangle + \sum_{k=1}^{N_A/2} \lambda^A_{ik}|\psi_k{}^A\rangle + \sum_{l=1}^{N_B/2} \lambda^B_{il}|\psi_l{}^B\rangle, \tag{4.44}$$

where

$$F = \hat{h} + \sum_{k=1}^{N_C/2} (2J_j^C - K_j^C). \tag{4.45}$$

The Lagrangian multipliers $\{\varepsilon_{ij}^C\}$ can be diagonalized as usual by a unitary transformation while the remaining multipliers, $\{\lambda_{ij}^A\}$ and $\{\lambda_{ij}^B\}$, can be processed by the coupling operator technique (Huzinaga, 1969b). Thus Eq. (4.44) can be brought to the form

$$F|\psi_i^C\rangle = \varepsilon_i^C|\psi_i^C\rangle + P_A F|\psi_i^C\rangle + P_B F|\psi_i^C\rangle \tag{4.46}$$

or

$$[1 - (P_A + P_B)]F|\psi_i^C\rangle = \varepsilon_i^C|\psi_i^C\rangle, \tag{4.47}$$

where, for $R \in \{A, B\}$,

$$P_R = \sum_{i=1}^{N_R/2} |\psi_i^R\rangle\langle\psi_i^R|. \tag{4.48}$$

If we write down the full expression of F in Eq. (4.45) we obtain

$$F = -\tfrac{1}{2}\Delta + V + \sum_{i=1}^{N_A/2} (2J_i^A - K_i^A) + \sum_{i=1}^{N_B/2} (2J_i^B - K_i^B) + \sum_{i=1}^{N_C/2} (2J_i^C - K_i^C). \tag{4.49}$$

which is the Hartree–Fock operator that determines the best orbitals in the *total* wave function Ψ_{ABC} of (4.1) [with (4.39) as group orbitals].

Generally speaking we have

$$[(P_A + P_B), F] \neq 0, \tag{4.50}$$

in which case $[1 - (P_A + P_B)]F$ is not Hermitian and, from the previous section, the proper Hermitian Hartree–Fock operator is then

$$\tilde{F} = [1 - (P_A + P_B)]F - F(P_A + P_B). \tag{4.51}$$

However, when

$$[(P_A + P_B), F] = 0 \tag{4.52}$$

$\tilde{F}$ can simply be

$$\tilde{F} = [1 - (P_A + P_B)]F. \tag{4.53}$$

E. Choice of "Core" Orbitals

The question of commutability between $(P_A + P_B)$ and F, of course, depends on the choice of the fixed orbitals $\{\psi_i^A\}$ and $\{\psi_i^B\}$. We shall consider three possibilities. The first choice is the Szász (1959) choice,

$$\hat{h}^A|\psi_i^A\rangle = \omega_i^A|\psi_i^A\rangle \tag{4.54}$$

and

$$\hat{h}^B|\psi_i^B\rangle = \omega_i^B|\psi_i^B\rangle, \tag{4.55}$$

where

$$\hat{h}^R = -\tfrac{1}{2}\Delta + V^R + \sum_{i=1}^{N_R/2} (2J_i^R - K_i^R) \tag{4.56}$$

is the Hartree–Fock operator for the "core"-R orbitals, R being A or B. Here V^R is such that $V^R(\mu)$ is the potential energy of electron μ in the field of the nuclei in "core" R. Since

$$V = V^A + V^B + V^C, \tag{4.57}$$

we see that

$$F = \hat{h}^A + \left[V^B + \sum_{i=1}^{N_B/2}(2J_i^B - K_i^B)\right] + \left[V^C + \sum_{i=1}^{N_C/2}(2J_i^C - K_i^C)\right] \tag{4.58}$$

or

$$F = \hat{h}^B + \left[V^A + \sum_{i=1}^{N_A/2}(2J_i^A - K_i^A)\right] + \left[V^C + \sum_{i=1}^{N_C/2}(2J_i^C - K_i^C)\right]. \tag{4.59}$$

In order for F and $(P_A + P_B)$ to commute it is necessary, but not sufficient, for the last term of (4.58) or (4.59) to vanish upon applying $P_A + P_B$ to it. As this is never the case we conclude that with this first (Szász) choice, F and $(P_A + P_B)$ do not commute and $\bar{F}$ must be written as (4.51).

Our second choice is simply

$$F|\psi_i^A\rangle = \lambda_i^A|\psi_i^A\rangle \qquad \text{with} \qquad \lambda_1^A < \cdots < \lambda_{N_A/2}^A \tag{4.60}$$

and

$$F|\psi_j^B\rangle = \lambda_j^B|\psi_j^B\rangle \qquad \text{with} \qquad \lambda_{N_A/2}^A < \lambda_j^B, \tag{4.61}$$

where, in Eq. (4.61), $j = 1, 2, \ldots, N_B/2$. From Eq. (4.49), this choice amounts to choosing the "core" orbitals to be the lowest set of Hartree–Fock orbitals from the set of Hartree–Fock orbitals of the *entire* system. Clearly $(P_A + P_B)$ and F commute and thus $\tilde{F}$ can be written as Eq. (4.53), which becomes, by Eqs. (4.48), (4.60), and (4.61),

$$\tilde{F} = F - \sum_{i=1}^{N_A/2} \lambda_i^A |\psi_i^A\rangle\langle\psi_i^A| - \sum_{i=1}^{N_B/2} \lambda_i^B |\psi_i^B\rangle\langle\psi_i^B|. \tag{4.62}$$

This suggests a new alternative form for $\mathscr{H}^C$ of Eq. (4.32):

$$\mathscr{H}^C_{\text{ALT}} = \sum_{\mu \in C} \tilde{h}(\mu) + \sum_{\substack{\mu<\nu \\ \mu,\nu \in C}} 1/r_{\mu\nu}, \tag{4.63}$$

where

$$\tilde{h}(\mu) = \hat{h}(\mu) - \sum_{i=1}^{N_A/2} \lambda_i^A |\psi_i^A\rangle\langle\psi_i^A| - \sum_{i=1}^{N_B/2} \lambda_i^B |\psi_i^B\rangle\langle\psi_i^B| \tag{4.64}$$

and $\hat{h}(\mu)$ is given in (4.43) as $\hat{h}$. By alternative we mean that upon optimizing $\langle\Phi_C|\mathscr{H}^C_{\text{ALT}}|\Phi_C\rangle$ using Φ_C of (4.39) and *only* the orthogonormality constraints (4.40) within $\{\psi_i^C\}$, i.e., upon taking

$$\delta\left[\langle\Phi_C|\mathscr{H}^C_{\text{ALT}}|\Phi_C\rangle - \sum_{i,j=1}^{N_C} \varepsilon_{ij}^C \langle\psi_i^C|\psi_j^C\rangle\right] = 0, \tag{4.65}$$

we obtain

$$\tilde{F}|\psi_i^C\rangle = \varepsilon_i^C|\psi_i^C\rangle, \tag{4.66}$$

where $\tilde{F}$ is given in (4.62). One might be tempted to take the last two terms in (4.62) or (4.64) and interpret them as, or replace them by, some kind of local pseudopotential, as is done by Szász and McGinn (1966). As may be recalled, this is not our main concern.

The use of $\mathscr{H}^C_{\text{ALT}}$ is of some interest. Suppose that we use in $\langle\Phi_C|\mathscr{H}^C_{\text{ALT}}|\Phi_C\rangle$ a normalized Φ_C which is more versatile than the single Slater determinant in Eq. (4.39) [and its constraints (4.40)] as, for example, the configuration interaction form in (4.37). Then, by the variation principle, this versatility will yield for us, upon optimization, a *lower* energy than the Hartree–Fock energy. We can, however, not guarantee anything on the comparison of this energy with the ones obtained when $\mathscr{H}^C$ of (4.32) or $\mathscr{H}^C_{\text{equiv}}$ of (4.38) is used.

Our final choice for the "core" orbitals is an intermediate case:

$$F_A|\psi_i^A\rangle = \varepsilon_i^A|\psi_i^A\rangle \tag{4.67}$$

and

$$F_B|\psi_i^B\rangle = \varepsilon_i^B|\psi_i^B\rangle \tag{4.68}$$

where, for $R \in \{A, B\}$,

$$F_R = \hat{h}^R + \sum_{i=1}^{N_{R'}/2}(2J_i^{R'} - K_i^{R'}) \tag{4.69}$$

is the Hartree–Fock operator of a subsystem having a "core" R and contributing $N_{R'}$ electrons to the region C (see Fig. 4.), and $\hat{h}^R$ is given in Eq. (4.56). Clearly, $N_C = N_{A'} + N_{B'}$ as mentioned in Fig. 4. As done in (4.58), the Hartree–Fock operator F of (4.49) can be written, for this case, as

$$\begin{aligned} F = F_A &+ \left[V^B + \sum_{i=1}^{N_B/2}(2J_i^B - K_i^B)\right] \\ &+ \left[V^C + \sum_{i=1}^{N_C/2}(2J_i^C - K_i^C) - \sum_{i=1}^{N_{A'}/2}(2J_i^{A'} - K_i^{A'})\right]. \end{aligned} \tag{4.70}$$

In parallel with (4.59), another form can be written where $A(A')$ and B are interchanged in (4.70). If the interacting system is sufficiently separated into its interacting components and $V^C = 0$ (as when C is a pure electron-bonding region) then

$$P_A\left\{V^B + \sum_{i=1}^{N_B/2}(2J_i^B - K_i^B)\right\} \simeq 0 \tag{4.71}$$

and

$$P_A\left\{V^C + \sum_{i=1}^{N_C/2}(2J_i^C - K_i^C) - \sum_{i=1}^{N_{A'}/2}(2J_i^{A'} - K_i^{A'})\right\} \simeq 0 \tag{4.72}$$

with a similar result holding when $A(A')$ and B are interchanged. If indeed the system is such that the approximations (4.71) and (4.72) hold, then $(P_A + P_B)$ and F very nearly commute and thus this case effectively reduces to that of the second choice. Equations (4.62) to (4.66) would then follow, with λ_i^R replaced by ε_i^R where $R \in \{A, B\}$.

F. The Diatomic Molecule

Before proceeding to the diatomic molecule case, we mention that the atomic case with "core" and "valence" electrons or, for that matter, any case with only a "core" and "valence" region, is obtainable from the previous treatment by taking, say, $B = 0$. Then only the mentioned cases, 1 and 2, of Section IV.E hold for the "core" orbitals. Consider now a diatomic molecule made from two atoms which are represented as noninteracting in Fig. 4. Let Z_A and Z_B be the nuclear charge of the atoms with "core" A and B, respectively, then

$$V^A(\mu) = -Z_A/r_{A\mu} \tag{4.73}$$

$$V^B(\mu) = -Z_B/r_{B\mu} \tag{4.74}$$

and

$$V^C(\mu) = 0. \tag{4.75}$$

If we include the nuclear repulsion term, $Z_A Z_B/R_{AB}$, in the total electronic Hamiltonian, then (4.9) becomes

$$\begin{aligned} H^{A,B} = {} & \langle\Phi_A|\mathscr{H}_0{}^A|\Phi_A\rangle - \langle\Phi_A|\sum_{\mu=1}^{N_A} Z_B/r_{B\mu}|\Phi_A\rangle \\ & + \langle\Phi_B|\mathscr{H}_0{}^B|\Phi_B\rangle - \langle\Phi_B|\sum_{\mu=1}^{N_B} Z_A/r_{A\mu}|\Phi_B\rangle \\ & + J^{AB} - K^{AB} + Z_A Z_B/R_{AB}, \end{aligned} \tag{4.76}$$

where in (4.9) and (4.10) we took, for example,

$$\mathscr{H}^A = \mathscr{H}_0{}^A - \sum_{\mu=1}^{N_A} Z_B/r_{B\mu}. \tag{4.77}$$

Here $\mathscr{H}_0{}^A$ is the Hamiltonian of "core" A. $\mathscr{H}^B$ is similarly defined provided A and B are interchanged in (4.77).

Let us assume that the two core regions are sufficiently separated so that

(a) $$E^A = \langle\Phi_A|\mathscr{H}_0{}^A|\Phi_A\rangle \tag{4.78}$$

and

$$E^B = \langle\Phi_B|\mathscr{H}_0{}^B|\Phi_B\rangle \tag{4.79}$$

represent well the "core" energies,

(b) $$K^{AB} \simeq 0 \tag{4.80}$$

and

$$\text{(c)}\quad Z_A Z_B/R_{AB} - \langle \Phi_A | \sum_{\mu=1}^{N_A} 1/r_{B\mu} | \Phi_A \rangle Z_B$$

$$- Z_A \langle \Phi_B | \sum_{\mu=1}^{N_B} 1/r_{A\mu} | \Phi_B \rangle + J^{AB}$$

$$\simeq (Z_A - N_A)(Z_B - N_B)/R_{AB} = z_A z_B/R_{AB} \tag{4.81}$$

where,[2] for example,

$$z_A = Z_A - N_A. \tag{4.82}$$

Then we have for (4.76),

$$H^{A,B} = E^A + E^B + z_A z_B/R_{AB}. \tag{4.83}$$

Since the above assumption is compatible with the approximation used to get (4.71) and (4.72) when we considered the third choice for the "core" orbitals, then we can write the total energy in the form

$$E = \langle \Phi_C | \mathscr{H}^C_{\text{ALT}} | \Phi_C \rangle + E^A + E^B + z_A z_B/R_{AB}, \tag{4.84}$$

which is a functional of Φ_C alone. This form, as mentioned in Section IV.E, also follows if the second choice for the "core" orbitals is taken. By noting the approximations taken to obtain (4.84) we can see the validity and limitations of the use of such an expression. Szász and McGinn (1966) proposed such an equation for treating diatomic molecules without any scrutiny of its validity. They also present this with a connection to pseudopotentials. as mentioned in Section IV.E, and, again, our purpose is their avoidance.

One might argue that the nonlocal property of our projection operators would cause difficulty. However, if one has recourse to the Roothaan expansion method such difficulties are remedied.

V. Concluding Remarks

As we stated at the beginning, our intention has been to present a review of some selected facets of the use of the projection operator technique in Hartree–Fock-type theories. However, the present article cannot be concluded without mentioning the profound and persistent influence of

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[2] Part (c) can be broken down into its individual approximations to obtain the final form given.

a number of well-known papers by Löwdin, their scope being well beyond the framework of Hartree–Fock-theory. We would also like to point out that a recent trilogy by Adams (1967, 1969a,b) should be an excellent place to learn how profitably one can employ the technique in sophisticated Hartree–Fock-type theories.

Appendix

We shall prove here the validity of the equivalence stated in Eq. (4.38). That is, given Φ_C of Eq. (4.37), then

$$\langle \Phi_C | \mathscr{H}^C | \Phi_C \rangle = \langle \Phi_C | \mathscr{H}^C_{\text{equiv.}} | \Phi_C \rangle. \tag{A.1}$$

In the following we shall suppress the index C and also we shall take for convenience, $1, 2, \ldots, n = N_C$ to be the electron labels for the C region rather than $N_A + N_B + 1, \ldots, N_A + N_B + N_C$.

The function Φ of Eq. (4.37) is of the form

$$\Phi = \sum_I C_I \Phi_I, \tag{A.2}$$

where we have taken the summing index to capital letters for notational convenience. Here each

$$\Phi_I = A[\phi_{I(1)} \phi_{I(2)} \cdots \phi_{I(n)}] \tag{A.3}$$

is a Slater determinant built from a common set of orthonormal spin orbitals and thus

$$\langle \phi_{I(k)} | \phi_{J(l)} \rangle = \delta_{I(k)J(l)}. \tag{A.4}$$

Using Eq. (A.2) we have

$$\langle \Phi | \mathscr{H} | \Phi \rangle = \sum_{I,J} C_I{}^* C_J \mathscr{H}_{IJ}, \tag{A.5}$$

where

$$\mathscr{H}_{IJ} = \langle \Phi_I | \mathscr{H} | \Phi_J \rangle, \tag{A.6}$$

and, by Eq. (4.32),

$$\mathscr{H} = (1 - Q)\mathscr{H} - \mathscr{H} Q. \tag{A.7}$$

Let us define, for $1 \leqslant k \leqslant n$, the orbital

$$\hat{\phi}_{I(k)}(\mu) = [1 - P_\mu{}^A - P_\mu{}^B] \phi_{I(k)}(\mu). \tag{A.8}$$

Then it follows from Eq. (A.4) and the strong orthogonality conditions that

$$\langle \hat{\phi}_{I(k)} | \phi_{J(l)} \rangle = \delta_{I(k)J(l)} \,. \tag{A.9}$$

Hence, since the antisymmetrizer, A, commutes with Q, we have that

$$(1 - Q)\Phi_I = \hat{\Phi}_I , \tag{A.10}$$

where

$$\hat{\Phi}_I = A[\hat{\phi}_{I(1)}\hat{\phi}_{I(2)} \cdots \hat{\phi}_{I(n)}]. \tag{A.11}$$

Upon using Eq. (A.11) and Eq. (A.7), Eq. (A.6) becomes

$$\tilde{\mathscr{H}}_{IJ} = \langle \hat{\Phi}_I | \hat{\mathscr{H}} | \Phi_J \rangle - \langle \Phi_I | \hat{\mathscr{H}} | \Phi_J \rangle + \langle \Phi_I | \hat{\mathscr{H}} | \hat{\Phi}_J \rangle. \tag{A.12}$$

From Eq. (4.14)

$$\hat{\mathscr{H}} = \sum_{\mu=1}^{n} \hat{h}(\mu) + \sum_{\mu<\nu}^{n} 1/r_{\mu\nu} \,. \tag{A.13}$$

By Eq. (A.9) we then have

$$\begin{aligned}
\tilde{\mathscr{H}}_{IJ} = \sum_{k} [&\langle \hat{\phi}_{I(k)} | \hat{h}(1) | \phi_{J(k)} \rangle - \langle \phi_{I(k)} | \hat{h}(1) | \phi_{J(k)} \rangle + \langle \phi_{I(k)} | \hat{h}(1) | \hat{\phi}_{J(k)} \rangle] \\
&+ \sum_{k<l} [\langle \hat{\phi}_{I(k)}\hat{\phi}_{I(l)} | (1/r_{12})(1 - P_{12}) | \phi_{J(k)}\phi_{J(l)} \rangle \\
&- \langle \phi_{I(k)}\phi_{I(l)} | (1/r_{12})(1 - P_{12}) | \phi_{J(k)}\phi_{J(l)} \rangle \\
&+ \langle \phi_{I(k)}\phi_{I(l)} | (1/r_{12})(1 - P_{12}) | \hat{\phi}_{J(k)}\hat{\phi}_{J(l)} \rangle],
\end{aligned} \tag{A.14}$$

where P_{12} permutes space-spin coordinates 1 and 2. Equation (A.14) can be written as

$$\begin{aligned}
\tilde{\mathscr{H}}_{IJ} = \sum_{k} &\langle \phi_{I(k)} | (1 - P_1{}^A - P_1{}^B)\hat{h}(1) - \hat{h}(1)(P_1{}^A + P_1{}^B) | \phi_{J(k)} \rangle \\
&+ \sum_{k<l} \langle \phi_{I(k)}\phi_{I(l)} | [1 - (P_1{}^A + P_1{}^B)][1 - (P_2{}^A + P_2{}^B)](1/r_{12}) \\
&+ (1/r_{12})[(P_1{}^A + P_1{}^B)(P_2{}^A + P_2{}^B) - (P_1{}^A + P_1{}^B) \\
&- (P_2{}^A + P_2{}^B)] | (1 - P_{12})\phi_{J(k)}\phi_{J(l)} \rangle.
\end{aligned} \tag{A.15}$$

This implies that

$$\tilde{\mathscr{H}}_{IJ} = \langle \Phi_I | \tilde{\mathscr{H}}_{\text{equiv.}} | \Phi_J \rangle,$$

where $\tilde{\mathscr{H}}_{\text{equiv.}}$ is given in Eq. (4.38) and thus the equivalence is proved.

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An Analytic Independent Particle Model for Atoms

I. Initial Studies

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I. Introduction

A systematic knowledge of basic atomic properties is needed to achieve an understanding of fundamental mechanisms in a number of disciplines such as chemistry, aeronomy, astrophysics, radiation physics, plasma physics, and laser physics. Properties such as ionization energies, excitation energies, transition probabilities, and elastic, excitation, and ionization cross sections are particularly needed in problems involving the deposition of charged particle energy in matter.

Motivated by this need a series of calculational studies have been undertaken which utilize a two-parameter analytic atomic independent particle model (IPM) potential (Green, Sellin, and Zachor, 1969) which is quite close to the average Hartree–Fock potential acting on the electrons in an atom. This paper will largely be devoted to a description of the results obtained in these studies.

At the outset it should be noted that a somewhat parallel series of works (Manson and Cooper, 1968; Manson, 1971; McGuire, 1968) has also been underway with a similar motivation. For the most part these works utilize numerical Hartree–Fock–Slater potentials (Slater, 1951, 1953, 1968). The two sets of studies go far beyond those based on hydrogenic potentials which have been used for over 45 years (Mott and Massey, 1965) in attempts to organize atomic properties. When the studies deal with the same atomic species the results usually compare quite favorably. An advantage of the analytic IPM approach is that one can directly use many techniques which have been developed and exploited in extensive studies involving the nuclear independent particle models, e.g., the shell and optical models (see Green, Sawada, and Saxon, 1968) and distorted wave analyses of nuclear collisions. Among these techniques is the ability to phenomenologically adjust the parameters of the model in relationship to experimental data or data acquired from more rigorous calculations. In many instances such an adjustment phenomenologically allows for small effects which for the most part are neglected at the present stage of applied atomic physics.

In applications of the independent particle model (IPM) approximation, one eventually arrives at the radial wave function for one-electron orbitals by solving numerically the radial Schrödinger equation

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - V(r) + E_{nl}\right] P_{nl}(r) = 0. \tag{1}$$

In this work r is in units of Bohr radii (a_0) and all energies are in Rydbergs. Here E_{nl} is the energy eigenvalue and $V(r)$ is a central atomic potential due to the Z units of nuclear charge and the average effect of the N remaining core electrons. The development of rapid numerical techniques for solving the radial Schrödinger equation permits one to concentrate on the massive body of physics that can be encompassed by the use of realistic electron–atom potentials.

II. Analytic Representations of the Thomas–Fermi Potential

Most analytic representations of atomic potentials have started with the screening function $[\phi(x)]$ of the statistical model of Thomas (1927) and Fermi (1928) which satisfies the nonlinear differential equation

$$x^{1/2}(d^2\phi/dx^2) = \phi^{3/2}, \tag{2}$$

where $x = rZ^{1/3}/\mu_0$, and $\mu_0 = \frac{1}{2}(3\pi/4)^{2/3} = 0.8853$. In the usual elementary treatment, the screening function ϕ is assumed to satisfy $\phi(0) = 1$ and $\phi(x) \to 0$ as $x \to \infty$. Equation (2) was first solved by Bush and Caldwell (1931) with a differential analyzer. The points in Fig. 1 are taken from their numerical values.

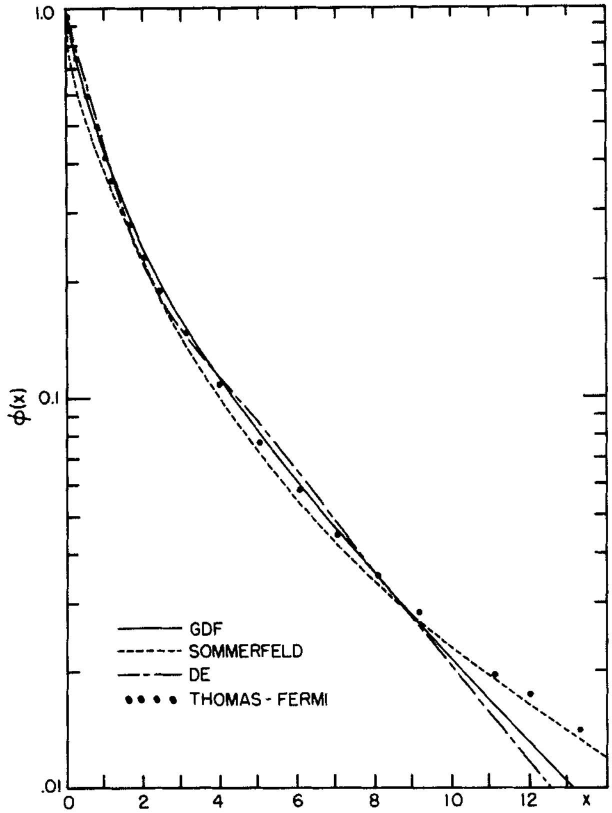

Fig. 1. Comparison of analytic representations of the Thomas–Fermi screening function. The Thomas–Fermi function appears as dots; the legend for various analytic representations is given in the diagram.

TABLE I

ANALYTIC THOMAS–FERMI SCREENING FUNCTIONS

	P_1	P_2	P_3
Sommerfeld (1932) $[1+(x/P_1)^{P_2}]^{-P_3}$	5.242	0.772	3.885
Gaspar (1952) $e^{-P_1x}/(1+P_2x)$	0.1837	1.050	—
Teitz (1955) $[1+P_1x]^{-2}$	0.5363	—	—
Latter[a] (1955) $[\sum_{i=0}^{6} P_jx^{j/2}]^{-1}$	0.02747	1.243	−0.1486
	$(0.2302)_4$	$(0.007298)_5$	$(0.006944)_6$
Green (DE) (1958) $P_1e^{-x/P_2}+(1-P_1)e^{-P_3x/P_2}$	0.349	3.56	5.22
Green *et al.* (GDF) (1969) $[P_2(e^{x/P_1}-1)+1]^{-1}$	4.478	$P_2=P_1+1$	—

[a] Note $P_0 = 1$. P_4,P_5 & P_6 are below P_1, P_2 and P_3.

The curves in Fig. 1 correspond to analytic forms which are among those described in Table I. The last form listed has been the starting point of a series of published studies which will be summarized in this paper. The abbreviation GDF stands for *generalized distribution function* since this function has as special cases the Fermi–Dirac function ($P_2 = H < 1$), the Maxwell–Boltzmann function ($H = 1$), and intermediate functions approaching the Einstein–Bose function ($H \to \infty$).

In the simplest form of the Thomas–Fermi model the potential energy of a single electron in a neutral atom is taken as $-2Z\phi/r$. In this form the vanishing of ϕ as $r \to \infty$ presents a problem since the potential fails to go to the hydrogen atom limit. Following Latter (1955) it has been customary to overcome this problem by using TF only out to the radius r_0 at which it equals $V_h = -2/r$, and by using $V = V_h$ for $r > r_0$. Effectively one uses the screening function ϕ_{TF} only for $x < x_0 = r_0Z^{1/3}/\mu_0$ and uses $\phi(x) = Z^{-1}$ for $x > x_0$.

To avoid this introduction of a discontinuity in the derivative of the potential at r_0 one may alternatively write the potential for an electron in a neutral atom in the form

$$V(r) = -2r^{-1}[(Z-1)\Omega + 1], \tag{3}$$

where Ω is an analytic screening function which approximates the TF function but which is readjusted to compensate for approximations made in the neighborhood of r_0. To deal with such effects it is convenient to use the independent variable r rather than x. In particular, GDF may be written in the form (Green, Sellin, and Zachor, 1969)

$$\Omega(r) = [H(e^{r/d}-1)+1]^{-1}, \tag{4}$$

where H is a shape parameter and d a scale parameter. Figure 2 illustrates this analytic screening function for a representative set of values of the shape parameter which encompasses all potentials used to date.

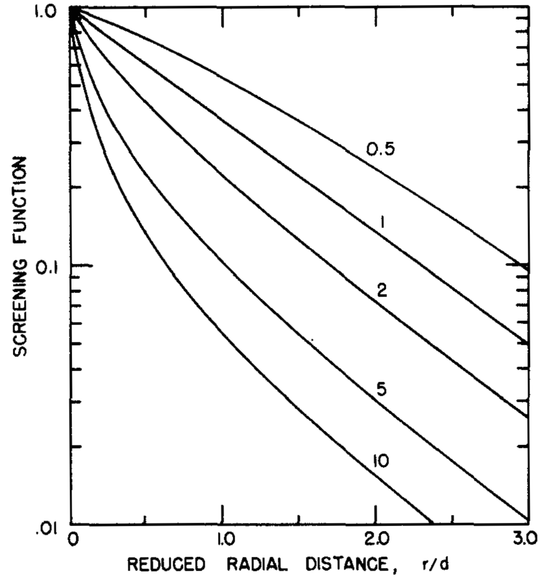

Fig. 2. Shapes of screening functions corresponding to various H ($d = 1$) (Green *et al.*, 1969).

The analytic fit of GDF to the Thomas–Fermi screening function (see Table I) suggests that one use the parameter values

$$H = 5.478 \qquad \text{and} \qquad d = 4.478\mu_0/Z^{1/3} = 3.962/Z^{1/3} \tag{5}$$

in conjunction with Eq. (4) to specify the potential seen by an electron in any neutral atom, and this was the initial potential used in the work of Green, Sellin, and Zachor (GSZ). However, while the energy eigenvalues which they found from the radial Schrödinger equation were fairly reasonable, they found that one could do somewhat better by holding d fixed (~ 0.8) and letting $H \sim Z^{1/3}$ while preserving the ratio

$$K = H/d = 1.382Z^{1/3}. \tag{6}$$

In the course of such exploratory studies, however, GSZ found that they could dramatically improve upon the results achievable with their analytic IPM model by adjusting the two parameters d and H for each element. This then became the starting point of the phenomenological IPM model of GSZ.

III. The Phenomenological Model of GSZ

The power of the phenomenological analytic potential approach is that one can adjust the two parameters d and H for each element in the light of many more "data" points acquired either from experiment or from more fundamental theoretical models, e.g., the Hartree-Fock model. Let us consider the various adjustments philosophies studied by GSZ.

A. Analytic Fits to HFS Screening Functions

Hartree-Fock-Slater (HFS) self-consistent field calculations (Slater, 1968) have been carried out by Herman and Skillman (HS) (1963) for neutral atoms for $Z = 2$ through 103. They express their one-electron potential energy in terms of a "normalized" potential U which is equivalent to our Ω. To avoid the Latter device GSZ transformed these to modified screening functions $\Omega_{\mathrm{HS}}(r)$, using

$$\Omega_{\mathrm{HS}}[x(r)] = [U(r) - Z^{-1}]/(1 - Z^{-1}) \tag{7}$$

For each Z, values of the parameters H and d were obtained by a least-squares fit of the GDF function [Eq. (4)] to Ω_{HS}. The values of the d's so obtained fluctuated around an average of about 0.8. The values of H tended generally to increase as a function of the number of core electrons $N = Z - 1$ but displayed local fluctuations which correlated directly with the fluctuations in d. Empirically it was found that

$$K = H/d = \alpha N^{\nu} \tag{8}$$

could be represented very well if $\nu = 0.4$ and $\alpha = 1.05$. Using these values of ν and α for all elements, least-squares fits were made to the Ω values given by Eq. (7) to obtain readjusted values of d. This one-parameter per element screening function proved to provide nearly as accurate a representation of Ω_{HS} as those obtained by varying both H and d.

B. Adjustment of Parameters to HFS Eigenvalues

A more direct way of adjusting the two parameters is to fit a set of energy levels acquired either from experimental data or more fundamental theoretical treatment. In such adjustments original estimates of d and

$\alpha = H/dN^{0.4}$ were revised by a least-squares procedure which minimized the sum

$$\chi^2 = \sum [E_j(\text{obs}) - E_j(\text{calc})]^2 / |E_j^p(\text{obs})|, \tag{9}$$

where E_j(obs) represents the "data," E_j(calc) the values computed from the Schrödinger equation and the power p determines the weight given to individual points. When $p = 2$, χ^2 represents simply the sum of the squares of the fractional deviations from the desired energies, with all levels given equal weighting. Since in most cases our main purpose is to reproduce observed energies, which decrease in reliability with increasing electronic energy, we may give greater weight to the inner electronic levels, by using the power $p = 1$.

TABLE II

COMPARISONS OF VARIOUS d AND α[a,b]

Z	$d^{(1)}$	$d^{(2)}$	$\alpha^{(2)}$	$d^{(3)}$	$\alpha^{(3)}$	$d^{(4)}$
5	0.877	0.977	1.120	0.780	1.02	0.979
10	0.466	0.443	0.997	0.466	1.04	0.500
15	0.920	1.060	1.140	0.919	1.08	0.867
20	1.140	1.080	1.010	1.170	1.05	1.154
30	0.593	0.559	1.000	0.598	1.02	0.612
40	0.951	1.010	1.090	0.942	1.06	0.866
50	0.846	0.789	1.000	0.841	1.03	0.841
70	0.725	0.752	1.090	0.632	1.00	0.654
90	1.060	1.090	1.080	0.924	1.02	0.927

[a] Green *et al.* (1969).

[b] (1) Fit of d to HFS screening functions with $\alpha = 1.05$. (2) Fits of d and α to HFS screening functions. (3) Fits of d and α to HFS eigenvalues. (4) Fit of d to HF (Mann) eigenvalues with $\alpha = 1.00$.

In applying this adjustment procedure GSZ used $p = 1$ and the eigenvalues E_j(obs) of Herman and Skillman (1963) from the Hartree–Fock–Slater model. Table II gives some representative comparisons of d and α obtained from the modified screening function adjusted to the HS eigenvalues. The average value of α so obtained is quite close to that obtained from fits to Ω_{HS}.

TABLE III

VALUES OF d TO FIT HARTREE–FOCK ENERGIES ($\alpha = 1.00$)[a, b]

II			III		
Z	Sym	d	Z	Sym	d
3	Li	0.563	11	Na	0.561
4	Be	0.858	12	Mg	0.621
5	B	0.979	13	Al	0.729
6	C	0.880	14	Si	0.817
7	N	0.776	15	P	0.868
8	O	0.708	16	S	0.885
9	F	0.575	17	Cl	0.881
10	Ne	0.500	18	A	0.862

IV			V		
Z	Sym	d	Z	Sym	d
19	K	1.006	37	Rb	0.744
20	Ca	1.154	38	Sr	0.798
21	Sc	1.116	39	Y	0.855
22	Ti	1.060	40	Zr	0.866
23	V	0.996	41	Cb	0.831
24	Cr	0.837	42	Mo	0.825
25	Mn	0.866	43	Tc	0.855
26	Fe	0.807	44	Ru	0.803
27	Co	0.751	45	Rh	0.788
28	Ni	0.700	46	Pd	0.737
29	Cu	0.606	47	Ag	0.754
30	Zn	0.612	48	Cd	0.775
31	Ga	0.631	49	In	0.810
32	Ge	0.649	50	Sn	0.841
33	As	0.663	51	Sb	0.870
34	Se	0.675	52	Te	0.896
35	Br	0.684	53	I	0.919
36	Kr	0.689	54	Xe	0.940

VI			VII		
Z	Sym	d	Z	Sym	d
55	Cs	1.022	87	Fr	0.818
56	Ba	1.108	88	Ra	0.859
57	La	1.150	89	Ac	0.899
58	Ce	1.081	90	Th	0.927
59	Pr	0.970	91	Pa	0.887
60	Nd	0.938	92	U	0.880
61	Pm	0.905	93	Np	0.872
62	Sm	0.873	94	Pu	0.832
63	Eu	0.842	95	Am	0.822
64	Gd	0.862	96	Cm	0.842
65	Tb	0.830	97	Bk	0.830
66	Dy	0.754	98	Cf	0.790
67	Ho	0.728	99	Es	0.778
68	Er	0.702	100	Fm	0.766
69	Tm	0.677	101	Mv	0.754
70	Yb	0.654	102	No	0.742
71	Lu	0.665	103	Lw	0.755
72	Hf	0.672			
73	Ta	0.676			
74	W	0.679			
75	Re	0.680			
76	Os	0.680			
77	Ir	0.679			
78	Pt	0.661			
79	Au	0.657			
80	Hg	0.671			
81	Tl	0.690			
82	Pb	0.708			
83	Bi	0.726			
84	Po	0.744			
85	At	0.761			
86	Rn	0.777			

[a] Green *et al.* (1969).

[b] Note for $Z = 1$ (H), d is indeterminate; for $Z = 2$ (He), $d = 0.215$.

C. Adjustment to Hartree–Fock Energies

Using the same weighted least-squares method and the same starting values, GSZ also obtained values for d and α by fitting the energies computed by Mann (1968) from the coupled Hartree–Fock equations in which exchange is represented exactly. Thus the IPM potentials for the d's and α's determined from the Hartree–Fock (HF) energies implicitly embody an "average" exchange potential.

A complete set of d's and α's from helium through lawrencium were obtained in this way. After these calculations were completed, GSZ found no significant loss of accuracy if α were set to 1.00 and the d values were readjusted using HF eigenvalues. Table III and Fig. 3 present the values of d so obtained. Column 5 of Table IV gives a sample set of energies computed from this analytic potential and the parameter values of Table III. Column 4 gives the corresponding HF energies. Column 3 gives HS–HFS energies. It should be noted that the differences between the computed energies and the HF energies are generally much smaller than the differences between the HS–HFS and the HF energies. Columns 6 and 7 give the derivatives of the energy with respect to parameters d and α. The wave functions obtained by GSZ are quite close to those obtained from HF and HFS calculations. This is illustrated in Fig. 4.

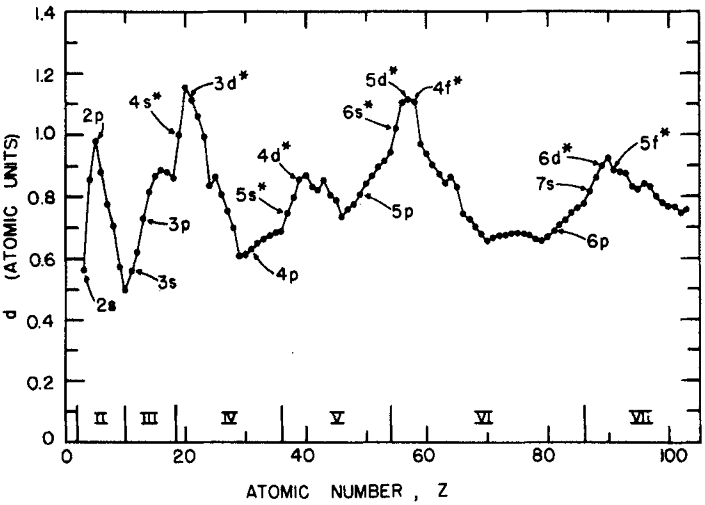

Fig. 3. Graph of the optimum values of d that were obtained by fitting Mann's HF energies with $\alpha = 1.0$. Symbols denote filling orbitals (*competitive) (Green *et al.*, 1969).

TABLE IV: ILLUSTRATIVE ENERGIES[a]

Shell	ESCA	HFS	HF	IPM	dE/dd	$dE/d\alpha$
		$Z = 10$	$d = 0.500$	$H = 1.203$		
1*s*	63.70	62.99	65.54	64.24	7.20	−25.90
2*s*	3.30	3.17	3.86	3.54	6.03	− 4.66
2*p*	1.30	1.47	1.70	1.88	6.22	− 5.02
		$Z = 20$	$d = 1.154$	$H = 3.747$		
1*s*	296.80	293.50	298.70	297.40	4.68	−80.30
2*s*	32.20	31.63	33.65	33.06	3.42	−30.90
2*p*	25.70	26.18	27.26	28.10	3.48	−35.20
3*s*	3.20	3.88	4.49	4.09	2.07	− 6.97
3*p*	1.90	2.48	2.68	2.72	1.97	− 6.60
4*s*	—	0.40	0.39	0.49	0.44	− 0.73
		$Z = 40$	$d = 0.866$	$H = 3.748$		
1*s*	1290.00	1291.00	1301.00	1303.00	6.97	−251.0
2*s*	177.60	178.00	182.80	182.90	12.10	−127.0
2*p*	164.00	163.80	167.00	169.80	11.90	−143.0
3*s*	30.00	29.80	32.12	31.97	11.10	− 45.0
3*p*	24.30	24.36	26.05	26.68	11.10	− 47.2
3*d*	13.20	14.32	15.05	16.58	11.40	− 49.2
4*s*	3.60	4.23	4.85	4.35	5.50	− 10.5
4*p*	2.00	2.73	2.99	2.80	4.97	− 9.24
4*d*	—	0.52	0.62	0.47	3.08	− 4j43
5*s*	—	0.44	0.42	0.44	0.76	− 0.85
		$Z = 90$	$d = 0.927$	$H = 5.580$		
1*s*	7066.00	7078.00	7102.00	7116.00	6.94	−893.00
2*s*	1253.00	1227.00	1239.00	1235.00	23.7	−559.00
2*p*	1258.00	1188.00	1196.00	1200.00	19.4	−617.00
3*s*	313.80	308.50	315.00	311.80	25.2	−286.00
3*d*	302.80	289.10	294.20	292.70	24.4	−305.00
3*d*	241.70	252.50	255.80	255.00	26.1	−338.00
4*s*	79.00	77.75	81.46	81.38	20.9	−124.00
4*p*	71.70	68.78	71.84	72.52	21.0	−126.00
4*d*	48.40	51.99	54.06	55.51	21.0	−129.00
4*p*	24.20	28.70	29.43	31.91	21.9	−125.00
5*s*	16.50	17.45	18.94	18.54	13.2	− 43.50
5*p*	13.50	14.00	15.09	15.02	12.9	− 41.80
5*d*	6.15	7.97	8.283	8.71	12.0	− 36.30
6*s*	3.42	2.98	3.386	2.90	5.65	− 10.50
6*p*	3.05	1.97	2.135	1.85	4.85	− 8.56
6*d*	—	0.52	0.592	0.38	2.51	− 3.52
7*s*	—	0.36	0.342	0.34	0.67	− 0.86

[a] Green *et al.* (1969).

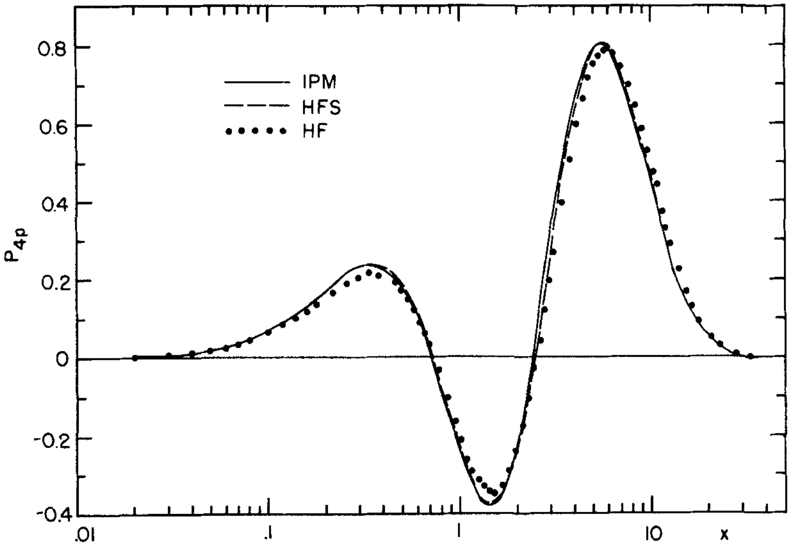

Fig. 4. Wave functions for the 4*p* state of argon (Green *et al.*, 1969).

D. Adjustment to Experimental Energies

In the study of GSZ, *d* and α were also adjusted to the experimental ionization (ESCA) (Siegbahn *et al.*, 1967) energies for selected elements. These experimental energies were first averaged with respect to spin–orbit splitting. For $Z < 40$, α and *d* vaues were readily found that provided reasonable agreement. However, for $Z > 50$ it was difficult to find reasonable sets of parameter. This problem was ascribed to relativistic effects.

As an interim approach the relativistic effects tabulated by Herman and Skillman were subtracted from the experimental energies for a sample of elements with $Z \geq 40$. Then values of *d* and α similar to those obtained from HFS and Hartree–Fock energies were found to give energies in reasonable agreement with those obtained from the experimental data. This agreement, however, deteriorates somewhat for very heavy elements.

IV. The Relativistic IPM Model

In an effort to cope with relativistic effects more simply Darewych, Green, and Sellin (DGS) (1971) have made use of the Dirac equation in place of the Schrödinger equation. This permits direct comparison with experimental data and with energies obtained from relativistic Hartree–Fock calculations.

The Dirac equation for an electron moving in a spherically symmetrical potential $V(r)$ is

$$[c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2 + V(r)]\psi = E\psi, \tag{10}$$

where all the symbols have their usual meaning. As is well known, Dirac's equation can be reduced to the coupled radial equations

$$\frac{dF}{dr} = \frac{-K}{r}F + \frac{\alpha}{2}\left[\varepsilon - V(r) + \frac{4}{\alpha^2}\right]G, \tag{11}$$

$$\frac{dG}{dr} = \frac{K}{r}G - \frac{\alpha}{2}[\varepsilon - V(r)]F, \tag{12}$$

where $F = F_{nlj}(r)$ and $G = G_{nlj}(r)$ are the large and small radial components, respectively, $\varepsilon = E - mc^2$, $\alpha = e^2/\hbar c$, $K = (l - j)(2j + l)$ here, while n, l, and $j = l \pm \frac{1}{2}$ are the usual principal, orbital angular momentum and total angular momentum quantum numbers.

TABLE V

Relativistic Electronic Energies for Zr ($Z = 40$)[a]

	E(ESCA)	E_1(GSZ) $d = .80197$ $H = 3.6429$ $p = 1$	P_1	E(RHF)	E_2(GSZ) $d = .94932$ $H = 4.2804$ $p = 1$	P_2	E_3(GSZ) $d = .96265$ $H = 4.3554$ $p = 2$	P_3
$1s^+$	1322.81	1324.31	0.11	1331.052	1327.18	0.29	1326.33	0.35
$2s^+$	186.10	184.28	0.97	189.690	187.06	1.38	186.75	1.55
$2p^-$	169.56	170.07	0.30	173.010	172.90	0.06	172.52	0.28
$2p^+$	163.39	163.52	0.08	166.644	166.34	0.18	165.97	0.40
$3s^+$	31.68	30.75	2.94	33.393	32.68	2.15	32.64	2.27
$3p^-$	25.36	25.16	0.79	27.068	27.11	0.14	27.06	0.03
$3p^+$	24.33	24.10	0.93	26.010	26.02	0.06	25.98	0.11
$3d^-$	13.45	13.77	2.39	14.918	15.76	5.66	15.72	5.37
$3d^+$	13.23	13.58	2.63	14.701	15.56	5.84	15.52	5.56
$4s^+$	3.82	3.79	0.88	5.019	4.63	7.69	4.66	7.23
$4p^-$	2.13	2.26	6.34	3.169	3.02	4.59	3.05	3.88
$4p^+$	2.13	2.13	0.07	2.911	2.87	1.52	2.89	0.75
$4d^-$	0.22	0.18	16.67	0.592	0.54	8.79	0.56	5.67
$5s^+$	—	—	—	0.429	0.49	14.82	0.50	16.41

[a] Darewych *et al.* (1971).

To determine solutions of Eqs. (11) and (12) numerically DGS used the second-order equation

$$(d^2u/dr^2) + Qu = 0, \tag{13}$$

where

$$Q = -\frac{1}{4B}\frac{d^2V}{dr^2} - \frac{3}{10B}\left(\frac{dV}{dr}\right)^2 + \frac{K}{2Br}\frac{dV}{dr} + \frac{\alpha^2}{2}(\varepsilon - V)B - \frac{K(K+1)}{r^2}, \tag{14}$$

and

$$B = \tfrac{1}{2}[\varepsilon - V + 4/\alpha^2], \tag{15}$$

which is obtained by eliminating G from (11) and (12) and setting $F = B^{1/2}u$. Equation (13) is then amenable to numerical solution using the relatively efficient Numerov technique (Piper, 1961; Hartree, 1957; Herman and Skillman, 1963). Table V gives a representative result (for $Z = 40$) with d and H adjusted in three different ways. The first and third entries [columns labeled E(ESCA) and E(RHF)] are experimental and relativistic Hartree–

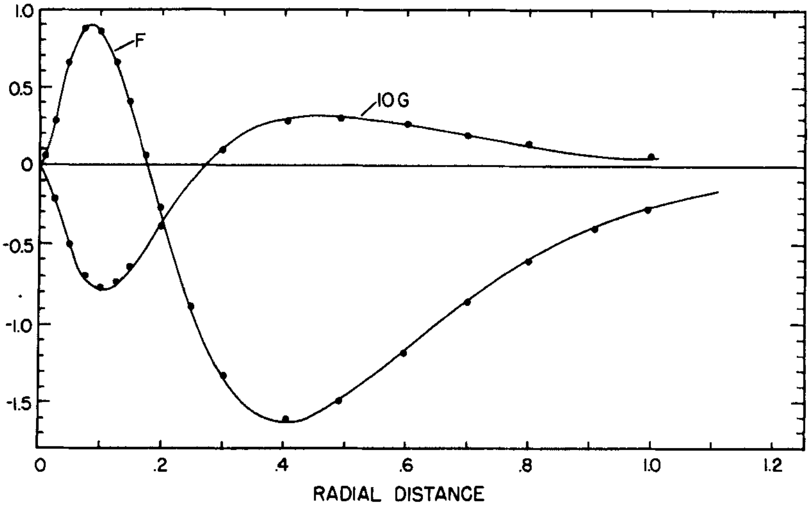

Fig. 5. Radial wave functions for $3p^+$ electrons of Zr ($Z = 40$). Solid curve: present model using potential parameters of Table I (the curves for the three sets of parameters are indiscernible on this scale). Circles: relativistic Hartree–Fock results of Mann (Darewych *et al.*, 1971).

Fock results. The column labeled E_1 gives the energies computed from the present model with parameters adjusted to fit experimental energies with lower levels given greater weighting [i.e., $p = 1$ in (7)]. The column labeled E_2 gives analogous results obtained by fitting to relativistic Hartree–Fock data. The column labeled E_3 is based upon fits to ESCA data but with weighting determined by $p = 2$. By examining the columns headed P_1, P_2, and P_3 (for percentage deviation) one notes that experimental data or relativistic Hartree–Fock data are approximated just about equally well. The parameters d and H, however, show substantial variations in the three computations.

Figure 5 is a plot of the wave functions F and G for the $4p$ state of $Z = 40$ in comparison with relativistic Hartree–Fock wave functions. Clearly the agreement is very good. Results for other atoms are similar.

V. The Thomas–Fermi–Dirac Energy Functional Model

A. The Energy Functionals

Thus far the analytic IPM model must be classified as a semiempirical or phenomenological model in that prior experimental or theoretical data are needed to adjust the two parameters. We shall next describe an attempt by Green, Sellin, and Darewych (GSD) (1971) using the energy functional form of the Thomas–Fermi (TF) statistical model, to place the systematics of d and H on a more fundamental basis. For the purposes of this study it is constructive to write our analytic IPM potential for an electron in a neutral atom in the form

$$V = V_e + V_n = 2r^{-1}[(Z - 1)\Upsilon - Z],$$

where $Z - 1$ is the number of core electrons and Z the number of nuclear protons. Here V_n is the nuclear potential, and V_e is the potential energy due to the electronic cloud and

$$\Upsilon(r) = 1 - \Omega(r) = 1 - [H(e^{r/d} - 1) + 1]^{-1}. \tag{16}$$

To obtain the average electronic radial charge density, we may use Poisson's equation

$$n(r) = -\frac{1}{4\pi r}\frac{d^2\Upsilon}{dr^2} = \frac{H}{4\pi d^2}\frac{e^{r/d}}{r}\frac{He^{r/d} + H - 1}{(He^{r/d} - H + 1)^3}. \tag{17}$$

In the statistical theory (cf. March, 1957; Herman, Van Dyke, and Ortenburger, 1969, and references cited therein) the total energy of a many-electron system containing N electrons and Z protons may be expressed in the form

$$E_T = \sum_i E_i, \tag{18}$$

where E_i represents the various identifiable components of the total energy expressed in terms of the electron density and the electrostatic potential. The main components include the energy of the electron cloud in the field of the nucleus

$$E_1 = E_n = -2ZN \int r^{-1} n(r)\, d\tau, \tag{19}$$

the electrostatic interaction energy between the various electrons

$$\begin{aligned} E_2 = E_e &= N^2 \int |\mathbf{r} - \mathbf{r}'|^{-1} n(r) n(r')\, d\tau\, d\tau' \\ &= N^2 \int r^{-1} \Upsilon(r) n(r)\, d\tau, \end{aligned} \tag{20}$$

and the main kinetic energy of the electrons

$$E_3 = E_k = C_k N^{5/3} \int n^{5/3}\, d\tau, \qquad C_k = \tfrac{3}{5}(3\pi^2)^{2/3}. \tag{21}$$

In addition, however, there are the von Weizsäcker (1935) correction to the kinetic energy as given by (Kompaneets and Pavlovskii, 1956)

$$E_4 = E_{kw} = C_{kw} N \int [(\nabla n)^2/n]\, d\tau, \qquad C_{kw} = \tfrac{1}{36}, \tag{22}$$

the exchange energy (Dirac, 1930)

$$E_5 = E_x = -C_x N^{4/3} \int n^{4/3}\, d\tau, \qquad C_x = \tfrac{3}{2}(3/\pi)^{1/3}, \tag{23}$$

and the inhomogeneity correction for the exchange energy

$$\begin{aligned} E_6 = E_{xw} &= -C_{xw} N^{2/3} \int [(\nabla n)^2/n^{4/3}]\, d\tau, \\ C_{xw} &= 2\pi/(3\pi^2)^{4/3}. \end{aligned} \tag{24}$$

Finally, we shall give some consideration to a correlation energy, which in the approximate form interpolated by Lewis (1958) may be given by

$$E_7 = E_c = -C_c N \int n \ln [1 + b(Nn)^{1/3}]\, d\tau, \tag{25}$$

where $C_c = 0.06225$ and $b = 10.86$. The initial strategy of GSD was to evaluate the various integrals given in Eqs. (18)–(25) to obtain each component energy in terms of the N, Z, and the parameters H and d. The stable atom should correspond to the parameters which give the least total energy. Let us see how such a conceptual procedure worked out.

We recall from Section II that a good fit to the universal Thomas–Fermi screening function is obtained if the reduced parameter $h = H/dZ^{1/3} = 1.382$. In the course of the GSZ study, it was found, however, that a closer approximation to HF and HFS results could be obtained by permitting the parameters H and d to take on values which varied throughout the periodic table. The values of d, H, and h obtained by fitting Ω_{HF} are given in Table VI for seven sample substances. Also given are the total

TABLE VI

HARTREE–FOCK "DATA"[a]

Z	d	H	h	$-E$	b
10	0.443	1.06	1.134	257	1.193
20	1.08	3.05	1.041	1354	1.247
30	0.559	2.15	1.238	3556	1.272
40	1.01	4.73	1.369	7078	1.294
50	0.789	3.74	1.286	12046	1.308
70	0.752	4.46	1.439	26783	1.326
90	1.09	7.10	1.453	48719	1.342

[a] Green *et al.* (1971).

energies and the reduced binding energies $b = -E_T/N^{7/3}$ which have been obtained from HF calculations. In attempting to adapt the statistical model GSD used the values for d, h, and b as empirical "data" which realistically characterize atoms.

The normalized electron density corresponding to Eq. (17) is singular at the origin as r^{-1}. While this is weaker than the $r^{-3/2}$ singularity of the strict TF model, it occasions a difficulty with E_{kw}, the inhomogeneity correction to the kinetic energy.

Except for the E_n and E_e terms, which can be evaluated analytically, the integrations were carried out numerically. In the case of E_{kw}, a cutoff procedure was employed in which the denominator in Eq. (22) was replaced by $n^{4/3}/\bar{n}^{1/3}$, where $\bar{n}$ is a reasonable nonsingular density which departs fron n only at very short range.

It is simple to establish the dependence of the integrals upon the parameter d by using d as the unit of length. Apart from the small correlation term, all potential energy components go as d^{-1}, wheras all kinetic energy components go as d^{-2}. This makes it simple to minimize the total energy with respect to d so that the further minimization problem need only be carried out with respect to H.

Numerical calculations showed that the total energy is a very slowly varying function of H, having a minimum at large unrealistic values ($H \sim 100$). To look at component energies GSD imposed the *ad hoc* rule $H = 1.3Z^{1/3}$. Minimization with respect to d then led to the component energies presented in Table VII for a sample of elements. The parameters H, d, h, the total energies, and reduced energies are given in Table VIII.

TABLE VII

INDIVIDUAL CONTRIBUTIONS TO TOTAL STATISTICAL ENERGY FOR CONSTRAINED CASE ($H = 1.3Z^{1/3}$)[a]

Z	E_k	E_{k2}	E_n	E_e	E_{kw}	E_{xw}	E_c
10	262.4	37.1	− 686.4	134.8	−22.7	− 24.8	− 1.6
20	1344.2	123.1	− 3474.1	661.1	− 71.3	− 50.2	− 3.6
30	3515.6	248.7	− 8997.8	1685.3	−140.0	− 76.0	− 5.8
40	6955.2	409.3	− 17679	3277.8	−226.0	−102.1	− 8.1
50	11803	601.8	− 29848	5494.0	−327.8	−128.3	−10.6
70	26177	1074.3	− 65724	11976	−574.2	−180.1	−15.7
90	47416	1653.5	−118473	21440	−872.8	−233.7	−21.0

[a] Green *et al.* (1971).

TABLE VIII

PARAMETERS AND ENERGIES FOR CONSTRAINED CASE[a]

Z	H	d	h	$-E$	b
10	2.80	0.8161	1.504	301	1.396
20	3.52	0.8120	1.602	1471	1.355
30	4.04	0.8081	1.609	3770	1.348
40	4.44	0.8048	1.616	7373	1.347
50	4.78	0.8023	1.620	12415	1.348
70	5.36	0.7989	1.628	27267	1.350
90	5.82	0.7966	1.632	49091	1.352

[a] Green *et al.* (1971).

Focusing on the reduced energies we note that at large Z the results (~ 1.35) are quite comparable to HF values (see Table VI). However, for small atomic numbers the GDF model is too large (~ 1.4) compared to HF (~ 1.2). Furthermore, the parameter h (~ 1.6) is also too large.

B. The Semiempirical Atomic Energy Formula

To explore the source of the difficulty GSD expressed the successive terms in Eqs. (18)–(25) in an approximate algebraic form. In the important inner region the screening function depends on H/d; accordingly, we use the dependence upon d to factor out the corresponding H/d. Thus, we write

$$E = -\alpha ZN \frac{H}{d} + \beta N^2 \frac{H}{d} + \gamma N^{5/3} \frac{H^2}{d^2} + \delta N \frac{H^2}{d^2} - \mu N^{4/3} \frac{H}{d} - \tau N^{2/3} \frac{H}{d}, \tag{26}$$

where the successive terms correspond to those defined by Eqs. (18)–(25), and we have discarded the correlation energy. Analytically it is possible to show that $\alpha = 2$ and $\beta = \beta_1 + \beta_0/H$, where $\beta_1 = 1/3$ and $\beta_0 = 1/6$. By numerical evaluations GSZ found that to good approximation $\gamma = 0.487$, and $\delta = \delta_0 + \delta_1 H$, where $\delta_0 = 0.270$ and $\delta_1 = 0.01$; $\mu = 0.298$; and $\tau = 1.57$. If all the integrals were independent of H (i.e., we neglect β_0 and δ_1) then we may readily minimize the total energy with respect to the reduced shape-scale parameter H/d. The terms β_0/H and $\delta_1 H$ in principle should permit us to solve for H and d simultaneously by minimizing the energy with respect to both parameters. By algebra GSD arrived at analytic expressions for the total energy of the atom and the parameters d and H in terms of N and Z and the integration constants α, β, γ, etc. In practice they used the reduced parameters $h = H/dN^{1/3}$ and $b = -E_T/N^{7/3}$ as quantities to compare with data from the GSZ study. They obtained reasonable values of b but $d \sim 1.95$ rather than ~ 0.8 and $h \sim 1.62$ rather than ~ 1.3. Thus, they were quite far from the empirical values of these screening function parameters.

At this juncture GSD approached the atomic-energy-formula work from a nuclear-energy-formula (Bethe and Bacher, 1936; Green, 1958) standpoint by exploring various empirical adjustments of the integral parameters.

To mechanize their search for good parameters they used a nonlinear least-squares program which minimized the composite χ^2.

$$\chi^2 = w_1(b - b_{\mathrm{HF}})^2 + w_2(h - h_{\mathrm{HFS}})^2 + w_3(d - d_{\mathrm{HFS}})^2. \tag{27}$$

To give the greatest emphasis to the well-defined energies, since h fluctuates and d fluctuates rather wildly, they chose the weights $w_1 = 1$, $w_2 = \frac{1}{2}$, and $w_3 = \frac{1}{4}$. After many searches, they arrived at a number of readjusted integral parameters listed in Table IX. The second column shows the initial integral parameters. The remaining columns show the results of various restricted searches in which the parameters indicated by stars or zeros are held fixed. Figure 6 shows the simultaneous fits to b, d, and h for the simple four-parameter-model case E. These fits are fairly representative of cases D, F, G, and H as well. One sees that GSD have found a variety of simple representations of the data.

TABLE IX

PARAMETERS FOR GDF[a,b]

	Initial	A	B	C	D	E	F	G
$\alpha-\beta_1$	1.666	1.956	1.98	1.99	2.00	2.04	2.04	2.04
β_0	0.1666	0.1666*	0.0973	0.130	0.162	0.277	0.388	0.527
μ	0.298	0.298*	0	0	0	0	0.298*	0.679
τ	1.57	1.57*	0	0	0	0	0	0
γ	0.487	0.683	0.719	0.712	0.705	0.637	0.664	0.635
δ_0	0.275	0.275*	0	0	0	0	0	0
δ_1	0.010	0.109	0.06*	0.08*	0.100*	0.177	0.248	0.339
$100\chi^2$	36.8	7.38	6.87	6.68	6.53	6.33	6.28	6.31

[a] Green *et al.* (1971).

[b] * denotes fixed parameters.

GSD explored several other potentials and their corresponding densities in an effort to determine whether the results of the TF model were limited by the original choice of the analytic potential. These results suggested that the difficulty with TDF is due, at least in part, to the assumption that Poisson's equation serves as a link connecting $n(r)$ to $\Omega(r)$, which is rather basic to the usual forms of the statistical model. This does not preclude the possibility that within the TF framework improvements can be made either by resorting to different potential or density functions or by introducing additional corrections to the energy functional. Their efforts with

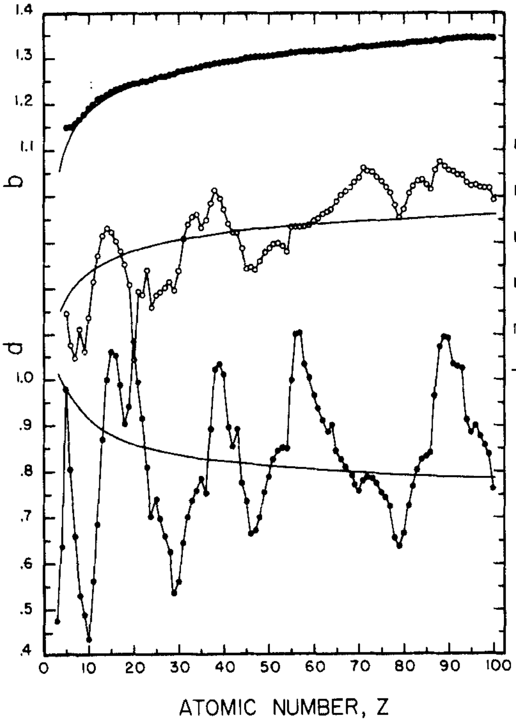

Fig. 6. Atomic energy formula based upon GDF model. The points for *d* and *h* are from GSZ based upon fitting HFS screening functions. The points for the reduced energy $b = -E/Z^{7/3}$ are from Mann's Hartree-Fock total energies. The curves represent the parameters of case E in Table IX with reduced energies at minima using the semiempirical atomic energy formula (Green *et al.*, 1971).

the semiempirical energy formula in which the various components in the energy functional are examined as to their parameter dependences suggested that a component which enhances the H^3N/d^2 term which arises out of the kinetic energy inhomogeneity correction is needed to obtain good energy minima at H and d parameter values consistent with our analytic fits to HFS screening functions and HF energies.

Figure 7 compares the radial charge distributions from the analytic IPM model and HFS model with densities calculated using Eq. (17). The absence of shell structure in the statistical model may be a limitation of the statistical model.

The study of GSD provided the background for another attempt (Bass, Green, and Wood, 1973) to fix the parameters of the GSZ analytic potential from first principles.

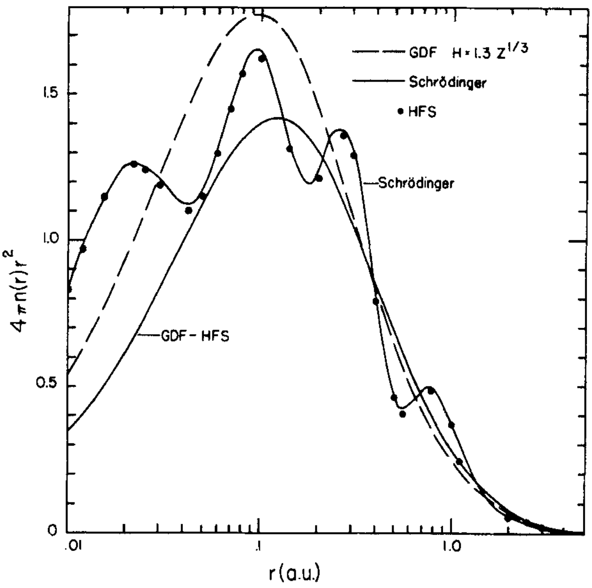

Fig. 7. The solid line labeled Schrödinger is the sum of the electron densities based upon the IPM using the GSZ potential with constants fitted to HF eigenvalues. The circles show the corresponding densities using Herman and Skillman's HFS program. The GDF–HFS is based upon parameters which fit HFS screening functions. GDF* is the constrained model (Green *et al.*, 1971).

VI. Electron–Atom Elastic Scattering

In this section we consider the application of analytic IPM to scattering problems. The simplest modification of Eq. (4) which will vanish asymptotically as $r \to 0$ is

$$V(r) = -2r^{-1}Z\Omega(r), \tag{28}$$

Berg, Purcell, and Green (BPG) (1971) have utilized this potential to calculate the elastic scattering of electrons from Ar, Kr, and Xe. The usual partial wave analysis was employed. The Schrödinger equation for the lth partial-wave radial function for the electron energy $E = k^2$ is

$$d^2u_l/dr^2 + [k^2 - l(l+1)/r^2 - V(r)]u_l = 0. \tag{29}$$

Equation (29) is solved subject to the boundary conditions $u_l(0) = 0$ and

$$u_l \to rj_l(kr) + kA_l(-rn_l + irj_l) \qquad \text{as} \qquad r \to \infty,$$

where j_l and n_l are the spherical Bessel and Neumann functions. The coefficients A_l are related to the phase shifts δ_l by

$$A_l = [e^{2i\delta_l} - 1]/2ik. \tag{30}$$

The scattering amplitude $f(\theta)$ and the differential cross section $d\sigma/d\Omega$ are obtained from the A_l's and the Legendre polynomials P_l

$$f(\theta) = \sum_{l=0}^{\infty} (2l + 1)A_l P_l(\cos\theta) \tag{31}$$

and

$$d\sigma/d\Omega = |f(\theta)|^2. \tag{32}$$

The usual procedure is then followed. Equation (29) is integrated numerically for partials waves $0 \leq l \geq L$, where L is chosen $L \geq 2kd$. A power-series expansion for u_l is used near $r = 0$, after which the Numerov method is used to integrate outward to a "matching radius" r_m. The mesh size is doubled periodically in the vicinity of $r = 0$ to allow a small grid where the potential is changing rapidly and a larger grid farther out. At the matching radius, the derivative of u_l is computed numerically and the equation

$$\frac{u_l'}{u_l}\,(\text{numerical}) = \frac{(rj_l)' + A_l k(-rn_l + irj_l)'}{(rj_l) + A_l k(-rn_l + rj_l)} \tag{33}$$

is used to obtain A_l and therefore δ_l from Eq. (30) and $d\sigma/d\Omega$ from Eqs. (31) and (32).

Figures 8 and 9 are illustrative of their results, which were obtained without any adjustment of constants. For d they used the values given in Table III; 0.862 (Ar) and 0.940 (Xe). For H they used $H = 1.00\, dZ^{0.4}$.

The data plotted in Figs. 8 and 9 were obtained from graphs given in the literature (Mehl, 1967; Schackert, 1968) and do not have absolute values assigned to them. The normalization process used was to require that the areas under the parts of the angular distribution which were common to both experiment and theory should be equal. It is clear that the calculations agree quite well with the observations both in detail of structure and in relative magnitude. Since the data do not extend to angles less than about 30°, no special treatment of small angles was necessary. In particular, it was unnecessary to use a polarization potential such as used by Purcell, Berg, and Green (1970) and Ganas, Dutta, and Green (1970) in studies of elastic scattering of electrons by He.

Fink and Green (FG) (1971) have used the same analytic potential in conjunction with the Dirac equation to calculate elastic scattering cross sections for 300 eV electrons on Hg. They found that the relativistic

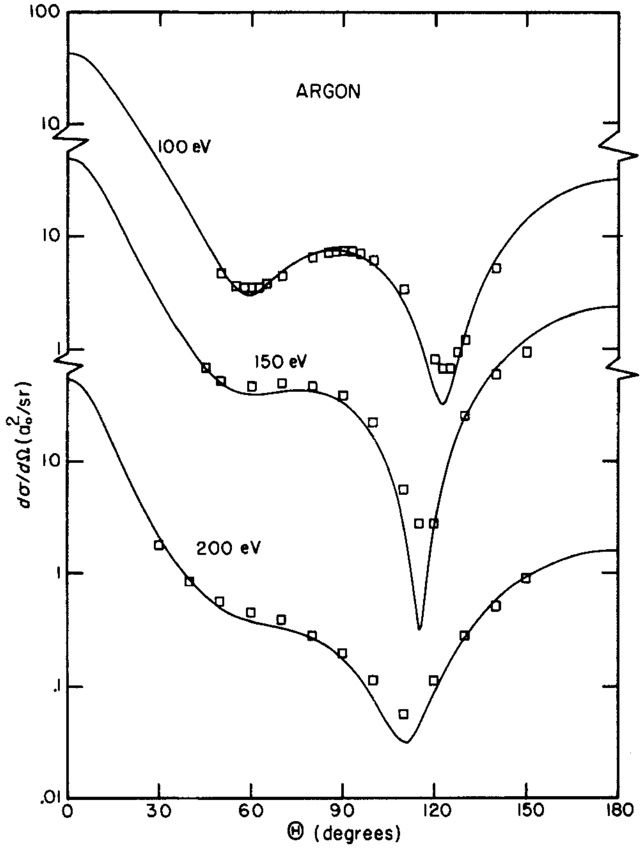

Fig. 8. Comparison of differential cross sections for electron scattering by argon. The boxes are normalized experimental results (see text). The vertical axis is logarithmic. The energy of the incident electron is listed next to the curve (Berg *et al.*, 1971).

potential parameters of Darewych *et al.* gave significantly better results than the nonrelativistic parameters of GSZ.

In both the BPG and FG studies the most remarkable result was that one can account for the gross properties of the currently known electron–atom elastic scattering cross sections with so simple a phenomenological potential. In all likelihood as more detailed experimental data are acquired it will be necessary to incorporate additional terms into the IPM potential to allow for inelastic processes, correlation effects, charge cloud polarization, and other residual effects. The results achieved to date suggested that it would be fruitful to use the analytic IPM model as a basic point of departure.

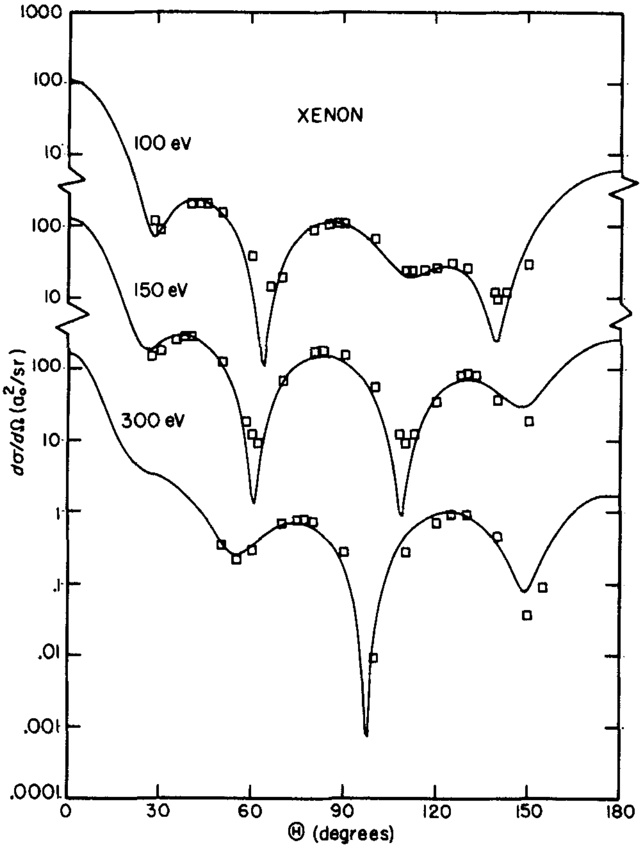

Fig. 9. Comparison of differential cross sections for electron scattering by xenon. See Fig. 8 for details (Berg *et al.*, 1971).

VII. Electron Impact Excitation Cross Sections

Ganas and Green (GG) (1971) have utilized the GSZ analytic atomic IPM model as a basis for calculating generalized oscillator strengths (GOS) for the single-particle excitations of Ne, Ar, Kr, and Xe by electron impact. These GOS may be used to calculate high-energy excitation cross sections. The underlying theory is essentially that of Bethe's classic paper in 1930 (Mott and Massey, 1965). The essential results of this paper in a form suitable for our use will now be summarized.

A. Bethe's Theory of Generalized Oscillator Strengths

Consider the transition of an N-electron atom from its ground state to the nth excited state with momentum transfer K. We define

$$x = K^2 a_0^2, \qquad x_t = W/R, \qquad \text{and} \qquad \xi = x/x_t = K^2 a_0^2 R/W, \tag{34}$$

where $\mathbf{K} = \mathbf{k}_0 - \mathbf{k}'$ is the momentum transfer with $\mathbf{k}_0$ the incident initial plane wave momentum and $\mathbf{k}'$ the outgoing momentum; $W = E_n - E_0$ is the excitation energy where E_n is the energy of the nth state, E_0 is the ground-state energy, a_0 is the Bohr radius, R is the Rydberg energy, and ξ is a reduced variable.

In terms of these quantities Bethe's generalized oscillator strength may be defined as

$$f(x) = \sum_{mom} |I|^2/\xi, \tag{35}$$

where

$$I = \sum_{j=1}^{N} \int \psi_n^* \exp(i\mathbf{K}\cdot\mathbf{r}_j)\psi_0 \, d\mathbf{r}_1 \cdots d\mathbf{r}_N \tag{36}$$

Here $\mathbf{r}_j$ is the position of the jth electron, and ψ_n and ψ_0 are the excited state and ground state many-electron wave functions. Generalized oscillator strength has the important feature that it goes over the usual optical oscillator strength as $K \to 0$ (or $x \to 0$).

The practical aspects of a study of generalized oscillator strengths arise from its usefulness in providing approximate electron impact cross sections. Thus, it can be shown that the differential cross section may be expressed as (Green and Dutta, 1967)

$$\frac{d\sigma}{d\Omega} = \frac{q_0}{\pi W^2}\left(1 - \frac{W}{E}\right)^{1/2} \frac{f(\xi)}{\xi}, \tag{37}$$

where $q_0 = 4\pi a_0^2 R^2$. For a given E and W the reduced quantity ξ depends upon the scattering angle θ according to the relation

$$\xi = \frac{2E}{W}\left[1 - \cos\theta\left(1 - \frac{W}{E}\right)^{1/2} - \frac{W}{2E}\right]. \tag{38}$$

The total cross section is given by

$$\sigma = \frac{q_0}{WE}\int_{\xi_l}^{\xi_u} \frac{f(\xi)}{\xi}\, d\xi, \tag{39}$$

where for ξ_l, forward scattering, $\cos\theta = 1$ and ξ_u, backward scattering, $\cos\theta = -1$. When expressing W and E in electron volts and cross sections in cm^2, $q_0 = 6.514 \times 10^{-14}$ cm^{2}eV^2.

B. The Use of the Analytic IPM Model

The usefulness of the analytic IPM model lies primarily in the fact that it provides realistic wave functions which may be used for the approximate calculation of I^2 and hence $f(\xi)$. Let us suppose that only one electron is involved in the transition, the core remaining undisturbed. Suppose the electron is promoted from its ground state with the usual central field quantum numbers n_0, l_0, m_0 to an excited state with quantum numbers n, l, m. Then, under these conditions the matrix element I simplifies to $I = C\mathscr{I}$ where

$$\mathscr{I} = \int \psi^*_{n_0 l_0 m_0}(\mathbf{r}) \exp(i\mathbf{K}\cdot\mathbf{r}) \psi_{nlm}(\mathbf{r})\, d\mathbf{r}, \tag{40}$$

where the wave functions are now the single-electron IPM wave functions. To establish the constant of proportionality would entail considerable angular momentum algebra and the results would depend on the angular momentum coupling scheme chosen. To circumvent these complications Ganas and Green normalize their calculated GOS to experimental or theoretical optical oscillator strengths.

To evaluate the integral in Eq. (40), we first separate the wave functions in the usual way into their radial and angular parts and make use of the Rayleigh expansion

$$\exp(i\mathbf{K}\cdot\mathbf{r}) = \sum_{l'=0}^{\infty} i^{l'}(4\pi)^{1/2}(2l'+1)^{1/2} j_{l'}(Kr)\, Y_{l'0}(\theta, \phi), \tag{41}$$

where $j_l(Kr)$ is a spherical Bessel function. Using the spherical harmonic property

$$\int Y_{a\alpha} Y_{b\beta} Y_{c\gamma} \sin\theta\, d\theta\, d\phi = \left[\frac{(2a+1)(2b+1)(2c+1)}{4\pi}\right]^{1/2} \times \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix} \begin{pmatrix} a & b & c \\ 0 & 0 & 0 \end{pmatrix} \tag{42}$$

where the arrays in brackets are $3j$ symbols. Using the properties of $3j$ symbols, it can be shown that the generalized oscillator strengths eventually reduce to

$$f(\xi) = C^2 \xi^{-1} \sum_{l'} (2l_0+1)(2l+1)(2l'+1) \begin{pmatrix} l_0 & l & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \mathscr{R}^2_{l'}(\xi), \tag{43}$$

where $\mathscr{R}_{l'}(\xi)$ are radial matrix elements

$$\mathscr{R}_{l'}(\xi') = \int_0^\infty P_{n_0 l_0}(r) j_{l'}(Kr) P_{nl}(r)\, dr. \tag{44}$$

Clearly the essence of any systematic behavior of generalized oscillator strengths depends upon the systematic properties of the reduced radial matrix elements $\mathscr{R}_{l'}(\xi)$. In a search for systematic behavior the analytic IPM model of GSZ proved particularly useful. Since Ganas and Green were concerned with excited states of the rare gases Ne, Ar, Kr, and Xe which have a complex multiplet structure, they started their effort by first establishing the underlying single particle structure.

C. Experimental Levels

The ground state of each rare gas atom is a p^6 configuration with all lower-energy shells filled. The known excited states of these atoms have p^5 cores, i.e., they correspond to configurations like p^5ns, p^5np, p^5nd, ..., where one electron is excited. The experimental energies show considerable fine structure which arise when the angular momentum of the core, J_c, is coupled to the angular momentum of the excited electron, j, to give various possible total angular momenta J. The core angular momentum J_c takes the values $\frac{3}{2}$ and $\frac{1}{2}$.

To arrive at the IPM levels GG replaced each multiplet by a center of gravity by averaging over J:

$$\Sigma_{nl} = \sum_J (2J+1)\bar{E}_{nlJ} \Big/ \sum_J (2J+1) \tag{45}$$

where all energies were converted to atomic units ($R = 1$ Rydberg). Here n, l are the principal quantum number and orbital angular momentum, respectively, of the excited state, and $\bar{E}_{nlJ}$ is the energy of the configuration p^5nl when the total angular momentum is equal to J. The configurations associated with $J_c = \frac{3}{2}$ were treated separately from configurations associated with $J_c = \frac{1}{2}$, i.e., two separate averages were performed, one corresponding to $J_c = \frac{3}{2}$ and the other to $J_c = \frac{1}{2}$. In this manner the tabulated spectra were reduced to two sets of single-particle states for each gas. An illustration of their results is given for the case of Ar in Fig. 10. To a good approximation any state nl differs from the corresponding state nl' by ΔI, the difference between the two ionization limits. Hence the two systems can be combined into a final average by subtracting ΔI from all of the energies of nl' system and combining these energies with the corresponding ones from the nl system in the ratio $\frac{1}{3}$ to $\frac{2}{3}$. These final averages,

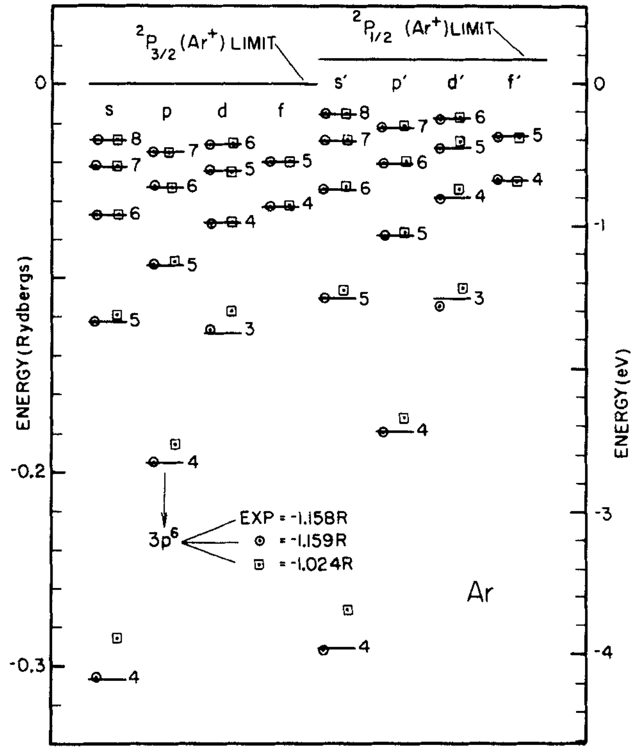

Fig. 10. Excited-state energies of argon. The lines denote average of experimental levels. The position of the ground state is indicated by numerical values. The symbols ○ and □ denote theoretical IPM energy levels based upon corresponding parameters in Table XI (Ganas and Green, 1971).

which serve as experimental single-particle energy levels, conform quite well to the Rydberg series formula

$$E_{nl} = -(n-\delta)^{-2} \qquad (\text{in } R). \tag{46}$$

Table X presents these quantum defects.

Having arrived at an experimental set of single-particle excitation energies GG compared these with the eigenvalues of the IPM model of GSZ which were based upon occupied levels. While the results were reasonable, it appeared that a tune-up of the parameters would improve the agreement. To this objective for each gas a search was carried out over the occupied plus the excited states. The best fits in this case for Ar are denoted by square symbols in Fig. 10, and the best-fit parameters are given in Table XI. (b) For each gas a search was made over the excited

TABLE X

QUANTUM DEFECTS AND IONIZATION LIMIT DIFFERENCES
(Units of ΔI are Rydbergs)

	s	p	d	f	ΔI
Ne	1.33	0.86	0.014	0.000	0.0071
Ar	2.19	1.73	0.212	0.010	0.0130
Kr	3.16	2.68	1.27	0.008	0.0489
Xe	4.11	3.61	2.42	0.025	0.0960

[a] Ganas and Green (1971).

TABLE XI

IPM POTENTIAL PARAMETERS[a]

		⊙	⊡	GSZ
Ne	d	0.715	0.465	0.500
	H	2.219	1.130	1.204
Ar	d	0.997	0.776	0.862
	H	3.469	2.462	2.677
Kr	d	1.055	0.617	0.689
	H	5.507	2.532	2.857
Xe	d	1.175	0.684	0.940
	H	6.805	3.109	4.600

[a] Ganas and Green (1971).

states only, including the ground state but not the inner occupied states. The best fits in this case are denoted by the circular symbol in Fig. 10, and the best-fit parameters are given in Table XI. The data points were weighted as the inverse of the experimental values. Also included in Table XI are the values obtained by GSZ, who searched over the occupied states only. It is evident that the best parameters from the three kinds of search vary somewhat.

Ganas and Green used the radial wave functions for the IPM model with parameters from search (b) above to calculate oscillator strengths and total cross sections for transitions from the ground state to the excited states. To illustrate their results we show in Fig. 11 the relative

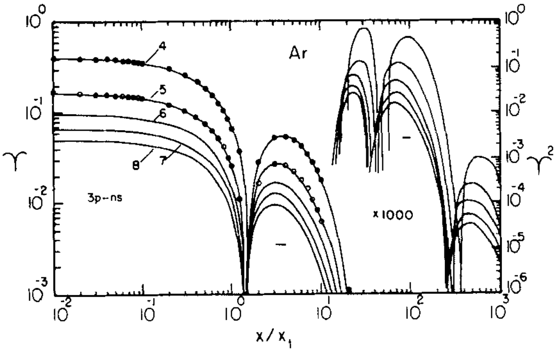

Fig. 11. Curves indicating reduced oscillator amplitude (left scale) and oscillator strengths (right scale) for argon vs. reduced square of momentum transfer. The solid dots give representative analytic fit using three adjustable parameters. The open circles give a representative fit using only one adjustable parameter (Ganas and Green, 1971).

oscillator amplitudes (Υ) and strengths ($f \sim Υ^2$) for $3p$–ns transitions in Ar.

Log–log paper is used to cover a large range of ξ and Υ and to further save space Υ values beyond the second node are multiplied by 10^3. The negative signs between the nodes (to be denoted by ξ_1, ξ_2, etc.) denote regions of negative Υ values which lie between ξ_1 and ξ_2; ξ_3 and ξ_4; ξ_5 and ξ_6; etc. Note that the regularities in the amplitudes for these Rydberg series when presented as a function of the reduced variable $\xi = a_0{}^2K^2R/W$ are indeed remarkable. A foretaste of such a regularity was noted earlier by Green and Dutta (1967) for helium transitions. However, their calculations involved results with much simpler structure and covered a far more restricted range of ξ.

The values of Υ(0) or $Υ^2(0)$ are measures of the relative optical oscillator strengths in Rydberg series. Previously Green and Dutta (1967), based upon their helium studies, proposed the rule

$$f_n = f^*/(n - \delta)^3. \tag{47}$$

This is a simplification of a rule which was suggested by Fano and Cooper (1965). Equation (47) suggests that $Υ_{0n} = Υ_0{}^*(n - \delta)^{-3/2}$. In Fig. 12, we show the values of $Υ_{0n}{}^{-2/3}$ vs. n. These follow straight lines rather well, thus confirming Eq. (47). The values of $Υ_0{}^*$ and δ for the various gases as determined by least-squares fits are given in Table XII. Note that the quantum defects obtained differ from those used to characterize the energies of the s states in the transition as given in Table X. This might have been expected since, of course, the quantum defects of the ground states are also involved.

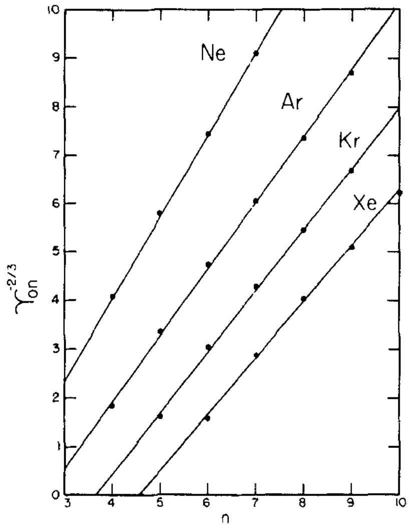

Fig. 12. The functions $\Upsilon_{0n}^{-2/3}$ vs. n for n_0p–ns transitions, illustrating validity of Eq. (47) (Ganas and Green, 1971).

TABLE XII

QUANTUM DEFECTS AND RELATIVE OPTICAL OSCILLATOR STRENGTH CONSTANTS FOR n_0p–ns TRANSITIONS[a]

	δ	Υ_0^*	Υ_0^{*2}
Ne	1.62	0.453	0.205
Ar	2.57	0.630	0.396
Kr	3.63	0.716	0.512
Xe	4.57	0.804	0.647

[a] Ganas and Green (1971).

While the behavior of Υ beyond ξ_2 is quite complicated, the behavior for $\xi < \xi_2$ is fairly simple. Since there is a rapid fall-off in each case beyond ξ_2, GG ignored this domain but sought a convenient quantitative representation of $\Upsilon(\xi)$ and hence $f(\xi)$ within ξ_2. They had good success with the representation

$$\Upsilon(\xi) = \Upsilon_0(e^{-\gamma_0\xi} - \kappa\xi e^{-\gamma_1\xi}). \tag{48}$$

The dots shown on Fig. 11 for Ar are examples of the fits within ξ_2 which can be achieved by fitting γ_0, κ, and γ_1, to the results of such calculations. Ganas and Green give the values of the parameters for various Rydberg series obtained by use of a nonlinear least-square program. Their studies indicated that $\gamma_0 \sim 1.25$, $\gamma_1 \sim 0.40$ for all cases. Thus good fits could be obtained simply by conducting restricted search on κ alone using the fixed decay lengths γ_0, γ_1, and the Υ_0 previously obtained. The open circles in Fig. 11 are illustrative of the fits so obtained.

In their study GG examined the literature on optical oscillator strengths and found that the rule $f_0 \approx 1.5\,\Upsilon_0{}^2$ was quite reasonable for normalizing their calculated GOS's.

One important advantage of Eq. (48) for the oscillator amplitudes is that the corresponding generalized oscillator strengths and differential cross sections are analytic [see Eq. (37)] and furthermore the total cross section [see Eq. (39)] is analytically integrable.

The utility of the work of GG lies not only in their direct usefulness in providing approximate high-energy electron impact cross sections, but in addition by the use of certain reasonable phenomenological rules proposed by Green and Dutta (1967) these results can be used to generate approximate distorted generalized oscillator strengths (DGOS) which are useful for low-energy impacts (e.g., 25–250 eV).

VIII. Distorted Wave Calculation of Excitation Cross Sections

A. The IPM Wave Functions

To extend the work of Ganas and Green to lower-energy regions, Sawada, Purcell, and Green (SPG) (1971) investigated the effects of distortion upon generalized oscillator strengths. For the incident and outgoing waves they used wave functions distorted by the same IPM potential that was used by Berg, Purcell, and Green for the elastic scattering analysis (see Section VI). As in GG the ground and excited state atomic wave functions ψ_0 and ψ_n were constructed from single-electron wave functions for bound states in the IPM potential of the form of Eq. (4) using the GG parameters. This same potential was used in the calculation of the exchange scattering amplitude.

The ground-state wave function ψ_0 was taken as the Slater determinant of $(n_0 p)^6$ electron wave functions, and the excited-state wave function ψ_n was constructed as a properly antisymmetrized combination of $(n_0 p)^5 n l_n$ product wave functions LS-coupled to produce a state with the given final state angular momenta (LSJM). The analysis proceeds utilizing advanced methods in collision theory which have been described by Goldberger and Watson (1964), Wu and Ohmura (1962), Messiah (1965), and others.

B. Scattering Amplitudes

Let us denote by $\phi_0(j)$ a plane wave function for the jth electron, by $\psi_0(\bar{j})$ the ground-state atomic wave function indicating the situation that the jth electron is the projectile and hence not present in ψ_0, and by $\Psi_0^{(+)}(j)$ the total wave function in which only the jth electron has an incoming plane wave in the incident channel but all electrons have outgoing spherical waves in all open channels. Similarly for ϕ_n, ψ_n, and $\Psi_n^{(-)}$ for the final state, where $\Psi_n^{(-)}$ now has the out going boundary condition. Then the exact amplitude for the direct process in which electron 0 comes in and is scattered out inelastically by exciting the atom from the $(n_0p)^6$ to the $(n_0p)^5nl_n$ configuration can be written as proportional to

$$M^{\mathrm{D}} = \langle \psi_n(\bar{0})\phi_n(0) | \sum_{j\neq 0} v_{0j} + U(0) | \Psi_0^{(+)}(0) \rangle \tag{49a}$$

$$= \langle \Psi_n^{(-)}(0) | \sum_{j\neq 0} v_{0j} + U(0) | \psi_0(\bar{0})\phi_0(0) \rangle \tag{49b}$$

in the post- and prior-interaction form, respectively. Here $U(j)$ is the nuclear Coulomb interaction acting upon the jth electron, and v_{ij} is the Coulomb interaction between the ith and the jth electrons. The sum $\sum v_{0j}$ is over all the $(n_0p)^6$ electrons in the ground-state atom, which will be denoted by $1, 2, \ldots, 6$.

The amplitude for the exchange process in which the incident electron 0 drops into the nl_n orbit while electron 1 is knocked out from the n_0p orbit is proportional to

$$M^{\mathrm{E}} = \langle \psi_n(\bar{1})\phi_n(1) | \sum_{j\neq 1} v_{1j} + U(1) | \Psi_0^{(+)}(0) \rangle \tag{50a}$$

$$= \langle \Psi_n^{(-)}(1) | \sum_{j\neq 0} v_{0j} + U(0) | \psi_0(\bar{0})\phi_0(0) \rangle \tag{50b}$$

in the post- and prior-interaction forms, respectively.

Introducing a distorting potential $V_0(j)$ and its eigenfunction $\chi_0^{(\pm)}(j)$ for an electron in the incident channel,

$$[(E - E_0) - K_j - V_0(j)]\chi_0^{(\pm)}(j) = 0, \tag{50c}$$

where K_j is the kinetic energy operator, E is the total energy, and E_0 is the eigenenergy of ψ_0, and similarly for $V_n(j)$ and $\chi_0^{(\pm)}(j)$ for the outgoing channel, and using the Gell–Mann–Goldberger relation for our problems with two potentials, we obtain from Eq. (49) and Eq. (50)

$$M^{\mathrm{D}} = \langle \psi_n(\bar{0})\chi_n^{(-)}(0) | \sum_{j \neq 0} v_{0j} + U(0) - V_n(0) | \Psi_0^{(+)}(0) \rangle \tag{51a}$$

$$= \langle \Psi_n^{(-)}(0) | \sum_{j \neq 0} v_{0j} + U(0) - V_0(0) | \psi_0(\bar{0})\chi_0^{(+)}(0) \rangle \tag{51b}$$

and

$$M^{\mathrm{E}} = \langle \psi_n(\bar{1})\chi_n^{(-)}(1) | \sum_{j \neq 1} v_{1j} + U(1) - V_n(1) | \Psi_0^{(+)}(0) \rangle \tag{52a}$$

$$= \langle \Psi_n^{(-)}(1) | \sum_{j \neq 0} v_{0j} + U(0) - V_0(0) | \psi_0(\bar{0})\chi_0^{(+)}(0) \rangle . \tag{52b}$$

The distorted wave approximation corresponds to approximating the exact total wave functions $\Psi_0^{(+)}$ and $\Psi_n^{(-)}$ by their elastic channel components, $\psi_0\chi_0^{(+)}$ and $\psi_n\chi_n^{(-)}$, respectively. This takes advantage of the fact that elastic scattering usually is the dominant process and hence other components in $\Psi_0^{(+)}$ and $\Psi_n^{(-)}$ can be ignored. In other words, the coupling between pairs of states is assumed to be small.

Under this approximation, the direct amplitude becomes

$$M^{\mathrm{D,DW}} = 6\langle \psi_n(\bar{0})\chi_n^{(-)}(0) | v_{01} | \psi_0(\bar{0})\chi_0^{(+)}(0) \rangle , \tag{53}$$

where the orthogonality of ψ_0 and ψ_n has been used to eliminate the contributions of $U(0) - V_n(0)$ and $U(0) - V_0(0)$ in Eq. (51), thereby eliminating the post–prior asymmetry. Due to the antisymmetry of ψ_0 and ψ_n, each $n_0 p^6$ electron contributes the same and hence the factor 6.

The potential of Berg, Purcell, and Green for elastic scattering from the rare gases was used for V_0 and V_n for the direct amplitude with the GG parameter. For V_n it was assumed that the influence of a single electron excited in the final state upon the outgoing electron is small compared to the rest of the interactions and V_n was set equal to V_0

Since $V(r)$ vanishes exponentially at large distance, the direct amplitude can be computed as

$$M^{\mathrm{D}} = (M^{\mathrm{D}} - M^{\mathrm{B}}) + M^{\mathrm{B}}, \tag{54}$$

where M^{B} is the Born amplitude. For the last term, i.e., M^{B}, SPG essentially used the results of Ganas and Green.

For the first term of Eq. (54), i.e., $M^{\mathrm{D}} - M^{\mathrm{B}}$, the partial wave expansion approach is used. This follows the strategy of work of Dutta, Wilson, and Green (1968), Ganas, Dutta, and Green (1970), and Purcell, Berg, and Green (1970) as applied to elastic scattering. Since the effect of distortion vanishes rapidly at moderately large l values due to the exponential damping of $V(r)$, the difference $M^{\mathrm{D}} - M^{\mathrm{B}}$ as a function of l vanishes rapidly at higher l values. This is unlike M^{D} itself, which requires a very large number of partial waves due to the long-range nature of the Coulomb interaction.

For the exchange amplitude, difficulties arise which are associated with a post–prior asymmetry. These difficulties can be circumvented if we use the potential for the bound-state wave functions for the distorting potential of the exchange amplitude. Then the bound states and scattering states become orthogonal to each other and the post–prior asymmetry of $M^{\mathrm{E,DW}}$ disappears. We find

$$M^{\mathrm{E,DW}} = \langle \psi_n(\bar{1})\chi_n^{(-)}(1)\,|\,v_{10}\,|\,\psi_0(\bar{0})\chi_0^{(+)}(0)\rangle. \tag{55}$$

This same expression has been obtained formally by Shelton and Leherissey (1971) and Cartwright (1967) who used HF potentials rather than phenomenological analytic potentials.

The total scattering amplitude for the transition $(n_0 p)^6 \rightarrow (n_0 p)^5 n l_n$ is

$$M^{\mathrm{DW}} = M^{\mathrm{D,DW}} - 6M^{\mathrm{E,DW}}. \tag{56}$$

To obtain the differential cross section we use (Goldberger and Watson, 1964)

$$\frac{d\sigma}{d\Omega} = \frac{k'}{k_0}\left(\frac{m_e}{2\pi\hbar^2}\right)^2 \frac{1}{2} \sum |M^{\mathrm{DW}}|^2, \tag{57}$$

where the sum is over initial and final magnetic substates. We may now define the DGOS by using the inverse of Eq. (37), i.e.,

$$f_d(\xi, E) = \frac{\pi}{q_0}\left(1 - \frac{W}{E}\right)^{-1/2} \xi W^2 \frac{d\sigma}{d\Omega}. \tag{58}$$

This goes over to the usual GOS in the limit of the Born approximation. The integrated cross section σ may be obtained using Eq. (39) but with $f_d(\xi, E)$ in place of $f(\xi)$.

C. Results

We refer the reader to SPG for the more tedious computational details which involve considerable angular momentum algebra.

The theoretical predictions of DGOS are illustrated in Fig. 13 for Ar $(3p)^6 \rightarrow (3p)^5 4s$ excitations at various incident energies. The solid curves represent the results of the Born approximation. The GOS when extrapolated to zero momentum transfer yield the optical oscillator strengths

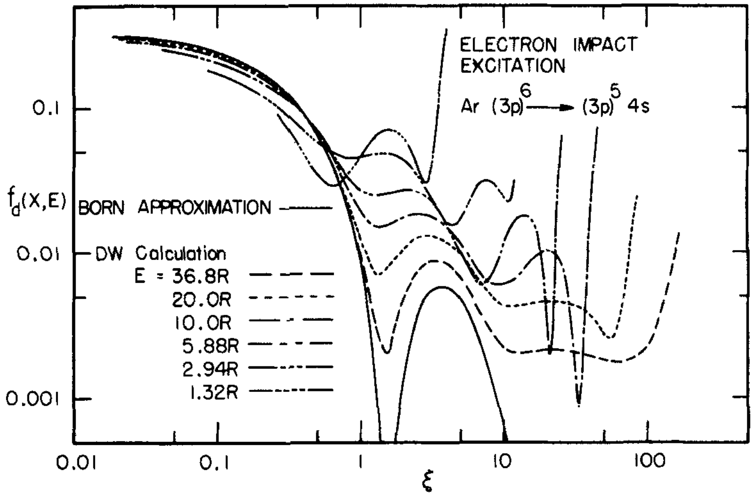

Fig. 13. Averaged DGOS for the electron impact excitation of Ar from $(3p)^6$ to $(3p)^5 4s$ configurations as a function of ξ at various incident energies as indicated in the figure (Sawada *et al.*, 1971).

0.327 for Ar. In reality, these strengths are split among components of the fine structure. Therefore, they should be compared with the sums of experimentally determined ^1P and ^3P strengths. The fact that the extrapolated values, although somewhat large, come fairly close to the experimental optical oscillator strengths (Lawrence, 1968; Lewis, 1967) indicates that the LS coupling scheme is reasonable at least for this excitation.

As can be seen from Fig. 13, the effect of distortion remains small, and hence the Born approximation remains good, for small momentum transfer even at energies as low as $10R$. The effect of distortion sets in for larger momentum transfer, and in fact even at $36.8R$ the Born limit is not quite reached beyond the first diffraction minimum. The results at low energies, where the exchange effects are appreciable, are presented as the sum of singlet and triplet excitations.

Not many data are available to compare with the SPG results. Fortunately the low-energy data (only relative) of Nicoll and Mohr (1933) in

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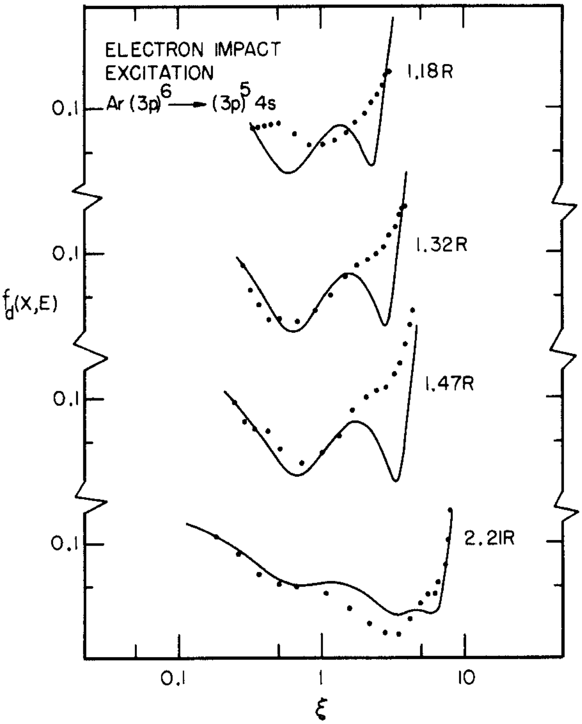
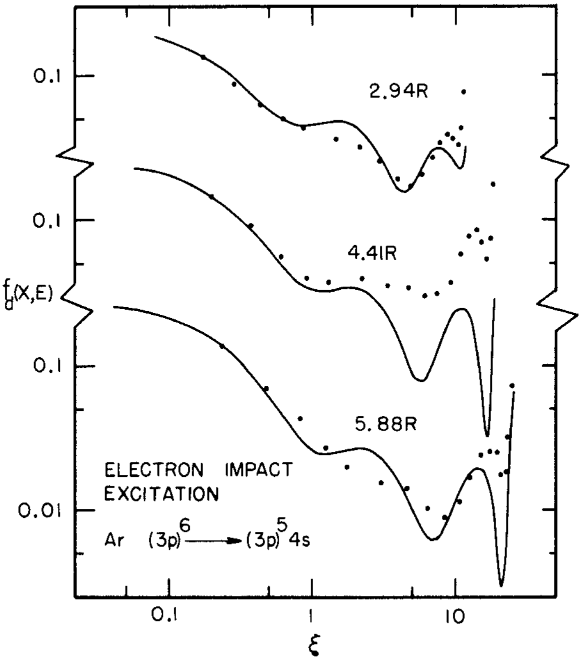
Fig. 14. Low-energy electron impact excitation of Ar $3p \rightarrow 4s$. The dots are the experimental DGOS transformed from the cross section data given by Nicoll and Mohr, and the solid curves are the sums of predictions for the singlet and triplet final states (Sawada *et al.*, 1971).


ELECTRON IMPACT
EXCITATION
Ar $(3p)^6 \rightarrow (3p)^5 4s$
1.18R
1.32R
1.47R
2.21R
0.1
0.1
0.1
0.1
$f_d(X,E)$
0.1
1
10
ξ


2.94R
4.41R
5.88R
ELECTRON IMPACT
EXCITATION
Ar $(3p)^6 \rightarrow (3p)^5 4s$
0.1
0.1
0.1
0.01
$f_d(X,E)$
0.1
1
10
ξ

which the energy resolution in their work is low allows a direct comparison with the average theoretical cross sections. For Ar the cross section data were first transformed to experimental DGOS using Eq. (58), by normalizing them arbitrarily to the theoretical values at $\theta = 10°$. These are shown in Fig. 14 along with the theoretical results.

At energies larger than $2.21R$ the theoretical values of the DGOS $f_d(x, E)$, for Ar have two peaks and all go up sharply at the extreme backward angles. These expectations seem to be borne out by the experimental data.

The integrated cross sections are presented in Fig. 15. Although the effect of distortion on the DGOS is important, as we have just seen, its

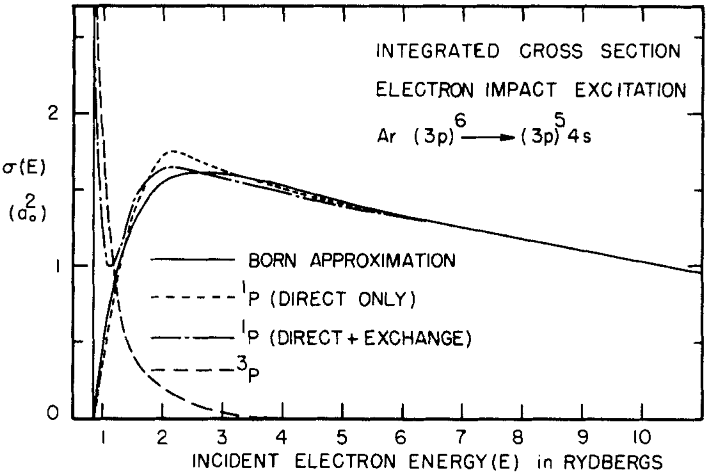


Fig. 15. Integrated cross section σ (in a_0^2) for Ar $3p \rightarrow 4s$ electron impact excitation. The solid curve is for the Born approximation, the short-dash curve is for the singlet cross section with direct process only, the dot-dash curve is for the singlet cross section including exchange, and the long-dash curve is for the triplet cross section (Sawada *et al.*, 1971).

effect on the integrated cross section σ is much less important, so that the Born approximation seemingly holds quite well down to fairly low energies. Apparently at forward angles where the main contribution to σ comes, the Born approximation is good down to relatively low energies. For even lower energies where the Born approximation fails at forward angles, there occurs a certain amount of compensation between the contributions from forward angles and those from backward angles.

There is a resonance-like peak in σ near threshold for Ar as shown in Fig. 15. There is no sharp resonance in phase shifts for Ar, although the d-wave phase shifts rise through 90° at around $2.8R$ in the incident channel and at the corresponding energy in the outgoing channel, which may be responsible for bringing σ closer to the Born approximation. The peak at threshold is, however, due to the finite contribution of the exchange amplitude at threshold caused by the use of the distorting potential with an attractive Coulomb tail (Massey and Burhop, 1969; Drukarev, 1965).

To summarize, the distorted wave method presented here gives a reasonably reliable estimate of averaged DGOS and integrated cross sections over a wide range of energies except perhaps at very low energies.

IX. Summary, Discussion, and Conclusions

In the work of GSZ a simple analytic atomic IPM potential with a continuous first derivative was found which uses only two parameters. With one parameter (α) established for the entire periodic table and one parameter (d) adjusted for each element, fits to all occupied state energies can be achieved within a few percent. The fact that these IPM energies also agree approximately with the experimental removal energies confirms the approximate validity of Koopmans (1933) theorem for atoms.

We have noted throughout this work that the adjustment of the two parameters of the GSZ–IPM model is quite sensitive to the "data" or weighting used in the adjustment. Part of this is due to the restrictive and oversimplified nature of the model, which might be removed in later studies. The radial wave functions obtained from the GSZ–IPM potential are less sensitive to parameter adjustments and are usually very close to Hartree–Fock wave functions or Hartree–Fock–Slater wave functions. Certainly for the sake of applications these wave functions are far more realistic than hydrogenic wave functions which despite the lapse of 45 years are still used in some studies (Inokuti, 1971).

Since our IPM central potential is common to all the electrons in an atom, it provides a complete and orthogonal basis which is very helpful for the study of residual perturbations. For some purposes it might be desirable to adjust the parameters d and H for each l value, which would permit greater precision yet still preserve the orthogonality property. This, in effect, would build in nonlocality, which may be a simple way to approximate the remaining exchange, polarization, and correlation effects. It remains for future work to explore such elaborations of the model.

For excited states the polarization potential would be expected to take on greater importance. The change of parameters noted by Ganas and Green is probably an empirical accommodation to this need.

For scattering calculations an imaginary potential should also be expected, at least from experience with the nuclear optical model. In addition, dynamical polarization and exchange terms such as those studied for the case of e–He scattering by Callaway *et al.* (1968) should also arise. It is reasonable to hope that the analytic IPM optical potential can be extended to incorporate such terms. At present, experimental data are lacking to test such models with complex atoms.

The primary purpose of this entire series of studies has been to use a realistic analytic IPM model of the electron–atom interaction to assist in the programmatic generation of atomic properties that are needed in applications. In particular, the problem of the deposition of electron energy in matter has been the specific focus of most of these studies. With such an IPM model we can by-pass some of the present obstacles such as the lack of Hartree–Fock excited-state wave functions or the general mathematical complexity of many-body theory. The simple analytic IPM model permits one to explore broad systematic gross structures and to seek out regularities which might be used to organize experimental data. An example of such regularities is the approximate analytic representation for the generalized oscillator strengths in Rydberg series. This provides a useful and compact way of introducing sets of cross sections into such applied calculations in which all channels of energy loss must be considered.

The work of Sawada, Purcell, and Green is a fitting conclusion for this study since it utilizes most of the tools developed in the previous bound state and scattering studies. The motivation of this work again has been the deposition problem, particularly for secondary electrons. No matter what the primary particles are the secondary particles are usually electrons in the low-energy region (10 to 100 eV) which lies below the domain of validity of the Born approximation. Thus a realistic attempt to deal with distortions is essential to a basic understanding of the energy deposition process. The SPG calculation can serve as a firmer basis for incorporating empirical DW modification into realistic Born approximation results than was previously available.

The two articles by Berg and Green (1973) and by Bass, Green, and Wood (1973) which follow are further studies in this series and serve to round out our view as to the usefulness of the present model, its limitations, and also the directions which might be taken to remove these limitations.

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The writer would like to thank Professors J. C. Slater and James Conklin for their help in the early phases of this work. He particularly wishes to express his appreciation to his collaborators Shureen Dutta, Alex Zachor, David Sellin, Jorg Darewych, Perry Ganas, James Purcell, Richard Berg, and Tatsuro Sawada, not only for their contributions to this series of studies, but also for the education in quantum mechanical techniques which has been concomitant to the entire endeavor.

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An Analytic Independent Particle Model for Atoms

II. Modified Hartree–Fock Calculations for Atoms*

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I. Introduction

Most atomic calculations are based on the Hartree–Fock self-consistent field model, in which the motion of each electron is governed by a potential field due to the others. True Hartree–Fock calculations are complicated because the potential is nonlocal and because the self-consistency requirement leads to an iterative procedure. Most local approximations to the nonlocal (exchange) term in the potential start from Slater's free-electron gas assumption (Slater, 1951).

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An alternative procedure is based on the analytic independent particle model (IPM), which has been applied in a number of studies which are summarized in the preceding chapter in this volume (Green, 1973).

It would be desirable to have an *ab initio* method of determining IPM potential parameters which include exchange effects. In this chapter we shall consider a method in which the total energy of an atom, whose one-electron wave functions are eigenfunctions of the IPM potential, is minimized with respect to the potential parameters. The total energy may be calculated either in the true HF sense or by using the HFS $X\alpha$ approximation.

II. Formulation of Variational Problems

We assume that the one-electron wave functions of the atom are

$$U_{nlmi}(\mathbf{r}, s) = r^{-1}P_{nl}(r)Y_{lm}(\theta, \phi)\Gamma_i(s), \tag{1}$$

where n is the principal quantum number; l, the orbital angular momentum; m, the magnetic quantum number; and $\Gamma_i(s)$ is the spin eigenfunction. These functions are constrained to satisfy the eigenvalue equation

$$[-\nabla^2 + V(r)]U_{nlmi}(\mathbf{r}, s) = E_{nl}\, U_{nlmi}(\mathbf{r}, s), \tag{2}$$

where $V(r)$ is the analytic IPM potential of Green, Sellin, and Zachor (GSZ) (1969)

$$V(r) = 2r^{-1}[N\Upsilon - Z], \qquad \Upsilon = 1 - \Omega(r) = 1 - [(e^{r/d} - 1)H + 1]^{-1}, \tag{3}$$

with adjustable parameters H and d, for an atom containing $N + 1$ electrons and a nuclear charge Z.

The expectation value of the total energy, averaged over all Slater determinants which can be constructed from a given configuration, is (Slater, 1960)

$$\bar{E} = \sum_{nl} W_{nl}[I_{nl} + \tfrac{1}{2} \sum_{n'l'} (W_{n'l'} - \delta_{nl;\, n'l'})M_{nl;\, n'l'}], \tag{4}$$

where

$$W_{nl} = \text{number of electrons in } nl \text{ shell}, \tag{5}$$

$$I_{nl} = \int_0^\infty P_{nl}(r)\left[-\frac{d^2}{dr^2} - \frac{2Z}{r} + \frac{l(l+1)}{r^2}\right]P_{nl}(r)\, dr, \tag{6}$$

$$\delta_{nl;n'l'} = 1 \qquad \text{if } n = n' \text{ and } l = l', \tag{7}$$
$$\qquad = 0 \qquad \text{otherwise.}$$

$$M_{nl;nl} = F^0_{nl;nl} - (4l+1)^{-1} \sum_{k=1}^{\infty} c^k(l0;\, l0) F^k_{nl;nl},$$

$$M_{nl;n'l'} = F^0_{nl;n'l'} - \tfrac{1}{2}[(2l+1)(2l'+1)]^{-1/2} \sum_{k=0}^{\infty} c^k(l0;\, l'0) G^k_{nl;n'l'},$$
$$n \neq n' \quad \text{or} \quad l \neq l', \tag{8}$$

with

$$F^k_{nl;n'l'} = 2 \int_0^\infty \int_0^\infty P_{nl}(r_1) P_{n'l'}(r_2) \frac{r<^k}{r>^{k+1}} P_{nl}(r_1) P_{n'l'}(r_2)\, dr_1\, dr_2,$$

$$G^k_{nl;n'l'} = 2 \int_0^\infty \int_0^\infty P_{nl}(r_1) P_{n'l'}(r_2) \frac{r<^k}{r>^{k+1}} P_{nl}(r_2) P_{n'l'}(r_1)\, dr_1\, dr_2, \tag{9}$$

where

$$\begin{aligned} r< &= \text{smaller of } (r_1, r_2), \\ r> &= \text{larger of } (r_1, r_2). \end{aligned} \tag{10}$$

The $c^k(lm;\, l'm')$ are tabulated (Appendix 20, Slater, 1960). The first term in Eq. (4) accounts for kinetic energy and nuclear attraction, while the second is due to interaction between electron pairs.

With the assumption that the $P_{nl}(r)$ satisfy the radial differential equation

$$\left[-\frac{d^2}{dr^2} + V(r) + \frac{l(l+1)}{r^2} \right] P_{nl}(r) = E_{nl} P_{nl}(r), \tag{11}$$

derived from Eq. (2), the variational problem of $\bar{E}$ with respect to the $P_{nl}(r)$ becomes a variational problem with respect to the parameters d and H of the potential $V(r)$. We thus obtain a first principles estimate of the "best" IPM potential of the form given by Eq. (3).

III. Calculational Procedures

Previous results (Green *et al.*, 1969) have indicated that to a good approximation

$$K = H/d \cong (N)^{0.4}. \tag{12}$$

This suggests that d and K $(=H/d)$ be used as variational parameters instead of d and H. In the calculations described here, this parameterization was used.

To locate the minimum of E in d–K space three methods are used: (A) the Brute Force (Roothan and Bagus, 1963); (B) the Grid Search (Arndt and MacGregor, 1966); and (C) the Quadratic Fit. In the last case if the location of the minimum is approximately known, $\bar{E}$ is computed at a set of six points in the vicinity. The minimum is located by fitting a quadratic surface through these points.

Method A proved to be the most reliable of the three methods, but since it was also the most costly this method was applied only for $Z \leq 21$. For $22 \leq Z \leq 30$, Method B was used with Method C serving as a check. It was found in this region that K approximately satisfied the relation

$$K(Z+1) = K(Z) + 0.045. \tag{13}$$

With this initial guess for K only one minimization was necessary for each parameter. Hence, it was decided to minimize only with respect to d for $30 < Z < 36$ and use Method C as a check.

IV. Results and Discussion

In Table I we present the potential parameters obtained for $2 \leq Z \leq 36$ and for $Z = 50$, 70, and 90. The fourth column gives the deviation of the results (in parts per million) with respect to the Hartree–Fock total energy. It is satisfying that most of the results are within 100 ppm from true Hartree–Fock. In cases where the total HFS energies were available, the BGW results were usually closer to HF.

The fifth column of Table I gives the results of the HFS $X\alpha$ method (Kmetko, 1971). The $X\alpha$ method differs from the original HFS method in that in the former the coefficient α of the Slater exchange term in the potential is varied to minimize the total energy. We see that the present results (BGW) are competitive with $X\alpha$, and are even better for most lighter atoms. The agreement between BGW and HF for helium is excellent, showing that two parameters are sufficient for describing a single shell.

In Figs. 1 and 2 we plot the BGW parameters d and K, for $Z \leq 36$, along with the results obtained by fitting eigenvalues to HF results (Green *et al.*, 1969). The correlation between the two sets of results is excellent.

TABLE I

VALUES OF d AND k MINIMIZING TOTAL ENERGY.
DEVIATION (D) GIVES 10^6 $(\mathrm{E}-\mathrm{E}_{\mathrm{HF}})/\mathrm{E}_{\mathrm{HF}}$

Z	d	K	D(BGW)	$D(X\alpha)$	Z	d	K	D(BGW)	$D(X\alpha)$
2	0.382	1.77	1.7	230.0	21	1.259	3.64	59.2	33.6
3	0.462	1.75	242.2	191.0	22	1.203	3.69	61.7	33.6
4	0.769	1.88	116.7	161.0	23	1.138	3.73	66.7	33.4
5	0.970	2.00	152.9	158.0	24	0.967	3.78	65.1	37.4
6	0.950	2.13	119.5	142.0	25	0.968	3.82	71.3	33.0
7	0.848	2.27	82.9	127.0	26	0.894	3.87	72.5	32.4
8	0.737	2.41	60.2	120.0	27	0.822	3.91	71.2	31.8
9	0.641	2.56	50.3	110.5	28	0.778	3.98	73.0	31.2
10	0.560	2.72	38.9	107.0	29	0.662	4.00	73.0	35.8
11	0.584	2.85	68.0	84.4	30	0.646	4.05	64.7	31.8
12	0.670	3.01	55.1	70.0	31	0.649	4.11	47.2	25.7
13	0.860	3.17	78.6	60.0	32	0.656	4.16	43.7	27.2
14	0.980	3.26	71.0	52.9	33	0.670	4.23	43.3	19.5
15	1.055	3.33	57.2	47.3	34	0.685	4.29	40.0	17.5
16	1.070	3.39	44.0	43.0	35	0.693	4.34	38.2	15.9
17	1.089	3.45	38.0	39.8	36	0.719	4.41	27.7	14.7
18	1.049	3.50	38.5	36.9	50	0.875	4.97	24.2	9.1
19	1.166	3.55	50.1	34.2	70	0.625	5.48	60.9	8.2
20	1.288	3.60	51.7	31.8	90	0.875	6.17	28.9	3.1

The parameter K for $Z \geq 10$ was found to fit very well the functional form (see Fig. 3).

$$K = 1.17Z^{0.37}. \tag{14}$$

This Z dependence is in agreement with Gaspar's results (1971) for the Z dependence of the linear scaling parameter for neutral atoms. In fact, from the effective electronic charge density

$$\rho(r) = (4\pi)^{-1}N\nabla^2 r^{-1}\Omega(r), \tag{15}$$

one finds

$$\langle r^{-1}\rangle = N^{-1}\int r^{-1}\rho(r)\,d\tau = K. \tag{16}$$

Although the actual charge density is not exactly given by Eq. (15), since $V(r)$ contains exchange effects, one nevertheless expects Eq. (16) to hold approximately, and Fig. 4 shows this to be the case, with K given

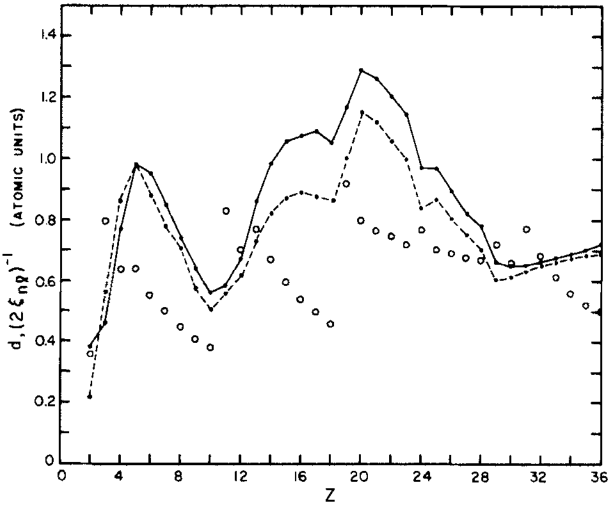

Fig. 1. Plot of parameter d vs. Z. Solid line gives present results. Dashed line represents results of Green, Sellin, and Zachor (1969). Open circles are $(2\xi_{nl})^{-1} = \frac{1}{2}(-\varepsilon_{nl})^{-1/2}$ for outermost orbitals using Mann's eigenvalues ε_{nl} of Mann (1968).

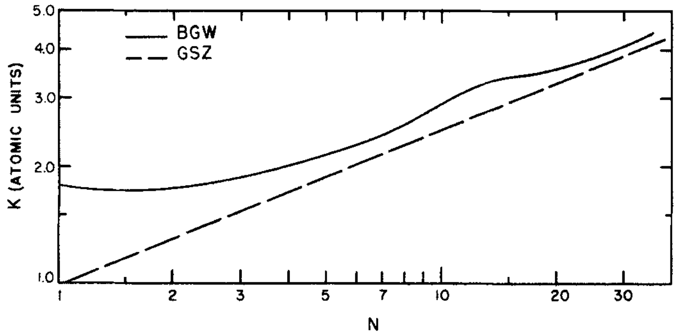

Fig. 2. Parameter K vs. $N = Z - 1$. Solid line gives present results, dashed line $K = N^{0.4}$ (Green *et al.*, 1969).

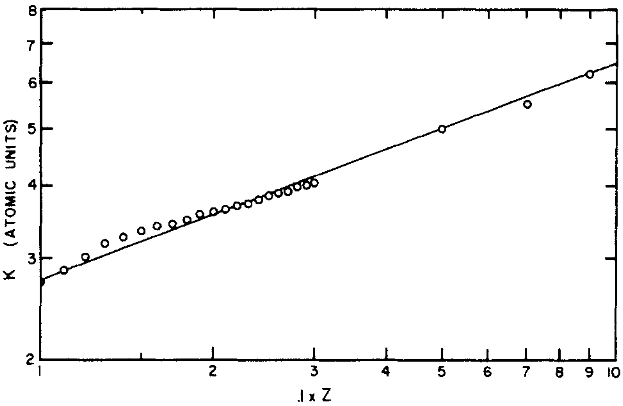

Fig. 3. Parameter K vs. Z using present results. Solid line is $K = 1.17\,Z^{0.37}$.

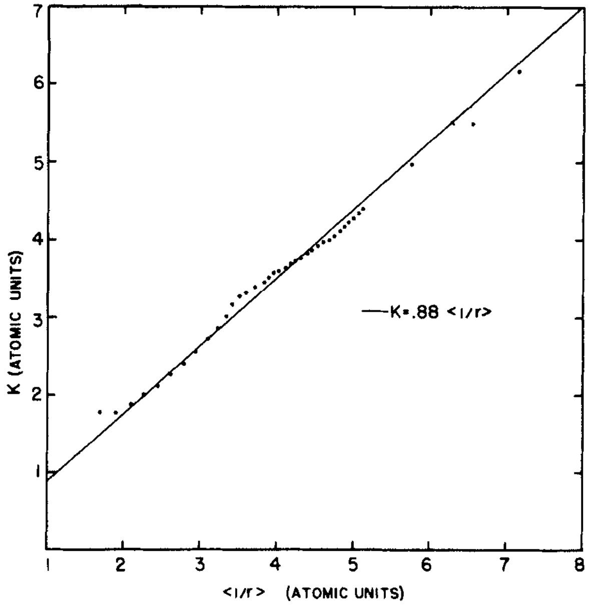

Fig. 4. Parameter K vs. $\langle r^{-1}\rangle$. Solid line is $K = 0.88\langle r^{-1}\rangle$.

approximately as

$$K = 0.88\langle r^{-1}\rangle. \tag{17}$$

For the parameter d it is a different story, however. The fluctuations of the parameter with Z, as obtained in the GSZ calculations, hinted that d depends in some way on the atomic shell structure. The excellent correlation between the values of d obtained in the present calculation and those obtained by GSZ is strong confirmation of this suspicion. We wish to analyze this situation a little further.

For asymptotically large r the screening function $\Omega(r)$ behaves as

$$\Omega \approx (1/Kd)e^{-r/d}; \qquad r \to \infty. \tag{18}$$

This corresponds to a radial charge density

$$4\pi r^2\rho(r) = r^2\nabla^2(N/Kdr)e^{-r/d} = (Nr/Kd^3)e^{-r/d}. \tag{19}$$

In HF or modified HF models the charge density at large r is dominated by the outermost orbital, whose contribution is, to lowest order

$$W_{nl}P_{nl}^2 \propto W_{nl}r^{\gamma_{nl}}e^{-2\xi_{nl}r}, \qquad r \to \infty, \tag{20}$$

where W_{nl} is the occupation number of the orbital, $-\xi_{nl}{}^2$ is the one-electron eigenvalue, and

$$\gamma_{nl} = 2(\xi_{nl})^{-1}. \tag{21}$$

This is derived by using Eq. (11) with the asymptotic behavior

$$V = -2/r, \qquad r \to \infty. \tag{22}$$

A comparison of (19) and (20) shows that the appropriate value of the parameter d depends on ξ_{nl}, i.e., how fast the density is decaying as $r \to \infty$, the occupation number W_{nl}, and the normalization factor for the right-hand side of (20). While the effect of the latter cannot be accurately assessed, we illustrate in Fig. 1 the effects of ξ_{nl} and W_{nl} by the plot of $(2\xi_{nl})^{-1}$ vs. Z. If d depended only on ξ_{nl} the plot should coincide with that of d. However, only a loose correlation occurs. The effect of increasing W_{nl} is clearly evident in all shells except the $2p$ shell. Increasing the occupation number W_{nl} increases the charge density at large r, requiring an increase in d in Eq. (19). This partly counterbalances the decreases in $(2\xi_{nl})^{-1}$ as electrons are being added to the shell.

In Fig. 5 we plot for krypton the differences between the screening functions $\Omega(r)$ of Eq. (3) obtained by other methods and that obtained by the present method. The GSZ results are for the parameters plotted in

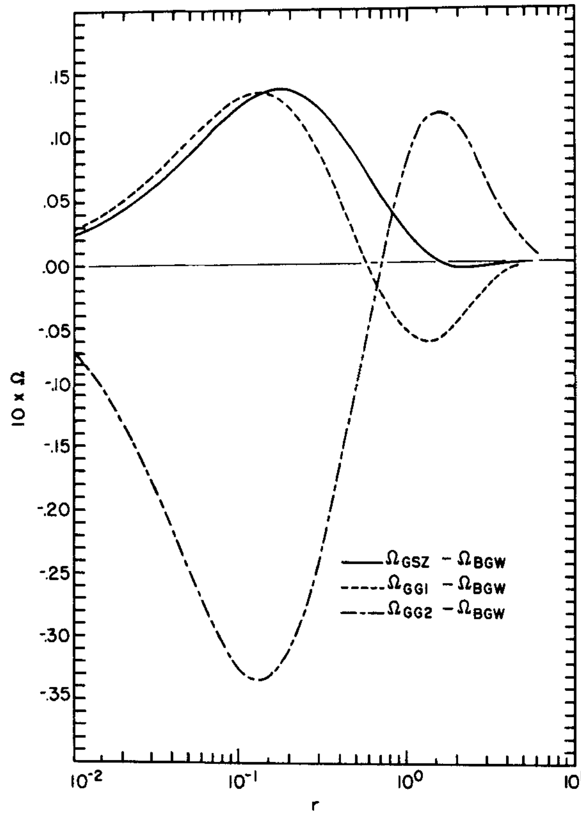

Fig. 5. Screening functions $\Omega(r)$ for krypton for different sets of parameters. Solid line is Ω_{GSZ}–Ω_{BGW}, dashed line is Ω_{GGI}–Ω_{BGW}, alternating dots and dashes Ω_{GGII}–Ω_{BGW}.

Figs. 1 and 2 (least-squares fit to HF eigenvalues), while GGI and GGII are results obtained by Ganas and Green (1971) by least-squares fits of eigenvalues to experimental data for the ground and excited states, including all orbitals of the ground state in GGI, but only the 4*p* shell of the ground state, and various excited states, in GGII. The parameters for these cases are given in Table II.

An inverse relationship exists between the amount of screening and the screening function Ω. Hence, decreasing Ω increases the amount of screening, making the potential less attractive. For small *r*, Ω is approximately independent of *d*, since

$$\Omega \approx (1 + Kr + \cdots)^{-1} \approx (1 - Kr + \cdots), \qquad r \to \infty. \tag{23}$$

TABLE II

PARAMETERS FOR KRYPTON

	BGW	GSZ	GGI	GGII
d	0.719	0.689	0.617	1.055
K	4.41	4.15	4.10	5.22

Hence, increasing K increases the amount of screening (i.e., decreases Ω), making the potential less attractive. This is certainly to be expected, in view of Eq. (16), since increasing K shrinks the charge distribution toward the nucleus.

The parameter K is always larger for the BGW results than for GSZ. This results in a less attractive potential curve in the region occupied by most of the electronic charge, a fact reflected in Fig. 5 and Table III,

TABLE III

EIGENVALUES FOR KRYPTON

	HF	GSZ	BGW
1*s*	1040.33	1040.83	1027.53
2*s*	139.81	138.65	132.85
2*p*	126.02	127.34	120.65
3*s*	21.70	21.02	19.45
3*p*	16.66	16.63	14.99
3*d*	7.65	8.29	6.71
4*s*	2.31	1.97	1.80
4*p*	1.04	0.97	0.86

which compares the BGW eigenvalues with HF eigenvalues. The fact that the potential which minimizes the total energy yields one-electron eigenvalues somewhat higher than HF is a result in common with HFS $X\alpha$ calculations (Slater, Wilson, and Wood, 1969).

The two Ganas–Green curves appear quite dissimilar. The GGI curve, which reflects the inner orbitals of the ground state, as well as excited states, is very similar to the GSZ curve. To understand some of the features of these two potentials we note that the 4p and excited orbitals are more effectively screened than are the inner orbitals. Thus one expects the parameter K to be higher for the excited orbitals, a fact clearly reflected by the two Ganas–Green potentials. This result is in common with those for the other rare gases studied in that work.

At large r the GGII potential is more attractive than the GGI potential despite the fact that K_{GGII} is larger. Thus the behavior of the potential at large r is influenced chiefly by the parameter d. The large r adjustment in GGII reflects the fact that the experimental data actually show higher ionization energies (lower-lying energy levels) for excited states than are predicted by GGI. This effect is apparently more important at large r than is screening and is not accounted for properly by the GGI potential.

In passing we compare our results with those obtained by the TFD approach of Green, Sellin, and Darewych (GSD) (1971). It was previously noted that the parameters H and d obtained by that method were unrealistic compared to other results. However, the value of K for $Z = 50$ ($H = 100$, $d = 17$) obtained by the TFD approach is 5.88, which is not far from the present calculation of 4.97. In the TFD work the GSZ potential was used to represent the electrostatic potential on a single electron due to all charges, including the electron itself. Hence the value of K should be appropriate to the entire electronic charge. Indeed a calculation from the wave functions obtained shows $\langle r^{-1}\rangle = 5.74$ for $Z = 50$. On the other hand, the potential on each of the electrons in the HF calculations is due only to the charge distribution of the others. The effective K value ($\langle r^{-1}\rangle$) for the distribution depends on which electron is excluded. The value of K should be much smaller than for the total charge distribution if an inner electron is excluded, but slightly larger if an outer electron is excluded. Hence on the average the value of K is smaller, as the inner electrons have more influence. The results obtained here verify this expectation.

The value of d (~ 17 for $Z = 50$) remains unexplainably large. While the results of GSD with other distributions suggest that the GDF function is overly restrictive, nevertheless, it would also appear that the problem in large part is a limitation of the statistical model.

V. The Statistical Exchange Energy

Minimizing the total energy (in HF) becomes very expensive as one proceeds to higher atomic numbers due to the increasing number of exchange integrals which must be computed. During the course of the calculations it occurred to the authors that one might minimize instead the HFS $X\alpha$ approximation to the total energy, in which the exchange term is replaced by

$$E_{X\alpha} = \tfrac{3}{4}\alpha \int V_s \rho(r)\, d\tau, \tag{24}$$

where V_s is the original Slater statistical approximation for the exchange term in the potential and ρ is the charge density. If one varies the resulting expression for the total energy with respect to the orbitals one obtains the HFS $X\alpha$ self-consistent equations. Kmetko (1970) has minimized the total energy of the solutions of these equations with respect to α. While the results showed that α fluctuates sharply, due to its dependence on shell structure, we may smooth out these bumps with the approximate relation

$$\alpha = 0.67 + 0.28Z^{-0.63}. \tag{25}$$

Using this relationship for α the statistical energy was minimized with respect to d and K for $Z = 10, 30, 50, 70, 90$. The agreement between these results and those obtained by minimizing HF energies is shown in Table IV.

TABLE IV

STATISTICAL ENERGY RESULTS

Z	d_{HF}	$d_{X\alpha}$	K_{HF}	$K_{X\alpha}$
10	0.560	0.547	2.72	2.69
30	0.646	0.644	4.05	4.05
50	0.875	0.872	4.97	4.97
70	0.625	0.630	5.47	5.50
90	0.875	0.904	6.17	6.18

VI. Conclusions

We have tested a new method for determining the parameters of the GSZ IPM potential for neutral atoms. This method, minimizing the total energy, gives good agreement with other methods while having the advantage of being *ab initio*. Thus the method may be applied to excited states and ions, for which few theoretical or experimental data currently exist.

Furthermore, we have reached some physical conclusions concerning the parameters d and K. The relationship between K and $\langle r^{-1}\rangle$ should allow one to estimate this parameter and reduce the problem to a minimization with respect to the shell parameter *d*.

We have explored the possibility of using the statistical approximation to the HF expression for total energy. This approximation is much simpler and faster to use and yields encouraging results. While this method, in the form presented here, is not strictly *ab initio*, Kmetko's results show that the parameter α, whose variations are related to atomic shell structure, never varies by more than a few percent from the analytic representation used here. Hence, one should expect to be able to use the same value of α for excited states and ions as for the ground state of the neutral atom.

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An Analytic Independent Particle Model for Atoms

III. Ionization of Rare Gas Atoms by Electrons in the Born Approximation

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I. Introduction

Interest in the problem of electron impact ionization of atoms both from a theoretical and experimental standpoint has increased greatly in recent times. References in the literature on the subject have been quite sporadic up until the late 1950s and early 1960s. Recent review articles on the subject detailing present and former approaches have been written by Rudge (1968) and on more specialized aspects of the subject by Inokuti (1971). Cooper (1962), Fano and Cooper (1965), and Manson and Cooper (1968) have carried out recent theoretical studies in the closely related topic of photoionization, utilizing a similar approach to that used in this paper. Very recently Manson (1971) has extended their work to electron impact ionization using the Hartree–Fock–Slater type wave functions tabulated by Herman and Skillman (1963) for bound-state wave functions.

In Section II we give a development of the GOS formalism for ionization emphasizing those calculational procedures which differ from the excitation formalism used by Ganas and Green (1971). Section III gives a comparison in the region of the ionization threshold between the p to s partial wave contribution to the ionization GOS and the appropriately energy-normalized p to s excitation GOS's of Ganas and Green (1971). In Section IV calculational results are given and it is shown that as one goes to higher Z atoms the differences between this model and simple hydrogenic results become very substantial. The Bethe continuum surface is shown as series of cuts at constant ejected electron energy and constant momentum transfer. In Section V the cross-section differential in both incident electron energy and ejected electron energy, $S(E, T)$, is compared with recent experiments of Opal, Beaty, and Peterson (1972). In Section VI we assess the present status of work and describe possible future directions.

II. GOS Formalism for Ionization

The GOS formalism for ionization has many features in common with the GOS formalism for excitation. It differs in that W, the energy loss, is now a continuous variable and that the wave function of the ejected electron with kinetic energy T must be characterized by continuous wave vector $\mathbf{k}'$. When these changes are introduced into the GOS formalism (Bethe, 1930, 1932; Mott and Massey, 1965) one arrives at a differential GOS given by

$$\frac{df}{dW} = \frac{W}{K^2(2l_0+1)} \sum_{m_0, m'} \int |I|^2 \, d\hat{k}'. \tag{1}$$

In our calculations the continuum wave function $U_{k'}(\mathbf{r})$ is normalized by matching logarithmic derivatives to a Coulomb wave function, which requires that

$$\frac{1}{(2\pi)^3} \int U_{k''}^*(\mathbf{r}) U_{k'}(\mathbf{r}) \, d\mathbf{r} = \delta(\mathbf{k}'' - \mathbf{k}'). \tag{2}$$

The relevant transition matrix element is now

$$I = (N_{n_0 l_0} k'/2(2\pi)^3)^{1/2} \langle U_{k'}(\mathbf{r}) | \exp(i\mathbf{K} \cdot \mathbf{r}) | U_{n_0 l_0}(\mathbf{r}) \rangle, \tag{3}$$

where $N_{n_0 l_0}$ is the number of electrons in the initial $(n_0 l_0)$ subshell.

Using the Rayleigh expansion for $\exp(i\mathbf{K}\cdot\mathbf{r})$ the usual spherical harmonic form for $U_{n_0 l_0}(\mathbf{r})$ and letting

$$U_{k'}(\mathbf{r}) = \frac{1}{k'r} \sum_{l'=0}^{\infty} \sum_{m=-l'}^{l'} 4\pi i^{l'} P_{l'}(k'r) Y_{l'}^{m'*}(\hat{k}') Y_l^{m}(\hat{r}), \tag{4}$$

it follows after a number of manipulations involving Wigner $3-j$ symbols that

$$\frac{df}{dW}=\frac{N_{n_0l_0}W}{\pi k'K^2}\sum_{l'=0}^{\infty}(2l'+1)\sum_{l=|l'-l_0|}^{l'+l}(2l+1)\begin{pmatrix} l' l l_0 \\ 0 0 0 \end{pmatrix}^2 |I_{l'll_0}|^2, \tag{5}$$

where

$$I_{l'll_0}=\int P_{l'}^{*}(k'r)j_l(Kr)P_{n_0l_0}(r)\,dr. \tag{6}$$

For the special case of an initial p subshell Eq. (5) becomes

$$\frac{df}{dW}=\frac{N_{n_0l_0}W}{\pi k'K^2}\sum_{l'=0}^{\infty}l'|I_{l'(l'-1)1}|^2+(l'+1)|I_{l'(l'+1)1}|^2. \tag{7}$$

We note that the s ($l'=0$) partial wave contribution to Eq. (7) is

$$\frac{df_{n_0l_0\to Ts}}{dW}=\frac{N_{n_0l_0}W}{\pi k'K^2}\,|I_{011}|^2. \tag{8}$$

For $P_{n_0l_0}(r)$ and $P_{l'}(k'r)$ we use the GSZ (1969) analytic potential for an electron in a neutral atom with the parameters of Ganas and Green (1971). These lead one to expect a relationship between the higher Rydberg states and the continuum GOS.

III. Calculational Results

A. Comparison with Excitation GOS

It can be shown that

$$\lim_{T\to 0}[df_{n_0l_0\to Tl'}/dW]=\lim_{n'\to\infty}[F_{n_0l_0\to n'l'}/2(-E_{n'l'})^{3/2}] \tag{9}$$

should be satisfied. It should be noted that this disagrees slightly with Cooper (1962), probably due to a typographical error.

Figure 1 is a plot of the s partial wave contribution to the ionization GOS to the right of zero with the appropriately energy-normalized excitation GOS's of Ganas and Green as the circles to the left of zero for Ne, Ar, and Xe. Zero represents the ionization threshold, with values to the right being ejected electron energies in rydbergs and values to the left being the energy levels of the various bound s-states, shown in rydbergs. The dashed curves are smooth extensions of the ionization curves to the negative bound-state energy region. We note that in all three cases chosen the agreement of both the function value and its slope at the ionization threshold is extremely good, indicating that our calculations are consistent with those of Ganas and Green.

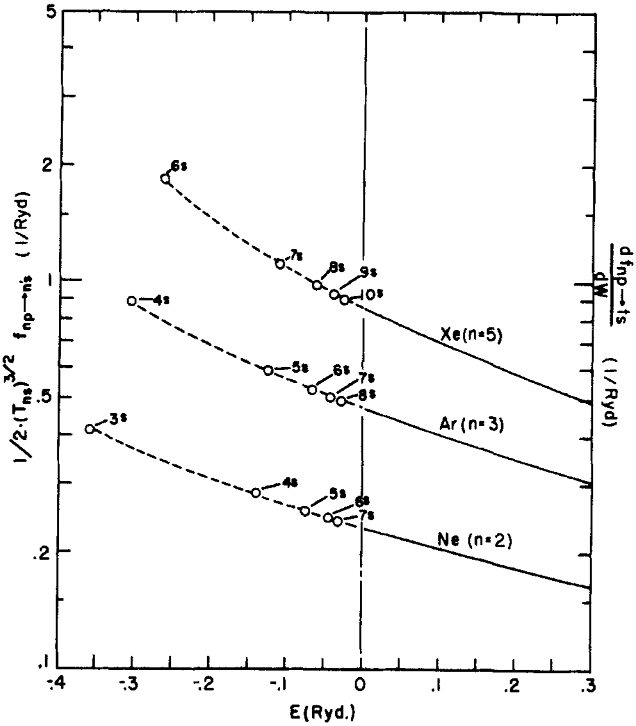

Fig. 1. Across ionization threshold comparison of appropriately normalized p to s excitation GOS's of Ganas and Green with p to s transitions of the ionization continuum.

B. Comparison with Manson's HFS Results

Manson (1971) has been performing similar calculations using wave functions from the Herman–Skillman HFS potential. Figure 2 shows the comparative results of both calculations for $df_{3p\to Td}/dW$ in Ar for T values of 1.5, 3., 6., and 10. Ry. We note first that the curves at all energies are quite similar. This is an indication that the potentials used in both models are similar, a fact borne out by plotting them. The potential we are using, however, does not have a discontinuous derivative as is characteristic of the Herman–Skillman potential. Our calculations indicate that, contrary to Manson's expectations, the minimum seen in the $p \to d$ transition would not be expected to be observed in the total GOS. We note that while a maximum is clearly in evidence, in all cases the minimum of the $3p$ to Td transition has disappeared due to the cumulative contributions from all significant partial waves. The reason for this is simply that at low T values, where the $3p$ to Td transition is dominant, the minimum is

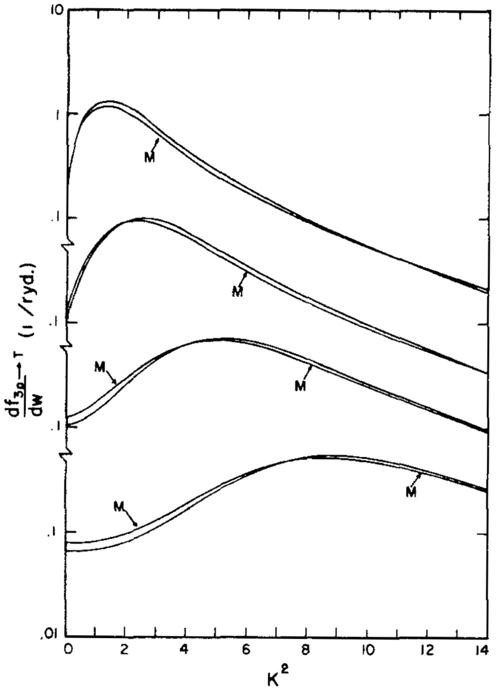

Fig. 2. Comparison of our calculation of Manson's total GOS for Ar with the present calculation. M denotes Manson's curves. The energy values for each pair of curves are, from top to bottom, $T = 1.5$, 3., 6., and 10. Ry. Note ordinate scale changes.

either very shallow or missing entirely and that, as one goes to higher T values, the minimum becomes a dominant feature of the transition, but the transition iteIf becomes a much less dominant contribution to the total GOS.

C. Comparison with McGuire's HFS Results

McGuire (1971) has also performed GOS calculations for various atoms from He to Na. His results are similar to ours and even more similar to Manson's. Like Manson, McGuire's potential is obtained from Herman and Skillman. However, in solving the reduced radial Schrödinger equation, he approximates the Herman–Skillman central potential with a series of straight-line segments. With this approximation Schrödinger's equation becomes analytically solvable within each line segment, the solutions being Whittaker functions. McGuire smoothly matches the solutions at the ends of each segment.

Since Ne is in this group we can compare with this atom. McGuire's results compare qualitatively with our total ionization GOS, however, quantitative differences of the order of 10% arise. These are probably due to (1) the different shape of the potentials, (2) the possible error associated with McGuire's straight-line segment approximation, and (3) the error of numerical calculations.

IV. Illustrative Results

Ionization GOS's were determined for the four rare gas atoms Ne, Ar, Ke, and Xe. These calculations indicate strong trends away from the Bethe continuum obtained with hydrogenic wave functions. In view of the great emphasis given to hydrogenic wave functions even in the recent literature (Inokuti, 1971) the fact that one obtains considerably different results when the wave functions are computed from a more realistic potential model is one of the main results of this paper.

The change between our Ne and hydrogenic continuum GOS are not very obvious quantitatively but quite significant qualitatively. As one

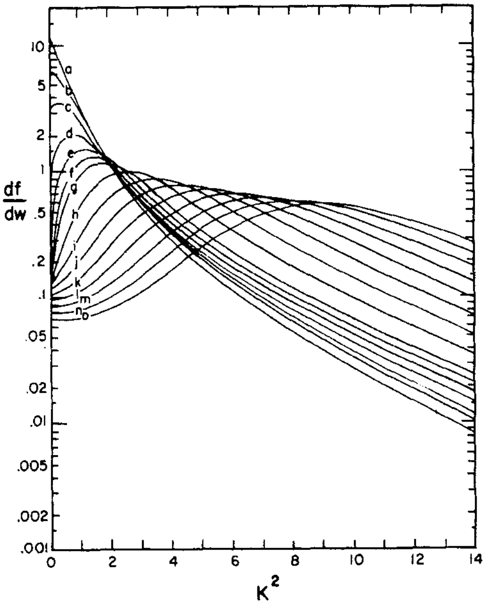

Fig. 3. Model calculation of the total GOS vs. K^2 at constant T in units of 1/Ry for Ar. The T values for the curves are as follows (in rydbergs): a, 10^{-6}; b, 0.2; c, 0.4; d, 0.8; e, 1.2; f, 1.6; g, 2; h, 3; i, 4; j, 5; k, 6; l, 7; m, 8; n, 9; o, 10.

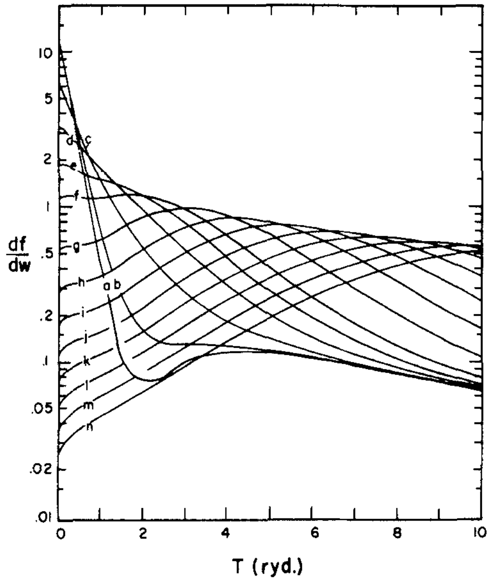

Fig. 4. Model calculation of the total GOS vs. T at constant K^2 for Ar. The K^2 values for the curves are as follows: a, 10^{-4}; b, 0.1; c, 0.5; d, 1.; e, 1.5; f, 2; g, 3; h, 4; i, 5; j, 6; k, 7; l, 8; m, 9; n, 10;.

starts at $T = 0$ and goes to higher energy for the very small K^2 curve the GOS builds up to a maximum at $T \neq 0$ and then falls off. In the hydrogenic case, the maximum is at $T = 0$ Ry. What this means in terms of the two-dimensional Bethe surface is that the Bethe ridge swings around and intersects the $K^2 = 0$ plane at a nonzero value of T. At large values of K^2 and T the surface is similar to the hydrogenic case, with the Bethe ridge centering over the $K^2 = T$ line.

Figures 3 and 4 give GOS for Ar at constant T and K^2, respectively. We note that for small K^2 and T the structure is distinctly different from the hydrogenic results. We see first that the near optical GOS in Fig. 4 has the usual dominant peak at $T = 0$ but also a secondary peak near $T = 5$. This broad flat peak disappears quickly as one goes to higher momentum transfer, but then another phenomenon takes over and is seen to be most pronounced in the $K^2 = 2.$ curve. The ridge at this point is actually a double ridge with a very shallow valley in between, as seen from the cuts at constant K^2. This behavior then slowly degenerates to the usual hydrogenic behavior as one goes to high T and K^2, showing a ridge centered at about K^2T. This "tructure" in the Bethe surface for small T and K^2 comes mainly from changes that have occurred in the p to d partial wave contribution to the GOS. The two major contributions to the GOS at small T and K^2 are made by the p to s and p to d transitions and the p to d makes by far (sometimes by an order of magnitude) the major contribution of the two.

The results for Kr and Xe display still more dramatic departures from the hydrogenic case in the low K^2 and T, departures that are difficult to characterize in a simple systematic way.

For Xe there is an extremely sharp falloff of the near-threshold curve ($T = 0$). There is much crossing and recrossing of the $E = 0.5$, 1., 1.5, 2., 2.5 Ry curves between the range $K^2 = 5.$ and $K^2 = 15.$, indicating a ripple structure to the Bethe surface in this region. In this case we see a more remarkable phenomenon. There is a distinct second ridge appearing in the higher K^2 curves which makes its first appearance in the $K^2 = 2.$ curve. This ridge becomes a shelf in the intermediate K curves and finally becomes a pronounced ridge again in the higher K curves. These behaviors can be traced back to changes which have occurred in the $p \rightarrow d$ transition amplitude, which for these higher Z atoms exhibits multiple nonzero minima when plotted vs. K^2 above a certain threshold T value.

V. Cross Sections

A cross section can be obtained by integrating out the angular dependence (or equivalently the K^2 or $\xi = a_0{}^2K^2R/W$ dependence) of the GOS, just as in the case of excitation cross sections. This cross section

$$S(E, W) = \frac{4\pi}{WE} \int_{\xi_l}^{\xi_u} \frac{df/dW}{\xi}\, d\xi, \tag{10}$$

which is differential with respect to energy loss (W) or secondary electron energy ($T = W - I$), is designated by $S(E, W)$ or $S(E, T)$.

Figure 5 illustrates our results for $S(E, T)$ vs. T for the case of Ar. The open circles, triangles, squares, crosses, and x's are our calculations of this quantity at the various incident energies listed. The filled circles are the experimental measurements of Opal, Beaty, and Peterson (1971) at an incident energy of 500 eV. The curves are fits to our data with the empirical function (Green and Sawada, 1972)

$$S(E, T) = A_0(E)\frac{\Gamma(E)^2}{[T - T_0(E)]^2 + \Gamma(E)^2}, \tag{11}$$

where $A_0(E)$, $T_0(E)$, and $\Gamma(E)$ are parameters whose dependence upon energy may be characterized by simple analytic forms.

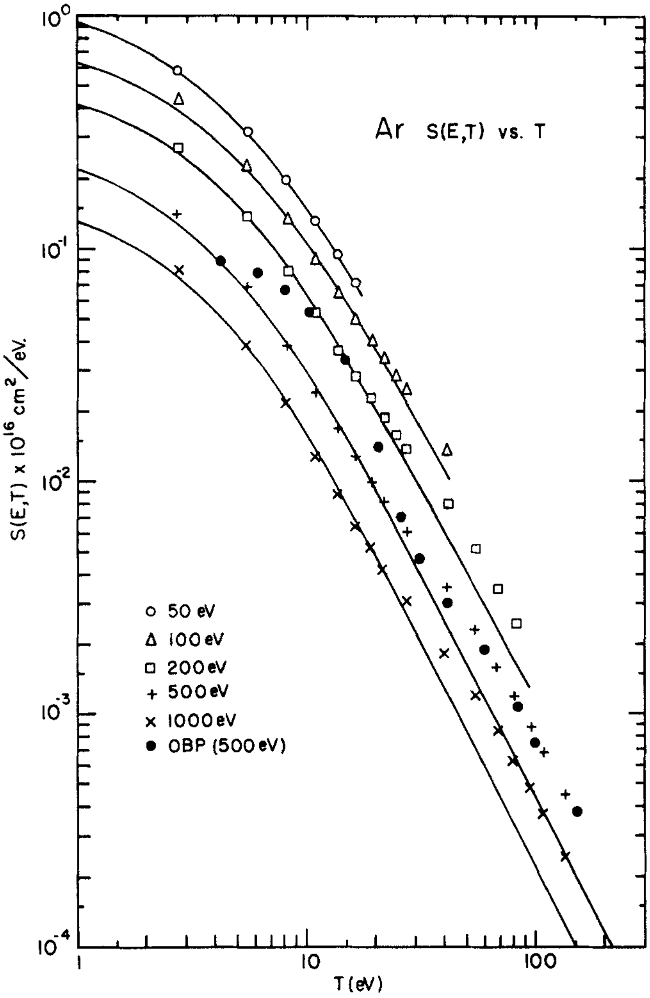

Fig. 5. Model calculation of the differential cross section $S(E, T)$ vs. T for Ar.

This function is analytically integrable with respect to T, giving the total ionization cross- section

$$\sigma(E) = A\Gamma\left[\tan^{-1}\frac{E - I - 2T_0}{2\Gamma} + \tan^{-1}\frac{T_0}{\Gamma}\right]. \tag{12}$$

We have used this formula to calculate approximate total cross sections for the noble gases and our results appear in Fig. 6. The data points are

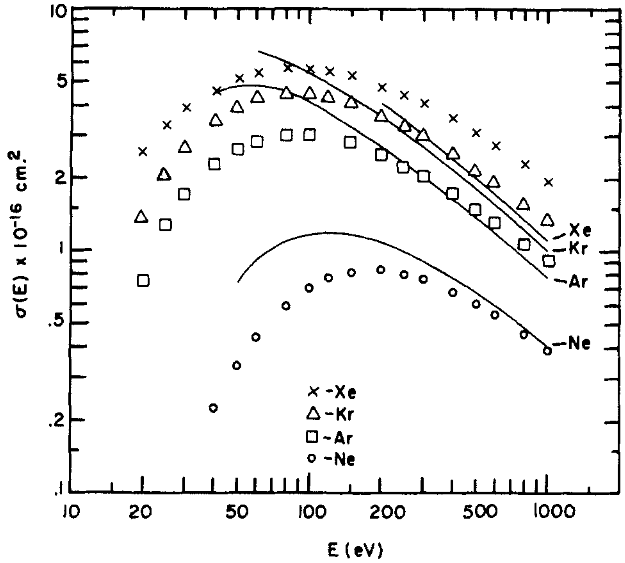

Fig. 6. Total cross sections.

from Green and McNeal (1971). The solid curves are calculations. The results for Ne and Ar are quite reasonable. It is known that the Born approximation goes characteristically high for lower energies and becomes quite good as higher energies are reached. The results, however, get progressively worse as we go to higher Z atoms. There are several possible reasons for this.

(1) Not enough partial waves were included in the calculation (we used a maximum of 14) for these higher Z cases.

(2) The fitting function Eq. (11) is not capable of reproducing an actual $S(E,T)$.

(3) There are discrepancies in the experimental data.

(4) The calculations which give the total cross section for an ionization from the outer p shell neglect the contribution of other shells.

(5) The experimental data include contributions from double, triple, etc., ionization.

Calculations are underway which will give estimates of these varying effects, and it is expected that better agreement for the higher Z elements will be achieved.

VI. Conclusion and Discussion

We have seen that the use of an analytic IPM potential for obtaining atomic wave functions provides a tractable means of exploring the trends of electron impact ionization cross sections. Furthermore, the analytic potential lends the calculation an adaptability which is not present in calculations using a fixed numerical potential such as the HFS potential. Our results indicate that there is much more structure in the GOS for low K^2 and T values than has been indicated by hydrogenic results. Hence the use of realistic wave functions is absolutely essential if one is to expect realistic results.

Our calculations of $S(E, T)$ and $\sigma(E)$ are quite reasonable for Ne and Ar but suggest that a number of other factors must be considered for heavier elements. The use of the Born approximation is a major weakness in these calculations. In energy deposition problems our calculations should yield reasonably accurate secondary electron spectra. However, since these electron energies are low (10–100 eV) our calculation cannot be used to predict such results as the tertiary electron spectra. At this time there are two directions which might be taken to resolve this difficulty. One is to use a distorted wave approximation of the nature used in excitation studies by Sawada, Purcell, and Green (1971). The second direction, which may be simpler calculationally, is to use the eikonal approximation. Both of these techniques go over to Born approximation at high energies so that the present work should serve as a useful point of departure for either direction.

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Note Added in Proof

In closing we should like to call attention to four additional studies which utilize the GSZ analytic IPM. Chen and Crasemann (1972) have obtained Auger and Coster–Kronig transition matrix elements for the L_2 subshell, which are very close to experimental values. Hahn and Watson (1973) have utilized the model to explore the systematics of multiple ionizations of ions by high energy electron impact. Whalen and Green (1972) have extended the model to spheroidal potentials for application to homonuclear diatomic molecules. Most recently, Riewe, Wallace, and Green (1973) have derived atom–atom potentials from electron–atom potentials provided by the model. In these studies the analytic IPM continues to give results close to those obtainable from Hartree–Fock methods but with major savings in computation time.

Solvent-Shift Effects on Electronic Spectra and Excited-State Dipole Moments and Polarizabilities

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I. Introduction

It is a well-known experimental fact that the spectrum of a substance in a solution is changed compared to its spectrum in the vapor state. In some cases the change is fairly profound (see, for example, Hayes and Timmons, 1965; Ledger and Suppan, 1967; Walker *et al.*, 1967) but in many cases the general shape of the spectrum is unaltered and the main effect is a shift of the various absorption or emission bands. This is known as the solvent-shift effect and is caused by a weak interaction between the solute and surrounding solvent molecules. The change in energy of the system due to this interaction will differ depending on whether the solute molecule is in its ground or excited state and consequently there will be the change in excitation energy observed experimentally.

The solvent–solute interaction, being weak, is best treated using quantum-mechanical perturbation theory, which allows it to be divided into electrostatic type interactions and dispersion interactions. The first of these is the more interesting (and much the easier to deal with), since it relates the solvent shift to the change in dipole moment and polarizability of the solute molecule on excitation from its ground state to its excited state and thus, in principle, can give experimental values—albeit once removed—of excited-state dipole moments and polarizabilities.

Over the past few years there have been a number of review articles on this topic (Liptay, 1966; Suppan, 1968a,b; Basu, 1964) but, unfortunately, most have used one particular type of approach based on the reaction-field method derived from classical electrostatics. Thus it is not always appreciated that there are other methods, in particular that due to Abe (1965), which ought also to be considered. Moreover the equations obtained by these different methods do not always agree; for example, those based on the reaction-field method generally suggest that excited-state polarizabilities differ little from those of the ground state, while the equation put forward by Abe (1965; Abe *et al.*, 1966) gives large changes. As far as we are aware there has been no real attempt to analyze and explain these differences or to consider how far it genuinely is possible to obtain "experimental" values of dipole moments and polarizabilities of excited states from solvent-shift data.

The purpose of this article is, therefore, to review the apparently different approaches and to show that as far as the electrostatic terms are concerned the theories are not very different. The great difference in results which have been obtained we trace to the treatment of the dispersion term and, because we think it quite impossible to decide exactly how this should be included in the theory, we believe that attempts to deduce excited-state polarizabilities from solvent-shift data will result in values subject to considerable uncertainty. On the other hand, it seems that at least order-of-magnitude values for excited-state dipole moments can be obtained from solvent shift data.

II. Solvent–Solute Interactions

Practically all solvent-shift theories are based on the assumption that solvent and solute molecules are sufficiently well separated that overlap of electronic distribution can be neglected. Actually this may not be quite correct for the solvent molecules closest to the solute molecules, but one hopes the effect is small. In some cases, however, hydrogen bonding between the solute and solvent molecules takes place and when this occurs the theory needs considerable modification (Hayes *et al.*, 1965; Ledger and Suppan, 1967; Walker *et al.*, 1967). These considerations apart, the interaction term between the solute and solvent molecules may be approximated by a point-dipole interaction operator (see Appendix 1) summed over all the solvent molecules, i.e.,

$$H' = \sum_{p=1}^{N} R_p^{-3} \mathbf{M}^u \cdot \boldsymbol{\Theta}^{uv(p)} \cdot \mathbf{M}^{v(p)} \tag{1}$$

where $\mathbf{M}^u$ and $\mathbf{M}^{v(p)}$ are the dipole-moment operators for the solute and pth solvent molecules,

$$\boldsymbol{\Theta}^{uv(p)} = \mathbf{1} - 3\hat{\mathbf{R}}_p \hat{\mathbf{R}}_p$$

is the angular term allowing for the relative orientations of two interacting molecules, and R_p is the distance between them. For H' to be a good approximation R_p is best measured as the distance between the centroids of charge in the solute and solvent molecules.

The zero-order function for the system will be a product of the wave functions of the individual molecules since in zero order the molecules do not interact, i.e.,

$$\Psi_0 = \phi_0^{v(1)} \phi_0^{v(2)} \cdots \phi_0^{v(N)} \phi_s^u, \tag{2}$$

where the solvent molecules are assumed to be in their ground states while the solute molecule is in state s, which can be either the ground or an excited state, but which is assumed to be nondegenerate.

It is a relatively simple matter to use perturbation theory to find the energy change in the solvent–solute system (see McRae, 1957). Full details can be found in Appendix 2. From the perturbation theory the main result is that the solvent shift of the energy level is

$$\begin{aligned} \Delta E_s = {} & \sum_{p=1}^{N} R_p^{-3} \boldsymbol{\mu}_s{}^u \cdot \boldsymbol{\Theta}^{uv(p)} \cdot \boldsymbol{\mu}_0^{v(p)} \\ & - \frac{1}{2} \sum_{p=1}^{N} R_p^{-6} \boldsymbol{\mu}_s{}^u \cdot \boldsymbol{\Theta}^{uv(p)} \cdot \boldsymbol{\alpha}_0^{v(p)} \cdot \boldsymbol{\Theta}^{uv(p)} \cdot \boldsymbol{\mu}_s{}^u \\ & - \frac{1}{2} \sum_{p,q=1}^{N} R_p^{-3} R_q^{-3} \boldsymbol{\mu}_0^{v(p)} \cdot \boldsymbol{\Theta}^{uv(p)} \cdot \boldsymbol{\alpha}_s{}^u \cdot \boldsymbol{\Theta}^{uv(q)} \cdot \boldsymbol{\mu}_0^{v(q)} + D_s, \end{aligned} \tag{3}$$

where D_s is the dispersion term, which we shall discuss later, and $\boldsymbol{\mu}_0{}^v$, $\boldsymbol{\mu}_s{}^u$, $\boldsymbol{\alpha}_0{}^v$, $\boldsymbol{\alpha}_s{}^u$ are the dipole moments and polarizability tensors for a solvent molecule (in its ground state) and the solute molecule (in state *s*).[1] Terms depending on properties of the solvent molecules only have been omitted.

The result given by Eq. (3) is obtained on the basis that all the molecules involved have fixed orientations and positions. Clearly different configurations will have different energies, so that in order to find the energy of the liquid system there has to be a statistical averaging over the various configurations. In principle, this could be done rigorously but in practice it is too complicated and, therefore, semiclassical and part empirical methods are used.

III. The Reaction-Field Method

In the procedure which uses the reaction field (Bakhshiev, 1961; Liptay, 1966; Suppan, 1968a,b; McRae, 1957; Lippert, 1957; Bilot and Kawski, 1962), terms in the perturbation theory result are identified with the electric field experienced by the solute molecule due to the dipole moments of each solvent molecule. This is on the basis of fixed positions and orientations. The statistical-mechanical averaging over all possible liquid configurations causes this to be replaced by its average value, which is the actual field—called the reaction field—at the solute molecule, and this can be computed from classical electrostatic theory. Actually, there are two ways of carrying out this procedure. The first, which is essentially that of McRae (1957), treats each term separately so that several different reaction fields are considered. For example, in the first term in Eq. (3) the field is that of the permanent dipole moment of the solvent molecules. The second procedure, which seems to be the more popular one, combines terms together so that the field considered is that due to the total dipole moment (actual and induced) of the solvent molecule (cf. Liptay, 1966). As it happens the two procedures give slightly different results, but from the point of view of comparison with Abe's theory McRae's method is the more useful, so that is the one we consider here.

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[1] Note that we neglect interactions between pairs of solvent molecules. The major terms which arise from this are the same both for ground and excited state and play no part in the solvent-induced shift of the excitation energy. However, in second-order perturbation theory there is a term which might be called a three-body interaction between the solute and two separate solvent molecules. As McRae points out, this is large only when the solvent is highly polar, in which case dipolar terms in first-order perturbation theory will be even larger. Thus it seems fair to neglect the second-order effect. In any case, by relating solvent effects to the macroscopic dielectric properties of the solvent it is probable that some empirical account is being taken of the solvent–solvent interactions. For details of terms neglected here, see Liptay and Walz (1971).

Following McRae, therefore, we rewrite the first term in Eq. (3) as $-\boldsymbol{\mu}_s{}^u \cdot \mathbf{E}_s{}^u$, where

$$\mathbf{E}_s{}^u = -\left\langle \sum_{p=1}^{N} R_p^{-3} \boldsymbol{\Theta}^{uv(p)} \cdot \boldsymbol{\mu}_0^{v(p)} \right\rangle \tag{4}$$

is the field due to the permanent dipoles of the solvent molecules and $\langle\ \rangle$ indicates the averaging over all orientations weighted according to their Boltzmann factor. In a similar fashion the third term in (3) is just

$$-\tfrac{1}{2}\, \mathbf{E}_s{}^u \cdot \boldsymbol{\alpha}_s{}^u \cdot \mathbf{E}_s{}^u, \tag{5}$$

which if we approximate the polarizability tensor by an isotropic tensor[2] becomes

$$-\tfrac{1}{2} |\mathbf{E}_s{}^u|^2 \alpha_s{}^u, \tag{6}$$

where $\alpha_s{}^u$ is the mean static polarizability of the solute molecule in the state s. To deal with the second term in (3) we introduce the field $\mathbf{E}_s^{v(p)}$ at the pth solvent molecule due to the permanent dipole of the solute molecule in its s state so that we obtain

$$-\tfrac{1}{2} \sum_{p=1}^{N} \mathbf{E}_s^{v(p)} \cdot \boldsymbol{\alpha}_0{}^v \cdot \mathbf{E}_s^{v(p)}. \tag{7}$$

Approximating $\boldsymbol{\alpha}_0{}^v$ by an isotropic tensor we obtain

$$-\tfrac{1}{2}\alpha_0{}^v \sum_{p=1}^{N} |\mathbf{E}_s^{v(p)}|^2. \tag{8}$$

An alternative expression for this can be found by introducing the induced dipole moment $\mathbf{m}_s^{v(p)}$ of the pth solvent molecule due to the field $\mathbf{E}_s^{v(p)}$ so that the second term becomes

$$-\tfrac{1}{2} \sum_{p=1}^{N} R_p^{-3} \boldsymbol{\mu}_s{}^u \cdot \boldsymbol{\Theta}^{uv(p)} \cdot \mathbf{m}_s^{v(p)}, \tag{9}$$

which is, therefore, $-\tfrac{1}{2}\boldsymbol{\mu}_s{}^u \cdot \mathbf{e}_s{}^u$, where $\mathbf{e}_s{}^u$ is the field at the solute molecule due to the solvent-induced dipoles.

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[2] Throughout this article we shall assume the polarizability tensors of both the solvent and solute molecules are isotropic. It is not essential to do this, of course, and it is perfectly possible to carry through the argument taking account of the polarizability anisotropy which is certainly present for most molecules. However, all this really does is to complicate the equations and introduce extra parameters. Our feeling is that, at the moment, the basic theory is too crude to allow for such refinements.

It is to be understood that these fields are Boltzmann-averaged over molecular orientations. They may, therefore, be identified with what are called, in classical electrostatics, reaction fields, i.e., the fields arising from an interaction between a dipole and a homogeneous polarizable dielectric (Onsager, 1936; Böttcher, 1952). Clearly the averaging of the liquid orientations of the solvent molecules is performed by assuming it is equivalent to replacing the solvent molecules by this dielectric. Writing $\mathbf{R}^s$ and $\mathbf{r}^s$ as the reaction fields due to the interaction between the solute molecule (in state s) and the permanent dipoles and the induced dipoles of the solvent, respectively, we can write for the first three terms in (3)

$$-\boldsymbol{\mu}_s{}^u \cdot \mathbf{R}^s - \tfrac{1}{2}\alpha_s{}^u |E_s{}^u|^2 - \tfrac{1}{2}\boldsymbol{\mu}_s{}^u \cdot \mathbf{r}^s, \tag{10}$$

and $\mathbf{R}^s$ and $\mathbf{r}^s$ have to be expressed in terms of the properties of the dielectric which "replaces" the solvent.

The "classical" formulas for $\mathbf{R}^s$ and $\mathbf{r}^s$ are

$$\mathbf{R}^s = \frac{2}{a^3}(\boldsymbol{\mu}_s{}^u + \alpha_s{}^u \mathbf{R}^s)\frac{D'-1}{2D'+1}$$

and, ignoring terms in $\alpha_s{}^u(\mathbf{R}^s - \mathbf{r}^s)$,

$$\mathbf{r}^s = \frac{2}{a^3}(\boldsymbol{\mu}_s{}^u + \alpha_s{}^u \mathbf{r}^s)\frac{D''-1}{2D''+1}, \tag{11}$$

calculated on the basis of a point dipole (the solute molecule) in the center of a spherical cavity of radius a surrounded by a homogeneous dielectric. The assumption that the solute molecule occupies a spherical cavity is not very significant, so that if the solute molecule is, for example, very flat, the radius a would just be that of a sphere with volume equal to that occupied in actuality by the solute molecule. (For further discussion of the value of a see below and, also, Appendix 3.)

In (11) D' represents the contribution of the permanent dipoles to the static dielectric constant and D'' is the contribution from the electronic-polarizable part of the dielectric properties of the solvent. There are two ways of obtaining $\mathbf{R}^s$ and $\mathbf{r}^s$ explicitly from (11). The first takes the permanent dipole term as the leading one so that, for example,

$$\mathbf{R}^s = \frac{2}{a^3}\frac{D'-1}{2D'+1}\boldsymbol{\mu}_s{}^u$$

with correcting terms depending on the polarizability. The second, which is actually more useful and, we believe, more accurate, is to note that $\alpha_s^u \approx \frac{1}{2}a^3$ (Basu, 1964; McRae, 1957) so that

$$\mathbf{R}^s = \frac{2}{a^3}\frac{D'-1}{D'+2}\boldsymbol{\mu}_s^u \tag{12}$$

and

$$\mathbf{r}^s = \frac{2}{a^3}\frac{D''-1}{D''+2}\boldsymbol{\mu}_s^u, \tag{13}$$

and the correcting terms depend on $(\alpha_s^u - \frac{1}{2}a^3)$, which should generally be small. The great advantage of this is that we can immediately make the identification

$$\frac{D'-1}{D'+2} = \frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \tag{14}$$

$$\frac{D''-1}{D''+2} = \frac{n^2-1}{n^2+2}, \tag{15}$$

where D is the static dielectric constant of the solvent and n the solvent refractive index extrapolated to zero frequency.

Combining these together we have

$$\Delta E_s = -\frac{1}{a^3}(\mu_s^u)^2\left\{\frac{2(D-1)}{D+2} - \frac{n^2-1}{n^2+2}\right\} - \tfrac{1}{2}\alpha_s^u|E_s^u|^2 + D_s. \tag{16}$$

Thus, except for the last term the energy shift is related to the dipole moment of the solute molecules and the dielectric properties of the solvent; since $|E_s^u|^2$ can either be expressed in terms of the dipole moment of the solvent molecules, as will be done in the next section, or else approximated by the square of the reaction field [cf., however, McRae (1957), who puts $|E_s^u|^2 \approx 3|R^s|^2$ for spherical molecules and $|E_s^u|^2 \approx |R^s|^2$ for rodlike molecules.]

Before this expression can be applied to both the ground and excited state of the solute molecule and subtracted to give the solvent shift, two further points should be made. The first is relatively minor and concerns the correcting terms to the explicit formulas for the reaction fields $\mathbf{R}^s$ and $\mathbf{r}_s$. These correcting terms when subtracted for the two different states give a term involving the differences in the polarizabilities of the ground and excited states (cf. Suppan, 1968a,b; McRae, 1957). This, however, will vanish if either (a) the solute molecule has no dipole moment, (b) the solvent is nonpolar, or (c) the difference in polarizabilities of the ground and excited state is small. In all other cases the term will be generally smaller than the dipole terms already included and the dispersion term we have yet to consider. Thus it seems reasonable to neglect them.

The second point is more serious and concerns the response time of the solute–solvent system to the excitation process. Normally the process is sufficiently rapid for the Franck–Condon principle to hold, which means that while the induced dipole of the solvent molecule can change in response to the change of solute dipole on excitation, the permanent dipoles cannot, i.e., there is negligible dipole reorientation. If this is the case the reaction field $\mathbf{R}^s$ for the excited state will be unchanged from the ground state, and this is determined by the ground-state dipole moment of the solute molecule. For such a system the ΔE for the excited state will be, instead of the formula (16),

$$-\frac{\boldsymbol{\mu}_e^u \cdot \boldsymbol{\mu}_g^u}{a^3}\left\{\frac{2(D-1)}{(D+2)} - \frac{2(n^2-1)}{(n^2+2)}\right\} + \frac{(\mu_e^u)^2}{a^3}\left(\frac{n^2-1}{n^2+2}\right) - \tfrac{1}{2}\alpha_e^u|E_e^u|^2 + D_e, \tag{17}$$

where the subscripts e and g refer to excited state and ground state, respectively.

Using Eq. (16) for the ground state and Eq. (17) for the excited state we obtain the reaction-field type expression for the solvent shift as

$$\begin{aligned}\Delta E_{e-g} = {} & \frac{\boldsymbol{\mu}_g^u \cdot (\boldsymbol{\mu}_g^u - \boldsymbol{\mu}_e^u)}{a^3}\left\{\frac{2(D-1)}{(D+2)} - \frac{2(n^2-1)}{(n^2+2)}\right\} \\ & + \frac{1}{a^3}[(\mu_e^u)^2 - (\mu_g^u)^2]\left(\frac{n^2-1}{n^2+2}\right) - \tfrac{1}{2}\alpha_e^u|E_e^u|^2 \\ & + \tfrac{1}{2}\alpha_g^u|E_g^u|^2 + D_e - D_g.\end{aligned} \tag{18}$$

Finally in this section we refer to the work of Ooshika (1954), which together with the work of McRae and Bayliss (Bayliss and McRae, 1954; McRae, 1957) represents the first quantum-mechanically based theory. Unlike most of the work which followed, Ooshika's theory used as zero-order wave functions products of wave functions of the solute molecule and the solvent treated as a whole. In spite of this, since the various terms in the perturbation expansion were related to reaction fields, the theory is basically the same as that just described. In particular, there are two terms equivalent to the first term in (16), although because the approximation

$\alpha_s^u \approx \frac{1}{2}a^3$ is not made, the functions $D - 1/D + 1$ and $n^2 - 1/n^2 + 1$ are replaced by $D - 1/2D + 1$ and $n^2 - 1/2n^2 + 1$. The E_s^u term in (16) was treated by Ooshika in rather a different way from that of, for example, McRae or from that we shall use in the next section. Ooshika's leading term for this is

$$\frac{1}{2D'' + 1}\frac{(\mu_0^v)^2\alpha_s^u}{a^3b^3},$$

where D'' is the part of the dielectric constant of the solvent due to the polarizability of the solvent molecules, and b is a cavity radius for a solvent molecule. [Actually Ooshika has μ, the solvent dipole moment in solution rather than μ_0^v, that in gas, but the difference is a term of higher order and arises because in Ooshika's theory solvent wave functions rather than molecular wave functions are used.] This should be compared with the formula $(\mu_0^v)^2\alpha_s^u/a^3r_v^3$ in the following section, to which it can be made equivalent by a suitable definition of b. The remaining part of this term in (16) was found by Ooshika to be of order $\alpha_s^u(R^s)^2$ and can probably be neglected. Of course, in Ooshika's theory there is also a dispersion term, but since, again, it involves wave functions for the solvent as a whole, it is more difficult to deal with than that derived in Appendix 2 using solvent molecular wave functions, so we shall not discuss this further.

IV. Abe's Theory

Abe's theory (1965) is, at first sight, rather different from that based on reaction fields but, as we shall see, it gives final results in agreement with those of the previous section. Essentially Abe takes the formula for the long-range interaction between two molecules averaged over all orientations (Margenau, 1939). This formula involves the dipole moments and polarizabilities of the interacting molecules as well as a temperature dependence arising from the Boltzmann factor. By considering the solute–solvent interaction as consisting of pairwise interactions of this type Abe is led to his final formula. In our opinion, while this is basically correct there are several points which need clarification and amendment. These are the following: (1) There are three-body type interactions not considered by Abe, and in any event the final expression should be derived explicitly from Eq. (3). (2) No account is taken of the rapidity of the electronic excitation process or, equivalently, the solvent dipoles are assumed to react instantaneously to the charge in the solute dipole on excitation. (3) Abe's method of summing over the distribution of solvent molecules leads to a most complicated expression which hides its basic simplicity and hinders comparison with the results of the reaction-field method. (4) The dipole moment and polarizability of the solvent molecules should be replaced by dielectric properties of the solvent liquid since this will more closely represent the physical situation. For these reasons we think it best to rederive the formula starting from Eq. (3) so that these points can be cleared up.

The most difficult point concerns the averaging process. Strictly speaking, we ought to compute the energy of each rotational state of the interacting molecule, multiply the interaction energy by the appropriate Boltzmann factor, and sum over the states. This is too difficult, of course, so instead we can use a semiclassical approach (Margenau, 1939) and compute $\langle V \exp(-V/kT)\rangle$, where V is the angular-dependent interaction term [i.e., Eq. (3)] and $\langle\ \rangle$ means average over all orientations of the interacting molecules. As explained by Margenau, this will not be valid for low temperatures since, in that case, only states of low energy will be occupied to any extent, so that the fully quantum mechanical treatment must be made. However, for normal laboratory temperatures the computation of $\langle V \exp(-V/kT)\rangle$ will suffice. Clearly the leading term in an inverse temperature expansion of this quantity will be $\langle V\rangle$ and, provided this is nonvanishing, the Boltzmann factor will not arise at all. Where it does arise is in the first term in (3), i.e., the dipole–dipole term, since this averaged over all orientations is zero. In this case we must go to the next term in the expansion of $\langle V \exp(-V/kT)\rangle$, which is the temperature-dependent one:

$$-\frac{1}{kT}\langle V^2\rangle. \tag{19}$$

On the assumption that $\boldsymbol{\alpha}_0{}^v$ and $\boldsymbol{\alpha}_s{}^u$ are isotropic tensors, the averaging of the orientation-dependent quantities in Eq. (3) gives

$$\langle \boldsymbol{\mu}_s{}^u \cdot \boldsymbol{\Theta}^{uv(p)} \cdot \boldsymbol{\mu}_0^{v(p)} \rangle = 0 \tag{20}$$

$$\langle \{\boldsymbol{\mu}_s{}^u \cdot \boldsymbol{\Theta}^{uv(p)} \cdot \boldsymbol{\mu}_0^{v(p)}\}^2 \rangle = \tfrac{2}{3}(\mu_s{}^u)^2(\mu_0^{v(p)})^2 \tag{21}$$

$$\langle \boldsymbol{\mu}_s{}^u \cdot \boldsymbol{\Theta}^{uv(p)} \cdot \boldsymbol{\alpha}_0{}^v \cdot \boldsymbol{\Theta}^{uv(p)} \cdot \boldsymbol{\mu}_s{}^u \rangle = 2\alpha_0{}^v(\mu_s{}^u)^2 \tag{22}$$

$$\begin{aligned} \langle \boldsymbol{\mu}_0^{v(p)} \cdot \boldsymbol{\Theta}^{uv(p)} \cdot \boldsymbol{\alpha}_s{}^u \cdot \boldsymbol{\Theta}^{uv(q)} \cdot \boldsymbol{\mu}_0^{v(q)} \rangle &= 2\alpha_s{}^u(\mu_0^{v(p)})^2 \qquad q = p \\ &= 0 \qquad\qquad\qquad q \neq p. \end{aligned} \tag{23}$$

The first of these shows, as we have said, that the first term of $\langle V \exp(-V/kT)\rangle$ vanishes for dipole–dipole interaction so that, for this, we must use $\langle V^2\rangle$, which is given by (22). The last result for $q \neq p$ corresponds to a three-body type interaction of the sort neglected by Abe. For this term we ought now to compute the $\langle V^2\rangle$ term, since this is the first nonvanishing one. However, this clearly would give terms much smaller than those we have already, so that we see Abe was indeed justified in neglecting them. Combining these together therefore we obtain

$$-\sum_{p=1}^{N} R_p^{-6}\left\{\frac{2}{3kT}(\mu_s{}^u)^2(\mu_0^{v(p)})^2 + \alpha_s{}^u(\mu_0^{v(p)})^2 + \alpha_0^{v(p)}(\mu_s{}^u)^2\right\}, \tag{24}$$

which apart from the dispersion term and terms involving solvent–solvent interactions is the equation used by Abe.

The next step is to evaluate the sum

$$\sum_{p=1}^{N} R_p^{-6}. \tag{25}$$

The most sensible procedure is to assume the solvent molecules are uniformly distributed with number density ρ [$\rho = Ad/M$, where d and M are the density and mass of the solvent molecules and A is Avogadro's number] outside a sphere of radius a—the cavity radius of the reaction field method. This gives the result

$$\sum_{p=1}^{N} R_p^{-6} = \frac{4\pi\rho}{3a^3} = \frac{4\pi Ad}{3Ma^3} \tag{26}$$

for the sum (25). Abe uses a rather different approach which leads to a very cumbersome expression for $\sum R_p^{-6}$. For a discussion of this point see Appendix 3.

Finally, if we use the Clausius–Debye equation,

$$\frac{4\pi\rho}{3}\left\{\frac{1}{3kT}(\mu_0{}^v)^2 + \alpha_0{}^v\right\} = \frac{D-1}{D+2} \tag{27}$$

and the relation between $\alpha_0{}^v$ and the refractive index

$$\frac{4\pi\rho}{3}\alpha_0{}^v = \frac{n^2-1}{n^2+2}, \tag{28}$$

we obtain

$$\Delta E_s = -\frac{(\mu_s{}^u)^2}{a^3}\left\{\frac{2(D-1)}{(D+2)} - \frac{n^2-1}{n^2+2}\right\} - \frac{4\pi\rho}{3a^3}\,\alpha_s{}^u(\mu_0{}^v)^2, \tag{29}$$

which agrees with the reaction-field result provided we make the identification, as clearly we should, that

$$|E_s{}^u|^2 = 2\,\frac{4\pi\rho}{3a^3}\,(\mu_0{}^v)^2. \tag{30}$$

It is a matter of opinion as to whether it is better to use the second term in (29) or the approximate reaction-field type expression for the term $-\frac{1}{2}\alpha_s{}^u|E_s{}^u|^2$. On the whole, we tend to favor that in (29) since it is a little more definite. Of course, it is only important in the case of a solute molecule with zero dipole moment in a polar solvent, in which case it relates the solvent shift to polarizability changes. However, in that case the dispersion term is of greater importance, as we shall see in the next section.

The final point we have to consider is the response time of the system to the excitation process. To allow for the negligible dipole reorientation of the system in the excited state, i.e., the Franck–Condon effect, we must reconsider the averaging process. We can approximate the physical situation by keeping the same type of Boltzmann distribution for the excited state as for the ground state and averaging $\langle V_e \exp - V_g/kT\rangle$, where V_e and V_g are the interaction potentials for the excited and ground states, respectively. This will have an effect only on the temperature-dependent term arising from the dipole–dipole interaction, which will be

$$-\frac{1}{kT}\langle V_g V_e\rangle. \tag{31}$$

Since

$$\langle \boldsymbol{\mu}_g{}^u \cdot \boldsymbol{\Theta}^{uv(p)} \cdot \boldsymbol{\mu}_0^{v(p)} \boldsymbol{\mu}_0^{v(q)} \cdot \boldsymbol{\Theta}^{uv(q)} \cdot \boldsymbol{\mu}_e{}^u\rangle = \tfrac{2}{3}\boldsymbol{\mu}_g{}^u \cdot \boldsymbol{\mu}_e{}^u (\mu_0{}^v)^2 \delta_{pq} \tag{32}$$

it follows that the value of ΔE for an excited state in which there is negligible dipole reorientation is

$$\begin{aligned}\Delta E_e = &-\frac{\boldsymbol{\mu}_g{}^u \cdot \boldsymbol{\mu}_e{}^u}{a^3}\left[\frac{2(D-1)}{(D+2)} - \frac{2(n^2-1)}{(n^2+2)}\right] \\ &-\frac{(\mu_e{}^u)^2}{a^3}\left(\frac{n^2-1}{n^2+2}\right) - \frac{4\pi\rho}{3a^3}\,\alpha_e{}^u(\mu_0{}^v)^2,\end{aligned} \tag{33}$$

which is in agreement with the reaction-field result. The final result for the solvent shift is therefore

$$\Delta E_{e-g} = -\frac{\boldsymbol{\mu}_g{}^u \cdot (\boldsymbol{\mu}_e{}^u - \boldsymbol{\mu}_g{}^u)}{a^3}\left[\frac{2(D-1)}{(D+2)} - \frac{2(n^2-1)}{(n^2+2)}\right] - \frac{1}{a^3}[(\mu_e{}^u)^2 - (\mu_g{}^u)^2]\left(\frac{n^2-1}{n^2+2}\right) - \frac{4\pi\rho}{3a^3}(\mu_0{}^v)^2(\alpha_e{}^u - \alpha_g{}^u) + D_e - D_g, \tag{34}$$

in agreement with the reaction-field result subject to the identification of the last term in (34) with the last term in (16) referred to earlier. This, therefore, confirms our remark in the introduction that Abe's theory and the reaction-field method differ by very little in the final analysis.

V. The Dispersion Term

If the solvent and solute molecules both have no permanent dipoles, the terms discussed in the previous two sections all vanish so that the energy change due to solvent–solute interactions is caused entirely by the dispersion term D_s in Eq. (3). Thus the solvent shift of the excitation energy will be given by the difference in the value of D_s in the ground and excited state. Since D_s is what remains of the second-order perturbation energy when all the terms which can be identified with the permanent and induced dipoles of the individual molecules are removed, it is a particularly difficult expression to deal with and, although by using the Unsold approximation it can be reduced to seemingly simple forms, such reductions are not very sound theoretically.

The full expression for D_s, where s refers either to the ground or excited state of the molecule, is

$$D_s = \left\langle -\sum_{p=1}^{N}\sum_{e\neq 0}\sum_{t\neq s} R_p^{-6}\,\frac{\boldsymbol{\mu}_{e0}^{v}\cdot\Theta^{uv(p)}\cdot\boldsymbol{\mu}_{ts}^{u}\,\boldsymbol{\mu}_{ts}^{u}\cdot\Theta^{uv(p)}\cdot\boldsymbol{\mu}_{e0}^{v}}{\varepsilon_e{}^v - \varepsilon_0{}^v + \varepsilon_t{}^u - \varepsilon_s{}^u}\right\rangle \tag{35}$$

where e refers to an excited state of a solvent molecule, and the sum is over all such states; t refers to a state of the solute molecule and the sum is over all states $t \neq s$, $\boldsymbol{\mu}_{e0}^{v} = \langle\phi_e{}^v|\mathbf{M}^v|\phi_0{}^v\rangle$ is the (vector) matrix element of the dipole-moment operator for a solvent molecule between the excited state e and the ground state 0, i.e., it is the transition dipole moment, and similarly for $\boldsymbol{\mu}_{ts}^{u} = \langle\phi_t{}^u|\mathbf{M}^u|\phi_s{}^u\rangle$; $\varepsilon_e{}^v$, $\varepsilon_0{}^v$, $\varepsilon_t{}^u$, $\varepsilon_s{}^u$ represent the energies of the appropriate states. The brackets in (35) indicate that the average over all orientations should be taken and when this has been done, and when in addition the $\sum_p R_p^{-6}$ is computed in a similar fashion to that described in Section IV, we obtain

$$D_s = -\frac{2}{3}\frac{4\pi Ad}{3M}\frac{1}{a^3}\sum_{t\neq s}\sum_{e\neq 0}\frac{(\mu_{ts}^u)^2(\mu_{e0}^v)^2}{\varepsilon_e{}^v - \varepsilon_0{}^v + \varepsilon_t{}^u - \varepsilon_s{}^u} = \frac{1}{a^3}\, d_{uv}^s \frac{4\pi Ad}{3M}, \tag{36}$$

where d_{uv}^s is the van der Waals coefficient for the interaction of two molecules.

Expressions similar to (36) have been considered by several authors (Ooshika, 1954; McRae, 1957; Bayliss, 1950; Longuet-Higgins and Pople, 1957; West and Geddes, 1964; Suppan, 1968a,b). In particular, Liptay (1966) has shown that $D_e - D_g$ is always negative, so that the dispersion term leads to a red shift.

In order to use (36) to obtain quantitative values for this red shift it is necessary to know or to be able to approximate the van der Waals coefficient. In fact, d_{uv}^s is practically never known, not even when s refers to the ground state. Usually, therefore, a form of Unsold approximation is applied to the energy denominator in (36). The simplest is to assume that

$$\varepsilon_e{}^v - \varepsilon_0{}^v + \varepsilon_t{}^u - \varepsilon_s{}^u \approx \Delta^{-1}(\varepsilon_e{}^v - \varepsilon_0{}^v)(\varepsilon_t{}^u - \varepsilon_s{}^u) \tag{37}$$

where Δ has the dimensions of energy, so that

$$D_s = -\frac{3}{2}\frac{n^2 - 1}{n^2 + 2}\frac{\Delta_s}{a^3}\alpha_s{}^u. \tag{38}$$

This is essentially the London approximation (London, 1937; see, also, Margenau and Kestner, 1969) which relates d_{uv}^s to $\alpha_0{}^v$ and $\alpha_s{}^u$, the mean polarizabilities. This approximation will be reasonable if the sum in (36) is dominated by one particular e value and one particular t value when, if the appropriate transition energies are Δ_1 and Δ_2, Δ is given by

$$\Delta = \frac{\Delta_1 \Delta_2}{\Delta_1 + \Delta_2}. \tag{39}$$

Usually this will not be the case so fictitious average states are introduced and Δ_1 and Δ_2 are approximated by the ionization potentials of the molecules. There are clearly many objections to this type of procedure. First of all it is at best highly approximate and one can scarcely hope to obtain anything but a rough order of magnitude from it. Second, it is not altogether clear how the values of Δ for the ground and excited states are related. Third, and this is connected with the second objection, it seems doubtful if, at least in the case of conjugated molecules, the average transition energy is as large as the ionization potential since there are low lying π-states which make significant contributions. Generally speaking, Unsold approximations work best when one value of the average energy can be used for a related series of molecules or when one has a considerable amount of extra experimental or theoretical information to thoroughly test the approximation and empirically determine the average energy. Neither of these cases apply here.

There are other "empirical" expressions of a similar type which can be obtained for D_s (cf. Margenau and Kestner, 1969). These usually involve the polarizabilities and some form or other for the average energies. For example, expressions involving the diamagnetic susceptibility can be used to replace Δ but this is scarcely of much help in the present problem.

Another rather different average energy approximation can be used to relate the spectral shift due to dispersion forces to the intensity of electronic transition (see, for example, Liptay, 1966). However, this is a rather cruder approximation than that which uses polarizabilities and leads to rather widely varying values so we prefer not to consider it.

On the whole, therefore, and in spite of its shortcomings, we believe that Eq. (38) is the best to use. Yet, as we shall see in the following section when we come to study particular examples, the lack of definiteness in the proper value to use for Δ means that it is almost impossible to obtain meaningful estimates of the polarizability of the solute molecule from it.

VI. Some Applications

A. Excited-State Dipole Moments

If we ignore any changes in the solute polarizability on excitation, then according to Eq. (34) the solvent shift is given by Eq. (40) (we now drop the superscript *u* since there can be no confusion). That is,

$$-\Delta E = \frac{2}{a^3}(\boldsymbol{\mu}_e - \boldsymbol{\mu}_g)\cdot\boldsymbol{\mu}_g\left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right] + \frac{\mu_e{}^2 - \mu_g{}^2}{a^3}\,\frac{n^2-1}{n^2+2} \tag{40}$$

if there is no solvent-dipole reorientation on excitation and

$$-\Delta E = \frac{\mu_e{}^2 - \mu_g{}^2}{a^3}\left[\frac{2(D-1)}{D+2} - \frac{n^2-1}{n^2+2}\right] \tag{41}$$

if there is. In most cases Eq. (40) will apply so that we predict the solvent shift is given by

$$-\Delta E = \frac{(\boldsymbol{\mu}_e - \boldsymbol{\mu}_g)\cdot\boldsymbol{\mu}_g}{a^3}[2\phi(D) - 2\phi(n^2)] + \frac{\mu_e^{\,2} - \mu_g^{\,2}}{a^3}\phi(n^2), \tag{42}$$

where

$$\phi(D) = \frac{D-1}{D+2}, \tag{43}$$

This should be compared with the theory of Lippert (1957), who uses

$$-\Delta E = \frac{(\boldsymbol{\mu}_e - \boldsymbol{\mu}_g)\cdot\boldsymbol{\mu}_g}{a^3}[f(D) - f(n^2)] + \frac{\mu_e^{\,2} - \mu_g^{\,2}}{a^3}f(n^2), \tag{44}$$

where

$$f(D) = \frac{2(D-1)}{2D+1}. \tag{45}$$

The difference can be traced to the formula for the reaction field. Theories which use $f(D)$ neglect terms of the order $\alpha^u f(D)$, while those which use $\phi(D)$ neglect terms of the order of $(\alpha^u - \tfrac{1}{3}a^3)f(D)$, which is more accurate. The use of $\phi(D)$ has the great advantage that the reaction-field result agrees with the Abe theory.

Unfortunately, it is not particularly easy to use the expressions as presented above due to the different dependence—linear and quadratic—of the terms in (42) and (44) on the excited-state dipole moment. One can avoid this by making any of the following approximations:

(1) Replace $\mu_e^{\,2} - \mu_g^{\,2}$ by $(\mu_e - \mu_g)(\mu_e + \mu_g)$ and approximate $(\mu_e + \mu_g)$ by $2\mu_g$ to get

$$-\Delta E = \frac{2(\boldsymbol{\mu}_e - \boldsymbol{\mu}_g)\cdot\boldsymbol{\mu}_g}{a^3}\phi(D) \tag{46}$$

or

$$-\Delta E = \frac{(\boldsymbol{\mu}_e - \boldsymbol{\mu}_g)\cdot\boldsymbol{\mu}_g}{a^3}[f(D) + f(n^2)]. \tag{47}$$

(2) Assume the dipole reorientation effect occurs for the permanent dipoles, so that

$$-\Delta E = \frac{\mu_e^{\,2} - \mu_g^{\,2}}{a^3}[2\phi(D) - \phi(n^2)] \tag{48}$$

or

$$-\Delta E = \frac{\mu_e{}^2 - \mu_g{}^2}{a^3} f(D). \tag{49}$$

(3) Assume there is no dipole reorientation effect even for the induced dipoles and hence

$$-\Delta E = \frac{(\boldsymbol{\mu}_e - \boldsymbol{\mu}_g) \cdot \boldsymbol{\mu}_g}{a^3} [2\phi(D) - \phi(n^2)], \tag{50}$$

and similarly for the f-type result, although this approximation will not be very good.

All of these will give a reasonable linear plot between the solvent shift and the appropriate solvent properties, i.e., the functions $f(D)$, $\phi(D)$, $\phi(n^2)$, and $f(n^2)$. Similarly, because $f(D)$ and $\phi(D)$ have a reasonably constant ratio to each other and $\phi(n^2)$ and $f(n^2)$ are more or less constant, it will not be possible, due to the basic inaccuracies in the theory, to say which gives a better correlation with experiment. For similar reasons, although Eq. (42) is the really accurate formula and therefore is to be preferred, nevertheless, the errors involved in using one of Eqs. (46), (47), (48), or (49) rather than (42) itself are not significant given the rather approximate nature of the whole theory.

TABLE I

DIPOLE MOMENT OF THE LOWEST EXCITED STATE OF NITROBENZENE[a] (IN DEBYES)

Solvent	Calculated from formula			
	(46)	(47)	(48)	(49)
n-Heptane	12.2	8.76	8.90	7.51
Cyclohexane	12.1	9.13	9.16	7.71
Computed by difference technique	4.30	4.29	4.29	4.29

[a] The dipole moments in ground and excited states are assumed to be parallel.

In Table I we give μ_e for the lowest state of nitrobenzene obtained from the solvent shifts in the two solvents, cycloheptane and *n*-heptane using the four formulas (46)–(49). It is clear from the table that the results are large and differ depending on which formula is used and, indeed, which solvent. Part of the problem is that we have taken no account of the dispersion term. To some extent we can hope to avoid this difficulty by adopting the device used by Suppan (1968a,b) and subtracting the solvent shifts for different solvents and relating this to the change in $\phi(D), f(D)$, etc., i.e., for example, replace (46) by

$$\Delta E_{1-2} = \frac{2}{a^3}(\boldsymbol{\mu}_e - \boldsymbol{\mu}_g)\cdot\boldsymbol{\mu}_g\,\Delta\phi_{1-2}(D), \tag{51}$$

where ΔE_{1-2}, $\Delta\phi_{1-2}$ mean the differences of the quantities in the two solvents 1 and 2. Provided the dispersion shift is more or less the same in solvents 1 and 2, and one might very well expect that for similar types of solvents this is so, then using difference formulas will eliminate this effect. In any event, this seems to work remarkably well for nitrobenzene since, as is shown in Table I, we then obtain a consistent value for μ_e, namely, 4.3 D, which is about the same as the ground-state value.

The reason that we obtain more or less the same $\boldsymbol{\mu}_e$ for formulas (46)–(49), provided we use the differencing technique, is that the graphs of $\phi(D), f(D)$, etc., against solvent shifts are nearly parallel so that when we take differences, the formulas become practically the same. This is the reason for our remark in Section V that the approximations in the theory make it impossible to judge which is the best of formulas (46)–(49) to use.

On the whole, however, it does seem to be the case that solvent-shift effects are related fairly simply to dipole-moment changes on excitation of the solute molecule. Thus solvent-shift data can be used to obtain at least order of magnitude estimates of excited-state dipole moments. From this point of view the situation is quite satisfactory.

B. Polarizability

The situation as regards polarizabilities is not nearly so clearcut as that for dipole moments. The simplest case to consider is that of a nonpolar solute, since we can then ignore all the terms which we discussed in the previous section, because they vanish. The solvent shift in this case reduces to

$$\Delta E_{e-g} = \frac{4\pi\rho}{3a^3}(\mu_0{}^v)^2(\alpha_g{}^u - \alpha_e{}^u) + D_e - D_g, \tag{52}$$

i.e., the change in the term given by Eqs. (6) and (23) plus the change in the dispersion term. In Table II we give the values of ΔE_{e-g} for the ${}^1B_{1u}$ and

$^1B_{2u}$ transitions of naphthalene in various solvents, together with various properties of these solvents. The first four solvents have no dipole moment, so that the solvent shift should be entirely due to the dispersion term, and we see that for all of these the value of ΔE_{e-g} is roughly the same. This is actually quite a pleasing result since it was assumed that this was so in the previous section where the differencing technique was used to eliminate the dispersion effects in order to obtain consistent values of μ_e. Except for the $^1B_{2u}$ transition in acetonitrile the fact that the solvent has a dipole moment seems to have relatively little effect, which suggests that the first term in Eq. (52) is negligible.

TABLE II

SOLVENT-SHIFT DATA FOR THE EXCITED STATES OF NAPHTHALENE[a]

Solvent	Solvent shift (cm^{-1})		Solvent properties		
	$^1B_{1u}$	$^1B_{2u}$	μ^v (D)	α^v (10^{-25} cm^3)	I^v (eV)
n-Pentane	260	870	0	99.5	10.3
n-Hexane	290	910	0	117.8	10.4
n-Heptane	290	920	0	136.1	10.3
Cyclohexane	300	950	0	108.7	9.9
Ethyl ether	240	920	1.18	87.3	9.5
Ethanol	260	980	1.68	53.1	10.5
Acetonitrile	270	1190	3.94	44.2	12.4

[a] Taken from the paper by Abe *et al.* (1966).

Table II, therefore, indicates that the dispersion shift for the two transitions of naphthalene are (approximately) 270 cm^{-1} and 900 cm^{-1}, respectively. Unfortunately it does not seem possible to correlate these very closely with either $\alpha_0{}^v$ or the ionization of the solvent molecules (see Table II). According to Eq. (38), where the London approximation is made, the dispersion shift should be

$$-\tfrac{3}{2}a^{-3}\phi(n^2)[\Delta_e\alpha_e{}^u - \Delta_g\alpha_g{}^u], \tag{53}$$

where the parameters Δ_e, Δ_g must clearly depend on the particular solvent. In the two papers we are aware of where calculations of this type have been made, Suppan (1968a,b) takes $\Delta_e = \Delta_g$ and by means of a differencing technique finds for the lowest state that $\alpha_e - \alpha_g \sim 20.10^{-25}$ cm^3. On the other hand, Abe *et al.* (1966) takes

$$\Delta_s = \frac{I_s{}^u I_0{}^v}{I_s{}^u + I_0{}^v}, \tag{54}$$

where $I_s{}^u$, $I_0{}^v$ are the ionization potentials of the solute molecule in state s and of a solvent molecule in its ground state. This method gives enormous polarizability changes, of about 200 and 400 × 10^{-25} cm^3, respectively. These large differences mainly arise because the values of Δ_e and Δ_g obtained from (54) are markedly different. A recent semiempirical calculation of the polarizability of the excited states of naphthalene obtains results more in line with Suppan (Amos and Burrows, 1972), which does perhaps suggest that Δ_e and Δ_g are almost the same.

It seems to us quite clear that the situation with regard to the polarizabilities of excited states has yet to be resolved. We believe that the first term in (52) is too small to give any reliable estimates of $\alpha_e - \alpha_g$ so that if any estimates are to be obtained they will have to come from the dispersion term. Yet to relate the polarizability to dispersion forces is in itself an approximation and its range of applicability is quite unknown, especially when it is applied to excited states. Until there have been more complete investigations of this topic it does not seem likely that reliable estimates of polarizability changes can be obtained from solvent-shift data. Notice, however, that a more optimistic impression can be gleaned from theories based on the classical Onsager model [see, for example, Suppan (1968) and Liptay *et al.* (1971)]. Results can be obtained in this way which certainly seem in reasonable agreement with the theoretical predictions of Amos and Burrows (1972).

Appendix I

Consider two neutral molecules A and B. The Hamiltonian for the combined system can be written as

$$H = H_A + H_B + H'$$

where H_A and H_B are Hamiltonians for the separate molecules and the interaction term H' includes the nuclear–nuclear, nuclear–electron, electron–electron interactions between all pairs of particles (i.e., nuclei and electrons) such that one is associated with molecule A and one with molecule B. Thus

$$H' = \sum_{\alpha\beta} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} - \sum_{ab} \frac{Z_\alpha}{r_{ab}} - \sum_{a\beta} \frac{Z_\beta}{r_{a\beta}} + \sum_{ab} \frac{1}{r_{ab}},$$

where α and β refer to nuclei and a, b electrons of molecules A and B, respectively, and Z_α, Z_β are the appropriate nuclear charges. If we choose origins O_A and O_B in the two molecules, put $O_A O_B = R$ and let the z direction be parallel to $O_A O_B$, each of the distances in H' can be expressed in terms of R and position coordinates $(x_\alpha, y_\alpha, z_\alpha)$, (x_a, y_a, z_a) relative to O_A and $(x_\beta, y_\beta, z_\beta)$, (x_b, y_b, z_b) relative to O_B. For example,

$$r_{\alpha\beta} = R\left[1 + \frac{2(z_\beta - z_\alpha)}{R} + \frac{(x_\beta - x_\alpha)^2 + (y_\beta - y_\alpha)^2 + (z_\beta - z_\alpha)^2}{R^2}\right]^{1/2}.$$

When all these terms are expanded as an inverse power series[3] in R, the terms in R^{-1} and R^{-2} vanish since the molecules are neutral and the leading term is

$$R^{-3}\left\{\sum_{\alpha\beta} Z_\alpha Z_\beta I_{\alpha\beta} - \sum_{\alpha b} Z_\alpha I_{\alpha b} - \sum_{a\beta} Z_\beta I_{a\beta} + \sum_{ab} I_{ab}\right\},$$

where $I_{\alpha\beta} = x_\alpha x_\beta + y_\alpha y_\beta - 2z_\alpha z_\beta$, etc.

Introducing the dipole-moment operators $\mathbf{M}^A$ and $\mathbf{M}^B$ and the angular tensor $\boldsymbol{\Theta}$ defined by

$$\mathbf{M}^A = \sum_\alpha Z_\alpha \mathbf{r}_\alpha - \sum_a \mathbf{r}_a,$$

$$\mathbf{M}^B = \sum_\beta Z_\beta \mathbf{r}_\beta - \sum_b \mathbf{r}_b,$$

$$\boldsymbol{\Theta} = 1 - 3\hat{\mathbf{R}}\hat{\mathbf{R}},$$

where $\hat{\mathbf{R}}$ means the unit vector, the interaction term becomes

$$H' = R^{-3}\mathbf{M}^A \cdot \boldsymbol{\Theta} \cdot \mathbf{M}^B + O(R^{-4}),$$

i.e., the leading term is a dipole–dipole interaction term. The higher order terms have the form of dipole–quadrupole, quadrupole–quadrupole, etc., interactions (see, for example, Margenau, 1939). These certainly contribute to the solvent shift but only through terms of order R^{-7} and greater, and so they may be ignored compared with the leading term.

Appendix 2

The unperturbed wave functions for the solvent–solute system will be products (we are assuming the molecules are sufficiently well separated for the anti-symmetry requirement to be relaxed) of wave functions of the

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[3] The validity of this presupposes that the nuclei and electrons in molecules A and B are confined within spheres of radii $(\sqrt{2} - 1)R$ about O_A and O_B, respectively.

separate molecules. A complete set of zero-order functions is obtained from Ψ_0 [Eq. (2)] by changing any of the solvent molecule ground-state wave functions to excited-state wave functions, i.e., replacing $\phi_0{}^v$ by $\phi_e{}^v$, and by changing the wave function of the solute molecule from $\phi_s{}^u$ to $\phi_t{}^u$, i.e., from that for state s to any other state t. However, since H' involves only one solvent molecule at a time, when perturbation theory is carried through second order the only members of the complete set of zero-order functions which contribute are those which differ from Ψ_0 in a change of wave function at, at most, one solvent molecule only. Thus for our set of zero-order wave functions we need consider only Ψ_0 and the sets:

$$\phi_0^{v(1)} \cdots \phi_0^{v(N)} \phi_t{}^u, \tag{A2a}$$

where t is any solute molecule state, $t \neq s$,

$$\phi_0^{v(1)} \cdots \phi_e^{v(p)} \cdots \phi_0^{v(N)} \phi_s{}^u, \tag{A2b}$$

where e is any solvent molecule excited state and p runs from 1 to N, and

$$\phi_0^{v(1)} \cdots \phi_e^{v(p)} \cdots \phi_0^{v(N)} \phi_t{}^u. \tag{A2c}$$

The first-order change in the energy of Ψ_0 due to the interaction term H' [Eq. (3)] is just $\langle \Psi_0 | H' | \Psi_0 \rangle$ which equals

$$\sum_{p=1}^{N} R_p^{-3} \langle \phi_0^{v(p)} \phi_s{}^u | \mathbf{M}^u \cdot \boldsymbol{\Theta}^{uv(p)} \cdot \mathbf{M}^{v(p)} | \phi_0^{v(p)} \phi_s{}^u \rangle .$$

Introducing $\boldsymbol{\mu}_s{}^u = \langle \phi_s{}^u | \mathbf{M}^u | \phi_s{}^u \rangle$ and $\boldsymbol{\mu}_0^{v(p)} = \langle \phi_0^{v(p)} | \mathbf{M}^{v(p)} | \phi_0^{v(p)} \rangle$, the s-state dipole moment of the solute molecule and the ground-state dipole moment of the solvent molecule, this becomes

$$\sum_{p=1}^{N} R_p^{-3} \boldsymbol{\mu}_s{}^u \cdot \boldsymbol{\Theta}^{uv(p)} \cdot \boldsymbol{\mu}_0^{v(p)}. \tag{A2d}$$

The second-order term is

$$-\sum_e{}' \frac{|\langle \Psi_0 | H' | \Psi_e \rangle|^2}{E_e - E_0}, \tag{A2e}$$

where the sum is over the complete set of zero-order states Ψ_e (but excluding Ψ_0) and E_e and E_0, the zero-order energies of the states Ψ_e and Ψ_0, equal the sum of the individual molecular energies. As explained above, because of the nature of H' the only nonzero terms in (A2e) arise when

Ψ_e is one of the states (A2a)–(A2c). Taking each of these in turn, from (A2a), we obtain

$$-\sum_{t\neq s}\sum_{p,q=1}^{N} R_p^{-3}R_q^{-3}\boldsymbol{\mu}_0^{v(p)}\cdot\boldsymbol{\Theta}^{uv(p)}\cdot\frac{\langle\phi_s^u|\mathbf{M}^u|\phi_t^u\rangle\langle\phi_t^u|\mathbf{M}^u|\phi_s^u\rangle}{\varepsilon_t^u-\varepsilon_s^u}\cdot\boldsymbol{\Theta}^{uv(q)}\cdot\boldsymbol{\mu}_0^{v(q)} \tag{A2f}$$

where ε_t^u and ε_s^u are the solute molecule energies in states t and s. Recognizing that the s-state polarizability tensor $\boldsymbol{\alpha}_s^u$ of the solute molecule is defined by

$$\boldsymbol{\alpha}_s^u = 2\sum_{t\neq s}\frac{\langle\phi_s^u|\mathbf{M}^u|\phi_t^u\rangle\langle\phi_t^u|\mathbf{M}^u|\phi_s^u\rangle}{\varepsilon_t^u-\varepsilon_s^u},$$

it follows that (A2f) becomes

$$-\tfrac{1}{2}\sum_{p,q=1}^{N} R_p^{-3}R_q^{-3}\boldsymbol{\mu}_0^{v(p)}\cdot\boldsymbol{\Theta}^{uv(p)}\cdot\boldsymbol{\alpha}_s^u\cdot\boldsymbol{\Theta}^{uv(q)}\cdot\boldsymbol{\mu}_0^{v(q)}. \tag{A2g}$$

In a similar fashion from (A2b) we obtain

$$-\tfrac{1}{2}\sum_{p=1}^{N} R_p^{-6}\boldsymbol{\mu}_s^u\cdot\boldsymbol{\Theta}^{uv(p)}\cdot\boldsymbol{\alpha}_0^{v(p)}\cdot\boldsymbol{\Theta}^{uv(p)}\cdot\boldsymbol{\mu}_s^u. \tag{A2h}$$

From (A2c) we obtain the dispersion term D_s, which is written out in full in Eq. (36).

Thus we see that the change in energy ΔE_s due to H' is given by the sum (A2d), (A2g), (A2h), and D_s, as shown by Eq. (3).

Appendix 3

In order to evaluate $\sum_{p=1}^{N} R_p^{-6}$, Abe assumes the solute and solvent molecules are spherical with radii

$$r_u = \left(\frac{3M_u}{4\pi A d_u}\right)^{1/3}$$

and

$$r_v = \left(\frac{3M}{4\pi A d}\right)^{1/3},$$

where M, d, M_u, d_u are molecular weights and liquid densities and A is Avogadro's number. Approximately, therefore, the values of R_p will be $r_u + r_v$, $r_u + 3r_v$, $r_u + 5r_v$, etc., and the number of solvent molecules at these distances will be $4\pi(r_u + r_v)^2/(2r_v)^2$, $4\pi(r_u + 3r_v)^2/(2r_v)^2$, etc. Thus the sum may be approximated by

$$\sum_{p=1}^{N} R_p^{-6} = 4\pi r_u^{-4}(2r_v)^{-2} \sum_{n=1}^{\infty} [1 + (2n - 1)r]^{-4}, \qquad \text{(A3a)}$$

where r is the ratio r_v/r_u. This should be compared with the result

$$\sum_{p=1}^{N} R_p^{-6} = r_v^{-3} a^{-3} \qquad \text{(A3b)}$$

obtained by assuming the solvent molecules are uniformly distributed outside a sphere of radius a. A comparison of (A3a) and (A3b) suggests that a should not be chosen to equal r_u as might be expected, but instead should lie between r_u and r_v, the exact value depending on the relative values of r_u and r_v. For example, if $r_u = r_v$, the two expressions (A3a) and (A3b) will be equal if $a \approx 1.67 r_u$. This is perhaps a larger value than is normally taken. The point is that the largest contribution to the sum comes from the solvent molecules nearest to the solute one, i.e., those at a distance $r_u + r_v$, simply because R^{-6} decreases so rapidly with increasing R. The number of solvent molecules at this nearest distance is approximately $4\pi(r_u + r_v)^2/(2r_v)^2$, so that by far the largest term is

$$\frac{4\pi A d}{3M} \frac{\pi r_v}{(r_u + r_v)^4},$$

which implies we should put

$$a^3 = r_u{}^3 \frac{(1 + r)^4}{\pi r}. \qquad \text{(A3c)}$$

As r_v varies from $\frac{1}{2} r_u$ to $2 r_u$ this gives a value of about $r_u + \frac{1}{2} r_v$ for a.

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Thermochemistry in the Hartree–Fock Approximation

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I. Introduction

One of the primary aims of quantum chemistry is to predict the enthalpies of reaction of molecules from *ab initio* calculations based directly on the Schrödinger equation. To be chemically useful such predictions must achieve an accuracy of 1 kcal/mole or better for simple reactions involving the formation and/or breaking of a single chemical bond (Boys and Rajagopal, 1965).

We shall find it convenient to adopt a slightly different notion of "chemical accuracy"; namely, an estimate of the total electronic energy of a molecule which is in error by not more than 0.001 au ($\sim$0.6 kcal/mole $\sim$0.03 eV)[1] per atom (other than hydrogen). Such an accuracy for the true total energy, that is the lowest eigenvalue of the electronic Schrödinger equation, corrected if necessary for relativistic effects, has so far been achieved only for systems containing four or fewer electrons.

A more modest aim is the Hartree–Fock limit, which, for a closed-shell

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[1] Conversion factors used here are 1 au (hartree) = 27.21070 eV = 627.51 kcal/mole = 219474.6 cm^{-1} (DuMond and Cohen, 1965).

ground state, may be defined as the lowest electronic energy obtainable with a variational trial wave function expressed as a single Slater determinant. For quite a range of small molecules we may use recent self-consistent-field molecular orbital (SCF–MO) calculations to estimate the Hartree–Fock limit to within near chemical accuracy. This is the first objective of the present article. Most calculations of adequate accuracy are for molecules composed of hydrogen and first-row elements and we restrict our attention to these.

The total energies obtained in this way are then used to investigate the utility of the Hartree–Fock approximation in thermochemical calculations. The basic SCF calculations themselves all employ some variant of the expansion technique introduced by Hall (1951) and Roothaan (1951). Recent comprehensive reviews of this HFR (Hartree–Fock Roothaan) method have been given by Nesbet (1967), Roothaan (1960), and Roothaan and Bagus (1963).

II. Hartree–Fock Total Energies to Near Chemical Accuracy

A. Types of Basis Function

In the expansion method the unknown SCF–MO's are expressed linearly in terms of a certain set of basis functions. As a consequence the integrodifferential equations of Hartree–Fock theory are reduced to nonlinear matrix eigenvalue equations which are solved iteratively. In principle, the SCF–MO's and the total energy converge to accurate Hartree–Fock results as the basis set is extended to comprise an infinite complete set of functions. In practice finite basis sets are used and, as far as the total energy is concerned, the problem is to achieve convergence to within chemical accuracy.

The most commonly used basis functions are of two types: Slater-type orbitals

$$\chi_{\mathrm{STO}}(n, l, m; \zeta) = N_s r^{n-1} \exp(-\zeta r) Y_{lm}(\theta, \phi) \tag{1}$$

(Basic) Gaussian-type orbitals

$$\chi_{\mathrm{GTO}}(l, m; \zeta) = N_g r^l \exp(-\zeta r^2) Y_{lm}(\theta, \phi). \tag{2}$$

Each basis function is usually centered on one of the nuclei; (r, θ, ϕ) are then local spherical coordinates. The functions Y_{lm} are spherical harmonics which permit a classification of both STO's and GTO's into $s, p, d, f, \ldots$ types. Polynomials in the local Cartesian coordinates (x, y, z)

are sometimes used instead of the spherical harmonics to express the angular dependence of the basis functions.

In atomic SCF calculations each atomic orbital 1*s*, 2*p*, 3*d*, ... contains contributions only from basis functions of the same type. Here it is feasible to fully optimize the nonlinear parameters ζ and to obtain convergence to numerical Hartree–Fock results with considerably better than chemical accuracy. Such calculations have established that, for atoms, STO bases are much more efficient than GTO bases. This is illustrated by the results for the ground ^4S state of N shown in Table I, which are typical of those for first-row atoms.

The final two calculations in Table I employ "contracted" or "combined" GTO bases (CGTO's). Here some basis functions are chosen as fixed linear combinations of basic GTO's of the same type, as indicated by the first notation in the table. Such bases have proved useful in molecular SCF calculations. Although the contraction process does not reduce the number of basic electrostatic integrals which must be computed initially, it does reduce substantially the number which must be stored and subsequently manipulated and, if care is taken, the loss in flexibility of the

TABLE I

SCF Total Energies for N, ^4S (au)

Type and number of basis functions	Total energy (E_{SCF})	$E_{\mathrm{SCF}} - E_{\mathrm{HF}}$
STO[a] (2*s*, 1*p*) ≡ {2, 1} ≡ {SZ}	−54.26890	0.1320
STO[a] (4*s*, 2*p*) ≡ {4, 2} ≡ {DZ}	−54.39795	0.0030
STO[a] (4*s*, 3*p*) ≡ {4, 3}	−54.40082	0.0001
STO[a] (5*s*, 4*p*) ≡ {5, 4}	−54.40093	0.0000
GTO[a] (6*s*, 3*p*) ≡ (6, 3)	−54.28328	0.1178
GTO[a] (10*s*, 6*p*) ≡ (10, 6) ≈ {DZ}	−54.39892	0.0020
GTO[a] (11*s*, 7*p*) ≡ (11, 7)	−54.40012	0.0008
CGTO[a] (3, 3, 2, 3; 3, 3) = [4, 2] ≈ {DZ}	−54.39880	0.0021
CGTO[b] (4, 2, 1, 2, 1, 1, 1, 1, 1, 1; 3, 2, 1, 1, 1) = [10, 5]	−54.40035	0.0006

[a] Huzinaga *et al.* (1971).

[b] Rauk *et al.* (1970).

basis and consequent increase in total energy are small. In Table I and subsequently such CGTO bases are specified using square brackets [ ] to distinguish them from STO bases { } and uncontracted GTO bases ( ). Inside the brackets the number of basis functions of *s*, *p*, ... type are listed successively.

A convenient intermediate level of accuracy between a single-zeta STO basis {SZ}, with one STO per atomic orbital, and chemical accuracy (0.001 au for N) is provided by the STO double-zeta basis {DZ}. Table I shows that to achieve this level of accuracy with GTO's we require between two and three times as many basis functions. As the tolerable error is further reduced below chemical accuracy the relative advantage of STO bases increases still more. Only the largest GTO and CGTO basis of Table I surpass chemical accuracy, whereas the STO basis {4, 3} is an order of magnitude better. Allowing for the three types of *p* function these bases contain 32, 39, and 13 functions, respectively.

The great attraction of GTO bases for molecular calculations is that all the electrostatic integrals which arise may be evaluated simply in closed form (Boys, 1950). The evaluation of the corresponding integrals for a STO basis is very much more difficult.

B. N_2 and NH_3

One of the most thorough studies of the convergence of a series of SCF–MO calculations towards the Hartree–Fock limit is that of Cade *et al.* (1966) on the nitrogen molecule. These authors carried out two series of calculations. The first started with the basis {SZ} of Table I on each atom, with ζ values optimized for the N_2 molecule, and this basis was gradually augmented by additional functions of *s*, *p*, *d*, and *f* types; different ζ values were used for the same basis function in different molecular symmetries and these ζ values were partially optimized at each stage.

The second series was similar except that it started from a large STO basis for N, ^4S. This "best-atom" basis, intermediate between the bases {4, 3} and {5, 4} of Table I will be denoted {BA}.

Key results of the two series of calculations and the estimated Hartree–Fock limit are shown in Table II. A prime indicates complete or partial optimization of the orbital exponents ζ and the symbol P represents polarization functions, that is basis functions with *l* values one or more units higher than any valence atomic orbital. The inclusion of such functions leads to an energy decrease of about 0.1 au and is, therefore, essential for chemical accuracy; for N_2 up to three *d* functions and one *f* function were included for each molecular symmetry type.

TABLE II

SCF–MO TOTAL ENERGIES FOR N_2, $X\,^1\Sigma_g^+$(au)

Calculation	Basis	Total energy (E_{SCF})	$E_{SCF} - E_{HF}$
1*B*	{SZ}′	−108.6459	0.3469
1*G*	{DZ}′	−108.8914	0.1014
1*S*	{BA + P}′	−108.9888	0.0040
2*A*	{BA}	−108.8967	0.0961
2*B*	{BA + P}	−108.9897	0.0031
2*D*	{BA + P}′	−108.9928	0.0014
	{BA + P}′	−108.9956[a]	0.0014

Estimated limit $E_{HF} = -108.997 \pm 0.002$

[a] At r_e (calc.) = 2.013 au, all other energies at r_e (exp) = 2.068 au.

The basis sets 1*S*, 2*B*, and 2*D* are identical apart from ζ values and the superior results with 2*B* and especially 2*D* reflect the inefficiency of the procedure of gradually building up the basis with partial optimization at each stage; it is much more efficient to start with large optimum atomic bases and perform limited molecular optimizations with all important basis functions included. Indeed, we see from Table II that the basis {BA + P} without any molecular optimization is already almost adequate for chemical accuracy (0.002 au for N_2).

Two SCF–MO calculations on NH_3 of accuracy comparable to the above study of N_2, have been carried out by Rauk *et al.* (1970) using a very large CGTO basis and by Rajagopal (1965) using a STO basis; both bases were expressed in local Cartesian coordinate systems. Total energies from these and simpler calculations are shown in Table III together with the estimated Hartree–Fock limit.

This estimate is based mainly on the work of Rauk *et al.* and the other Gaussian calculations. Although the final wave function of Rajagopal's calculation may be of comparable accuracy, the grids used in the numerical integration technique (Boys and Rajagopal, 1965) are such that the final two decimals quoted in the total energy are not significant. As for N_2, the inclusion of polarization functions, here *d* functions on nitrogen and *p* functions on the hydrogens, is essential for near chemical accuracy. Their effect may be estimated as the greater part of $E_{SCF} - E_{HF}$ for the 16-function STO basis of Guidotti and Salvetti, that is about 0.05 au.

TABLE III

SCF–MO TOTAL ENERGIES FOR NH_3, $X\,^1A_1$ (au)

Basis	Total energy (E_{SCF})	$E_{SCF} - E_{HF}$
8STO[a], N {2, 1} H {1}	−56.096	0.129
16STO[b], N {4, 2} H {2}	−56.1678	0.0572
23STO[c], N {4, 3, 2} H {1}	(−56.2268)	(−0.0018)
45GTO[d], N (9, 5) H (4, 1)	−56.2015	0.0235
67GTO[e], N [7, 8, 1] H [3, 2]	−56.2109	0.0141
91GTO[f], N [10, 5, 2] H [4, 1]	−56.2219	0.0031
Estimated limit $E_{HF} = -56.225 \pm 0.002$		

[a] Duncan (1957).
[b] Guidotti and Salvetti (1968).
[c] Rajagopal (1965).
[d] Ritchie and King (1967).
[e] Body *et al.* (1968).
[f] Rauk, *et al.* (1970).

C. Basis Function Requirements

From these examples and others in the literature (cf. especially, McLean and Yoshimine, 1967b) we may formulate the following requirements for an HFR calculation to converge to the Hartree–Fock limit to within chemical accuracy.

(*i*) The basis set should include for each atom sufficient functions to approximate the Hartree–Fock limit for the isolated atom to within 0.0005 au or less, that is, considerably better than chemical accuracy. For a typical first-row atom (N) the "nominal" Slater basis {4, 3} of Bagus and Gilbert (1967) with a total of 13 functions satisfies this requirement comfortably, whereas the Gaussian basis (15, 8), with 39 functions, contracted to [10, 5] is barely adequate (Table I).

(*ii*) In addition several polarization functions should be included for each atom. The most important of these have l values 1 greater than the highest l value for the valence electrons. The nonlinear parameters (ζ) in the polarization functions should be optimized in a molecular calculation of at least double-zeta quality. In the case of a Slater basis, the ζ's for the two or three s functions needed on each hydrogen atom should be optimized at this stage since this is not possible for the isolated atom. Limited experience would suggest that, for polarization functions, Gaussian bases are almost as efficient as Slater bases. That is, for chemical accuracy comparable numbers of polarization functions are needed for the two types of basis. With Gaussian bases it is also simple to introduce additional functions centered at points other than the nuclei, for example, bond functions consisting of 1*s* Gaussians distributed along chemical bonds. For CH_4 such functions have proved an attractive alternative to the more conventional *d* functions on carbon and *p* functions on the hydrogens (Rothenberg and Schaefer, 1971).

(*iii*) All basis functions from (*i*) and (*ii*) are to be used in a final HFR calculation. If rather small Slater bases are used in step (*i*) it may be necessary to carry out extensive optimization of many ζ's at this stage. A more efficient procedure is to use large atomic bases; little or no optimization of the ζ's in the final calculation may then be required for chemical accuracy. The Gaussian bases required to satisfy the conditions of step (*i*) are so extensive that molecular optimization is unnecessary except, perhaps, for hydrogen functions. Indeed it is usually possible to reduce the flexibility of the basis by contraction and still retain chemical accuracy.

D. Extrapolated Hartree–Fock Total Energies

The Hartree–Fock total energies listed in Table IV are the results of HFR calculations which satisfy, or come close to satisfying, the above requirements. The best-atom Slater bases {BA} for the linear molecules are at least as extensive as the basis {4, 3} of Table I. Both the lowest calculated energy and the estimated Hartree–Fock limit are given for each molecule. The estimated limits and their uncertainties are basesd mainly on estimates of the original authors of the calculations modified in some cases for mutual consistency and to ensure what are intended to be safe estimates. Thus, for the linear molecules taken from the work of McLean and Yoshimine (1967a), their estimate, *d*, of the "probable" distance from the Hartree–Fock limit was assumed to be a lower limit to this distance with an uncertainty $\pm d$.

For O_2 and C_2 results are given for some excited states as well as the ground states. We note that the observed ground state of C_2 is the $x\ {}^1\Sigma_g^+$ state arising (principally) from the closed-shell configuration, $(2\sigma_u)^2(1\pi_u)^4$, whereas the Hartree–Fock calculations predict that the $A\ {}^3\Sigma_g^-$ state from the configuration $(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^2$ lies almost 3 eV lower than the $x\ {}^1\Sigma_g^+$ state. This rather large error is understandable from the correlation

TABLE IV

HARTREE–FOCK TOTAL ENERGIES AND BINDING ENERGIES FOR SOME SMALL MOLECULES

Molecule and state	Basis functions	$-E_{\mathrm{HF}}$(au)		D_e(HF) (eV)	δD_e (eV)	D_e(obs)[b] (eV)	D_e'(HF) (eV)
		Lowest calculated[a]	Estimated limit				
H_2, $X\,^1\Sigma_g^+$	elliptic	1.1336	1.1336	3.64	1.11	4.75	4.78
LiH, $X\,^1\Sigma^+$	{BA + P}′	7.9873	7.9878 ± 0.0003	1.50	1.02	2.52	2.82
BeH, $X\,^2\Sigma^+$	{BA + P}′	15.1531	15.1536 ± 0.0003	2.19	0.41	2.6 ± 0.2	3.01
BH, $X\,^1\Sigma^+$	{BA + P}′	25.1315	25.1320 ± 0.0003	2.80	0.78	3.58	3.96
CH, $X\,^2\Pi$	{BA + P}′	38.2796	38.2801 ± 0.0003	2.49	1.16	3.65	3.82
NH, $X\,^3\Sigma^-$	{BA + P}′	54.9784	54.9789 ± 0.0003	2.12	1.68	3.8 ± 0.2	4.00
OH, $X\,^2\Pi$	{BA + P}′	75.4213	75.4218 ± 0.0003	3.06	1.57	4.63	4.80
FH, $X\,^1\Sigma^+$	{BA + P}′	100.0708	100.071 ± 0.0003	4.41	1.71	6.12	6.25
Li_2, $X\,^1\Sigma_g^+$	{BA + P}′	14.8718	14.873 ± 0.001	0.21	0.84	1.05	—
C_2, $x\,^1\Sigma_g^+$	{BA + P}′	75.4062	75.408 ± 0.002	0.84	5.56	6.4 ± 0.2	—
C_2, $A\,^3\Sigma_g^-$	{BA + P}′	75.5152	75.517 ± 0.002	3.80	1.80	5.6 ± 0.2	—
N_2, $X\,^1\Sigma_g^+$	{BA + P}′	108.9956	108.997 ± 0.002	5.31	4.59	9.90	—
O_2, $X\,^3\Sigma_g^-$	{BA + P}′	149.6659	149.670 ± 0.003	1.39	3.79	5.21	—
O_2, $a\,^1\Delta_g$	{BA + P}′	149.6172	149.621 ± 0.003	0.06	4.17	4.23	—
O_2, $b\,^1\Sigma_g^+$	{BA + P}′	149.5683	149.572 ± 0.003	−2.50	6.07	3.57	—
F_2, $X\,^1\Sigma_g^+$	{BA + P}′	198.7814[c]	198.785 ± 0.003	−0.92	2.57	1.65 ± 0.05	—
LiO, $X\,^2\Pi$	{BA + P}′	82.3111	82.312 ± 0.001	1.90	1.54	3.5 ± 0.2	—
LiF, $X\,^1\Sigma^+$	{BA + P}	106.9916	106.993 ± 0.001	4.11	1.89	6.0 ± 0.3	—
BeO, $X\,^1\Sigma^+$	{BA + P}′	89.4541	89.455 ± 0.001	1.98	2.72	4.7 ± 0.1	—
BF, $X\,^1\Sigma^+$	{BA + P}	124.1671	124.169 ± 0.001	6.28	1.62	7.9 ± 0.2	—
CO, $X\,^1\Sigma^+$	{BA + P}′	112.7891	112.791 ± 0.001	7.97	3.25	11.22	—
CF, $X\,^2\Pi$	{BA + P}′	137.2259[c]	137.229 ± 0.002	3.57	1.93	5.5 ± 0.2	—

NO, $X^2\Pi$	{BA + P}′	129.2837	129.286 ± 0.002	2.06	4.55	6.61	—
NF, $X^3\Sigma^-$	{BA + P}′	153.8353[c]	153.838 ± 0.002	0.75	3.25	4 ± 1	—
OF, $X^2\Pi$	{BA + P}′	174.1950[d]	174.199 ± 0.003	−0.54	2.94	2.4 ± 0.4	—
HCN, $X^1\Sigma^+$	{BA + P}	92.9160	92.918 ± 0.001	8.94	4.64	13.58	—
CO_2, $X^1\Sigma_g^+$	{BA + P}	187.7254	187.729 ± 0.002	11.47	5.38	16.85	—
NNO, $X^1\Sigma^+$	{BA + P}	183.7567	183.771 ± 0.007	4.35	7.37	11.72	—
FCN, $X^1\Sigma^+$	{BA + P}	191.7798	191.796 ± 0.008	8.08	—	—	—
C_2H_2, $X^1\Sigma_g^+$	{BA + P}	76.8540	76.858 ± 0.002	13.08	4.45	17.53	—
LiCCH, $X^1\Sigma^+$	{BA + P}	83.7305	83.742 ± 0.006	11.76	—	—	—
FCCH, $X^1\Sigma^+$	{BA + P}	175.7236	175.740 ± 0.008	12.34	—	—	—
C_2N_2, $X^1\Sigma_g^+$	{BA + P}	184.6568	184.677 ± 0.009	13.55	8.10	21.65	—
H_2O, X^1A_1	O(10, 6, 2), H(4, 2)	76.0596	76.070 ± 0.005	7.09	2.99	10.07	10.67
	O{3, 3, 1}, H{2, 1}	76.0047					
NH_3, X^1A_1	N[10, 5, 2], H[4, 1]	56.2219[e]	56.225 ± 0.002	8.82	4.07	12.89	14.29
	N{4, 3, 2}, H{1}	(56.2268)					
H_2O_2, X^1A_1	O(11, 7, 1), H(6, 1)	150.7993	150.850 ± 0.009	6.29	5.19	11.48	—
CH_4, X^1A_1	C[4, 2, 2], H[2, 1]	40.2045[f]	40.220 ± 0.005	14.46	3.72	18.18	20.80
	C{5, 3, 1}, H{2, 1}	40.2045					
H_2CO, X^1A_1	C, O[5, 3, 2], H[2, 1]	113.8917	113.932 ± 0.009	11.81	4.43	16.24	—
C_2H_6, X^1A_{1g}	C(11, 7, 1), H(6, 1)	79.2377[g]	79.270 ± 0.008	24.29	6.53	30.82	—
C_2H_4, X^1A_{1g}	C[5, 3, 2], H[2, 1]	78.048[h]	78.080 ± 0.008	19.12	5.25	24.37	—

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[a] Values from Krauss (1967) and Richards *et al.* (1971) where detailed references are given.

[b] Values for diatomic molecules from Gaydon (1968); for polyatomic molecules from Lewis and Randall (1961) supplemented by NBS Technical Note 270-3 (Wagman *et al.*, 1968). Zero-point vibrational energies from Herzberg (1950, 1966).

[c] O'Hare and Wahl (1971).

[d] O'Hare and Wahl (1970).

[e] Rauk *et al.* (1970).

[f] Rothenberg and Schaefer (1971).

[g] Veillard (1969).

[h] Neumann and Moskowitz (1969).

[i] *Note added in proof.* This value, ascribed by Krauss to Horsley and Richards (1967), is incorrect (Richards, private communication). Replacing it by 198.7761 (LMSS 1967) gives the limit 198.780 ± 0.003.

diagram for homonuclear diatomic molecules (Mulliken, 1932) and the calculations of Fougere and Nesbet (1966) which indicate that the MO's $3\sigma_g$ and $1\pi_u$ are almost equal in energy. Thus there is a second ${}^1\Sigma_g^+$ state from $(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^2$ which, in the single configuration approximation, is almost degenerate with $x\ {}^1\Sigma_g^+$; we have a case of strong first-order configuration interaction (Moffitt, 1954) or "nondynamical correlation" (Sinanoglu, 1964) and the energy of $x\ {}^1\Sigma_g^+$ is substantially lowered. On the other hand, $A\ {}^3\Sigma_g^-$ is the only low-lying state of ${}^3\Sigma_g^-$ symmetry and is, therefore, not affected by strong first-order CI. A similar, although less marked, failure of the Hartree–Fock calculations is the substantial (~2 eV) overestimation of the $X\ {}^3\Sigma_g^- - b\ {}^1\Sigma_g^+$ interval for O_2. This is again attributable to neglect of first-order CI, which lowers the state $b\ {}^1\Sigma_g^+$ relative to $X\ {}^3\Sigma_g^-$.

III. Hartree–Fock Binding Energies

The Hartree–Fock binding energies D_e(HF) in Table IV were obtained from the extrapolated Hartree–Fock total energies and atomic Hartree–Fock energies (Huzinaga *et al.*, 1971). Also listed are the observed binding energies and the discrepancies

$$\delta D_e = D_e(\text{obs}) - D_e(\text{HF}). \tag{3}$$

Assuming that the observed total energy of an atom or molecule may be obtained from the Hartree–Fock value by adding the correlation energy E_{corr} and a relativistic correction E_{rel} we have

$$\delta D_e = -\Delta E_{\text{corr}} - \Delta E_{\text{rel}}, \tag{4}$$

where Δ denotes the change in a quantity in going from the separated atoms to the molecule.

Estimates of relativistic corrections for atoms (Clementi, 1963) indicate that contributions from the valence shell are negligible to within chemical accuracy, at least for first-row elements. Appreciable contributions arise only from inner-shell electrons and it is reasonable to assume that these are almost unchanged on molecular formation. Hence, in Eq. (4) $\Delta E_{\text{rel}} \approx 0$ and

$$\delta D_e = -\Delta E_{\text{corr}}, \tag{5}$$

that is, the deficiency in the Hartree–Fock dissociation energy is given by the change in correlation energy on molecular formation. Calculations of the relativistic corrections are, therefore, not required to obtain these changes in correlation energy.

Estimates of the total correlation energies of the first-row atoms have been obtained by Clementi (1963) and Cade and Huo (1967) from experimental atomic energies, Hartree–Fock total energies, and calculated relativistic corrections.

From Table IV we see that δD_e (often referred to as the extra molecular correlation energy or the correlation contribution to binding) is substantial often amounting to several electron volts even for diatomic molecules. Hartree–Fock estimates of binding energies are, therefore, not directly useful. These large changes in correlation energy reflect the extensive electronic reorganization on molecular formation.

The description of molecules in terms of localized molecular orbitals (LMO's) is convenient for interpreting these correlation energy changes. These LMO's, which correspond closely to the chemical concepts of inner shells, bonds, and lone pairs, are obtained by applying a suitable unitary transformation to the molecular orbitals obtained directly from the canonical Hartree–Fock equations (Lennard-Jones, 1949). Various criteria have been suggested to determine this unitary transformation and hence the LMO's uniquely. The criterion used here is the maximization of the intraorbital Coulomb interactions at the expense of the interorbital interactions (Lennard-Jones and Pople, 1950; Hurley *et al.*, 1953; Edmiston and Ruedenberg, 1965). In terms of this LMO picture the formation of each new chemical bond leads to an additional pair of electrons in a localized molecular orbital. Since the LMO's are defined to maximize intraorbital interactions at the expense of interorbital contributions, it is to be expected that the formation of these new electron pairs will dominate the correlation energy changes. The values of Table IV bear out this view in a qualitative way, the δD_e values for closed-shell molecules amounting to some 1.0–2.0 eV per bond. A more thorough analysis along these lines requires the introduction of appropriate valence states for the separated atoms in place of the spectroscopic states.

IV. Conditions for the Invariance of the Correlation Energy

The picture in terms of LMO's suggests that the correlation energy should remain almost invariant in any change that preserves the number of electron pairs and, as far as possible, their local spatial relationship to each other. The Hartree–Fock approximation should then provide quite an accurate estimate of the change in total energy.

One of the simplest changes of this sort is the formation of a hydride by the extraction of one or more protons from the nucleus of the united atom. Assuming conservation of the electronic correlation energy in this process we obtain improved estimtes $D_e'(\mathrm{HF})$ of hydride binding energies from the equation

$$D_e'(\mathrm{HF}) = D_e(\mathrm{HF}) - E_{\mathrm{corr}}(\mathrm{UA}) + E_{\mathrm{corr}}(\mathrm{SA}). \tag{6}$$

In applying this equation to the diatomic hydrides of Table IV it is necessary to employ those states of the united atom (UA) and separated atoms (SA) which correlate with the appropriate hydride state (Cade and Huo, 1967). These states and their electronic correlation energies are listed in Table V.

TABLE V

UNITED AND SEPARATED ATOMS FOR FIRST-ROW DIATOMIC HYDRIDES

E_{corr} (au)	United atom	Hydride, AH	Separated atom A[a]	E_{corr} (au)
−0.0943	$\mathrm{Be}(1s^2 2s^2,\ {}^1S)$	$\mathrm{LiH}(1\sigma^2 2\sigma^2,\ X\,{}^1\Sigma^+)$	$\mathrm{Li}(1s^2 2s,\ {}^2S)$	−0.0454
−0.1248	$\mathrm{B}(1s^2 2s^2 2p,\ {}^2P)$	$\mathrm{BeH}(1\sigma^2 2\sigma^2 3\sigma,\ X\,{}^2\Sigma^+)$	$\mathrm{Be}(1s^2 2s^2,\ {}^1S)$	−0.0943
−0.1673	$\mathrm{C}(1s^2 2s^2 2p^2,\ {}^1D)$	$\mathrm{BH}(1\sigma^2 2\sigma^2 3\sigma^2,\ X\,{}^1\Sigma^+)$	$\mathrm{B}(1s^2 2s^2 2p,\ {}^2P)$	−0.1248
−0.2057	$\mathrm{N}(1s^2 2s^2 2p^3,\ {}^2D)$	$\mathrm{CH}(1\sigma^2 2\sigma^2 3\sigma^2 1\pi,\ X\,{}^2\Pi)$	$\mathrm{C}(1s^2 2s^2 2p^2,\ {}^3P)$	−0.1565
−0.2579	$\mathrm{O}(1s^2 2s^2 2p^4,\ {}^3P)$	$\mathrm{NH}(1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2,\ X\,{}^3\Sigma^-)$	$\mathrm{N}(1s^2 2s^2 2p^3,\ {}^4S)$	−0.1886
−0.3220	$\mathrm{F}(1s^2 2s^2 2p^5,\ {}^2P)$	$\mathrm{OH}(1\sigma^2 2\sigma^2 3\sigma^2 1\pi^3,\ X\,{}^2\Pi)$	$\mathrm{O}(1s^2 2s^2 2p^4,\ {}^3P)$	−0.2579
−0.3896	$\mathrm{Ne}(1s^2 2s^2 3p^6,\ {}^1S)$	$\mathrm{HF}(1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4,\ X\,{}^1\Sigma^+)$	$\mathrm{F}(1s^2 2s^2 2p^5,\ {}^2P)$	−0.3220

[a] Plus $\mathrm{H}(1s,\ {}^2S)$, $E_{\mathrm{corr}} = 0$.

Equation (6) may also be applied to the closed-shell polyhydrides H_2O, NH_3, and CH_4, all of which correlate with ground-state separated atoms and the same united atom $\mathrm{Ne}(1s^2 2s^2 2p^6,\ {}^1S)$. The $D_e'(\mathrm{HF})$ values obtained in this way are listed in the final column of Table IV. We see that Eq. (6) works well for H_2 and the diatomic hydrides, the binding energies being consistently overestimated by a small fraction of an electron volt. However, for the ten-electron isoelectronic series

$$\mathrm{Ne} \to \mathrm{HF} \to \mathrm{H_2O} \to \mathrm{NH_3} \to \mathrm{CH_4} \tag{7}$$

the discrepancy increases rapidly and amounts to more than 2.5 eV for CH_4. Recent theories of electronic correlation are consistent with some decrease in the magnitude of the correlation energy in going from Ne to CH_4 in the isoelectronic sequence (7) but adequate quantitative calculations are lacking (Sinanoglu, 1964).

We may use the δD_e values of Table IV to compute the change in correlation energy for many chemical reactions involving the listed molecules. When both the products and reactants are closed-shell molecules we find quite small correlation energy changes, very much smaller than the δD_e themselves. For example, for the reaction

$$N_2 + 3H_2 \rightarrow 2NH_3, \tag{8}$$

the change in correlation energy is given by

$$\begin{aligned}\Delta_{\text{corr}}(N_2 + 3H_2 \rightarrow 2NH_3) &= 2E_{\text{corr}}(NH_3) - E_{\text{corr}}(N_2) - 3\,E_{\text{corr}}(H_2)\\ &= -2\delta D_e(NH_3) + \delta D_e(N_2) + 3\delta D_e(H_2)\\ &= -0.22 \pm 0.15\text{ eV}.\end{aligned} \tag{9}$$

Here we have used Eq. (5) and values of δD_e from Table IV. The uncertainty arises from errors in the experimental binding energies (negligible in this case) and in the extrapolated Hartree–Fock limits for N_2 and NH_3.

This near invariance of the correlation energy for closed-shell reactions is clearly consistent with the conditions enunciated above in terms of LMO's. In such reactions the number of electron pairs is always preserved and changes in their local spatial relationship are quite minor. In this connection we note that, for N_2, the localization criterion we have adopted leads to three equivalent bent bonds rather than the alternative picture in terms of one σ-bond and two π-bonds (Edmiston and Ruedenberg, 1965).

There are several ways of exploiting this property of closed-shell reactions. Thus Matcha (1968) has used formulas of the type

$$\begin{aligned}D_e(\text{NaCl}) = D_e(\text{HF,NaCl}) - E_{\text{corr}}(\text{Na}^+) - E_{\text{corr}}(\text{Cl}^-)\\ + E_{\text{corr}}(\text{Na}) + E_{\text{corr}}(\text{Cl}),\end{aligned} \tag{10}$$

which may be based on the near invariance of the correlation energy in the ionic decomposition

$$\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^- \tag{11}$$

to obtain binding energies of near chemical accuracy for NaCl and other alkali halide molecules.

Again Snyder (1967) has used Hartree–Fock electronic energies together with estimates of translational, rotational, and vibrational energies to calculate enthalpies of reaction, ΔH°_{298}, for a number of closed-shell molecules. However, deficiencies in the then available Hartree–Fock energies, especially for nonlinear molecules, made it difficult to separate the error inherent in the Hartree–Fock approximation itself from inadequacies in the HFR calculations.

Here we use the data of Table IV to calculate Hartree–Fock enthalpies of formation ΔH_0° for the listed molecules but first we must consider an appropriate choice of reference states.

V. Reference States for the Elements

Any compilation of enthalpies of formation depends on some definition of reference states, both for the molecules concerned and for the elements. For our purposes the most convenient reference state for the molecules is the standard perfect-gas state at a temperature of absolute zero. In this state both the internal energy U and enthalpy H are given by

$$H = U = E + v_0, \tag{12}$$

where E is the total electronic energy and v_0 is the zero-point vibrational energy. The term v_0 could, in principle, be calculated to near chemical accuracy using Hartree–Fock total energies for a range of nuclear configurations. However, such calculations are not available for many of the molecules of Table IV and we use spectroscopic values in all cases.

For the elements various choices of reference state are possible. The usual thermodynamic standard state (Lewis and Randall, 1961) is chosen for experimental convenience and differs for different elements; for example, we have Li (metal), C (graphite), and O_2 (gas). This choice is clearly unsuitable for our purpose since we have no estimate of the Hartree–Fock limit for many of these states.

On the other hand, theoretical discussions are usually based on the binding energies D_e of Table IV. The use of these quantities, or more properly $D_0 = D_e - v_0$, corresponds to the choice of a monatomic gas in the ground electronic state as the reference state for each element. The enthalpy of formation of any molecule is then given by $\Delta H_0^\circ = -D_0$. The large values of δD_e in Table IV show that this choice of reference state is a very bad one from the point of view of invariance of the correlation energy, and the considerations of Section IV suggest that some different choice may lead to much more accurate enthalpies of formation.

The best choice of reference state for each element would seem to be some simple closed-shell molecule which contains one atom of the element and which is easily accessible both experimentally and theoretically. Closed-shell hydrides satisfy these requirements and we have chosen these hydrides, in the perfect-gas state at absolute zero, as reference states for the elements.

One temporary disadvantage of these reference states is that in two cases (H_2O, CH_4) the best available HFR calculations are hardly adequate to estimate the Hartree–Fock limit to within chemical accuracy and for two others (BeH_2, BH_3) no adequate HFR calculations have been carried out. For these reasons compounds containing Be are omitted in the following tables and the reference state of B is chosen as the closed-shell diatomic hydride $BH(X\,^1\Sigma^+)$ rather than BH_3, which is probably more appropriate from correlation energy considerations.

The standard enthalpies of formation ΔHf_0° of these closed-shell hydrides, relative to the thermodynamic standard states for the elements, are listed in Table VI. These values are used to convert enthalpies of formation from thermodynamic standard states to values relative to the closed-shell hydride reference states and vice versa.

TABLE VI

STANDARD ENTHALPIES OF FORMATION ΔHf_0° FOR ELEMENTARY REFERENCE STATES

Element:	H	Li	B	C	N	O	F
Hydride:	H_2	LiH	BH	CH_4	NH_3	H_2O	HF
ΔHf_0° (kcal/mole):	0.0[a]	30.0[b]	106.7[c]	−15.970[c]	−9.34[c]	−57.102[c]	−64.789[c]

[a] By definition.

[b] From NBS Circular 500 (Rossini *et al.*, 1952).

[c] From NBS Technical Note 270-3 (Wagman *et al.*, 1968).

VI. Hartree–Fock Enthalpies of Formation

In Table VII enthalpies of formation ΔH_0° are listed for molecules appearing in Table IV; all values are relative to the reference states for the elements specified in the previous section (Table VI). The experimental values are based on the data of Gaydon (1968) for diatomic molecules, and on the data of Lewis and Randall (1961), supplemented by the National Bureau of Standards Technical Note 270-3 (Wagman *et al.*, 1968,) for polyatomic molecules.

The Hartree–Fock values, $\Delta H_0^\circ(\mathrm{HF})$, were derived from the estimated Hartree–Fock limits of Table IV and spectroscopic values for the zero-point vibrational energies (Herzberg, 1950, 1966). For each molecule, the listed uncertainty in $\Delta H_0^\circ(\mathrm{HF})$ corresponds only to the uncertainty in the Hartree–Fock limit for that molecule; if the molecule contains C, N, or O, additional errors in $\Delta H_0^\circ(\mathrm{HF})$ arise from the uncertainties 3, 1, and 3 kcal/mole, respectively, in the Hartree–Fock limits of the reference states

TABLE VII

ENTHALPIES OF FORMATION ΔH_0° FROM CLOSED-SHELL HYDRIDE REFERENCE STATES (kcal/mole)

Compound (gas)	ΔH_0°(exp)	ΔH_0°(HF)	ΔH_0°(HF) $-\Delta H_0^\circ$(exp)	ΔH_0°[DZ]	ΔH_0°[DZ] $-\Delta H_0^\circ$(exp)
a. Closed-shell molecules					
H_2	0	0	—	0	—
LiH	0	0	—	0	—
BH	0	0	—	0	—
CH_4	0	0 ± 3	—	0	—
NH_3	0	0 ± 1	—	0	—
H_2O	0	0 ± 3	—	0	—
HF	0	0	—	0	—
Li_2	−17 ± 1	−16.7 ± 1	0.3	—	—
(C_2, $x\,^1\Sigma_g^+$	229 ± 5	285.5 ± 1	56.5)	—	—
F_2	130 ± 2	136.4 ± 2	6.4	127.6	−2.4
LiF	−49 ± 8	−42.1 ± 1	6.9	—	—
C_2H_6	15.4	20.1 ± 5	4.7	22.2	6.8
H_2O_2	83.1	90.9 ± 6	7.8	82.8	−0.3
		Mean[a]	5.2	Mean	1.3
C_2H_4	46.5	47.3 ± 5	0.8	55.5	8.2
CH_2O	46.0	45.5 ± 6	−0.5	58.7	13.2
LiCCH	—	76.2 ± 4	—	—	—
FCCH	—	126.0 ± 5	—	—	—
		Mean	0.2	Mean	10.7
N_2	18.7	13.7 ± 1	−5.0	39.7	21.0
BF	−71 ± 4	−63.3 ± 1	7.7	—	—
CO	45.9	43.3 ± 1	−2.6	63.2	17.3
C_2H_2	86.3	94.3 ± 2	8.0	101.5	15.2
HCN	57.7	60.0 ± 1	2.3	71.7	14.0
FCN	—	94.3 ± 5	—	—	—
		Mean	2.1	Mean	16.9
CO_2	36.2	39.7 ± 1	3.5	70.5	34.3
C_2N_2	124.0	132.3 ± 6	8.3	—	—
N_2O	96.2	112.3 ± 4	16.1	—	—
b. Open-shell states					
C_2, $A\,^3\Sigma_g^-$	246 ± 5	217.0 ± 1	29.0	—	—
O_2, $X\,^3\Sigma_g^-$	114.2	116.1 ± 2	1.9	—	—
O_2, $a\,^1\Delta_g$	136.7	146.7 ± 2	10.0	—	—
O_2, $b\,^1\Sigma_g^+$	151.7	177.3 ± 2	25.6	—	—
LiO, $X\,^2\Pi$	39 ± 5	24.8 ± 1	14.2	—	—
NO, $X\,^2\Pi$	88.1	94.6 ± 1	6.5	—	—
OF, $X\,^2\Pi$	144 ± 10	144.2 ± 2	0.2	—	—
CF, $X\,^2\Pi$	142 ± 5	127.7 ± 1	14.3	—	—

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[a] Omitting C_2, $x\,^1\Sigma_g^+$ (see text).

CH_4, NH_3, and H_2O. For example, in the case of CO_2 the maximum error in the estimate of ΔH_0°(HF) is $1 + 1 \times 3 + 2 \times 3 = 10$ kcal/mole. The molecules are arranged in groups with similar types of bonding and the mean deviation ΔH_0°(HF) − ΔH_0°(exp) is listed for each group.

For the closed-shell molecules of Table VIIa, the agreement between ΔH_0°(HF) with ΔH_0°(exp) is quite remarkable, in view of the large errors in the Hartree–Fock dissociation energies, and vindicates our choice of reference states for the elements. Apart from C_2, $x\,^1\Sigma_g^+$ which, as we have seen above (Section II.D), hardly qualifies as a closed-shell state, the largest discrepancy is for N_2O, where $\Delta H_0^\circ(\mathrm{HF}) - \Delta H_0^\circ(\mathrm{exp}) = 16.1 \pm 9$ kcal/mole. In all other cases the discrepancy is less than 10 kcal/mole and is usually less than the combined computational and experimental uncertainties. We conclude that, relative to the closed-shell hydrides as reference states for the elements, accurate Hartree–Fock calculations would yield ΔH_0° values for closed-shell molecules correct to within a few kilocalories per bond, and that existing HFR calculations are hardly adequate to assess the errors of such calculations, even for the molecules of Table VIIa.

The results for the open-shell diatomic states in Table VIIb show some interesting trends. As is to be expected, most of the discrepancies are larger than for the closed-shell molecules. However, good agreement with experiment is obtained for the chemically stable species O_2, $X\,^3\Sigma_g^-$ and NO, $X\,^2\Pi$. This, together with the large positive discrepancies for O_2, $b\,^1\Sigma_g^+$ and the formally closed-shell state C_2, $x\,^1\Sigma_g^+$, which are both strongly affected by first-order CI (Section II.D), suggests that the criterion for the accuracy of the ΔH_0°(HF) values is not so much the closed-shell nature of the molecular electronic state, but rather the absence of the strong first-order CI which is characteristic of isolated atoms and reactive free radicals.

It is sometimes convenient to have estimates of Hartree–Fock total energies for molecules for which adequate HFR calculations are not available. Such estimates are commonly obtained from Hartree–Fock atomic energies, experimental binding energies D_e (Table IV) and empirical estimates of correlation energies (Hollister and Sinanoglu, 1966). We may obtain much simpler and more accurate estimates by reversing the procedure leading to the ΔH_0°(HF) values of Table VII. That is, we use the estimates of Table IV for the Hartree–Fock total energies of the closed-shell hydrides and experimental enthalpies of formation relative to the thermodynamic standard states of the elements. For any closed-shell hydro-carbon $C_m H_n$ this procedure, and the numerical value of Tables IV, VI, and VII, lead to the simple formula (in au).

$$E_{\mathrm{HF}}(\mathrm{C}_m\mathrm{H}_n) + v_0(\mathrm{C}_m\mathrm{H}_n) = \Delta Hf_0^\circ - 37.9039\mathrm{m} - 0.56185\mathrm{n}. \qquad (13)$$

Here v_0 is the zero-point vibrational energy and ΔHf_0° is the standard enthalpy of formation of $\mathrm{C}_m\mathrm{H}_n$ both expressed in atomic units.

Formula (13), which is readily extended to molecules containing other first-row atoms, depends on the conservation of correlation energy in reactions involving only closed-shell molecules. From the $\Delta H_0^\circ(\mathrm{HF}) - \Delta H_0^\circ(\mathrm{exp})$ values of Table VII it appears that Hartree–Fock total energies estimated in this way should be accurate to within about 0.005 au per carbon atom.

VII. Simpler SCF Calculations

As we have seen, accurate Hartree–Fock total energies provide quite a good account of the thermochemistry of those (relatively few) chemically stable small molecules for which current SCF calculations are adequate to estimate the Hartree–Fock limit. However, we have also seen that the basis function requirements for such calculations are stringent and difficult to satisfy even for a molecule as small as NH_3 (Section II.B). The task of reducing the uncertainties in the Hartree–Fock limits of Table IV and extending the table to include larger molecules is, therefore, difficult and expensive despite the fact that computer programs of sufficient generality are available (Clementi, 1969). It is of interest to see whether simpler SCF calculations with smaller basis sets can produce comparable results.

For linear molecules McLean and Yoshimine (1967a), showed that the near-Hartree–Fock binding energies D_e from their best calculations ({BA + P} of Table IV) could be reproduced to within about 1kcal/mole, by the consistent use of a smaller basis {DZ + P} despite a substantial rise in all total energies. It seems likely that, if such a {DZ + P} basis were used consistently for all the molecules in Table VII, the enthalpies of formation obtained would be close to the Hartree–Fock values, but such calculations are not available for the nonlinear molecules. The most comprehensive set of calculations using a comparable basis set for many small molecules seems to be that of Snyder (1969), who treats most of the molecules of Table VII and a number of others using a CGTO basis set [DZ] which is comparable in quality to a double-zeta Slater set. Snyder's results, converted to ΔH_0° values relative to our reference states for the elements are shown in the last two columns of Table VII.

We see that, for the first group of molecules containing only single bonds, the [DZ] results are about as good as those from the estimated Hartree–Fock limits, but that for molecules containing multiple bonds the [DZ] results are consistently too high, the error increasing with both the number of such bonds and their multiplicity.

As a result of these errors hydrogenation reactions such as

$$C_2H_4 + H_2 = C_2H_6 \tag{14}$$

$$CH_2O + 2H_2 = H_2O + CH_4 \tag{15}$$

are predicted to be too exothermic by the [DZ] calculations, the average error being about 7 kcal/mole for each hydrogen molecule added. This effect was noted by Snyder (1969), who attributed it principally to changes in electronic correlation energy. Since the effect is absent for the ΔH_0°(HF) values of Table VII, it seems more likely that it arises from the inadequacy of the [DZ] basis set for multiply bonded molecules. That is, the introduction of polarization functions would lead to greater energy lowerings for multiply bonded molecules and the errors would be much reduced.

However, the small number of cases in Table VII and the uncertainties in the estimated Hartree–Fock limits make this conclusion tentative. Better HFR calculations for a wider variety of molecules are needed to assess the true role and limitations of Hartree–Fock theory in thermochemistry.

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On Physical Properties and Interactions of Polyatomic Molecules: With Application to Molecular Recognition in Biology

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I. Introduction

A key problem in both chemistry and molecular biology is the analysis of interactions between noncovalently bonded molecules. In chemical terminology these interactions are referred to as van der Waals forces, electrostatic and dispersion interactions, hydrogen bonding, stacking interactions, etc. The fundamental role which these types of nonbonding interactions play in biological phenomena has been increasingly recognized in recent years (see Pullman, 1968).

However, the biological aspect, important as it may be, is not the only reason for the interest in these interactions. The treatment of intermolecular forces is of equal importance for theories concerned with the structure of solids and liquids as well as for the explanation of a host of physicochemical phenomena. It is therefore not surprising that the subject of intermolecular forces from its very beginning, nearly a century ago, remains in the mainstream of interest in molecular physics.

The formal treatment of intermolecular forces is generally based on quantum mechanical perturbation theory. The formal aspects of the theory and the advances which have been made in the application of the theory to small systems are extensively treated in Hirschfelder *et al.* (1954) and Margenau and Kestner (1971).

Until the late 1950s, application of the theory to the treatment of interactions between large molecules had been restricted to the use of the semiempirical theory developed by London (1937). Since then there has been an ever-increasing interest in this area. Progress in molecular orbital theory of polyatomic molecules has provided the basis for efforts to improve the application of theory beyond the crudest form of the semiempirical method. Early efforts in this direction have been concerned with the use of calculated rather than experimental values of quantities such as dipole moments, ionization potentials and polarizabilities (DeVoe and Tinoco, 1962; Bradley *et al.*, 1964; Haugh and Hirschfelder, 1955; Rein and Pollak, 1967) which are required in the theory. The applicability of some of the approximations underlying the semiempirical treatment to certain molecular situations of interest has been questioned and alternative treatments have been proposed (Haugh and Hirschfelder, 1955; Coulson and Davies, 1952). Since the first wave functions for large polyatomic systems were on the π-electron level, most of this work was restricted mainly to explicit considerations of the π-electron aspect of the theory. The rapid development of molecular orbital theory in the 1960s, with increasingly more sophisticated calculations of all-electron wave functions, offered the conditions for extending the studies to explicit consideration of all the electronic terms contributing to the interactions.

In an attempt to evaluate the quantitative features and predictive value of such interaction studies, a number of problems stemming from the approximations used in the theory have to be considered. This chapter is designed to examine two of the more important of these problems. The first one is concerned with the question of the reliability of wave functions for large molecules, a question which is also of great interest in quantum chemistry. The second is related to the convergence problem connected to the expansions of the interaction potential ($1/r_{12}$) used in most interaction treatments.

Various aspects of these two general problems have been studied during the recent years in the author's laboratory by J. Rabinowitz, T. Swissler, G. Pack, V. Renugopalakrishnan, A. Hartman, S. Nir, M. Stamatiadou, and other co-workers. A unified outline of the analysis employed in these studies and a survey of the most outstanding of their results are presented in the latter sections of the present work. Some of these results have been published in greater detail elsewhere and some others will be discussed in a separate context in forthcoming publications.

Let us turn now to an examination of the two problems to be dealt with in this presentation.

The problem of reliability arises because only approximate wave functions can be computed for many-particle systems. Therefore the electron densities are approximate and so are the corresponding expectation values. Depending on the approximations employed, i.e., the nature and size of the basis set and the way the integrals are treated, the accuracy of the description may vary from one case to another and from one region in a molecule to another. As a consequence the reliability of a wave function for predicting physical quantities may vary with the properties examined. Putting this in somewhat different terms: the question of the usefulness of approximate wave functions depends on the particular application for which they are designed. As an illustrative example, consider the usefulness of a wave function in predicting the value of a nuclear quadrupole coupling constant and the value of diamagnetic susceptibility. The former would require an accurate behavior of the wave function near the nucleus, while the latter quantity is not as sensitive to features in this region and depends only on a correct global distribution of charge between the atoms (see below). The two quantities pose obviously different requirements on the wave functions.

There are currently three major approaches to the calculation of the electronic structure of large polyatomic molecules:

(a) Gaussian *ab initio* calculations (Clementi and Davis, 1966; Preuss, 1956; Moscowitz, 1965).

(b) Methods based on neglect of differential overlap (Pople and Beveridge, 1970).

(c) Refined versions of the extended Hückel method (Rein *et al.*, 1970a).

The analysis of the detailed features of the ground-state wave function obtained by any of these methods and its value for predicting physical properties has been carried out in the past in two general ways. The most frequent one has been to look on the agreement between the calculated and the experimental value of the molecular dipole moment and to use this as the main test criterion for the accuracy of the wave function. A second test criterion has been the analysis of the correlations between formal atomic charges calculated from the wave function and chemical shifts obtained by spectroscopic methods (Pople, 1962; Barber and Clark, 1970). Considering the arbitrariness in the definition of formal charges and the fact that this arbitrariness is frequently carried over into the calculation of the dipole moment, as well as the fact that the relation between formal charges and observed shifts is often little more than intuitive, one is led to question the conclusiveness of the results of these procedures in establishing the accuracy of the wave function. In this chapter it will become evident that these conventional criteria are not always sufficient and that this is the case not only for the intermolecular force application but also in the context of the calculation of other physical properties of interest.

To anticipate the nature of the requirements on the wave function for calculating molecular interactions and to establish the connection with the second major subject of this study, it is useful to introduce into the discussion at this point the problem of convergence.

As is well known, there are three infinite series expansions which underlie the perturbation treatment of intermolecular interactions. The first of these infinite series arises from the Taylor expansion of the perturbation $(1/r_{12})$ to the Hamiltonian. The second one is due to the perturbation expansion in terms of successive orders. The third expansion is employed to express the perturbation correction in terms of the excited-state functions of the unperturbed Hamiltonian. For a perturbation treatment of a given molecular interaction to provide meaningful results, a rapid convergence of each one of these expansions must be assured. At short molecular separation distances, where the assumption of electronic separability of the interacting molecules breaks down, the treatment is further complicated by the appearance of terms due to antisymmetrization.

As has already been stated, one of the major objectives of this chapter is to consider the results of the investigations which have been carried out in our laboratory (Rein *et al.*, 1972c) concerning the convergence of the first one of these expansions, i.e., the expansion of the interaction term in a Taylor series. This expansion leads to a decomposition of the interaction into a series of terms comprised of interactions between successive electrical moments of the two molecules. The question to which we will try to provide an answer is how many of these successive moments have nonnegligible contributions to the interaction for a given geometry and separation distance of the interacting molecules. If the answer to this question is that more than the dipole–dipole term is required, as in fact will turn out to be the case in many instances of interest, then this poses an obviously much more stringent requirement on the wave function than the conventional test criterion would. To state this in a more explicit form: The wave function must be sufficiently detailed to give a quantitative prediction of quadrupole moments and, in some instances, of even higher moments, and this requirement cannot be ascertained just on the basis of the conventional criteria referred to earlier. Hence the intimate connection between the two problems, i.e., of the reliability of wave functions and the convergence of the series, which are the two major aspects of this study.

The two major objectives of this chapter having been stated, there remains to examine the practical importance of this analysis within the broader context of formulation of a complete and computationally manageable method for calculation of intermolecular interactions. There are a number of aspects which have to be stressed in this connection.

First, the interaction operator $(1/r_{12})$ expansion is the most general one among the three expansions appearing in the theory. It is most general because it underlies the perturbation treatment of any order and thus is involved in every level of the calculation. It follows that the insight gained from the analysis of the convergence of the first-order interaction energy will be a useful guideline also in the consideration of second and higher order interaction energies. That is, the rapidity of convergence in inverse powers of separation observed in the first-order case will provide a good indication for the acceptable cutoff point of the expansion in the second-order case for a given geometry. This question of the convergence condition of the second-order energy is indeed of great practical interest. This stems from the fact that, at present, the analysis can hardly be carried out further than the inverse sixth-order term since there are no experimental values of higher-order polarizabilities available for a semiempirical approach, nor are there large enough sets of accurate excited-state wave functions available for *ab initio* calculations. Thus, until convergent sets of excited states for their perturbation expansion are available, the best that can be achieved with regard to calculation of the second-order term is to establish the geometrical limits within which the inverse sixth-power term is leading the expansion. This indeed will follow within reasonable limits from this study.

Second, the chemical literature of the past few decades contains a host of applications of the dipole theory of molecular interactions. The dipole approximation is equivalent to terminating the operator expansion after the first nonvanishing term. While the validity of this approximation has been questioned, it appears that no systematic effort was made in the past to verify the geometrical conditions for which this approximation is acceptable. The studies on which this article is based furnish, thus, for the first time, the criteria needed to decide which of these past applications are justifiable and which of them will have to be rejected.

Third, the relevance of this study in the biological context requires some introductory comments. The basic theoretical problem in modern biology is the explanation of the nature and magnitude of the physical interactions involved in molecular recognitions which universally underlie the genetic, physiological, and morphological expressions of life. To emphasize this point further, I would like to suggest that the quantitative explanation of these interactions is of the same value for a rational explanation of molecular biology as the quantum mechanical explanation of the covalent chemical bond was for a rational explanation of chemistry.

Qualitatively, it has long been realized that electrostatic interactions play an important part in these recognition processes. The theoretical developments in this chapter provide the equipment for a quantitative approach to these interactions. This will be demonstrated by a detailed analysis of the quantitative role of electrostatic interactions in two important biological phenomena. One of these phenomena is the hydrogen bonding between complementary bases, which underlies the expression of the genetic code. The other one is a typical enzyme–substrate recognition, the 3′-cytidine monophosphate interaction with ribonuclease.

II. Method

Before proceeding with the analysis of the interaction schemes employed in these studies we are going to describe the alternative multipole representations of charge distribution on which these schemes are based, as well as the alternative definitions of moment and the respective computational methods employed.

A. Multipole Representations of Molecular Charge Distribution

1. Molecular Dipole Moments

The molecular dipole moment is defined

$$\boldsymbol{\mu} = \sum_{\substack{\mathrm{A} \\ \text{atoms}}} Z_{\mathrm{A}} \mathbf{R}_{\mathrm{A}} - \sum_{\lambda\sigma} P_{\lambda\sigma} \boldsymbol{\mu}_{\lambda\sigma} \tag{1}$$

where Z_A and $\mathbf{R}_A$ are the charge and position, respectively, of the Ath nucleus, in a space-fixed axial system, $P_{\lambda\sigma}$ is the element of the charge bond order matrix, and $\boldsymbol{\mu}_{\lambda\sigma}$ is the moment arising from the density in the same coordinate system as $\mathbf{R}_A$.

A displacement equation defines the moment component with respect to a new origin

$$\boldsymbol{\mu}_{\lambda\sigma} = \langle\lambda|\mathbf{r}|\sigma\rangle = \langle\lambda|\mathbf{r}'|\sigma\rangle + \mathbf{R}\langle\lambda|\sigma\rangle, \tag{2}$$

where $\mathbf{R}$ is the displacement to the new origin (R connects the space-fixed axial system with the new origin), and $\mathbf{r}$ is the position vector defined with respect to the original reference point, and $\mathbf{r}'$ is the position vector defined with respect to the new origin.

After partitioning the second term of Eq. (1) into integrals arising from one- and two-center densities, respectively, and introducing Eq. (2) to simplify the integration, the expression for the dipole moment becomes

$$\begin{aligned}\boldsymbol{\mu} = \sum_{\mathrm{A}} \Bigg[&\mathbf{R}_A\Big(Z_A - \sum_{\lambda} P_{\lambda\lambda}\Big) - \tfrac{1}{2}\sum_{\lambda}\sum_{\sigma\neq\lambda} P_{\lambda\sigma}\langle\lambda|\mathbf{r}'|\sigma\rangle \\ &- \tfrac{1}{2}\sum_{\mathrm{B}\neq\mathrm{A}}\sum_{\lambda}\sum_{\nu} P_{\lambda\nu}\big(\langle\lambda|\mathbf{r}'|\nu\rangle - \mathbf{R}_{AB}\langle\lambda|\nu\rangle\big)\Bigg]\end{aligned} \tag{3}$$

where the sums A and B are over atoms, the sums λ and σ are over orbitals on center A, the sum ν is over orbitals on center B, and $\mathbf{R}_A$ and $\mathbf{R}_{AB}$ are the displacement vectors from the molecular origin to a local origin, the origin of $\mathbf{r}'$.

The first three terms in Eq. (3) correspond to the one-center density contributions and the last two terms to the two-center density contributions to the dipole moment. Dipole moments calculated from IEHT wave functions contain both contributions, while for CNDO wave functions the second contribution vanishes.

There are several alternative ways to perform the calculation of the two-center density contributions. These alternatives depend on the choice of the local coordinate systems in which the integrations implied in Eq. (3) are performed. More specifically, there are alternative ways of defining the origin of the integration variable r' in the respective local coordinate systems in which the densities are specified. This amounts to choosing the points in the molecules, i.e., atomic or interatomic centers (R_{AB} specifies such a point), that the bicentric density moments are referred to in the intermediate stages of calculation. While the final result for the molecular dipole moment is independent of this choice, it is of substantial interest in the context of the alternative atomic segmental multipole representation of molecular charge distributions. Hence we digress from the topic of molecular dipole moments to introduce this alternative representation.

2. *Atomic Multipole Representation*

We will review the earlier work relevant to the development of atomic multipole representation and the discussion of its significance for interaction calculations in Section III. At present we confine the discussion to the definition of this representation and some of its more important aspects. The molecular density matrix, ρ, can be partitioned

$$\rho(1) = \sum_i \rho_i(1), \tag{4}$$

where $\rho_i(1)$ are the densities assigned to the ith atom.

$$\begin{aligned}\rho_i(1) = \sum_\lambda &\left[P_{\lambda\lambda}\chi_\lambda(1)\chi_\lambda(1) + \tfrac{1}{2}\sum_{\sigma\neq\lambda} P_{\lambda\sigma}\chi_\lambda(1)\chi_\sigma(1) + \sum_\nu P_{\lambda\nu}f_{\lambda\nu}\chi_\lambda(1)\chi_\nu(1)\right]\\ &+ Z_i\,\delta(\mathbf{R}_i - \mathbf{r}_1),\end{aligned} \tag{5}$$

where the sums λ and σ are over all orbitals on atom i and the sum ν is over all orbitals on all centers except atom i. The subscripts λ, σ, and ν are indications of all the quantum numbers and parameters in the Slater orbitals (χ_λ, χ_σ, and χ_ν) and the center from which the orbital is defined; $f_{\lambda\nu}$ is the fraction of the density in the case where the Slater orbitals are referred to two different centers and this is the part assigned to center χ_λ. Obviously,

$$f_{\lambda\nu} + f_{\nu\lambda} = 1. \tag{6}$$

It is easy to recognize that the integral of ρ_i corresponds to formal atomic charge on atom i. Various definitions of formal atomic charges then correspond to various definitions of ρ_m. A choice of ($f_{\lambda\nu} = \frac{1}{2}$) corresponds, for example, to formal charge defined according to the Mulliken division.

By a straightforward generalization, formal atomic multipoles can be defined as

$$\langle {}_m x^k \rangle = \int {}_m x^k \rho_m \, d\tau, \tag{7}$$

where the subscript on the left indicates that the operator component x^k is defined relative to the atomic origin m.

We list a number of interesting properties which follow from the definition:

(a) Any molecular multipole moment referred to an arbitrary single origin is defined uniquely in terms of the corresponding set of atomic multipole components of the type defined in Eq. (7) and the corresponding transformation equations that are generalizations of Eq. (2). For quadrupole moment this transformation is

$$M_{ij} = R_i R_j q' + R_i \mu_j' + R_j \mu_i' + M'_{ij}, \tag{8}$$

where M_{ij} is a quadrupole-like operator (an operator from which all the components of the quadrupole moment can be obtained), R_i and R_j are vector components from the unprimed origin to the primed one, and

$$M_{ij} = \langle 0 | X_i X_j | 0 \rangle \tag{9}$$

(b) The electrostatic potential of the molecular charge distribution can be expressed as the superposition of potentials of an atomic multipole series. Such a representation in certain instances may be of substantial practical advantage relative to a single-center multipole representation. The most important advantage is the applicability in certain interaction situations which are not tractable in the single-center representation because the geometrical conditions do not justify the underlying expansion. We will return to discuss this aspect in greater length in a later section.

(c) For the domain of convergence of the potential represented by a molecular multipole series truncated after *n* terms, the *n* truncated series of sets of formal atomic multipoles is also a convergent representation. Furthermore, even when the *n*th truncated molecular representation is not convergent, it may happen that the *n*th truncated formal atomic set is convergent.

What the above statement implies can best be explained by an example. Let us say that at a given exterior point the potential of a neutral molecule is represented by its dipole potential. Then any set of formal atomic monopoles (formal atomic charge) and atomic dipoles is also a convergent representation. However, it may happen that an optimal choice of $f_{\lambda\sigma}$ exists for which the potential of the set of formal atomic charges is already convergent. Results of our calculations illustrating this conclusion appear in Table VIII. It is useful to recognize how very interesting this consideration is in providing for the concept of formal atomic charges. The essence of it is that all the efforts in the past to define formal atomic charges can be rationalized as an effort to improve the representation of the dipole field by a set of monopoles only. If the representation is not incomplete, i.e., in the example above, atomic dipoles are also included, then the interest in the ways that the formal charge is defined becomes irrelevant, since one definition is as good as the other.

B. Definition of Moments and Their Calculation

We return now to a general definition of multipole moments and their calculation.

The computational procedures for dipole and quadrupole moments from IEHT or any Slater basis LCAO wave function have been discussed in our earlier papers. Here we present an extended description including also the calculation of the atomic multipole moments. The description will have the additional advantage that it will set the stage for a formal discussion of the interaction problem that is covered in the next section.

The calculation of the moments includes the following main steps.

(i) Partitioning of the density matrix according to Eq. (5) leads to a set of atomic and diatomic densities with orbital components defined relative to atomic centers A and A,B, respectively. These centers are designated by Cartesian coordinates X_{A}, Y_{A}, and Z_{A} relative to a fixed axis system which is the same for all orbitals.

The orbitals have the form

$$\chi_\mu{}^A = B_n r^{n-1} e^{-\delta r} Y_{lm}(\theta, \phi) \tag{10}$$

and are specified in spherical coordinate systems centered at atom A with the polar axis in the $+z$ direction and $+x$ direction defining the reference meridian. The subscript μ stands for (n, l, m, δ), and B_n is the normalization factor

$$B_n = \left[\frac{(2\delta)^{2n+1}}{(2n)!}\right]^{1/2}. \tag{11}$$

It is to be noted that the orbitals in a bicentric density are not aligned properly at this stage.

(ii) Assignment of local operator components and specification of coordinate systems in which they are defined. These are

$X_{i\mathrm{A}}$, Cartesian component of the dipole operator defined relative to origin on atomic center A;

$X_{i\mathrm{AB}}$, Cartesian component of the dipole operator defined in an axis system whose polar direction is along the directed line from center A toward center B and whose origin is at the midpoint between A and B,

$X_{iA} X_{jA}$, Cartesian component of a type of quadrupole operator relative to origin A,

$X_{iAB} X_{jAB}$, Cartesian component of the quadrupole operator in the A,B midpoint coordinate system.

(iii) Application of the operators defined in (ii) to their corresponding densities defined in (i) yields the following integrals:

$$\mu_{iA} = \int X_{iA} \rho_A(\mathbf{r})\, d\mathbf{r} \tag{12}$$

$$\mu_{iAB} = \int X_{iAB} \rho_{AB}(\mathbf{r})\, d\mathbf{r} \tag{13}$$

$$m_{iAjA} = \int X_{iA} X_{jA} . \rho_A(\mathbf{r})\, d\mathbf{r} \tag{14}$$

$$m_{iAjB} = \int X_{iAB} X_{jAB} \rho_{AB}(\mathbf{r})\, d\mathbf{r}. \tag{15}$$

These integrals are the components of the local one-center and two-center electronic moments and their set, i.e., all A and all A,B, in fact corresponds to a unique moment representation of the molecular electron distribution (see below), where $\rho_A(\mathbf{r})$ is a local one-center charge density and $\rho_{AB}(\mathbf{r})$ is a local two-center charge density.

(iv) The one-center dipole moment integral [Eq. (12)] after expansion of ρ_A is

$$\mu_{iA} = \sum_{\mu\nu}^{\substack{\text{on atom}\\ \text{A}}} P_{\mu\nu} \int \chi_\mu{}^A X_{iA} \chi_\nu{}^A \, d\mathbf{r}. \tag{16}$$

The only nonzero contributions to μ_{iA} are from Slater orbitals for which $l_\mu = l_\nu \pm 1$. Formulas for these cases in terms of one-center overlap integrals have been presented in an earlier paper (Rein *et al.*, 1970a). The one-center quadrupole integral [Eq. (14)] after expansion is

$$M_{iAjA} = \sum_{\mu\nu}^{\substack{\text{on atom}\\ \text{A}}} P_{\mu\nu} \int \chi_\mu{}^A X_{iA} X_{jA} \chi_\nu{}^A \, d\mathbf{r}. \tag{17}$$

These integrals have been discussed elsewhere (Rabinowitz and Rein, 1972). Their calculation proceeds by expressing $X_{iA} X_{jA}$ in terms of r^2 multiplied by a linear combination of even spherical harmonics. By virtue of this decomposition and the orthogonality of spherical harmonics, the only nonzero integrals are χ_μ and χ_ν, both p functions with different m value, or $\chi_\mu\ \chi_\nu$ the same function.

It is interesting to remark here that the only nonzero atomic moments for a CNDO wave function are the dipoles and quadrupole moments arising from the nonzero terms of Eqs. (12) and (14) and the monopoles. For an S, P basis all the higher one-center moments are zero.

(v) We now consider the two-center case which is necessary for the IEHT wave function or for any *ab initio* wave function in a Slater orbital basis set. Equations (13) and (15) after expansion are

$$\mu_{i\mathrm{AB}} = \overset{\text{on atom}}{\sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}}} P_{\mu\nu} \int \chi_\mu{}^{\mathrm{A}} X_{i\mathrm{AB}} \chi_\nu{}^{\mathrm{B}}\, d\mathbf{r} \tag{18}$$

$$m_{i\mathrm{A}j\mathrm{B}} = \overset{\text{on atom}}{\sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}}} P_{\mu\nu} \int \chi_\mu{}^{\mathrm{A}} X_{i\mathrm{AB}} X_{j\mathrm{AB}} \chi_\nu^{\mathrm{B}}\, d\mathbf{r}. \tag{19}$$

We observe that (18) and (19) are not yet in a form convenient for integration. In order to bring this expression to a more convenient form for integration the orbitals have to be expressed in the coordinate system in which the operators are referred, i.e., in a system where their polar axes are along the line joining the centers and their reference meridian coincides. The coordinate rotation affects only the spherical harmonics. The unrotated spherical harmonics can be expressed as a linear combination of harmonics Y_{lm} in the rotated system

$$Y_{lm} = \sum_{\sigma=-l}^{l} D_l^{m\sigma}(\phi, t)\ Y_{l_\sigma}, \tag{20}$$

where t stands for $\cos\theta$; ϕ and θ are angular coordinates of the new orientation from the position coordinates of the centers; and $D_l^{m\sigma}(\phi, t)$ are the well-known rotational coefficients.

The integrals of (18) and (19) after inserting (20) are

$$\int \chi_{nlm\delta}^{\mathrm{A}} \begin{matrix} X_{i\mathrm{AB}} \\ \text{or} \\ X_{i\mathrm{AB}} X_{j\mathrm{AB}} \end{matrix} \chi_{n'l'm'\delta'}^{\mathrm{B}}\, d\mathbf{r} = \sum_{\sigma=-l}^{l} \sum_{\sigma=-l'}^{l'} D_{l\mathrm{A}}^{m\mathrm{A}\sigma}(\phi, t) \times D_{l'\mathrm{B}}^{m'\mathrm{B}\sigma'}(\phi, t) \left\langle nl\sigma\delta \left| \begin{matrix} X_{i\mathrm{AB}} \\ X_{i\mathrm{AB}} X_{j\mathrm{AB}} \end{matrix} \right| n'l'\sigma'\delta' \right\rangle. \tag{21}$$

The integrals in Eq. (21) are calculated by expressing the respective operators in terms of cylindrical operators. The further details in the specification of the local coordinate origin will be given in the computational section. The dipole operators are z, $\rho e^{i\phi}$, $\rho e^{-i\phi}$, and the quadrupole components can be expressed as a linear combination of the six cylindrical operators

$$zz, \qquad z\rho e^{i\phi}, \qquad z\rho e^{-i\phi}, \qquad \rho^2 e^{+2i\phi}, \qquad \rho^2 e^{-2i\phi}, \qquad \rho^2.$$

These cylindrical operators have ellipsoidal representation and the integrals are reduced to ellipsoidal expression; details of this procedure and a list of ellipsoidal expressions are given in our earlier papers (Rein *et al.*, 1970a).

(vi) In order to complete the calculation of the atomic moments three further steps are required. First, the moments have to be rotated into a new local coordinate system with axes parallel to the fixed axis system. This is accomplished by the standard rotational matrices.

Second, they have to be translated to the respective atomic origin to which they are referred according to the partitioning of the densities. For this partitioning we have to consider two cases. The first case is straight forward. It corresponds to $f_{\lambda\sigma}^{AB} = \frac{1}{2}$, and it effects a translation of one-half of each moment component to center A and one-half to center B. As we have already indicated for the monopoles, this just corresponds to the Mulliken division of overlap charge. The translation is effected by Eq. (2) and Eq. (8) for the dipole and quadrupole components respectively.

The second case is somewhat more complicated; $f_{\lambda\sigma}^{AB}$ is defined in this case by the operators

$$f_{\lambda\sigma}^{AB} = \left(1 - \frac{2z}{R}\right), \qquad f_{\sigma\lambda}^{AB} = \left(1 + \frac{2z}{R}\right), \tag{22}$$

where z is the position operator component along the polar axis in the A,B axis system measured from the midpoint, and R is distance between centers A and B. This leads to a formal division of bicentric densities in a way in which the part of the density associated with center A is

$$f_{\lambda\sigma}^{AB}\chi_\lambda\chi_\sigma = \left(1 - \frac{2z}{R}\right)\chi_\lambda\chi_\sigma = \chi_\lambda\chi_\sigma - \frac{2z}{R}\chi_\lambda\chi_\sigma. \tag{23}$$

The part of the overlap charge associated with center A is

$$f_{\lambda\sigma}^{AB}S_{\lambda\sigma} = S_{\lambda\sigma}\frac{-2(\mu_z)}{R}\lambda\sigma$$

and with center B is

$$f_{\sigma\lambda}^{\mathrm{BA}} S_{\lambda\sigma} = S_{\lambda\sigma} + \frac{2(\mu_z)_{\lambda\sigma}}{R}\,. \tag{24}$$

The definition of formal change involving this division has been used in most of our earlier reported IEHT results (Rein *et al.*, 1970a). This division has the value that it preserves the bond dipole moment.

The final step of the calculation of the local moments is transformation of the atomic moments into the traceless definition

$$Q_{ij}^{\mathrm{A}} = \tfrac{1}{2} \int \rho_{\mathrm{A}}(\mathbf{r})(3X_i X_j - r^2\delta_{ij}]\, d\mathbf{r}. \tag{25}$$

This is the form in which the calculated atomic moment values appear in the tables.

The molecular origin related moments which are in comparable form with experimentally measured quantities are

$$\boldsymbol{\mu} = \sum_{\mathrm{A}} Z_{\mathrm{A}} \mathbf{R}_{\mathrm{A}} - \sum_{\mu\nu} P_{\mu\nu} \boldsymbol{\mu}_{\mu\nu}\,, \tag{26}$$

where the components are connected with the local moments through the translational and rotational relations discussed before. Or more explicitly, for a dipole component

$$(\mu_x)_{\mu\nu}^{\mathrm{AB}} = \tfrac{1}{2}(X_{\mathrm{A}} + X_{\mathrm{B}})S_{\mu\nu} + \tfrac{1}{2}R(\cos\theta\cos\phi X_{\mu\nu} - \sin\phi Y_{\mu\nu} + \sin\theta\cos\phi z_{\mu\nu}) \tag{27}$$

where $(\mu_x)_{\mu\nu}^{\mathrm{AB}}$ is the x component of the dipole moment $\mu_{\mu\nu}$ due to the overlap density ${\chi_\mu}^{\mathrm{A}}{\chi_\nu}^{\mathrm{B}}$ and expressed relative to the fixed axial system.

X_{A}, X_{B}, ϕ, θ are as defined previously, R is the intercenter distance; $S_{\mu\nu}$ is the overlap integral; and $X_{\mu\nu}$, $Y_{\mu\nu}$, and $Z_{\mu\nu}$ are the bicentric moment components in the AB axis system in which system the integration has been performed.

The components of the traceless quadrupole tensor relative to the fixed axial system, which is the form comparable with the recently reported experimental values, is

$$Q_{ij} = \tfrac{1}{2}|e| \int \rho(\mathbf{X})(3X_i X_j - r^2\delta_{ij})\, d\mathbf{X} + \tfrac{1}{2}\sum_{\mathrm{A}}^{N} |e| Z_{\mathrm{A}}(3\bar{X}_{\mathrm{A}i}\bar{X}_{\mathrm{A}j} - {R_{\mathrm{A}}}^2\delta_{ij}), \tag{28}$$

where $\rho(\mathbf{X})$ is the density matrix; $\mathbf{X}_i\mathbf{X}_j$ are the Cartesian components of the position operator $\mathbf{r}$ relative to the fixed axial system; Z_{A} is the core or nuclear charge on atom A; and $\bar{X}_{\mathrm{A}i}$, $\bar{X}_{\mathrm{A}j}$ are the components of the position vector R_{A} of the Ath nucleus in the fixed axis system and the sum is over all atoms in the molecule.

The connection between Q_{ij} and the density moments which have been calculated in the local coordinate system is established via the following relations:

The electronic contribution to Q_{ij} is

$$M_{ij} = \int \rho(\mathbf{r}) X_i X_j \, d\mathbf{r} = \sum_{\mu\nu} P_{\mu\nu} \langle \mu | X_i X_j | \nu \rangle. \tag{29}$$

The integral in (29) is related to the local moments by the translational Eq. (8)

$$\langle \mu | X_i X_j | \nu \rangle = (m_{ij})^{\mathrm{rot}}_{\mu\nu} + X_{i\overline{\mathrm{AB}}} (\mu_j)^{\mathrm{rot}}_{\mu\nu} + X_{j\overline{\mathrm{AB}}} (\mu_i)^{\mathrm{rot}}_{\mu\nu} - |e| X_{i\overline{\mathrm{AB}}} X_{j\overline{\mathrm{AB}}} S_{\mu\nu}, \tag{30}$$

where the first term is the local quadrupole integral of Eq. (29) after rotational alignment with the fixed axis system. Similarly, the $(\mu_i)^{\mathrm{rot}}_{\mu\nu}$ are the rotated dipole components of Eq. (27). The $X_{i\overline{\mathrm{AB}}}$'s are the Cartesian components of the midpoint between centers A and B on which orbitals μ and ν's are defined, respectively.

C. Interaction Schemes

In this section the interaction energy between nonoverlapping molecules is considered using expansion techniques to express the interaction in a series of terms between the multipoles of molecule 1 with those of molecule 2. Part of the analysis is similar to that of Buckingham (1954) and McLean and Yoshimine (1967) in their discussion of the interaction of a molecular charge distribution with an external electric field. These considerations are extended to deal with interaction formulas in terms of the atomic multipoles which have been treated in the previous section.

These two interaction schemes are related to earlier formulations of London and subsequent workers in such a way that the two London methods appear as first approximations to the more general expansions of the present work. More specifically, the molecular dipole approximation (London, 1937) and the replacement of the molecule by point charges at the atomic centers (called the point charge or monopole approximation), the two alternative interaction schemes which were in general use for electrostatic (first order) interactions, are both equivalent to terminating the expansion after one nonzero term. In the latter case the molecule is first divided in segments and a separate expansion is made for each segment.

For the molecular dipole approximation, it had been previously suggested that this termination was not valid in many instances, particularly in biological systems. Subsequent studies used the monopole method. Based on Löwdin's (1956) criterion of spherically disconnected charges it had been shown (Pollak and Rein, 1967) that for segments the expansion is valid for distances of interest, whereas for the first scheme it is not valid. The assumption had been that the first term of each segment would dominate, but this was never shown explicitly.

The immediate purpose of this analysis is, therefore, to investigate the convergence of the electrostatic term in the two interaction schemes for larger molecules. Toward this objective we presented above the definition and computational method of the molecular and atomic moments. This, together with the formulas which will be presented here, constitutes a complete computational scheme. Starting from molecular LCAO wave functions, the electrostatic interaction between the two molecules up to and including quadrupole–quadrupole terms can be calculated in either of the two approximations. The computational methods can be extended to higher moments as well and can be used in a perturbation formulation to obtain higher-order interaction terms when suitable excited-state wave functions are available.

We have used this formulation to calculate the successive contributions to the electrostatic interaction between a number of molecules typical for those of interest in organic chemistry and biochemistry, and for a wide range of separations between the interacting molecules. The results of these calculations are surveyed in Table VII, followed by a consideration of the main conclusions concerning the convergence problem which can be reached from these results.

Derivation of Multipole Interaction Series

If a charge distribution $\rho(\mathbf{r})$ is placed in an external field $\Phi(\mathbf{r})$ then the electrostatic energy of the system is

$$W = \int \rho(\mathbf{r})\, \Phi(\mathbf{r})\, d\mathbf{r}; \tag{31}$$

$\mathbf{r}$ is the position vector over the charge distribution and the origin is within the distribution. If the external potential Φ is due to another continuous charge distribution (an atom or a molecule) that does not overlap with the charge distribution $\rho(r_i)$ then

$$\Phi(\mathbf{r}) = \int \frac{\rho'(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}'. \tag{32}$$

If $\rho(r)$ and $\rho'(r')$ are composed of segmental or atomic densities as defined above

$$\rho(r) = \sum_{\alpha} \rho_{\alpha}(r) \tag{33}$$

(31) and (32) can be rewritten as

$$W = \sum_{\alpha} \int \rho_{\alpha}(\mathbf{r})\,\Phi(\mathbf{r})\,d\mathbf{r} \tag{34}$$

$$\Phi(\mathbf{r}) = \sum_{\beta} \Phi_{\beta}(\mathbf{r}) = \sum_{\beta} \int \frac{\rho_{\beta}'(r')}{|\mathbf{r} - \mathbf{r}'|}\,d\mathbf{r}', \tag{35}$$

where **r** and **r**′ are position vectors over the segmental densities with origins chosen at the respective atomic centers. There are two Taylor expansions which are utilized to express W in terms of multipole series. In considering these expansions we will use them alternatively in the sense of Eqs. (31) and (34) and Eqs. (32) and (35), respectively, to derive the two alternative interaction schemes.

First, we begin with a Taylor expansion of the potential Φ about a suitable origin (by convention the center of mass is chosen as this origin for the molecular scheme, and the set of atomic origins in the segmental scheme). For this expansion it is assumed the Φ is slowly varying about the origin,

$$\Phi(\mathbf{r}) = \Phi(\mathrm{o}) + \mathbf{r} \cdot \nabla\Phi(\mathrm{o}) + \frac{1}{2} \sum_{i,j} r_i r_j \frac{\partial^2 \Phi}{\partial r_i\, \partial r_j}(\mathrm{o}) + \cdots, \tag{36}$$

where Φ and all its derivatives are evaluated at the origin. Since Φ is assumed to be due to another molecule (or its segments) that does not overlap with the one represented by the charge distribution $\rho(\mathbf{r})$, then in the region of ρ $\nabla^2\Phi = 0$, and we can subtract

$$\frac{1}{6} r^2 \nabla^2 \Phi = 0. \tag{37}$$

Substituting (36) and (37) into Eq. (31) and identifying the multipole moments as in Section II,A

$$W = q\Phi(\mathrm{o}) + \boldsymbol{\mu} \cdot \nabla\Phi(\mathrm{o}) + \frac{1}{2} \sum_{i,j} Q_{ij} \frac{\partial \Phi}{\partial r_i\, \partial r_j}(\mathrm{o}) + \cdots. \tag{38}$$

The same steps but with $\rho(\mathbf{r})$ first partitioned according to Eq. (33) leads to

$$W = \sum_{\alpha} \sum_{\beta} W_{\alpha\beta}$$

$$W_{\alpha\beta} = \left[q_\alpha \Phi_\beta(r) + \bar{\mu}_\alpha \cdot \nabla\Phi(r) + \frac{1}{2} \sum_{i,j} (Q_{ij}) \frac{\partial\Phi_\beta}{\partial r_i \, \partial r_j} (r) \right]_{r=r_\alpha} \tag{39}$$

where q_α, μ_α, and $(Q_{ij})_\alpha$ are the atomic charge dipole and quadrupole components as previously defined.

The external potential we are considering arises from the nonoverlapping charge distribution of the second molecule according to Eq. (39) or Eq. (35). The operators can be expanded in a second Taylor expression which, after the interactions implied either by Eq. (39) or by Eq. (35), leads to the two alternative expressions for the potential

$$\Phi(R) = \frac{q'}{|\mathbf{R}|} + \frac{\boldsymbol{\mu}' \cdot \mathbf{R}}{|\mathbf{R}|^3} + \frac{\mathbf{R} \cdot Q' \cdot \mathbf{R}}{|R|^5} + \cdots \tag{40}$$

$$\Phi(\mathbf{r}_\beta) = \sum_{\beta} \frac{q_\beta'}{|\mathbf{r}_\beta|} + \frac{\boldsymbol{\mu}_\beta' \cdot \mathbf{r}_\beta}{|\mathbf{r}_\beta|^3} + \frac{\mathbf{r}_\beta \cdot Q_\beta' \cdot \mathbf{r}_\beta}{|\mathbf{r}_\beta|^5} + \cdots, \tag{41}$$

where $\mathbf{R}$ is the vector from the origin of the primed charge distribution; the $\mathbf{r}_\beta$'s are similarly the vectors from the respective atomic origins in the primed charge distribution; q', $\boldsymbol{\mu}'$, Q' are the multipole moments of the primed charge distribution referred to the molecular origin; and q_β', μ_β', and Q_β' are the respective atomic multipole moments of the primed charge distribution.

Substituting Eq. (40) and its respective derivatives into Eq. (38) and repeating the whole procedure by interchanging the roles of molecules 1 and 2, then the interaction energy appears as a series of interactions of successive multipoles of the two molecules

$$W = \sum_{i=0} \sum_{j=0} W_{ij}, \tag{42}$$

where the successive interaction terms up to quadrupole–quadrupole interactions are

Monopole–monopole

$$W_{00} = \frac{qq'}{|R|} \tag{43}$$

Monopole–dipole

$$W_{01} = (q'\boldsymbol{\mu} \cdot \mathbf{R})|R|^{-3} \tag{44}$$

Dipole–monopole

$$W_{10} = -(q\boldsymbol{\mu}' \cdot \mathbf{R})|R|^{-3} \tag{45}$$

Dipole–dipole

$$W_{11} = (\boldsymbol{\mu} \cdot \boldsymbol{\mu}')|R|^{-3} - 3(\boldsymbol{\mu} \cdot \mathbf{R})(\boldsymbol{\mu}' \cdot \mathbf{R})|R|^{-5} \tag{46}$$

Monopole–quadrupole

$$W_{02} = (q'\mathbf{R} \cdot Q \cdot \mathbf{R})|R|^{-5} \tag{47}$$

Quadrupole–monopole

$$W_{20} = (q\mathbf{R} \cdot Q' \cdot \mathbf{R})|R|^{-5} \tag{48}$$

Dipole–quadrupole

$$W_{12} = 2(\boldsymbol{\mu}' \cdot Q \cdot \mathbf{R})|R|^{-5} - [5(\boldsymbol{\mu}' \cdot \mathbf{R})(\mathbf{R} \cdot Q \cdot \mathbf{R})]|R|^{-7} \tag{49}$$

Quadrupole–dipole

$$W_{21} = -2(\boldsymbol{\mu} \cdot \mathbf{Q}' \cdot \mathbf{R})|R|^{-5} + [5(\mathbf{R} \cdot Q' \cdot \mathbf{R})(\boldsymbol{\mu} \cdot \mathbf{R})]|R|^{-7} \tag{50}$$

Quadrupole–quadrupole

$$W_{22} = \tfrac{2}{3}\,\tfrac{1}{6}[Q : Q']|R|^{-5} - \tfrac{20}{3}[\mathbf{R} \cdot Q' \cdot Q \cdot \mathbf{R}][R]^{-7} + \tfrac{35}{3}(\mathbf{R} \cdot Q \cdot \mathbf{R})(\mathbf{R} \cdot Q' \cdot \mathbf{R})[R]^{-9}, \tag{51}$$

where **R** points from the unprimed origin to the primed origin and

$$Q : Q' = \sum_{ij} Q_{ij} Q'_{ij} = \text{trace of } Q \cdot Q'.$$

The expression for the interaction energy in terms of a series of interactions between successive atomic multipoles of molecule 1 with those of molecule 2 is obtained by a straightforward generalization of the procedure by which Eq. (42) has been obtained, i.e., the potential defined by Eq. (10) for successive atomic positions is substituted into the interaction equation

$$W = \sum_{\alpha} \sum_{\beta'} \sum_{i=0} \sum_{j=0} W_{ij}^{\alpha\beta'}, \tag{52}$$

where the interaction W is decomposed as in Eqs. (42)–(51) for each atomic pair α',β'. Thus, for example, a typical term $W_{12}^{02'}$ has the following meaning,

$$W_{20}^{\alpha\beta'} = (\tfrac{1}{2}q^{\alpha}\mathbf{R}_{\alpha\beta'}Q^{\beta'} \cdot R_{\alpha\beta'})|R_{\alpha\beta'}|^{-5},$$

so that this term represents the interaction between the monopole of atom α of molecule 1 with the quadrupole tensor of atom β' of molecule 2 with $R_{\alpha\beta'}$, the vector pointing from atom α to atom β'.

This completes the description of the two interaction schemes which are used in this study.

III. Analysis of Wave Functions

This section is designed to contribute a relative evaluation of the various wave functions by presenting a range of calculated physical properties and comparing them with corresponding experimental values. Two types of wave functions are used: wave functions calculated according to (a) the iterative extended Hückel theory (IEHT) and (b) the complete neglect of differential overlap method (CNDO). The physical properties considered are (a) diamagnetic susceptibilities, (b) dipole and quadrupole moments, and (c) inner shell electron binding energy shifts (ESCA shifts).

An outline of the theory and computational methods used in the calculation of these properties was given in the foregoing sections. A more complete discussion of these methods has been published elsewhere (Rein *et al.*, 1972a,b; Rabinowitz and Rein, 1972; Hartman *et al.*, 1972). The experimental values used in these comparisons were collected from the literature.

The purpose of the comparative analysis presented in this section is threefold. First, it aims to establish the relative usefulness of the two types of wave functions in predicting values for various physical properties. Second, it seeks an understanding of what aspects—or what regions—of the molecular structure contribute most to a given molecular property. Third, it attempts to determine the particular electronic aspects to which a given type of wave function is most sensitive and thereby evaluate the relative applicability of these wave functions to the various physical problems under study.

A. Diamagnetic Susceptibilities

Diamagnetic susceptibilities are calculated according to the Van Vleck (1932) equation

$$\chi_{xx}^{d} = \frac{e^2}{4mc^2}\langle 0|y^2 + z^2|0\rangle. \tag{53}$$

In order to calculate the χ_{xx}^d's, we first calculate the second moments of the electronic distribution.

These moments are

$$\langle 0|y^2|0\rangle = \sum_{\mu\nu} P_{\mu\nu}\langle\mu|y^2|\nu\rangle,$$

where $P_{\mu\nu}$ is the ground-state density matrix and y is by convention measured from the center of mass.

The value of the moment integral after displacement to a new origin is

$$\langle\mu|y^2|\nu\rangle = \langle\mu|y'^2|\nu\rangle + 2Y\langle\mu|y'|\nu\rangle + Y^2\langle\mu|\nu\rangle, \tag{54}$$

where Y is the component of the displacement and prime indicates integration variable with respect to the new origin. We can use this equation to express moment integrals in the most convenient coordinate system for integration.

There are two different cases: orbits μ and ν are either about the same center or about different centers. The common center in the former case and the midpoint of the two centers in the latter case were chosen as the new origins; the method of calculation of these integrals is discussed in connection with the quadrupole moments (Section III,C). Full details of these calculations have been given elsewhere (Rabinowitz and Rein, 1972).

The second moments for a set of polyatomic molecules using both CNDO/II and IEHT wave functions are depicted in Table I, where they are compared with recently measured experimental values and with a set of moments obtained for the case where unperturbed atomic charges of the centers are assumed. The components for the diamagnetic susceptibility tensors for the same set of molecules using both types of wave function are shown in Table II, where they are compared also with the corresponding experimental values. The main observation that can be made is that the calculated moments and susceptibilities appear to agree very well with the experimental values. The results indicate that the IEHT wave functions are somewhat more accurate than the CNDO/II wave functions in predicting diamagnetic susceptibilities and that both are remarkably successful. This interpretation is correct only because both the moments of the electronic distribution and the diamagnetic susceptibilities are very insensitive measures of the details of the electronic distribution. That this is indeed the case is further apparent from the additional data in Table I, which show that assuming all electrons to be at atomic centers gives a gross agreement with experimental values. This can best be understood

TABLE I

SECOND MOMENTS OF THE ELECTRIC DISTRIBUTIONS[a,b]

$\langle X^2 \rangle$
$\langle Y^2 \rangle$
$\langle Z^2 \rangle$

		Method		
Molecule	Experimental	IEHT	CNDO	Independent atom
Benzene	60.1 ± 1.5	60.42	61.52	53.6
	60.1 ± 1.5	60.42	61.52	53.6
	7.7 ± 1.2	8.02	7.65	0
Pyridine	57.1 ± 0.8	57.05	58.27	49.5
	56.2 ± 0.8	56.81	57.97	50.48
	7.9 ± 0.8	7.59	7.25	0
Furan	36.2 ± 0.7	37.29	38.17	31.33
	37.8 ± 0.7	37.91	38.73	32.77
	6.8 ± 0.7	6.30	6.04	0
Cyclopentadiene	42.3 ± 2.2	43.27	44.00	37.16
	41.8 ± 2.2	42.45	43.28	36.62
	8.4 ± 2.2	8.12	8.12	1.58
Pyrrole	39.1 ± 0.6	39.76	40.56	34.54
	38.6 ± 0.6	40.57	41.32	34.88
	7.4 ± 0.6	6.68	6.41	0
Methyl cyanide	34.7 ± 0.4	34.84	35.63	30.73
	5.2 ± 0.3	5.07	5.23	1.65
	5.2 ± 0.3	5.07	5.23	1.65
Methyl isocyanide	32.5 ± 0.6	32.92	33.49	28.09
	5.4 ± 0.5	5.02	5.23	1.60
	5.4 ± 0.5	5.02	5.23	1.60
Methyl acetylene	38.72 ± 0.30	38.91	39.70	35.78
	5.44 ± 0.25	5.53	5.58	1.65
	5.44 ± 0.25	5.53	5.58	1.65
Dimethyl ether	33.9	33.64	34.51	30.40
	11.0	10.54	11.19	6.6
	7.5	6.83	7.43	3.17

[a] Values from Rein *et al.* (1972a) and references therein.
[b] In $\text{cm}^2\ 10^{-16}$.

TABLE II

DIAMAGNETIC SHIELDING TENSORS[a,b]

χ^d_{xx}
χ^d_{yy}
χ^d_{zz}

		Method	
Molecule	Experimental	IEHT	CNDO
Benzene	−286 ± 10	−290.79	−293.88
	−286 ± 10	−290.79	−293.88
	−508 ± 20	−513.46	−522.77
Pyridine	−271.9 ± 1.6	−273.64	−277.15
	−275.7 ± 2.0	−274.66	−278.43
	−480.6 ± 2.2	−483.78	−493.93
Furan	−189.5 ± 1.8	−187.86	−190.20
	−182.5 ± 1.8	−185.22	−187.84
	−313.9 ± 1.8	−319.55	−326.75
Cyclopentadiene	−213.0 ± 5.8	−214.87	−218.42
	−211.8 ± 5.0	−218.33	−221.47
	−356.9 ± 5.1	−364.21	−370.85
Pyrrole	−195.7 ± 1.1	−200.80	−202.82
	−197.6 ± 1.3	−197.33	−199.58
	−329.8 ± 0.2	−341.33	−347.94
Methyl cyanide	− 44.2 ± 1.0	− 43.08	− 44.44
	−169.4 ± 1.1	−169.57	−173.59
	−169.4 ± 1.1	−169.57	−173.59
Methyl isocyanide	− 46.2 ± 2.0	− 42.67	− 44.43
	−160.9 ± 2.1	−161.22	−164.51
	−160.9 ± 2.1	−161.22	−164.51
Methyl acetylene	− 46.1 ± 2.1	− 46.97	− 47.93
	−187.3 ± 2.1	−188.83	−192.77
	−187.3 ± 2.1	−188.83	−192.77
Dimethyl ether	− 78.5	− 73.79	− 79.14
	−175.7	−171.94	−178.22
	−190.6	−187.72	−194.20

[a] Values from Rein *et al.* (1972a) and references therein.
[b] In erg G^{-2} $mole^{-1}$.

by an examination of the magnitude of the terms in Eq. (54). It is the last term that dominates the equation. This is further intensified by the fact that for the sum over each atom the last term always has a plus sign, while the other terms can have either sign. The last term is a measure of the electron density about each atom. The other terms are a measure of the anisotropy of the electrons about these centers.

This small difference between IEHT and CNDO/II wave functions may become decisive when considering other properties that depend more sensitively on charge distributions and atomic anisotropies that will become apparent in Section concerned with multipole moments.

B. Dipole Moments

Dipole moments calculated from IEHT and CNDO wave functions and corresponding experimental values are listed in Table IIIa. Separately appended in Table IIIb are the magnitude and angle to reference axis of the DNA nucleotide bases, as obtained by both our investigations and those of others. A more complete list of dipole moments calculated from IEHT wave functions can be found in earlier reports of ours (Rein *et al.*, 1970a).

In general, the agreement of our calculated values with those obtained by other investigators and with the corresponding experimental values is fairly good. For some molecules, the CNDO method appears to lead to slightly better predictions. However, for the nucleic acid bases where both directions and magnitudes are compared, the IEHT method is at least as successful as the CNDO.

The IEHT charges according to Method II charge division (Table IV) are very much smaller than the CNDO charges and the dipole moment in the two methods arises in different ways. For the IEHT wave function, the contribution to the dipole moment from each of the two terms, i.e., the atomic moments and the charge term, dominates. Thus the dipole moment in the CNDO method arises essentially from the segregation of charges among atoms in the molecule, while in the IEHT method the segregation and the anisotropy of charges contribute equally. This leads to consistent results regardless of the type of the scheme followed in assigning the bicentric densities.

For the IEHT calculation of the dipole moment vector there is at least indirect evidence to the effect that both the magnitude and the direction are both fairly correct. This follows from the definition of quadrupole components according to Eq. (28) and from IEHT wave functions (see

TABLE IIIa

Dipole Moments[a,b]

Molecule	Dipole moment Calc. from IEHT	Calc. from CNDO/II	Experimental
Benzene	0.	0.	0.
Pyridine	1.61	2.16	2.23
Cyclopentadiene	1.31	0.61	0.53
Pyrrole	2.27	1.69	1.80
Furan	0.61	0.86	0.63
Propynal	2.75	2.50	2.46
Propene	0.77	0.34	0.35
Dimethyl ether	2.18	1.79	1.29
Acetaldehyde	2.88	2.72	2.69
Formic acid	1.45	1.36	1.35–2.00
Formamide	4.57	3.97	3.20–3.86
Methyl formate	2.24	1.46	1.77
Keten	1.75	1.08	1.31–1.52
Methyl cyanide	3.51	3.12	3.08–3.96
Methyl isocyanide	4.75	4.05	3.80
Methyl acetylene	1.10	0.46	0.72–0.77
Water	2.23	2.24	1.81

[a] Values from Rabinowitz and Rein (1972) and references therein.
[b] In Debye units.

TABLE IIIb

Calculated Dipole Moments of DNA Bases[a]

	CNDO[b]		IEHT[b]		*Ab initio*[c]		IBMOL SCF[d]		Hückel $(\pi+\sigma)$[e]	
	μ_{tot}	θ[f]	μ_{tot}	θ[f]	μ_{tot}	θ[f]	μ_{tot}	θ[f]	μ_{tot}	θ[f]
Thymine	4.51	44°	4.03	39°	4.22	50°	3.3	34°	3.5	33°
Adenine	3.30	107°	3.50	88°	2.83	93°	2.6	85°	2.8	88°
Cytosine	7.64	97°	6.49	109°	6.76	103°	6.4	100°	8.0	108°
Guanine	8.11	327°	9.26	327°	—	—	6.94	328°	6.9	324°

[a] In Debye units.
[b] This investigation.
[c] Flygare and Benson (1971).
[d] Wyckoff *et al.* (1970).
[e] DeVoe and Tinoco (1962).
[f] Reference axis is the C_4—C_5 bond axis for guanine and adenine and the N_3—C_6 axis for thymine and cytosine.

below). The quadrupole moment components include contributions from both atomic charges and dipoles. Thus, the agreement of calculated quadrupole moments with corresponding experimental values implies that the lower moments are also correct. Since these quantities entirely specify both the magnitude and the direction of the dipole moment, this would indicate that the dipole vector quantities are also usually correct. However, it should be remarked here that these theoretical considerations are of little practical importance, as the differences encountered in this context are rather small.

TABLE IV-1a

PYRIDINE

	X (Å)	Y (Å)	Z (Å)	Q^{I}	Q^{II} (Units, electrons)	$Q^{\mathrm{III}f}$
C	0.69	−1.14	0.0	0.138	0.029	−0.180
C	−0.69	−1.19	0.0	−1.068	0.008	−0.202
C	−1.41	0.0	0.0	0.072	0.008	−0.204
C	−0.69	1.19	0.0	−0.068	0.008	−0.202
C	0.69	1.14	0.0	0.138	0.029	−0.180
H	1.28	−2.04	0.0	−0.030	0.010	0.231
H	−1.17	−2.16	0.0	0.014	0.014	0.227
H	−2.49	0.0	0.0	−0.011	0.010	0.221
H	1.28	2.04	0.0	−0.030	0.010	0.231
H	−1.17	2.16	0.0	0.014	0.014	0.227
N	1.39	0.0	0.0	−0.169	−0.143	−0.169

	I	II	III	
P_x	−2.16	−1.613	−1.613	Debyes
P_y	0.0	0.0	0.0	
P_z	0.0	0.0	0.0	
Q_{xx}	−13.408	− 5.620	− 5.620	10^{-26} esu-cm^2 (referenced to center of mass coordinate system)
Q_{xy}	0.0	—	—	
Q_{yy}	4.983	11.925	11.925	
Q_{xz}	0.0	—	—	
Q_{yz}	0.0	—	—	
Q_{zz}	8.425	− 6.306	− 6.306	

TABLE IV-1b

ATOMIC MOMENTS FOR PYRIDINE[a]

				Dipole[d]		Quadrupole[e]				
Atom	X[b]	Y[b]	Charge[c]	μ_x	μ_y	Q_{xx}	Q_{yy}	Q_{zz}	Q_{xy}	
N_1	1.39	0.0	−0.169	0.0	0.0	0.0	0.0	0.0	0.0	I[f]
			−0.144	−0.208	0.0	−0.131	0.102	0.029	0.0	II[f]
			−0.170	−0.176	0.0	−0.129	0.062	0.067	0.0	III[f]
C_2	0.69	−1.14	0.138	0.005	0.035	−0.011	0.010	0.001	−0.001	
			0.030	0.011	0.054	0.027	0.162	−0.189	−0.136	etc.
			−0.181	−0.106	0.251	0.002	0.055	−0.057	0.086	
C_3	−0.69	−1.19	−0.068	0.013	0.029	−0.004	0.017	−0.013	0.008	
			0.008	0.023	0.012	0.008	0.179	−0.187	−0.125	
			−0.202	0.108	0.194	0.051	−0.024	−0.027	−0.063	
C_4	−1.41	0.0	0.073	0.029	0.0	0.008	−0.025	0.017	0.0	
			0.009	0.022	0.0	0.050	0.038	−0.088	0.0	
			−0.205	0.226	0.0	−0.056	0.080	−0.024	0.0	
C_5	−0.69	1.19	−0.068	0.013	−0.029	−0.004	0.017	−0.013	−0.008	
			0.008	0.023	−0.012	0.008	0.179	−0.187	−0.125	
			−0.202	0.108	−0.194	0.051	−0.024	−0.027	0.063	
C_6	0.69	1.14	0.138	0.005	−0.035	−0.011	0.010	0.001	0.001	
			0.030	0.011	−0.054	0.027	0.162	−0.189	0.136	
			−0.181	−0.106	−0.251	0.002	0.055	−0.057	−0.086	

(*Continued*)

TABLE IV-1b—*Continued*

Atom	X^b	Y^b	Charge[c]	Dipole[d] μ_x	Dipole[d] μ_y	Quadrupole[e] Q_{xx}	Quadrupole[e] Q_{yy}	Quadrupole[e] Q_{zz}	Quadrupole[e] Q_{xy}	
H_7	1.28	−2.04	−0.031	0.0	0.0	0.0	0.0	0.0	0.0	
			0.010	0.004	−0.011	0.020	−0.013	−0.007	0.022	
			0.231	−0.013	0.016	0.019	0.052	−0.071	−0.041	
H_8	−1.17	−2.16	0.015	0.0	0.0	0.0	0.0	0.0	0.0	
			0.014	−0.001	−0.008	0.015	−0.011	−0.004	−0.018	etc.
			0.228	0.012	0.016	0.009	0.061	−0.070	0.038	
H_9	−2.49	0.0	−0.012	0.0	0.0	0.0	0.0	0.0	0.0	
			0.010	−0.004	0.0	0.160	−0.066	−0.094	0.0	
			0.222	0.024	0.0	0.082	−0.011	−0.071	0.0	
H_{10}	1.28	2.04	−0.031	0.0	0.0	0.0	0.0	0.0	0.0	
			0.010	0.004	0.011	0.020	−0.013	−0.007	−0.022	
			0.231	−0.013	−0.016	0.019	0.052	−0.071	0.041	
H_{11}	−1.17	2.16	0.015	0.0	0.0	0.0	0.0	0.0	0.0	
			0.014	−0.001	0.008	0.015	−0.011	−0.004	0.018	
			0.228	0.012	−0.016	0.009	0.061	−0.070	−0.038	

[a] Multipole moments not expressed are identically zero.

[b] Coordinates in Ångstroms.

[c] $|e|$ units.

[d] $10^{-8}\ |e| \cdot \text{cm}$.

[e] $10^{-16}\ |e| \cdot \text{cm}$.

[f] Corresponding to Methods I, II, and III, respectively.

TABLE IV-2a

ADENINE

	X (Å)	Y (Å)	Z (Å)	Q^{I}	Q^{II} (Units, electrons)	Q^{III}
N	−0.54	−0.10	0.0	−0.324	−0.180	−0.202
C	−1.03	−1.34	0.0	0.294	0.024	−0.176
N	−2.32	−1.65	0.0	−0.310	−0.173	−0.196
C	−3.21	−0.65	0.0	0.274	0.085	0.095
C	−2.77	0.65	0.0	−0.103	0.030	0.077
C	−1.42	0.90	0.0	0.345	0.091	0.105
N	−3.83	1.52	0.0	−0.235	−0.194	−0.234
C	−4.89	0.68	0.0	0.206	0.045	−0.124
C	−4.58	−0.60	0.0	−0.175	−0.010	−0.180
N	−0.98	2.17	0.0	−0.327	−0.069	−0.461
H	−0.31	−2.17	0.0	−0.061	0.002	0.218
H	−0.01	2.41	0.0	0.154	0.097	0.285
H	−1.71	2.85	0.0	0.155	0.097	0.288
H	−5.93	1.04	0.0	−0.039	0.022	0.228
H	−5.52	−1.11	0.0	0.147	0.130	0.276

	I	II	III	
P_x	− 3.304	− 3.27	− 3.27	Debyes
P_y	0.122	1.24	1.24	
P_z	0.0	0.0	0.0	
Q_{xx}	9.219	22.312	22.312	10^{-26} esu–cm^2 (Referenced to center of mass coordinate system)
Q_{yy}	−22.741	−12.732	−12.732	
Q_{zz}	13.522	− 9.580	− 9.580	
Q_{xy}	+24.562	27.485	27.485	

TABLE IV-2b

ADENINE SEGMENTAL MOMENTS

	P_x	P_y	P_z	Q_{xx}	Q_{xy}	Q_{yy}	Q_{xz}	Q_{yz}	Q_{zz}
		(10^{-8} el-cm)				(10^{-16} el-cm^2)			
N_1	−0.373	−0.057	0.0	−0.142	−0.057	0.121	0.0	0.0	0.020
	−0.219	−0.025	0.0	−0.246	−0.081	0.248	0.0	0.0	−0.001
	−0.194	−0.022	0.0	−0.224	−0.077	0.157	0.0	0.0	0.067
C_2	0.022	0.017	0.0	−0.012	−0.007	−0.014	0.0	0.0	0.027
	0.056	0.055	0.0	0.175	−0.301	0.253	0.0	0.0	−0.429
	−0.209	0.245	0.0	0.110	0.106	0.101	0.0	0.0	−0.212
N_3	0.092	0.358	0.0	0.110	−0.094	−0.138	0.0	0.0	0.027
	0.048	0.220	0.0	0.124	−0.145	−0.148	0.0	0.0	0.024
	0.045	0.198	0.0	0.067	−0.126	−0.148	0.0	0.0	0.080
C_4	−0.071	−0.006	0.0	0.107	−0.014	−0.083	0.0	0.0	−0.024
	−0.070	0.030	0.0	0.358	−0.085	0.029	0.0	0.0	−0.387
	−0.054	0.048	0.0	0.433	−0.269	0.074	0.0	0.0	−0.508
C_5	−0.019	−0.016	0.0	0.081	−0.023	0.029	0.0	0.0	−0.110
	0.001	−0.046	0.0	0.316	0.010	0.053	0.0	0.0	−0.369
	−0.042	−0.033	0.0	0.469	−0.035	0.045	0.0	0.0	−0.515
C_6	0.025	0.034	0.0	−0.082	0.020	0.018	0.0	0.0	0.064
	0.007	0.010	0.0	0.122	0.053	0.175	0.0	0.0	−0.298
	0.013	0.011	0.0	0.019	0.069	0.427	0.0	0.0	−0.447
N_7	−0.010	−0.409	0.0	0.107	0.002	−0.113	0.0	0.0	0.006
	0.011	−0.241	0.0	0.120	−0.012	−0.142	0.0	0.0	0.021
	0.018	−0.213	0.0	0.076	−0.051	−0.158	0.0	0.0	0.078

C_8	0.029	−0.075	0.0	0.007	−0.038	0.031	0.0	0.0	−0.038
	0.076	−0.104	0.0	0.227	−0.220	0.049	0.0	0.0	−0.276
	0.298	−0.232	0.0	0.076	0.006	0.207	0.0	0.0	−0.284
N_9	−0.026	0.067	0.0	0.149	0.044	0.056	0.0	0.0	−0.206
	−0.012	0.054	0.0	0.147	0.204	0.182	0.0	0.0	−0.329
	0.105	0.099	0.0	0.045	0.018	0.103	0.0	0.0	−0.149
N_{10}	−0.014	−0.021	0.0	0.190	−0.007	0.133	0.0	0.0	−0.323
	−0.013	−0.000	0.0	0.131	−0.072	0.309	0.0	0.0	−0.440
	−0.041	−0.135	0.0	−0.001	0.071	0.155	0.0	0.0	−0.153
H_{11}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.011	−0.012	0.0	0.073	0.041	−0.030	0.0	0.0	−0.043
	−0.008	0.009	0.0	0.054	−0.087	0.079	0.0	0.0	−0.134
H_{12}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.040	−0.003	0.0	0.165	−0.004	−0.069	0.0	0.0	−0.095
	−0.025	−0.013	0.0	0.170	0.063	−0.043	0.0	0.0	−0.127
H_{13}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	−0.045	0.010	0.0	0.029	0.075	−0.021	0.0	0.0	−0.007
	0.009	−0.037	0.0	0.036	−0.116	0.093	0.0	0.0	−0.130
H_{14}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	−0.012	0.005	0.0	0.257	0.014	−0.104	0.0	0.0	−0.152
	0.008	−0.002	0.0	0.138	−0.057	−0.010	0.0	0.0	−0.127
H_{15}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	−0.049	0.010	0.0	0.102	−0.030	−0.047	0.0	0.0	−0.055
	−0.022	0.041	0.0	0.034	0.116	0.066	0.0	0.0	−0.100

TABLE IV-3a

THYMINE

	X (Å)	Y (Å)	Z (Å)	Q^{I}	Q^{II} (Units, electrons)	Q^{III}
N	2.39	0.26	0.	−0.3302	−0.0129	−0.1904
C	3.22	−0.84	0.	0.5331	0.1652	0.1760
N	4.58	−0.60	0.	−0.2456	−0.0005	−0.1651
C	5.09	0.65	0.	0.2282	0.0502	−0.1523
C	4.24	1.74	0.	−0.1973	0.0118	0.0526
C	2.84	1.57	0.	0.4499	0.1134	0.1269
O	2.77	−1.97	0.	−0.4061	−0.3145	−0.3399
O	2.07	2.52	0.	−0.3853	−0.3118	−0.3446
H	1.40	0.10	0.	0.1776	0.1181	0.3044
H	5.25	−1.43	0.	0.1586	0.1116	0.2718
H	6.18	0.80	0.	−0.0192	0.0267	0.2314
C	4.83	3.16	0.	0.0297	0.0133	−0.7281
H	4.50	3.68	−0.85	0.0070	0.0125	0.2537
H	5.88	3.09	0.0	−0.0074	0.0043	0.2496

	I	II	III	
P_x	4.357	3.94	3.94	Debyes
P_y	− 1.154	− 0.86	− 0.86	
P_z	0.0	0.0	0.0	
Q_{xx}	18.060	23.787	23.787	10^{-26} esu–cm^2 (referenced to center of mass coordinate system)
Q_{yy}	−43.701	−32.251	−32.251	
Q_{zz}	25.641	8.464	8.464	
Q_{xy}	− 1.924	− 2.933	− 2.933	

TABLE IV-3b

THYMINE SEGMENTAL MOMENTS

	P_x	P_y	P_z	Q_{xx}	Q_{xy}	Q_{yy}	Q_{xz}	Q_{yz}	Q_{zz}
		(10^{-8} el-cm)				(10^{-16} el-cm^2)			
N_1	0.003	−0.020	0.0	0.145	−0.006	0.110	0.0	0.0	−0.256
	−0.011	−0.013	0.0	0.076	0.051	0.242	0.0	0.0	−0.318
	0.132	0.010	0.0	−0.014	−0.019	0.216	0.0	0.0	−0.201
C_2	0.033	0.051	0.0	0.011	−0.017	−0.062	0.0	0.0	0.051
	0.033	0.084	0.0	0.203	−0.004	0.090	0.0	0.0	−0.294
	0.031	0.074	0.0	0.213	0.014	0.225	0.0	0.0	−0.438
N_3	0.014	0.025	0.0	0.118	−0.020	0.135	0.0	0.0	−0.254
	−0.008	−0.012	0.0	0.095	−0.146	0.301	0.0	0.0	−0.396
	−0.100	0.093	0.0	0.088	0.111	0.078	0.0	0.0	−0.167
C_4	−0.029	−0.066	0.0	−0.032	0.056	−0.008	0.0	0.0	0.040
	0.040	−0.081	0.0	0.065	0.089	0.196	0.0	0.0	−0.261
	−0.237	−0.148	0.0	−0.223	0.082	0.396	0.0	0.0	−0.172
C_5	0.022	−0.030	0.0	0.044	−0.012	0.066	0.0	0.0	−0.111
	−0.046	−0.044	0.0	0.171	−0.033	0.099	0.0	0.0	−0.271
	−0.061	0.000	0.0	0.145	0.070	0.174	0.0	0.0	−0.320
C_6	−0.015	−0.054	0.0	−0.084	0.032	0.017	0.0	0.0	0.066
	−0.021	−0.066	0.0	0.121	−0.035	0.150	0.0	0.0	−0.272
	−0.044	−0.062	0.0	0.112	−0.003	0.290	0.0	0.0	−0.402
O_7	0.109	0.270	0.0	−0.131	0.107	0.090	0.0	0.0	0.041
	0.069	0.174	0.0	−0.149	0.107	0.083	0.0	0.0	0.066
	0.062	0.158	0.0	−0.102	0.032	−0.029	0.0	0.0	0.132

(Continued)

TABLE IV-3b—*Continued*

	P_x	P_y	P_z	Q_{xx}	Q_{xy}	Q_{yy}	Q_{xz}	Q_{yz}	Q_{zz}
		(10^{-8} el-cm)				(10^{-16} el-cm^2)			
O_8	0.176	−0.227	0.0	−0.072	−0.148	0.009	0.0	0.0	0.063
	0.116	−0.139	0.0	−0.096	−0.149	−0.000	0.0	0.0	0.097
	0.104	−0.125	0.0	−0.076	−0.050	−0.073	0.0	0.0	0.150
H_9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	−0.032	−0.004	0.0	0.189	−0.022	−0.071	0.0	0.0	−0.117
	0.029	0.005	0.0	0.168	0.034	−0.039	0.0	0.0	−0.128
H_{10}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.028	−0.031	0.0	0.032	0.060	−0.032	0.0	0.0	0.000
	0.000	0.007	0.0	0.034	−0.079	0.079	0.0	0.0	−0.114
H_{11}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.009	0.014	0.0	0.301	−0.015	−0.119	0.0	0.0	−0.182
	−0.011	0.010	0.0	0.148	0.003	−0.017	0.0	0.0	−0.131
C_{12}	−0.014	−0.040	0.0	0.010	−0.006	−0.010	0.0	0.0	−0.000
	−0.003	0.006	0.0	−0.204	−0.199	−0.084	0.0	0.0	0.289
	−0.093	−0.213	0.0	−0.068	0.152	0.285	0.0	0.0	−0.217
H_{13}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	−0.014	0.003	−0.02552	−0.024	0.032	0.062	−0.04187	0.03968	−0.038
	0.004	−0.020	0.02009	−0.067	−0.030	−0.009	0.06924	−0.11463	0.007
H_{14}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.026	−0.017	0.0	0.317	0.038	−0.141	0.0	0.0	−0.175
	−0.030	−0.010	0.0	0.180	0.001	−0.070	0.0	0.0	−0.109
H_{15}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	−0.014	0.003	0.02552	−0.024	0.032	0.062	0.04187	−0.03968	−0.038
	0.004	−0.020	−0.02009	−0.067	−0.030	−0.009	−0.06924	0.11463	0.077

TABLE IV-4a

CYTOSINE

	X (Å)	Y (Å)	Z (Å)	Q^{I}	Q^{II} (Units, electrons)	Q^{III}
N	2.35	0.19	0.	−0.420	−0.182	−0.196
C	3.22	−0.84	0.	0.513	0.110	0.139
N	4.58	0.60	0.	−0.250	−0.006	−0.194
C	5.09	0.65	0.	0.289	0.057	−0.145
C	4.20	1.71	0.	−0.284	−0.008	−0.193
C	2.85	1.42	0.	0.436	0.096	0.101
O	2.80	−1.99	0.	−0.448	−0.350	−0.378
N	1.99	2.45	0.	−0.321	−0.061	−0.455
H	5.15	−1.43	0.	0.159	0.117	0.302
H	6.18	0.82	0.	−0.030	0.028	0.230
H	4.56	2.75	0.	0.055	0.009	0.212
H	2.28	3.41	0.	0.145	0.094	0.286
H	1.00	2.33	0.	0.155	0.093	0.289

	I	II	III	
P_x	5.185	3.29	3.29	Debyes
P_y	5.619	5.60	5.60	
P_z	0.0	0.0	0.0	
Q_{xx}	8.063	13.230	13.230	10^{-26} esu–cm^2 (referenced to center of mass coordinate system)
Q_{yy}	−17.230	− 3.632	− 3.632	
Q_{zz}	9.167	− 9.597	− 9.597	
Q_{xy}	−31.444	−31.040	−31.040	

TABLE IV-4b

CYTOSINE SEGMENTAL MOMENTS

	P_x	P_y (10^{-8} el-cm)	P_z	Q_{xx}	Q_{xy}	Q_{yy} (10^{-16} el-cm^2)	Q_{xz}	Q_{yz}	Q_{zz}
N_1	0.372	0.087	0.0	−0.109	−0.033	0.163	0.0	0.0	−0.054
	0.218	0.030	0.0	−0.261	−0.081	0.300	0.0	0.0	−0.039
	0.195	0.014	0.0	−0.244	−0.085	0.217	0.0	0.0	0.026
C_2	0.074	0.029	0.0	0.041	0.014	−0.097	0.0	0.0	0.055
	0.069	0.057	0.0	0.203	0.031	0.098	0.0	0.0	−0.301
	0.084	0.057	0.0	0.160	0.039	0.307	0.0	0.0	−0.468
N_3	0.048	0.029	0.0	0.069	−0.014	0.145	0.0	0.0	−0.214
	−0.007	−0.020	0.0	0.068	−0.162	0.337	0.0	0.0	−0.405
	−0.095	0.090	0.0	0.101	0.083	0.065	0.0	0.0	−0.166
C_4	−0.026	−0.059	0.0	−0.045	0.052	−0.045	0.0	0.0	0.090
	−0.048	−0.099	0.0	0.104	0.110	0.110	0.0	0.0	−0.214
	−0.244	−0.154	0.0	−0.152	0.057	0.272	0.0	0.0	−0.119
C_5	0.006	−0.057	0.0	0.060	−0.005	0.096	0.0	0.0	−0.156
	−0.042	−0.027	0.0	0.059	0.157	0.411	0.0	0.0	−0.470
	−0.137	−0.212	0.0	0.268	−0.114	−0.099	0.0	0.0	−0.168
C_6	−0.025	0.049	0.0	−0.067	−0.056	−0.049	0.0	0.0	0.116
	−0.036	0.018	0.0	0.127	−0.088	0.144	0.0	0.0	−0.272
	−0.029	0.016	0.0	0.110	−0.165	0.299	0.0	0.0	−0.409

O_7	0.103	0.272	0.0	−0.127	0.107	0.101	0.0	0.0	0.026
	0.062	0.173	0.0	−0.152	0.098	0.086	0.0	0.0	0.066
	0.056	0.161	0.0	−0.108	0.030	−0.018	0.0	0.0	0.126
N_8	0.005	−0.002	0.0	0.156	0.017	0.156	0.0	0.0	−0.312
	−0.004	0.013	0.0	0.024	0.125	0.427	0.0	0.0	−0.452
	0.101	−0.115	0.0	0.070	−0.089	0.074	0.0	0.0	−0.145
H_9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.014	−0.030	0.0	0.028	0.066	−0.039	0.0	0.0	0.010
	−0.020	0.018	0.0	0.038	−0.099	0.090	0.0	0.0	−0.129
H_{10}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.009	0.014	0.0	0.297	−0.011	−0.121	0.0	0.0	−0.176
	−0.011	0.012	0.0	0.149	0.005	−0.018	0.0	0.0	−0.130
H_{11}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.005	0.007	0.0	0.029	−0.018	−0.017	0.0	0.0	−0.011
	−0.000	−0.013	0.0	−0.015	0.054	0.145	0.0	0.0	−0.129
H_{12}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.020	0.038	0.0	0.026	−0.068	−0.059	0.0	0.0	0.033
	−0.009	−0.025	0.0	−0.027	0.067	0.157	0.0	0.0	−0.129
H_{13}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	−0.042	−0.013	0.0	0.194	−0.049	−0.092	0.0	0.0	−0.102
	0.030	0.005	0.0	0.179	0.036	−0.048	0.0	0.0	−0.131

TABLE IV-5a

GUANINE

	X (Å)	Y (Å)	Z (Å)	Q^{I}	Q^{II} (Units, electrons)	Q^{III}
N	−0.58	−0.13	0.0	−0.291	−0.009	−0.198
C	−1.07	−1.39	0.0	0.482	0.145	0.142
N	−2.37	−1.68	0.0	−0.397	−0.192	−0.216
C	−3.21	−0.65	0.0	0.272	0.068	0.094
C	−2.77	0.65	0.0	−0.165	0.008	0.065
C	−1.40	0.98	0.0	0.431	0.090	0.113
N	−3.83	1.52	0.0	−0.183	−0.202	−0.243
C	−4.89	0.68	0.0	0.172	0.035	−0.151
N	−4.58	−0.60	0.0	−0.156	−0.012	−0.208
N	−0.20	−2.41	0.0	−0.344	−0.052	−0.447
O	−1.06	2.15	0.0	−0.405	−0.340	−0.379
H	0.41	0.0	0.0	0.152	0.118	0.306
H	−0.48	−3.37	0.0	0.174	0.100	0.293
H	0.77	−2.28	0.0	0.161	0.102	0.306
H	−5.93	1.04	0.0	−0.035	0.018	0.224
H	−5.15	−1.43	0.0	0.132	0.120	0.298

	I	II	III	
P_x	1.986	2.32	2.32	Debyes
P_y	− 7.856	− 8.96	− 8.96	
P_z	0.0	0.0	0.0	
Q_{xx}	47.444	53.632	53.632	10^{-26} esu–cm^2 (referenced to center of mass coordinate system)
Q_{yy}	−58.850	−41.009	−41.009	
Q_{zz}	11.406	−12.622	−12.622	
Q_{xy}	−16.852	−16.935	−16.935	

TABLE IV-5b—Guanine Segmental Moments

	P_x	P_y	P_z	Q_{xx}	Q_{xy}	Q_{yy}	Q_{xz}	Q_{yz}	Q_{zz}
		(10^{-8} el-cm)				(10^{-16} el-cm^2)			
N_1	0.013	−0.038	0.0	0.136	0.022	0.098	0.0	0.0	−0.235
	0.006	−0.014	0.0	0.084	0.044	0.231	0.0	0.0	−0.316
	−0.137	−0.030	0.0	0.017	−0.050	0.179	0.0	0.0	−0.197
C_2	0.066	0.006	0.0	−0.078	−0.018	0.012	0.0	0.0	0.066
	0.045	0.043	0.0	0.188	−0.085	0.144	0.0	0.0	−0.332
	0.057	0.058	0.0	0.201	−0.147	0.265	0.0	0.0	−0.466
N_3	0.131	0.365	0.0	0.166	−0.067	−0.103	0.0	0.0	−0.062
	0.074	0.224	0.0	0.170	−0.175	−0.133	0.0	0.0	−0.037
	0.065	0.204	0.0	0.121	−0.168	−0.134	0.0	0.0	0.012
C_4	−0.059	−0.017	0.0	0.086	−0.034	−0.077	0.0	0.0	−0.009
	−0.049	0.020	0.0	0.313	−0.093	0.061	0.0	0.0	−0.374
	−0.051	0.011	0.0	0.425	−0.278	0.101	0.0	0.0	−0.527
C_5	−0.030	−0.015	0.0	0.105	−0.019	0.056	0.0	0.0	−0.162
	−0.017	−0.035	0.0	0.310	0.035	0.078	0.0	0.0	−0.389
	−0.045	−0.023	0.0	0.499	−0.015	0.038	0.0	0.0	−0.538
C_6	0.049	−0.058	0.0	−0.064	−0.080	−0.001	0.0	0.0	0.066
	0.034	−0.081	0.0	0.149	−0.015	0.138	0.0	0.0	−0.288
	0.064	−0.072	0.0	0.103	−0.005	0.338	0.0	0.0	−0.442
N_7	−0.009	−0.408	0.0	0.092	0.004	−0.124	0.0	0.0	0.031
	0.005	−0.236	0.0	0.125	−0.005	−0.153	0.0	0.0	0.028
	0.015	−0.209	0.0	0.088	−0.046	−0.171	0.0	0.0	0.082
C_8	0.034	−0.087	0.0	0.020	−0.041	0.069	0.0	0.0	−0.090
	0.085	−0.131	0.0	0.216	−0.243	0.107	0.0	0.0	−0.324
	0.321	−0.229	0.0	0.107	−0.053	0.192	0.0	0.0	−0.299

(*Continued*)

TABLE IV-5b—*Continued*

	P_x	P_y	P_z	Q_{xx}	Q_{xy}	Q_{yy}	Q_{xz}	Q_{yz}	Q_{zz}
		(10^{-8} el-cm)				(10^{-16} el-cm^2)			
N_9	0.014	0.006	0.0	0.084	0.047	0.117	0.0	0.0	−0.201
	0.008	0.007	0.0	0.050	0.233	0.344	0.0	0.0	−0.394
	0.074	0.122	0.0	0.095	0.013	0.064	0.0	0.0	−0.159
N_{10}	−0.004	0.013	0.0	0.159	0.011	0.153	0.0	0.0	−0.321
	0.004	−0.006	0.0	0.026	0.124	0.430	0.0	0.0	−0.457
	−0.105	0.117	0.0	0.072	−0.089	0.072	0.0	0.0	−0.144
O_{11}	−0.069	−0.282	0.0	−0.164	0.065	0.118	0.0	0.0	0.045
	−0.057	−0.180	0.0	−0.167	0.092	0.098	0.0	0.0	0.068
	−0.054	−0.163	0.0	−0.103	−0.053	−0.028	0.0	0.0	0.132
H_{12}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.030	0.006	0.0	0.195	−0.018	−0.075	0.0	0.0	−0.119
	−0.031	−0.001	0.0	0.172	0.029	−0.046	0.0	0.0	−0.126
H_{13}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	−0.018	−0.039	0.0	0.026	−0.064	−0.060	0.0	0.0	0.034
	0.010	0.025	0.0	−0.031	0.071	0.160	0.0	0.0	−0.128
H_{14}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.039	0.013	0.0	0.198	−0.052	−0.094	0.0	0.0	−0.103
	−0.035	−0.007	0.0	0.186	0.039	−0.054	0.0	0.0	−0.132
H_{15}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	−0.012	0.006	0.0	0.258	0.015	−0.106	0.0	0.0	−0.152
	0.009	−0.000	0.0	0.143	−0.058	−0.017	0.0	0.0	−0.125
H_{16}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	−0.009	−0.029	0.0	0.025	−0.046	−0.033	0.0	0.0	0.007
	0.021	0.012	0.0	0.033	0.112	0.084	0.0	0.0	−0.117

C. Quadrupole Moments

A comparison of quadrupole moments calculated from IEHT and CNDO wave functions with corresponding experimental values may be made from the data listed in Table V. It appears that the quadrupole moments calculated from the IEHT wave functions are in general correspondence with the experimentally measured moments and this statement may be borne out by the following detailed considerations. First, we note that, for all but 2 of 54 quadrupole moments which are depicted in the tables, the moments calculated from IEHT wave functions and corresponding experimentally determined ones have the same sign. Even where the signs are different it may be noted that a change in the experimentally determined sign is within the limits of error of the experiment. It may further be remarked that due to the technical difficulties involved in the experimental determination and the fact that the obtained quadrupole moments represent the differences between two quantities of similar magnitude, i.e., the electronic part of the moment and the nuclear part, the error for most of the experimental moments reported in Table V is about ± 10% and may be as high as ± 50% in a few cases. A great many of the values calculated from IEHT wave functions also fall within this spread. Thus, the data of Table V may justify the statement that the IEHT-predicted quadrupole moments are in semiquantitative agreement with the experimentally determined values.

In contrast to this trend, inspection of Table V shows that the quadrupole moments calculated from CNDO/II wave functions completely fail to reproduce the experimental values with any consistency. It may be noted that of the 18 molecules considered 12 have at least one component differing in sign from the corresponding experimental value and many more have the wrong ordering of the components.

The principal difference in the contributions to multipole moments between the IEHT method and the CNDO/II method is that in the IEHT method there are two-center contributions to the moments (see Section II). If we decompose the contributions to the moments calculated from the IEHT wave function into one-center and two-center parts, we can see that, in general, the two-center part is of the order of magnitude of the moment itself. This is true because, in general, the nuclear contribution is about equal to or greater than the one-center electronic contribution. It is this cancellation that makes the multipole moment a very sensitive quantity in comparing molecular wave functions.

TABLE V[a]

Q_{xx}
Q_{yy}
Q_{zz}

Molecule	Experimental	Calc. from IEHT W.F.	Calc. from CNDO/II W.F.
Benzene	2.8 ± 1.6	2.86	−0.32
	2.8 ± 1.6	2.86	−0.32
	− 5.6 ± 2.8	−5.72	0.64
Pyridine	− 3.5 ± 0.9	−2.81	−6.70
	9.7 ± 1.1	5.96	2.49
	− 6.2 ± 1.5	−3.15	4.21
Cyclopentadiene	1.4 ± 0.4	0.34	−1.18
	3.7 ± 0.4	2.38	0.77
	− 5.1 ± 0.4	−2.72	1.01
Pyrrole	6.6 ± 1.2	4.67	1.95
	5.8 ± 1.6	1.23	−1.10
	−12.4 ± 2.5	−5.90	−0.85
Furan	0.2 ± 0.4	−1.15	−3.52
	5.9 ± 0.3	4.73	2.03
	− 6.1 ± 0.4	−3.58	1.49
Propynal	3.1 ± 1.3	5.87	2.62
	1.1 ± 2.2	−4.35	−5.58
	− 4.2 ± 2.4	−1.53	2.96
Propene	0.6 ± 0.3	0.05	−0.96
	2.9 ± 0.5	1.70	0.56
	− 3.5 ± 0.7	−1.75	0.40
Dimethyl ether	3.3 ± 0.6	2.73	3.13
	− 2.0 ± 0.5	−2.37	−3.92
	− 1.3 ± 1.0	−0.36	0.79
Acetaldehyde	− 1.2 × 1.5	−3.17	1.53
	1.0 ± 0.9	2.12	3.16
	0.2 ± 1.8	1.05	−4.69
Formic acid	5.2 ± 0.6	6.67	5.55
	− 5.3 ± 0.6	−7.13	−9.33
	0.1 ± 0.6	0.46	3.78

TABLE V—*Continued*

Molecule	Experimental	Calc. from IEHT W.F.	Calc. from CNDO/II W.F.
Formamide	3.4 ± 0.4	2.80	2.59
	−0.3 ± 0.5	−0.49	−3.67
	−3.1 ± 0.8	−2.21	1.08
Glycol aldehyde	−5.6 ± 2.0	−6.15	2.91
	3.8 ± 1.8	3.52	5.01
	1.8 ± 3.3	2.63	−7.92
Methyl formate	1.0 ± 0.9	1.22	4.73
	−1.2 ± 1.5	−1.90	−9.03
	0.2 ± 1.8	0.68	4.30
Ketene	−0.7 ± 0.3	−1.86	−6.31
	3.8 ± 0.4	3.42	4.73
	−3.1 ± 0.4	−1.56	1.58
Methyl cyanide	−1.8 ± 1.2	−3.32	−6.36
	0.9 ± 1.2	1.66	3.18
	0.9 ± 1.2	1.66	3.18
Methyl isocyanide	−2.7 ± 1.6	−6.78	−8.50
	1.35	3.39	4.25
	1.35	3.39	4.25
Methyl acetylene	4.82 ± 0.23	3.56	0.40
	−2.41	−1.78	−0.20
	−2.41	−1.78	−0.20
Water	−0.13 ± 0.03	0.02	−0.32
	2.63 ± 0.02	1.70	1.00
	−2.50 ± 0.02	−1.72	−0.77

[a] Values from Rabinowitz and Rein (1972) and references therein.

D. ESCA Shifts

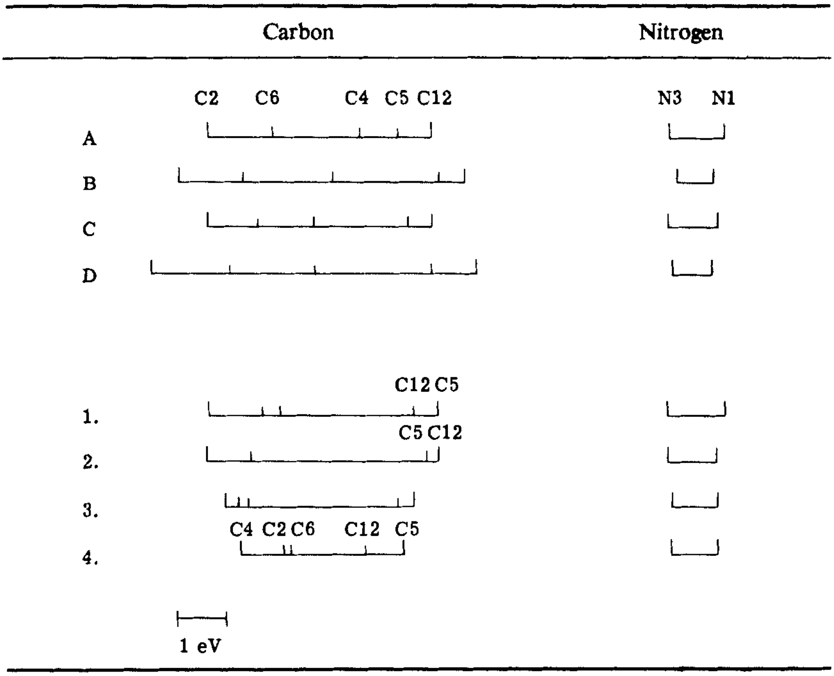
An additional approach to the investigation of the wave functions is offered by studies of physical properties which can be treated semiclassically in terms of the intramolecular electric field or, more correctly, in terms of the potential. That is, certain molecular properties are well approximated by the first-order perturbation correction. A particularly clear-cut example is offered in the case of the shifts in the 1*s* electron binding energies.

These shifts can be viewed as reflecting the perturbations to the atomic core energies induced by the molecular environment. These perturbations can be written in terms of one- and two-center integrals and the corresponding elements of the molecular bond order matrix; a point charge approximation of this method is the one used by Siegbahn *et al.* (1967). Shifts which are different from those obtained with the earlier analysis, inasmuch as all the appropriate integrals are calculated by exact methods, have been reported by us (Rein *et al.*, 1972b). We reproduce in Table VI our results obtained from CNDO wave functions for thymine. Comparison

TABLE VI

CALCULATED AND EXPERIMENTAL ESCA SHIFTS

Thymine



NOTE

A stands for experimental data (Barber and Clark, 1970); B, C, and D stand for *ab initio* calculations (Clementi *et al.*, 1969; Snyder *et al.*, 1970; Mely and Pullman, 1969, respectively).

1, 2, 3, 4, stand for our calculations (all CNDO wave functions): 1. Point charge approximation; 2. Integrals calculated by exact methods distinguishing between 2*s* and 2*p* orbitals; 3. Integrals calculated by exact methods, including 2*s* orbitals; 4. Integrals calculated by exact methods, including one-center overlaps.

of these numbers with corresponding experimental values and with values calculated by *ab initio* Gaussian methods show a fair agreement, as far as the general features (band width, relative position of bonds) are concerned. However, the predictions of the finer details of these spectra, i.e., level ordering, are more ambiguous.

These results, then, confirm once again that the charge distribution obtained from CNDO wave functions are in the first approximation correct, but they are insufficient to describe properties that depend on finer details of electronic structure.

IV. On the Problem of Convergence and Molecular Moment Representations

The alternative atomic moment representation of pyridine, the external molecular potential calculated from these representations, and finally the electrostatic interaction energy between a pair of stacked pyridine molecules, and for a wide range of successive separations, are represented in Tables VII and VIII. Most of the data appearing in these tables are reproduced from T. Swissler's and J. Rabinowitz's unpublished work. Some preliminary results on pyridine point moments and interactions have appeared elsewhere (Rein *et al.*, 1972c).

There are a number of very interesting observations which can be made in connection with these results.

We begin by observing that the three methods of calculation, i.e., Method I based on CNDO wave functions and definition of moments, Method II based on IEHT wave functions and division of two-center densities, and Method III, based also on IEHT wave functions but with equally divided overlap densities, yield very different magnitudes for the successive atomic moments. For example, some of the atomic charges defined according to Methods II and III, respectively, may be more than an order of magnitude different. However, the molecular moments and potentials calculated from these two methods are in exact agreement. This can be seen clearly from the fact that the molecular dipole and quadrupole moments as obtained from Methods II and III agree up to five decimal places and, similarly, the atomic moment potentials for distances for which both methods have converged do agree very well, as can be seen from Table VIII. These findings are very important indeed, first because they show that our analysis is consistent, and second because they clearly corroborate our earlier contention regarding the minor influence of a given arbitrary assignment of formal atomic charges on the final results of a rigorous analysis.

TABLE VIIa

INTERACTION ENERGIES
PYRIDINE WITH PYRIDINE AND APART FROM MOLECULAR CENTERS ON Z AXIS

	Segmental[a]			Molecular[a]		
R (Å)	E_M	E_D	E_Q	E_D	E_Q	
3	822.0	13720.0	14060.0	10800.0	45430.0	I
	1765.0	5068.0	7947.0	6019.0	27960.0	II
	35840.0	8010.0	8027.0	6019.0	27960.0	III
5	182.0	2779.0	2811.0	2333.0	5026.0	
	470.0	1167.0	1151.0	1300.0	3006.0	
	7547.0	1061.0	1050.0	1300.0	3006.0	
7	71.2	957.0	963.0	850.0	1351.0	
	184.0	441.0	439.0	474.0	791.0	
	2254.0	383.0	389.0	474.0	791.0	
10	25.8	313.0	314.0	292.0	376.0	
	65.5	156.0	158.0	162.0	216.0	
	577.0	143.0	148.0	162.0	216.0	
20	3.39	37.3	36.4	36.4	39.10	
	8.41	20.1	20.2	20.3	22.0	
	43.2	19.6	20.1	20.3	22.0	
30	1.01	10.9	10.9	10.8	11.1	
	2.51	5.99	6.01	6.02	6.24	
	10.8	5.93	6.00	6.02	6.24	
40	0.429	4.59	4.60	4.56	4.64	
	1.06	2.53	2.54	2.54	2.59	
	4.23	2.52	2.54	2.54	2.59	
50	0.220	2.53	2.35	2.33	2.36	
	0.543	1.30	1.30	1.30	1.32	
	2.09	1.29	1.30	1.30	1.32	
100	0.027	0.293	0.293	0.292	0.292	
	0.068	0.162	0.162	0.162	0.163	
	0.248	0.162	0.162	0.162	0.163	

[a] 10^{-5} eV.

TABLE VIIb

INTERACTION ENERGIES
GUANINE WITH CYTOSINE AND APART FROM MOLECULAR CENTERS ON BOND AXIS

	Segmental[a]			Molecular[a]		
R(Å)	E_M	E_D	E_Q	E_D	E_Q	
5.69	−35380.0	−83326.0	−94620.0	−19180.0	−72740.0	I
	−39710.0	−81453.0	−118700.0	−20450.0	−65680.0	II
	−78400.0	−77890.0	−113800.0	−20450.0	−65680.0	III
7.69	−9938.0	−23618.0	−25190.0	−7657.0	−23330.0	
	−12490.0	−22921.0	−26190.0	−8211.0	−21700.0	
	−22330.0	−20768.0	−25880.0	−8211.0	−21700.0	
10.69	−2885.0	−6872.0	−7116.0	−2816.0	−6904.0	
	−3798.0	−6696.0	−7146.0	−3034.0	−6606.0	
	−6510.0	−6525.0	−7106.0	−3034.0	−6606.0	
15.69	−729.0	−1728.0	−1726.0	−882.0	−1740.0	
	−990.0	−1705.0	−1769.0	−953.0	−1713.0	
	−1651.0	−1674.0	−1765.0	−953.0	−1713.0	
20.69	−280.0	−657.0	−667.0	−382.0	−662.0	
	−386.0	−657.0	−675.0	−414.0	−663.0	
	−633.0	−647.0	−674.0	−414.0	−663.0	
30.69	−74.3	−172.2	−173.8	−116.0	−173.0	
	−104.0	−175.2	−178.7	−126.0	−177.0	
	−167.0	−173.0	−178.7	−126.0	−177.0	
55.69	−10.7	−24.4	−24.6	−19.4	−24.5	
	−15.4	−25.5	−25.8	−21.1	−25.7	
	−24.0	−25.3	−25.8	−21.1	−25.7	
105.69	−1.44	−3.21	−3.22	−2.83	−3.22	
	−2.08	−3.41	−3.44	−3.08	−3.44	
	−3.18	−3.40	−3.44	−3.08	−3.44	

[a] 10^{-5} eV.

TABLE VIIc

INTERACTION ENERGIES
ADENINE WITH THYMINE AND APART FROM MOLECULAR CENTERS ON BOND AXIS

	Segmental[a]			Molecular[a]		
R(Å)	E_M	E_D	E_Q	E_D	E_Q	
6.11	−10580.0	−31807.0	−38180.0	7454.0	4248.0	I
	−8903.0	−28305.0	−56480.0	6148.0	2338.0	II
	−26400.0	−28811.0	−53200.0	6148.0	2338.0	III
8.11	−1038.0	−2400.0	−2795.0	3168.0	1700.0	
	−903.0	−2522.0	−4245.0	2600.0	713.0	
	−2653.0	−2597.0	−4443.0	2600.0	713.0	
10.11	−115.0	−156.0	99.0	1629.0	908.0	
	−45.0	−126.0	−469.0	1333.0	381.0	
	−235.0	−140.0	−535.0	1333.0	381.0	
15.11	40.1	284.6	278.3	485.0	309.0	
	75.4	174.0	121.0	395.0	158.0	
	142.0	169.0	116.0	395.0	158.0	
20.11	25.9	114.8	142.4	205.0	144.0	
	44.6	98.7	80.6	167.0	83.5	
	90.0	96.2	79.7	167.0	83.5	
30.11	10.05	48.7	48.05	60.9	47.7	
	16.8	35.6	31.6	49.5	31.3	
	35.6	34.9	31.4	49.5	31.3	
55.11	2.00	7.84	8.68	9.91	8.64	
	3.28	6.73	6.32	8.03	6.29	
	7.27	6.64	6.32	8.03	6.29	
105.11	0.320	1.33	1.33	1.43	1.33	
	0.522	1.05	1.02	1.15	1.02	
	1.19	1.04	1.02	1.15	1.02	

[a] 10^{-5} eV.

TABLE VIII

PYRIDINE POTENTIAL FOR ^{+}Q AT POSITION OF N AND OUT ON X AXIS

	Segmental[a]			Molecular[a]		
R (Å)	E_M	E_D	E_Q	E_D	E_Q	
3	−51300.0	−246600.0	−280800.0	−72040.0	−146600.0	I
	−64520.0	−162960.0	−207300.0	−53780.0	−85020.0	II
	−123700.0	−162500.0	−192800.0	−53780.0	−85020.0	III
5	−12350.0	−49490.0	−52710.0	−25940.0	−42040.0	
	−17090.0	−34480.0	−36540.0	−19360.0	−26110.0	
	−30590.0	−34280.0	−36330.0	−19360.0	−26110.0	
7	−5494.0	−20584.0	−21470.0	−13230.0	−19100.0	
	−7837.0	−14584.0	−14720.0	−9879.0	−12340.0	
	−13610.0	−14333.0	−14740.0	−9879.0	−12340.0	
8	−4041.0	−14841.0	−15390.0	−10130.0	−14060.0	
	−5821.0	−10574.0	−10561.0	−7563.0	−9211.0	
	−10070.0	−10363.0	−10570.0	−7563.0	−9211.0	
9	−3097.0	−11208.0	−11570.0	−8005.0	−10770.0	
	−4496.0	−8017.0	−7955.0	−5976.0	−7133.0	
	−7778.0	−7849.0	−7962.0	−5976.0	−7133.0	
10	−2449.0	−8760.0	−9012.0	−6484.0	−8496.0	
	−3579.0	−6289.0	−6214.0	−4841.0	−5684.0	
	−6200.0	−6152.0	−6217.0	−4841.0	−5684.0	
20	−551.0	−1877.0	−1903.0	−1621.0	−1873.0	
	−832.0	−1371.0	−1347.0	−1210.0	−1316.0	
	−1483.0	−1247.0	−1346.0	−1210.0	−1316.0	
40	−131.0	−434.0	−439.0	−405.0	−437.0	
	−201.0	−321.0	−317.0	−302.0	−316.0	
	−369.0	−318.0	−317.0	−302.0	−316.0	
50	−83.0	−275.0	−277.0	−259.0	−275.0	
	−128.0	−203.0	−201.0	−194.0	−200.0	
	−236.0	−201.0	−201.0	−194.0	−200.0	
100	−20.3	−66.8	−67.0	−64.8	−66.8	
	−31.6	−49.5	−49.2	−48.4	−49.2	
	−59.1	−49.2	−49.3	−48.4	−49.2	
150	−8.99	−29.43	−29.5	−28.8	−29.4	
	−14.0	−21.8	−21.7	−21.5	−21.8	
	−26.3	−21.8	−21.7	−21.5	−21.8	
200	−5.03	−16.47	−16.5	−16.2	−16.5	
	−7.85	−12.22	−12.2	−12.1	−12.2	
	−14.8	−12.20	−12.2	−12.1	−12.2	

[a] 10^{-5} eV.

Proceeding with our analysis of the convergence of the interaction series, we examine the data of Table VIII, which are tabulated as follows: For a given separation distance (column 1) the potentials obtained with the atomic multipole representation and arising from (a) monopoles only, (b) monopoles and dipoles, and (c) all terms up to, and including, quadrupoles are given in columns 2, 3, and 4, respectively. If, as more terms are included, there is no substantial difference between successive columns, it is assumed that the series is terminated, i.e., that convergence has been reached with the last term significantly contributing to the potential. The same procedure is applied for the case of columns 5 and 6 which contain, respectively, the potentials arising from (a) molecular dipoles and (b) molecular dipoles and quadrupoles. The difference in rapidity of convergence between the atomic and molecular representations can be studied by comparing the convergence of the potential values listed in corresponding columns and rows of the two representations. In each case, potential values were obtained with the previously described three types of calculations (Method I, II, and III) and are listed in successive rows as indicated in Table VIII. The molecular interaction data listed in Tables VIIa–c may be examined in a similar manner.

Our observations, then, are as follows: The convergence of the atomic multipole representation of the external potential is much more rapid than that of the molecular representation. In fact the former is very likely quadrupole convergent already at 3 Å and dipole convergent of 7 Å or even less. By contrast, the molecular representation approaches quadrupole convergence only at about 10 Å from the molecular boundary and dipole convergence at distances larger than 20 Å. The conclusions which may be drawn from the molecular interaction data essentially confirm the foregoing conclusions and even further accentuate the rapidity of the convergence of the atomic interaction series. Thus, for example, the dipole convergence of Method III of the pyridine interactions for 3 Å separation is apparent from the table. This same result shows clearly the effect of the charge definition, i.e., division of bicentric densities, on convergence. It appears that the equal division of densities (Method III) is of some advantage in achieving dipole convergence.

It should be noted that the monopole representation of the interaction energies fails at all ranges. This is clearly because the point charge accounts only for part of the molecular dipole vector. It is indeed interesting that this is the case also for the CNDO method, where the overlap densities are suppressed, and thus one would anticipate that an atomic point charge representation of the molecular charge distribution would be more successful. Carrying this point further, these results seem to emphasize the basic ambiguity in the interpretation of CNDO densities, which stems from the inherent contradiction in implying a Slater orbital basis in one respect and a nonlocalizable Löwdin orthogonalized basis in another. This contradiction is then brought up by our results, which clearly show that the moment contributions of the two-center overlap densities are necessary to achieve even relatively meaningful representation of potentials. These densities are neglected even in the CNDO method.

In summary, the results presented in this section have shown that the dipole approximation for short separation distances and for molecules of the size and complexity of pyridine is clearly inadequate and that the monopole approximation fails for all considered separation distances.

However, our results clearly show that the atomic multipole representations are the only correct ones at short separations where the Löwdin criterion of spherical disconnection of charges is violated for a molecular expansion as Pollak and Rein (1967) have already argued. The main new aspect which is borne out by the present analysis is that the first nonvanishing term (interactions of monopoles) does not dominate the series, but terms at least as high as quadrupoles have to be included in dealing with molecules at van der Waals separation distances.

V. Applications to Problems of Molecular Recognition in Biology

The theory of electronic structure and intermolecular interactions developed in this work is applied in this section to the central theme of molecular biology, which is the characterization of the nature of physical interactions involved in molecular recognition processes.

Broadly speaking, we can consider two fundamental types of recognition processes (Rein, 1971; Rein *et al.*, 1970b; Rendall *et al.*, 1971).

The first, which we can refer to as a simple template mechanism, involves direct physical interaction, for instance, between a molecule and part of a macromolecule. It has often been assumed that these interactions are to a major extent electrostatic in nature, with some additional contribution from dispersion, polarization, and overlap forces. A very good example of this type of interaction is hydrogen bonding as encountered in the case of the nucleic acid bases.

A second type of molecular recognition process known as steric template mechanism operates in a number of biological situations such as enzyme–substrate complexes, antigen–antibody interactions, or drug–receptor interactions. The requirements that have to be satisfied in the case of the steric template are more stringent than in the case of the electronic template mechanism, since the former requires a stereospecific environment of a cavity embedded in a macromolecule for trapping the relatively small substrate or ligand. However, the underlying physical forces are probably similar for the two types of mechanisms.

A. Hydrogen Bonding Between Complementary DNA Bases

The role of hydrogen bonding in the recognition between complementary nucleotide bases necessary for the stability of the helical structure as well as for replication and translation of the genetic information has long been recognized. From the early 1960s quantum chemists have displayed considerable interest in hydrogen bonding in nucleic acids. The problem has been approached in two basic ways: One way is to treat the interacting system as a single complex molecule by methods of molecular orbital theory (Rein and Harris, 1964a,b, 1965, 1966). The second approach, with which we are mainly concerned in this study, has been to use some approximate form of perturbation theory. DeVoe and Tinoco (1962) performed the first calculation of this type for the hydrogen bonding energies of the bases. They approximated the electrostatic interaction by interacting dipoles and treated the second-order energies by the London theory of dispersion forces. However, these calculations were criticized in subsequent studies on the ground that the adequacy of the dipole approximation is questionable for the short distances of separation involved. In the subsequent calculations by Pullman, Claverie, and Caillet (1966); Bradley, Lifson and Honig (1964); Pollak and Rein (1966); and Rein, Claverie, and Pollak (1968) the dipole approximation has been replaced successively with the atomic monopole method and in the case of the last group of investigations the molecular polarizability was replaced by bond polarizabilities. Pollak and Rein have also presented formal arguments to show that the expansions underlying the monopole method are valid even for cases where the expansion of the previous method is not valid. However, the monopole approximation was hinged on the *ad hoc* assumption that the monopole–monopole interactions dominate the atomic multipole interaction series.

Our justification for reopening this problem is twofold. First, it is due to the broad biological significance which those interactions typify. It is sufficient to say in this respect that a successful quantitative treatment of the complementary hydrogen bonding between nucleic acid bases opens up the whole realm of molecular recognition processes in biology for quantitative investigations. Second, the theoretical developments presented in the foregoing sections pointed to the necessity of extending the treatment to higher multipoles and provided as well a strong support for the adequacy of the available IEHT wave functions for this task.

We shall discuss here results of such studies performed by Stamatiadou, Swissler, Rabinowitz, and Rein (1972). The discussion of these results clearly follows the type of considerations previously presented.

The obtained data on electrostatic interactions between the DNA bases in the Watson–Crick hydrogen bonding configurations are listed in Tables VIIa and b, where the same tabulation procedure has been followed as in the previously described cases of intermolecular interactions. The following observations can be made: At hydrogen bonding distances (6.11 and 5.69 Å for the molecular mass centers of the A–T and G–C pairs, respectively) both the atomic monopole and the molecular dipole approximations yield inadequate descriptions of the interactions in all three methods and this is also true for all distances examined as the two molecules of each pair are drawn apart along the N_1—H ··· N_1 hydrogen bond direction. In the case of the G–C pair (Table VIIb), after inclusion in the atomic representation of terms as high as the quadrupole–quadrupole, the series shows a tendency to convergence, which is already obvious at a separation distance of 2–4 Å farther from the hydrogen-bonded position of the two bases. With regard to the three methods of calculation, only differences of rather minor significance are observed, i.e., the absolute magnitude of the atomic monopole–monopole term is always greatest in the case of Method III, reflecting a similar trend observed with the formal charges of the bases. Also, convergence between the molecular and the atomic representation is in some instances better in the case of the CNDO wave functions (Method I), but it should be remembered that this is a feature of the CNDO method resulting from the vanishing of higher atomic moments, as has already been pointed out in previous sections. It appears that the alternative divisions of bicentric densities (Methods II and III) are of no particular advantage in achieving convergence, thus corroborating the fact that these representations are equivalent and further showing that the final results of rigorous analysis are independent of the type of arbitrary (but consistent) assignment of formal charges.

That convergence is achieved with the inclusion of terms arising from quadrupole moments is important in itself. On the other hand, the contribution of these terms at the hydrogen bonding distance is comparatively small, as can be seen by comparing corresponding rows of columns 3 and 4 in Table VIIb. We thus have reason to be optimistic that even at the hydrogen bonding distance our results are close to convergence and that the inclusion of terms arising from the next higher moment, i.e., octopole, will be sufficient to assure complete convergence. Determination of octopole moments is currently in progress in our laboratory. In the case of the A–T pair the convergence with the IEHT wave functions is slower (it is achieved at a separation distance of about 10 Å farther from the hydrogen-bonded position of the two bases). As may be seen by a comparison among the rows of column 3, or of column 4, in Table VIIc which correspond to a given distance, the discrepancy in the asymptotic values obtained from the two different types of wave functions (CNDO and IEHT) while not very drastic, is still substantial. Thus, although the convergence values obtained from the CNDO wave functions cannot be considered as definitely representative, for the reasons previously elaborated upon, they nonetheless are likely to lie in the vicinity of the true values. There is little ground to doubt that the inclusion in the atomic representation of the interaction terms arising from octopole moments will yield convergence at shorter separation distances. It is important to remark that the observed differences in rapidity of convergence between the two cases examined here in no way impair the general validity of the treatment; they simply indicate that, depending on the case, terms arising from higher moments may have to be included.

B. Interaction of 3′-Cytidine Monophosphate with the Active Site of RNase

A typical example of the second type of molecular recognition process is offered by the enzyme–substrate interactions. A rigorous treatment of these interactions requires the acquisition of detailed information as to the three-dimensional architecture in which the active site of the enzyme is embedded, which is a difficult problem in itself. Recently obtained data from X-ray crystallography (Perutz, 1969), NMR spectroscopy (Roberts and Jardetsky, 1970), and several other physicochemical probes have helped elucidate the three-dimensional structures of several enzymes. However, the difficulties encountered in dealing with enzyme–substrate interactions are not confined to the enzyme structure problem only. Environmental, and most notably solvent, effects are likely to affect these interactions more severely than in the previously discussed case of the DNA base horizontal interactions. And precisely these effects complicate even further the problem of the conformation of the participating structures. It is important to realize that in considering a certain conformation for a participating structure there is no certainty as to the degrees of departure from the conformation actually encountered in the crystal form.

Despite, and at the same time because of, such shortcomings, investigations of the various energetic aspects of enzyme–substrate interactions can yield valuable insight as to the relative magnitude of the various factors contributing to the binding of the substrate to the active site. As an example of such studies we present here the salient features of results we obtained on the interaction of the active site of RNase (Kartha *et al.*, 1967; Wyckoff *et al.*, 1967) with the inhibitor 3′-CMP (Roberts and Jardetsky, 1970; Hammes, 1968). The case which we have treated here is the one known from chemical and kinetic evidence to be involved in the reaction of the enzyme with true substrate and is intended to be an approach to the geometry of substrate binding.

For the problem to become tractable, the following simplifying assumptions were made in our studies: (1) When the substrate is embedded in the active site domain, the positions of the active site residues are very strongly affected by their interaction with the substrate and therefore, as a first approximation, we ignore in our treatment the influence of neighboring or distant residues of the protein on these relative positions; (2) it is assumed that the interaction energies between active site and substrate are much stronger than the difference in the free energies of conformations of macromolecular structures (Gibson and Scheraga, 1967) and therefore they are likely to be overwhelming; (3) only the intrinsic intermolecular forces of the complex are considered, exclusive of the unknown contribution of environmental effects such as solvation, desolvation, etc.; and (4) since there are two histidine residues involved in the active site their interaction with 3′-CMP is treated pairwise.

We have evaluated the electrostatic and second-order interaction energies for the interaction of a system of imidazoles—comprising most of the active site of RNase—with cytidine 3′-phosphate. The numerical values of the interaction energies are given in Table IX and the geometric positions corresponding to the minimum energy values are shown in Fig. 1. We see that the geometric positions found in Fig. 1 for maximum interaction involve a direct approach of the imidazole 119 to the phosphate of 3′-CMP. The topography of the complex as deduced from our results is in good agreement with X-ray crystallography (Perutz, 1969), NMR spectroscopy (Roberts and Jardetsky, 1970), and other physicochemical studies.

Our study predicts a conformation change at the active site as a result of binding of the inhibitor, which is in good agreement with CD (Cathou *et al.*, 1965) and EPR (Smith, 1968) studies. The magnitude of the conformational change is shown in Table X. It is interesting to note that the predicted enlargement of the active site is consistent with the large entropy of binding (Hammes, 1964; Cathou and Hammes, 1965).

TABLE IX

INTERACTION ENERGIES (IN eV) FOR THE INTERACTION OF 3′-CMP WITH RNASE-ACTIVE SITE

System[a]	Electrostatic	Polarization[b]	Dispersion[b]	Total interaction energy (ΔH)
3′-CMP-imidazole 119	−0.7956 (−0.8761)$^+$	−0.1127	−0.0199	−0.9282 (−1.0087)[b]
3′-CMP-imidazole 12	(−0.2180)$^+$	−0.0750	−0.0590	(−0.3520)[b]
3′-CMP-lysine 41	(−0.8670 to −1.1704)$^+$	−0.0867 to −0.1300	Less than −0.0433	(−0.9970 to −1.3437)[b]

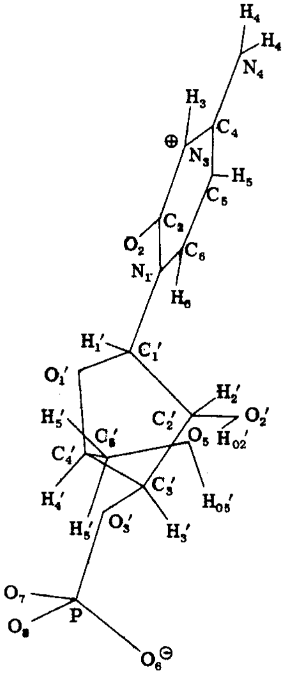
[a] Imidazole 119 is protonated; imidazole 12 is unprotonated; lysine 41 is protonated. 3′-CMP is the monoanion. Cytosine of 3′-CMP is protonated.

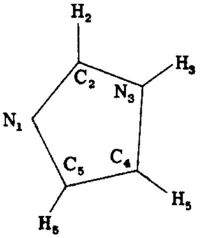
[b] Values obtained as in Rein *et al.* (1971).

It is noteworthy that the relative ordering of the energy values for the various geometries (Fig. 1) is the same as that which we obtained in previous studies (Rein, 1971) using the atomic monopole approximation (Table XI). Since we are dealing with interactions of molecules involving ionic forms (protonated imidazole) the contribution of the monopole–monopole term is considerable and hence, for obvious reasons, the earlier data obtained with the atomic monopole approximation are not drastically different from those obtained here with the inclusion of terms arising from higher moments in the interaction series.

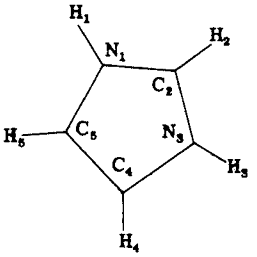
An interesting aspect of our results is that the substrate-active site pairwise electrostatic interactions are substantially larger than the calculated energies involved in going from one conformation to another (Pullman, 1971), which means that these electrostatic interactions are sufficient to account for a considerable resiliency in the backbone conformation, obviously required for the enzyme–inhibitor complex formation.

Having carried this analysis to this point we are now in the process of refining it by simultaneously considering the relative contribution of the two imidazole residues, as well as that of the participating lysine residue, to the total intrinsic electrostatic interactions of the complex and examining the energetics of the particular conformational changes induced by these interactions.





Imidazole II or 12



Imidazole I or 119

Fig. 1. Calculated model for the 3′-CMP–ribonuclease-active site complex. Projection on XY plane. Drawn to scale.

TABLE X

MAGNITUDE OF CONFORMATIONAL CHANGE

Bond	Distance in free RNase[a] (Å)	Distance in complex[b] (Å)
$C_2(12) \cdots C_2(119)$	6.13	13.88
$N_3(12) \cdots N_3(119)$	5.30	13.03
$N_1(12) \cdots N_1(119)$	5.68	14.94
$C_5(12) \cdots C_5(119)$	3.86	14.80
$C_4(12) \cdots C_4(119)$	4.08	13.60

[a] Observed [Wyckoff *et al.* (1970)].
[b] Calculated, this study.

TABLE XI

COMPARISON OF MOLECULAR INTERACTION ENERGIES (IN eV) OBTAINED BY THE MULTIPOLE APPROXIMATIONS FOR THE INTERACTION OF IMIDAZOLE I WITH 3′-CMP

Position of imidazole I	Multipole approximation
1[a]	−0.7434
2[b]	−0.7956
3[a]	−0.6424
4[a]	−0.6294

[a] Positions 1, 3, and 4 are in the vicinity of the minimum energy position of imidazole I.
[b] Corresponds to the minimum energy geometry of Table IX.

VI. Discussion and Summary

One of the objectives of this paper has been to evaluate the properties of semiempirical all-valence-electron molecular orbital theory for description of the charge distribution of polyatomic molecules. Our study has been concerned specifically with two of the more important of the available methods, i.e., the IEHT method as developed in our laboratory and the CNDO method developed by Pople and co-workers. The question to which we have particularly addressed ourselves was whether the description of the molecular charge distribution as obtained by these methods is sufficiently accurate and reliable to provide a quantitative description of the external molecular electric field and the related problem of electrostatic interactions between molecules. Our main criteria in investigating this problem were extensive comparisons between predicted and experimental values of molecular electrical moments and diamagnetic susceptibilities, quantities depending directly on the charge distribution, as well as comparisons of the molecular field as obtained from the two methods. Both types of wave functions which we have studied emerged rather successfully from this scrutiny, with the IEHT wave functions yielding better results in certain aspects. A significant difference detected from our studies was with respect to the molecular quadrupole tensor, which is treated much more reliably in the IEHT method than in the CNDO method. The reason for this appears to lie in the fact that the IEHT method provides a better description of the anisotropies in the charge distribution introduced by bonding, which anisotropies have an important contribution to the quadrupole moment but a lesser one to the rest of the quantities we have studied. It was interesting to find that in spite of these differences the atomic multipole representations of the potentials yield similar results for the two methods, i.e., the differences are of the order of 10–20% only.

However, this is not without exception. Thus, for example, in the case of the adenine–thymine pair, both the convergence is much slower and the discrepancy in the asymptotic values of the two methods, while not drastic, is still substantially larger than in the case of the guanine–cytosine pair. Which of the two somewhat opposing observations is the typical one and which is the exception is not possible to decide on the basis of current results. Thus it is safer to take the less optimal case as the more typical one. In this interpretation the atomic potential described by CNDO wave functions, in the domain of separations for which the quadrupole terms are important and for which the quadrupole moments as obtained from the CNDO wave functions are very different from those obtained from the calibrated IEHT values, may not be meaningful.

The conclusions of these studies we believe transcend, in a sense, the question of the two specific methods dealt with here. They reflect on the more general question of the adequacy of the limited basis set of Slater orbitals with the two-center densities included to describe in the context of judiciously parametrized semiempirical theory the gross features of the molecular charge distribution to the extent it is required for characterization of the external potential. Similar investigations with other all-valence-electron methods such as INDO (Pople *et al.*, 1967) and Arcana (Corrington and Cusachs, 1968, 1969; Corrington *et al.*, 1972) are in progress in our laboratory.

The second major topic we studied in this work was concerned with the question of convergence in the multipole description of potentials and molecular interactions. Our major findings are summarized as follows: The molecular dipole and even the quadrupole theory of these interactions is qualitatively incorrect when interacting molecules of the size we have studied are at nearly contact distances. For such molecules the separation distance must be at least 20 Å or greater for the molecular moment treatment up to quadrupole to yield relatively meaningful results. On the other hand, the atomic multipole decomposition of the interactions converges much more rapidly and thus a quadrupole treatment is likely to be convergent for short separation distances, at least for some of the cases. In those cases where convergence may be somewhat slower, inclusion of octopole moments, which we are currently in the process of calculating, is expected to be sufficient. The monopole approximation of these series is in most cases a poor one, although some of our data indicate that, for obvious reasons, the monopole treatment may be valid in the case where at least one of the interacting species is charged. The implications of these findings for the validity of a vast amount of past physicochemical considerations involving the dipole theory of interactions are indeed obvious. Rather than elaborating on this point we shall leave it to the reader to draw his own conclusions.

Finally, we wish to make some additional comments on the biological applications. Electrostatic interactions play a fundamental role in molecular recognition processes, as we have argued in earlier sections. The development of quantitative treatment for these interactions as described in this paper makes now possible an unambiguous evaluation of the degree to which these interactions participate in such fundamental biological events as hydrogen bonding formation and stability, and enzyme–substrate interactions.

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Quantum Theory of DNA
Summary of Results and Study Program

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I. Introduction

Deoxyribonucleic acid (DNA) plays a central role in molecular biology. As the carrier of genetic information DNA determines through messenger RNA the sequence of amino acids in proteins and with this their secondary and tertiary structure. Determining the enzymes and the structural proteins of the cell, in the last analysis the sequences of the nucleotide bases in the DNA molecules of a cell are responsible for the structure and function of the whole cell.

The chemical and stereo structure of DNA is fairly well known today; in other words, the positions of the atomic nuclei in this macromolecule have been determined. Thus, using the Born–Oppenheimer approximation, it was possible to start the quantum-mechanical calculation of the electronic structure of DNA.

The purpose of these calculations is to compute step by step always larger segments and more realistic models of DNA (see the next section), first of all to obtain approximate wave functions for different DNA constituents and DNA models. On the basis of these it was possible to perform approximate calculations for different physical and chemical properties of these systems. This also made possible interpretation of the UV absorption spectrum of DNA and has given deeper insight into the mechanism of charge transportation in this macromolecule. The knowledge of charge distribution in different DNA constituents had also helped in the understanding of their behavior in different chemical reactions.

The interpretation of the physical and chemical properties of more and more realistic models of DNA is not the last aim of its quantum-mechanical investigation. The investigation of the potential surfaces acting on the protons in the hydrogen bonds of the nucleotide base pairs has given a mechanism for point mutations (Löwdin, 1965). The results already obtained for the effect of electric field on the electronic structure of nucleotide bases and base pairs (see Section II.E.) make possible better understanding. of the mechanism of DNA duplication. All these first biologically significant conclusions obviously may help in the future to establish microphysical mechanisms for different important biological processes such as induced mutations, aging, and tumor development. Thus the final goal of the rather cumbersome calculations is to find correlations between the electronic structure of DNA and its biological functions.

II. Methods

A. The Strategy of the Investigations

Biologically active native DNA is a rather complicated macromolecule. Therefore it seems hopeless to perform a quantum-mechanical investigation which takes immediately into account in one step all its structural features (including its aperiodicity, impurities, lattice imperfections, surface effects, the effect of surrounding water, of ions, and of the protein chain). On the other hand, it is possible to investigate step by step its constituents and more and more realistic models of the real DNA molecule, respectively.

For all these investigations the Watson–Crick stereomodel (Watson and Crick, 1953; Crick and Watson, 1954) of the *in vivo* stable B form of DNA has been used. As a first step only the π-electrons of the single nucleotide bases have been investigated. If we restrict the investigation to the nucleotide bases of the DNA double helix (i.e., we neglect the sugar-phosphate chain and the surrounding medium and ions) we have two different kinds of interactions between the delocalized π-electron systems of the single nucleotide bases. There is on the one hand the interaction of the π-electrons of the two members of a base pair through the hydrogen bonds connecting them (A. Pullman and Pullman, 1959) and on the other hand the more important σ-type interaction of the π-orbitals of the stacked base pairs (Ladik, 1960).

First of all the question arises of how these interactions should be treated. The wave function of a composite system containing subsystems A and B with n_A and n_B electrons, respectively, can be written in a good approximation in the simple product form

$$\Psi = \Psi_A \Psi_B \tag{II.1}$$

if the overlap matrix formed from the overlap integrals between AO's belonging to the two different subsystems is negligible, $\mathbf{S}^{AB} \approx \mathbf{0}$. Here Ψ_A and Ψ_B are the Slater determinants of subsystems A and B, respectively. In this case the interactions between the subsystems are van der Waals type interactions. If we have a composite system consisting of many subsystems interacting by van der Waals forces, its excited states can be described with the aid of the localized (Frenkel) excitons.

On the other hand, if the overlap integrals $S_{\alpha,\beta}^{A,B} = \langle \chi_\alpha{}^A | \chi_\beta{}^B \rangle$ which form the matrix $\mathbf{S}^{A,B}$ are not negligible ($\chi_\alpha{}^D$ is the αth AO of subsystem D; D = A or B) and therefore $\mathbf{S}^{A,B} \neq \mathbf{0}$, the wave function of the composite system can be constructed only from MO's delocalized over both subsystems (intermolecular MO's),

$$\Psi = \mathscr{A}[\varphi_1(1)\alpha(1)\varphi_1(2)\beta(2) \cdots \varphi_{n/2}(n)\beta(n)], \qquad n = n_A + n_B, \tag{II.2}$$

where

$$\varphi_j = \sum_{r=1}^{m} C_{j,r}\chi_r, \qquad m = m_A + m_B. \tag{II.3}$$

Here $\mathscr{A}$ is the antisymmetrizer and finally m_A and m_B are the number of orbitals in subsystems A and B, respectively.

In the case of DNA the σ-type overlap integral between the π-orbitals of two carbon atoms belonging to two different bases is 0.03 (Ladik, 1960), if the distance between them is 3.36 Å (this is the distance between the planes of the stacked bases in DNA), while the values of the overlap integral between the π-orbitals of two carbon atoms in benzene (1.39 Å bond distance) is 0.26. Thus the former value is more than 10% of the latter.[1]

According to the Watson–Crick model the nucleotide bases are stacked

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[1] If we take into account the rotation of 36° of the stacked bases relative to each other in the plane perpendicular to the long axis of the DNA double helix, the value 0.03 decreases somewhat, but it remains also then for most of the overlaps about 10% of the value of 0.26.

on each other by planes. Therefore we have about 100 such nonnegligible overlaps between the AO's of two superimposed bases. So *a priori* (before performing the calculation) one can expect that the delocalized and not the van der Waals-type formalism is more correct to describe the interactions between the stacked bases.

The overlap integral values between the π-orbitals interacting through the hydrogen bonds of the base pairs are smaller than the previously mentioned values between the π-orbitals of the stacked bases. Yet, following the Pullmans' (A. Pullman and Pullman, 1959) original suggestion, we are of the opinion that also in this case the delocalized description is the more appropriate.[2] Combining the two different π-electron interactions in DNA and taking into account that there are usually 10^6–10^8 stacked base pairs in DNA with at least nonnegligible first-neighbor interactions, we can treat the electrons of the whole DNA double helix as a common delocalized π-electron system.

Native DNA is, of course, aperiodic (the sequence of the four nucleotide bases, A, T, G, and C, determines the genetic information carried by a particular DNA molecule). On the other hand, since the π-electron structure of an A–T base pair is not very different from that of a G–C base pair (their overall geometry is rather similar, and both have 24 π-electrons), we can consider DNA from the point of view of π-electrons as a quasiperiodic system. In this connection it should be mentioned that a previous investigation of this problem (Beleznay and Biczó, 1964) has shown that the band structure of a quasiperiodic DNA molecule (knowing its composition and its first-neighbors frequencies from experiment we can define in it an average elementary cell and also average interactions) is rather similar to the band structure of such a periodic DNA model[3] in which all the four different nucleotide bases are present in the elementary cell. (For further details see Section III.B.) Therefore we can expect that the investigation of the band structures of different periodic DNA models will also give valuable information about the π-electron structure of the real DNA macromolecule. On the other hand, from the point of view of σ-electrons A–T and G–C

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[2] It should be emphasized that for well-known quantum-mechanical reasons the delocalized description is also more exact in the $S^{A,B} \approx 0$ case. It is not worthwhile, however, to perform it in the case of weak interactions, because a van der Waals treatment can provide equally good results with less computational efforts.

[3] In a periodic DNA model a single nucleotide base, a base pair, two different stacked bases or base pairs, etc., form the elementary cell and this cell is repeated infinite times. For the stacked bases or base pairs the same relative positions have been taken as in the Watson–Crick stereostructure of real DNA. It should be mentioned that the simpler periodic DNA models have been synthesized in the laboratory.

differ more strongly. Therefore it seems probable that semiempirical all-valence-electron or *ab initio* band structure calculations for periodic DNA models will approximate less accurately the all-valence-electron or *ab initio* electronic structure of aperiodic DNA than the π-bands of periodic DNA models approximated its π-electron structure.

After all these remarks we can summarize the five basic approximations with which most of the until now executed DNA calculations have been performed: (1) Born–Oppenheimer approximation with nuclear positions given by Spencer (1959) and Langridge *et al.* (1960); (2) one-electron approximation (one single Slater determinant as many-electron wave function with two electrons on each level); (3) neglect of the sugar-phosphate backbone; (4) neglect of aperiodicity, impurities, and environmental effects; and (5) application of the π-electron approximation.

There are, however, some exceptions in which the calculations performed do not apply one or the other of the above-listed five approximations. Only for the single bases have different semiempirical all-valence electron calculations been performed, while *ab initio* calculations were done both for the single bases and for the G–C base pair (for details and references see Section III.A). The question of aperiodicity of DNA has been investigated in one early paper (see above), and model calculations on the effect of impurities are described in a few recent papers (see Section III.B). There exists also a DODS PPP crystal orbital (CO) calculation on polyC.

Applying all the five mentioned approximations, the calculations have taken into account step by step always larger segments of DNA. After the single nucleotide bases the pairs were treated as common delocalized π-systems. The next step was the investigation of two stacked bases as common systems (we have 16 such "dinucleotides") followed by the calculation of interacting base pairs (we have here 10 different cases).

To investigate the infinite DNA chain with the aid of solid-state physical methods (see the Section II.B) first a single base was taken as elementary cell (together with polyU we have five such homopolynucleotides). As the next step the poly(A–T) and poly(G–C) double helices were calculated. The most complicated calculated periodic DNA models for which calculations have been performed are

$$\mathrm{poly}\begin{pmatrix}\text{A—T}\\ \text{G—C}\end{pmatrix} = \begin{matrix}\text{A} & \text{G} & \text{A} & \text{G} & \text{A} & \text{G}\\ | & | & | & | & | & |\\ \text{T} & \text{C} & \text{T} & \text{C} & \text{T} & \text{C}\end{matrix}, \quad \mathrm{poly}\begin{pmatrix}\text{A—T}\\ \text{C—G}\end{pmatrix},$$

$$\mathrm{poly}\begin{pmatrix}\text{A—T}\\ \text{T—A}\end{pmatrix}, \quad \text{and} \quad \mathrm{poly}\begin{pmatrix}\text{G—C}\\ \text{C—G}\end{pmatrix}$$

systems. All these π-electron calculations have been done both in the Hückel and in the PPP MO and CO approximations, respectively, for all existing cases.

B. Band Structure Calculation Methods

If we should like to calculate the energy-band structure of an organic solid like a periodic DNA model, we are facing the problem that we have many atoms within the elementary cell and there are many interactions between the cells. As starting point for the treatment of such systems we can consider our solid as a giant molecule and we can write down its MO's delocalized over the whole solid in an LCAO form. We obtain in the standard way the

$$\mathbf{H}\mathbf{C}_j = \varepsilon_j \mathbf{S}\mathbf{C}_j \qquad \text{(II.4)}$$

matrix equation, where **H** and **S** are $n(2N+1) \times n(2N+1)$ matrices; n is the number of AO's within the elementary cell; and $2N+1$ is the number of cells (for the sake of simplicity we treat here only the one-dimensional problem; the derivation for the general three-dimensional case follows the same lines).

Taking into account the translational symmetry of our linear chain, we can recognize that **H** and **S** have the structure

$$\begin{pmatrix} \boxed{\mathbf{0}} & \boxed{\mathbf{1}} & \boxed{\mathbf{2}} & & \cdots & \boxed{\mathbf{2N}} \\ \boxed{\mathbf{-1}} & \boxed{\mathbf{0}} & \boxed{\mathbf{1}} & \boxed{\mathbf{2}} & & \boxed{\mathbf{2N-1}} \\ \vdots & & & & & \vdots \\ \boxed{\mathbf{-2N}} & & & & \boxed{\mathbf{-1}} & \boxed{\mathbf{0}} \end{pmatrix}, \qquad \text{(II.5)}$$

where the submatrix **0** denotes interactions within the elementary cell, the submatrices **1** and **−1** correspond to first neighbors, interactions and so on (all the submatrices have the dimension of n only). Introducing the Born–von Kármán periodic boundary condition, we obtain the relations $\boxed{\mathbf{2N}} = \boxed{\mathbf{-1}}$, $\boxed{\mathbf{2N-1}} = \boxed{\mathbf{-2}}$ and so on. Therefore the hypermatrices (II.5) will become cyclic hypermatrices. As is well known, for a cyclic matrix it is always possible to find a unitary transformation which diagonalizes it. In the same way there exists the unitary matrix **U** with the blocks $\mathbf{U}_{p,q}$ ($\mathbf{U}_{p,q}$ is the block of **U** belonging to the pth row of blocks and qth column of blocks)

$$\mathbf{U}_{p,q} = \frac{1}{(2N+1)^{1/2}} \exp\left(\frac{2\pi i p q}{2N+1}\right) \mathbf{1} \qquad \text{(II.6)}$$

(Del Re *et al.*, 1967), which block diagonalizes the cyclic hypermatrix. So we can write

$$\mathbf{H}' = \mathbf{U}^{+}\mathbf{H}\mathbf{U} = \begin{pmatrix} \square & & & & \\ & \square & & & \\ & & \square & & \\ & & & \ddots & \\ & & & & \square \end{pmatrix}, \qquad \mathbf{S}' = \mathbf{U}^{+}\mathbf{S}\mathbf{U}, \qquad \text{(II.7)}$$

where only the diagonal $n \times n$ blocks differ from zero. According to the detailed derivation (Del Re *et al.*, 1967), if $N \to \infty$ and therefore we can take

$$k = \frac{2\pi p}{a(2N+1)}, \qquad p = 0, 1, \ldots, 2N$$

as a continuous variable, we obtain for the different diagonal blocks $\mathbf{H}(k)$ and $\mathbf{S}(k)$, respectively of (II.7) (they are characterized by a given value of k) in the case of all neighbors' interactions the expressions:

$$\mathbf{H}(k) = \sum_{q=-\infty}^{+\infty} \exp(iqka)\mathbf{H}(q); \qquad \mathbf{S}(k) = \sum_{q=-\infty}^{+\infty} \exp(ikqa)\mathbf{S}(q). \qquad \text{(II.8)}$$

Here the matrices $\mathbf{H}(q)$ and $\mathbf{S}(q)$, respectively, are the submatrices of the original matrices (II.5) and a is the elementary translation.

Multiplying Eq. (II.4) from the left by $\mathbf{U}^{+}$ and inserting the unit matrix in the form of $\mathbf{U}\mathbf{U}^{+}$ we obtain $\mathbf{U}^{+}\mathbf{H}\mathbf{U}\mathbf{U}^{+}\mathbf{C}_j = \varepsilon_j \mathbf{U}^{+}\mathbf{S}\mathbf{U}\mathbf{U}^{+}\mathbf{C}_j$ or (introducing the notation $\mathbf{U}^{+}\mathbf{C}_j = \mathbf{D}_j$).

$$\mathbf{H}'\mathbf{D}_j = \varepsilon_j \mathbf{S}'\mathbf{D}_j. \qquad \text{(II.9)}$$

Since the matrices $\mathbf{H}'$ and $\mathbf{S}'$ are block diagonal, Eqs. (II.9) split to the matrix equations

$$\mathbf{H}(k)\mathbf{d}_j(k) = \varepsilon_j(k)\mathbf{S}(k)\mathbf{d}_j(k), \qquad \text{(II.10)}$$

in which all matrices have only the order of n.

Equation (II.10) can be used for the calculation of the band structure of any linear chain, or, using the more general formalism of the paper of Del Re *et al.* (1967), for a two- or three-dimensional solid both in *ab initio* and in different semiempirical forms. In the case of the *ab initio* SCF–LCAO crystal orbital (CO) method the elements of matrices $\mathbf{H}(q)$ [which define through (II.8) the matrix $\mathbf{H}(k)$] are given by the expression (Del Re *et al.*, 1967)

$$\begin{aligned}[\mathbf{H}(q)]_{u,v} = {} & \langle \chi_u{}^0(1) | \hat{H}^{\text{core}} | \chi_v{}^q(1) \rangle \\ & + \sum_{r,s=1}^{n} \sum_{q_1,q_2=-N}^{N} p_{r,s}(q_1 - q_2) \\ & \times [\langle \chi_u{}^0(1) \chi_r^{q_1}(2) | \chi_v{}^q(1) \chi_s^{q_2}(2) \rangle \\ & - \tfrac{1}{2} \langle \chi_u{}^0(1) \chi_r^{q_1}(2) | \chi_s^{q_2}(1) \chi_v{}^q(2) \rangle], \qquad \text{(II.11)}\end{aligned}$$

$$\hat{H}^{\text{core}} = -\tfrac{1}{2}\Delta - \sum_{q_1=-N}^{N} \sum_{\alpha=1}^{\tilde{n}} \frac{z_\alpha}{|\mathbf{r}_1 - \mathbf{R}_\alpha^{q_1}|}. \qquad \text{(II.12)}$$

Here, for instance, $\chi_v{}^q$ is the vth AO in the qth cell, n is the number of atomic nuclei in the cell, z_α is the charge of the αth nucleus, $\mathbf{r}_1$ is the position vector of the electron, and $\mathbf{R}_\alpha^{q_1}$ stands for the position vector of the αth nucleus in the cell characterized by q_1. Further the four-center integral

$$\langle \chi_u{}^0(1) \chi_r^{q_1}(2) | \chi_v{}^q(1) \chi_s^{q_2}(2) \rangle \equiv \int \chi_u{}^0(\mathbf{r}_1)^* \chi_r^{q_1}(\mathbf{r}_2)^* \frac{1}{r_{12}} \chi_v{}^q(\mathbf{r}_1) \chi_s^{q_2}(\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2$$

and the matrix elements of the generalized charge–bond order matrix are defined by

$$p_{r,s}(q_1 - q_2) = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} 2 \sum_{j=1}^{n_f} d_{j,r}(k)^* d_{j,s}(k) \exp[ik(q_1 - q_2)a]\, dk \qquad \text{(II.13)}$$

(for the proof, see Del Re *et al.*, 1967), where n denotes the number of filled bands.

To perform an *ab initio* CO calculation Löwdin's symmetric orthogonalization procedure (Löwdin, 1950) has to be used to eliminate the matrix $\mathbf{S}(k)$. It was shown (Del Re *et al.*, 1967) that this can be done in a straightforward way also for the Hermitian complex matrix $\mathbf{S}(k)$. Thus we are also left with the eigenvalue problem of the $n \times n$ Hermitian matrix

$$\tilde{\mathbf{H}}(k) = \mathbf{S}^{-1/2}(k)\mathbf{H}(k)\mathbf{S}^{-1/2}(k),$$

which can be solved either by rewriting it as the eigenvalue problem of a $2n$-dimensional real symmetric matrix, or by using complex arithmetic.

If there are n orbitals within the elementary cell, as is well known, the number of four-center integrals occurring in an *ab initio* calculation is $\sim n^4$. If we use only first neighbors' interations ($q = 0, +1, -1$) in a strict sense[4] (which is quite justified in the case of periodic DNA models)

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[4] That is, we neglect all multicenter integrals in which any two centers are not first neighbors.

it is easy to prove (see Ladik, 1971) that the number of *different* integrals occurring in the CO calculation will be only $\sim 4n^4$. Therefore if it is possible to perform an *ab initio* calculation on a molecule, the *ab initio* calculation of a linear chain constructed from the same molecules will require only ~ 6 times the computer time necessary for the investigation of the single molecule (if the approximation of first neighbors' interaction in a strict sense can be used).

The described *ab initio* SCF–LCAO–CO method (Del Re *et al.*, 1967) was programmed (POLYMOL) and applied for a chain of H_2 molecules recently by André (1969) in the IBM Research Laboratory (San José, California). Hopefully this program can also be used in the not too distant future for different periodic DNA models.

Taking for $\mathbf{S}(k) = \mathbf{1}$ and introducing the same approximations in the elements of $\mathbf{H}(k)$ as the PPP (Pariser and Parr, 1953; Pople, 1953) method and the CNDO method (Pople *et al.*, 1965; Pople and Segal, 1965), respectively, does in the case of molecules, we can obtain the PPP CO (Ladik, 1965) and CNDO CO (Ladik and Biczó, 1971b) schemes for crystals and polymers.

Writing down the elements of $\mathbf{H}(k)$ as is done in the case of the Hückel approximation for the molecules we obtain for the matrix elements $\mathbf{H}(k)_{r,s}$ in the simple LCAO CO method in the case of first neighbors' interactions

$$\mathbf{H}(k)_{r,s} = \beta_{r,s}(0) + \beta_{r,s}(1)e^{ika} + \beta_{r,s}(-1)e^{-ika}; \qquad [\beta_{r,s}(-1) = \beta_{s,r}(1)]. \tag{II.14}$$

Here the parameters $\beta_{r,s}(0)$, $\beta_{r,s}(1)$, and $\beta_{r,s}(-1)$ refer to the interaction between AO's r and s centered in the same cell, to the case where the AO r is centered in one cell and s in the right (1) or left (-1) neighborhood cell, respectively. We can further see from Eq. (II.14) that the matrix $\mathbf{H}(k)$ is Hermitian.

In the case of the PPP CO method we can derive for the matrix elements $\mathbf{H}(k)_{r,s}$ (Ladik, 1965; Ladik *et al.*, 1968a) the expressions

$$\begin{aligned}\mathbf{H}(k)_{r,r} = {} & -I_r + \tfrac{1}{2}(I_r - E_r)p_{r,r}(0) + \sum_{\substack{s=1\\ s\neq r}}^{n} [p_{s,s}(0) - z_s]\gamma_{r,s}(0) \\ & + \sum_{s=1}^{r} [p_{s,s}(0) - z_s][\gamma_{r,s}(1) + \gamma_{r,s}(-1)] + [\beta_{r,r}(1) - \tfrac{1}{2}p_{r,r}(1) \\ & \times \gamma_{r,r}(1)]e^{ika} + [\beta_{r,r}(-1) - \tfrac{1}{2}p_{r,r}(-1)\gamma_{r,r}(-1)]e^{-ika},\end{aligned} \tag{II.15a}$$

$$\begin{aligned}\mathbf{H}(k)_{r,s} = {} & \beta_{r,s}(0) - \tfrac{1}{2}p_{r,s}(0)\gamma_{r,s}(0) + [\beta_{r,s}(1) - \tfrac{1}{2}p_{r,s}(1)]\gamma_{r,s}(1)e^{ika} \\ & + [\beta_{r,s}(-1) - \tfrac{1}{2}p_{r,s}(-1)\gamma_{r,s}(-1)]e^{-ika},\end{aligned} \tag{II.15b}$$

where I_r and E_r are the ionization potential and electron affinity, respectively, of the rth atom in its appropriate valence state (their values were taken from Hinze and Jaffé, 1962) and z_r is the core charge of the rth atom. The quantities $\beta_{r,s}(0)$, $\beta_{r,s}(1)$, and $\beta_{r,s}(-1)$ are the core integrals (treated as parameters) between the atoms r and s in the same cell [in the case of application to periodic DNA models their values were taken from the previous PPP calculation of the single bases by Ladik and Appel (Ladik and Appel, 1966) and between atoms r and s belonging to neighboring cells [the parameters $\beta_{r,s}(1)$ and $\beta_{r,s}(-1) = \beta_{s,r}(1)$ have been taken proportional to the corresponding overlap integrals $S_{r,s}(1)$ and $S_{r,s}(-1)$, respectively]. The $\gamma_{r,s}(0)$, $\gamma_{r,s}(1)$, and $\gamma_{r,s}(-1) = \gamma_{s,r}(1)$ are Coulomb integrals between AO's r and s in the above-mentioned three cases. For them the

$$\gamma_{r,s}(q) = \frac{e^2}{a_{r,s} + R_{r,s}(q)}; \qquad \frac{e^2}{a_{r,s}} = \frac{1}{2}[I_r + I_s - E_r - E_s] \qquad q = 0, \pm 1 \tag{II.16}$$

Mataga–Nishimoto approximation (Mataga and Nishimoto, 1957) has been applied, where $R_{r,s}(q)$ is the distance between centers r and s in the cases $q = 0, \pm 1$. Finally, from the general expression (II.13) of the charge–bond order elements $p_{r,s}(q_1 - q_2)$ we obtain for $p_{r,s}(0)$ and $p_{r,s}(\pm 1)$, respectively,

$$\begin{aligned} p_{r,s}(0) &= \frac{a}{\pi} \int_{-\pi/a}^{\pi/a} \sum_{j=1}^{n_f} d_{r,j}(k)^* d_{s,j}(k)\, dk \\ &= \frac{2a}{\pi} \operatorname{Re}\left[\int_0^{\pi/a} \sum_{j=1}^{n_f} d_{r,j}(k)^* d_{s,j}(k)\, dk\right], \end{aligned} \tag{II.17a}$$

$$p_{r,s}(\pm 1) = \frac{2a}{\pi} \operatorname{Re}\left[\int_0^{\pi/a} \sum_{j=1}^{n_f} d_{r,j}(k)^* d_{s,j}(k) e^{\pm ika}\, dk\right], \quad p_{r,s}(-1) = p_{s,r}(1). \tag{II.17b}$$

Since the k dependence of the $d_{r,j}(k)$ eigenvector components is not known analytically, the (II.17a) and (II.17b) integrations have to be performed numerically in each iteration step. To be able to do this the eigenvalue problem of the Hermitian complex matrix $\mathbf{H}(k)$ has to be solved in each iteration step by different k values, which makes the calculations time consuming. The SCF criteria used in the calculations of periodic DNA models were

$$|p_{r,s}^{(n+1)}(0) - p_{r,s}^{(n)}(0)| \leqq 10^{-3}, \qquad |p_{r,s}^{(n+1)}(1) - p_{r,s}^{(n)}(1)| \leqq 10^{-3}, \qquad \text{(II.18)}$$

which had to be fulfilled simultaneously for all r and s.

In the case of the CNDO CO scheme we have in the first neighbors' interaction approximation

$$\mathbf{H}(k) = \mathbf{H}(0) + \mathbf{H}(1)e^{ika} + \mathbf{H}(-1)e^{-ika} \qquad \text{(II.19)}$$

with

$$\begin{aligned}\mathbf{H}(0)_{r,r} = {} & -I_r + [p_{\mathrm{A,A}}(0) - \tfrac{1}{2}p_{r,r}(0)]\gamma_{\mathrm{A,A}}(0) + \sum_{\substack{\mathrm{B} \\ \mathrm{B} \neq \mathrm{A}}} [p_{\mathrm{B,B}}(0)\gamma_{\mathrm{A,B}}(0) \\ & - V_{\mathrm{A,B}}(0)] + \sum_{\mathrm{B}} [p_{\mathrm{B,B}}(0)(\gamma_{\mathrm{A,B}}(1) + \gamma_{\mathrm{A,B}}(-1)) \\ & - V_{\mathrm{A,B}}(1) - V_{\mathrm{A,B}}(-1)], \qquad r \in A; \qquad \text{(II.20a)}\end{aligned}$$

$$\mathbf{H}_{r,s}(0) = -\tfrac{1}{2}p_{r,s}(0)\gamma_{\mathrm{A,A}}(0), \qquad r, s \in A, r \neq s; \qquad \text{(II.20b)}$$

$$\mathbf{H}_{r,s}(0) = \beta^0_{\mathrm{A,B}} S_{r,s}(0) - \tfrac{1}{2}p_{r,s}(0)\gamma_{\mathrm{A,B}}(0), \qquad r \in A, s \in B \qquad \text{(II.20c)}$$

$$\mathbf{H}_{r,s}(\pm 1) = \beta^0_{\mathrm{A,B}} S_{r,s}(\pm 1) - \tfrac{1}{2}p_{r,s}(\pm 1)\gamma_{\mathrm{A,B}}(\pm 1), \qquad \text{(II.20d)}$$

$$r \in A, s \in A, \text{ or } s \in B \neq A, \qquad r = s \text{ or } r \neq s.$$

Here

$$p_{\mathrm{A,A}}(0) = \sum_{r \in \mathrm{A}} p_{r,r}(0), \qquad \text{(II.21a)}$$

and with a generalization of the integral expressions occurring in the CNDO method

$$\gamma_{\mathrm{A,B}}(q) = \int |\chi_{\mathrm{A}}{}^0(1)|^2 \frac{1}{r_{12}} |\chi_{\mathrm{B}}{}^q(2)|^2 \, dV_1 \, dV_2, \qquad q = 0, \pm 1, \qquad \text{(II.21b)}$$

$$V_{\mathrm{A,B}}(q) = \int \chi_{\mathrm{A}}{}^0(1)^* \frac{z_{\mathrm{B}}}{|\mathbf{r}_1 - \mathbf{R}_{\mathrm{B}}{}^q|} \chi_{\mathrm{A}}{}^0(1) \, dV_1, \qquad q = 0, \pm 1, \qquad \text{(II.21c)}$$

where $\chi_{\mathrm{A}}{}^0$ is an appropriate valence s orbital centered on atom A in the cell 0 and $\mathbf{R}_{\mathrm{B}}{}^q$ is the position vector of atom B in the cell q.

This method has already been programmed and applied by several authors for different one-dimensional periodic systems, including polyglycine (see, for instance, Fujita and Imamura, 1970; Morokuma, 1971). Most recently the refined INDO and MINDO/2 versions of this crystal orbital method have been programmed and applied to polyacetylene, polyethylene, and polyglycine by Beveridge *et al.* (1972). It is very probable that in the near future the different forms of semiempirical all-valence electron crystal orbital methods will be applied also to periodic DNA models to calculate their σ- and π-bands together.

To take into account at least partially the electron correlation in polymers like periodic DNA models we can write down all the described methods (*ab initio*, PPP, CNDO CO) in different orbitals for different spins (DODS) form. Then we have instead of (II.10) the two matrix equations

$$\mathbf{H}^{\alpha}(k)\mathbf{d}_j^{\alpha}(k) = \varepsilon_j^{\alpha}(k)\mathbf{S}(k)\mathbf{d}_j^{\alpha}(k), \tag{II.22a}$$

$$\mathbf{H}^{\beta}(k)\mathbf{d}_j^{\beta}(k) = \varepsilon_j^{\beta}(k)\mathbf{S}(k)\mathbf{d}_j^{\beta}(k), \tag{II.22b}$$

for electrons with spin α and β, respectively, where in the case of the first neighbors' interaction approximation

$${}^{\eta}\mathbf{H}(k) = \mathbf{H}(0) + {}^{\eta}\mathbf{H}(1)e^{ika} + {}^{\eta}\mathbf{H}(-1)e^{-ika}, \qquad \eta = \alpha, \beta. \tag{II.23}$$

For the elements of the matrices $\mathbf{H}(q)(q = 0, \pm 1)$ in the *ab initio* case the following expressions can be derived (see Biczó *et al.*, 1972):

$$\begin{aligned}[{}^{\eta}\mathbf{H}(q)]_{u,v} = {} & \left\langle \chi_u^0 \left| -\tfrac{1}{2}\Delta - \sum_{q_1=0,\pm 1}{}' \sum_{\alpha=1}^{n} \frac{Z_{\alpha}}{|\mathbf{r}_1 - \mathbf{R}_{\alpha}^{q_1}|} \right| \chi_v^q \right\rangle \\ & + \sum_{r,s=1}^{n} \sum_{q_1,q_2=0,\ \pm 1}{}' \{[p_{r,s}^{\alpha\alpha}(q_1 - q_2) + p_{r,s}^{\beta\beta}(q_1 - q_2)]\langle \chi_u^0 \chi_r^{q_1} | \chi_v^q \chi_s^{q_2} \rangle \\ & - p_{r,s}^{\eta\eta}(q_1 - q_2)\langle \chi_u^0 \chi_r^{q_1} | \chi_s^{q_2} \chi_v^q \rangle\}, \qquad \eta = \alpha, \beta; \qquad q = 0, \pm 1,\end{aligned} \tag{II.24}$$

where now

$$p_{r,s}^{\eta\eta}(q_1 - q_2) = \frac{a}{\pi} \operatorname{Re}\left[\int_0^{\pi/a} \sum_{j=1}^{n_{\mathrm{f}}^{\eta}} {}^{\eta}d_{j,r}(k)^{*\,\eta}d_{j,s}(k)\exp^{[ik(q_1-q_2)a]}\,dk,\right. \qquad \eta = \alpha, \beta. \tag{II.25}$$

The primes after the summation signs according to q_1 and q_2, respectively, in (II.24) indicate that only such integrals are not neglected in the summation which do not contain any two centers which are not first neighbors and n_{f}^{η} stands for the number of filled bands of electrons with spin $\eta(\eta = \alpha, \beta)$.

A DODS many-electron wave function, as is well known, is not an eigenfunction of $\hat{S}^2$. Therefore to obtain a singlet ground state we have to apply on it the spin projection operator Θ_s. This of course would complicate a DODS band structure calculation to a great extent. It was possible to prove (Martino and Ladik, 1971), however, on the basis of a newly formulated extended Hartree–Fock scheme (DODS with spin projection before variation) in the one-λ approximation (Martino and Ladik, 1970; Ladik and Martino, 1970) that if the number of electrons goes to infinity the expectation value of any one- or two-electron operator and the one-electron functions are the same in the spin-projected and unprojected cases.[5] Therefore we can neglect spin projection in DODS band structure calculations.

Introducing again in the matrix elements (II.24) the neglections and the approximations of the PPP and CNDO methods, we can formulate the DODS PPP CO (Ladik and Biczó, 1971a) and DODS CNDO CO (Ladik and Biczó, 1971b) schemes. Since until now only the DODS PPP CO method has been applied, we give here only the elements ${}^{\eta}H(k)_{r,r}$ and ${}^{\eta}H(k)_{r,s}$ $(r \neq s)$ of the matrix (II.23) in this approximation:

$$\begin{aligned}{}^{\eta}H(k)_{r,r} = {} & -I_r + (I_r - E_r)p^{\bar{\eta}\bar{\eta}}_{r,r}(0) + \sum_{\substack{s=1\\ s\neq r}}^{n} [p^{\alpha\alpha}_{s,s}(0) + p^{\beta\beta}_{s,s}(0) - z_s]\gamma_{r,s}(0) \\ & + \sum_{s=1}^{n} [p^{\alpha\alpha}_{s,s}(0) + p^{\beta\beta}_{s,s}(0) - z_s][\gamma_{r,s}(1) + \gamma_{r,s}(-1)] \\ & + [\beta_{r,r}(1) - p^{\eta\eta}_{r,r}(1)\gamma_{r,r}(1)]e^{ika} \\ & + [\beta_{r,r}(-1) - p^{\eta\eta}_{r,s}(-1)\gamma_{r,r}(-1)]e^{-ika}, \qquad \text{(II.26a)}\end{aligned}$$

$$\begin{aligned}{}^{\eta}\mathbf{H}(k)_{r,s} = {} & \beta_{r,s}(0) - p^{\eta\eta}_{r,s}(0)\gamma_{r,s}(0) + [\beta_{r,s}(1) - p^{\eta\eta}_{r,s}(1)\gamma_{r,s}(1)]e^{ika} \\ & + [\beta_{r,s}(-1) - p^{\eta\eta}_{r,s}(-1)\gamma_{r,s}(-1)]e^{-ika}, \qquad \eta = \alpha, \beta, \end{aligned} \qquad \text{(II.26b)}$$

where $\bar{\eta} = \beta$ if $\eta = \alpha$ and $\bar{\eta} = \alpha$ if $\eta = \beta$, and all other quantities have been defined before.

Generalizing the expression

$$E_0 = \frac{1}{2}\left[\sum_{j=1}^{n_f^{\alpha}} (I_j^{\alpha} + \varepsilon_j^{\alpha}) + \sum_{j=1}^{n_f^{\beta}} (I_j^{\beta} + \varepsilon_j^{\beta})\right];$$

$$I_j^{\eta} = \langle \varphi_j^{\eta} | \hat{H}^{\text{core}} | \varphi_j^{\eta} \rangle, \qquad \eta = \alpha, \beta \qquad \text{(II.27)}$$

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[5] More precisely, this statement is true, if $\tilde{\eta} \to \infty$ and $\tilde{\eta} \gg s$, where $\tilde{\eta} = n(2N + 1)$ and s is the multiplicity. The proof for the general many $\lambda_l - s$ case is in progress.

of the total energy of a molecule in the DODS scheme (here I_j^η is the core integral calculated with the aid of the *molecular orbital* φ_j^η) to a linear chain in the first neighbors' iterations approximation and using the PPP method we obtain after a simple derivation for the total energy per elementary cell

$$\frac{E_0}{2N+1} = \frac{a}{4\pi}\int_{-\pi/a}^{\pi/a}\left[\sum_{j=1}^{n_f^\alpha}\varepsilon_j^\alpha(k) + \sum_{j=1}^{n_f^\beta}\varepsilon_j^\beta(k)\right]dk + \tfrac{1}{2}\,\mathrm{Tr}\{\boldsymbol{\beta}(0)[\mathbf{p}^{\alpha\alpha}(0) + \mathbf{p}^{\beta\beta}(0)] + \boldsymbol{\beta}(1)[\mathbf{p}^{\alpha\alpha}(1) + \mathbf{p}^{\beta\beta}(1)] + \boldsymbol{\beta}(-1)[\mathbf{p}^{\alpha\alpha}(-1) + \mathbf{p}^{\beta\beta}(-1)]\}. \tag{II.28}$$

Here the matrices $\boldsymbol{\beta}(\pm 1)$ have as elements the core integrals $\beta_{r,s}(\pm 1)$; the off-diagonal elements of $\boldsymbol{\beta}(0)$ are the $\beta_{r,s}(0)$ core integrals, while its diagonal elements are, according to the PPP CO scheme,

$$\beta_{r,r}(0) = -I_r - \sum_{s=1}^{n} z_s[\gamma_{r,s}(0) + \gamma_{r,s}(1) + \gamma_{r,s}(-1)] + z_r\gamma_{r,r}(0).$$

The matrices $\mathbf{p}^{\eta\eta}(q)$ ($q = 0, \pm 1$; $\eta = \alpha, \beta$) have the elements $p_{r,s}^{\eta\eta}(q)$ defined by (II.25).

In the closed-shell PPP CO case $\varepsilon_j^\alpha(k) = \varepsilon_j^\beta(k)$ and $\mathbf{p}^{\alpha\alpha}(q) = \mathbf{p}^{\beta\beta}(q) = \frac{1}{2}\mathbf{p}(q)$ ($q = 0, \pm 1$). Then (II.28) simplifies to

$$\frac{E_0}{2N+1} = \frac{a}{2\pi}\int_{-\pi/a}^{\pi/a}\sum_{j=1}^{n_f}\varepsilon_j(k)\,dk + \tfrac{1}{2}\mathrm{Tr}\{\boldsymbol{\beta}(0)\mathbf{p}(0) + \boldsymbol{\beta}(1)p(1) + \boldsymbol{\beta}(-1)\mathbf{p}(-1)\}. \tag{II.29}$$

Having performed both a closed-shell and a DODS PPP CO calculation for a linear polymer, one can calculate its total energy with the aid of the obtained SCF matrices $\mathbf{p}(q)$ and $\mathbf{p}^{\eta\eta}(q)$ ($q = 0, \pm 1$; $\eta = \alpha, \beta$) using expressions (II.29) and (II.28), respectively. In this way the improvement given by using the DODS scheme can be studied.

Finally, it should be mentioned that in the case of the DODS PPP CO calculation performed for polyC (Kertész *et al.*, 1972) 30 iteration steps were needed to reach self-consistency using *the not very severe* (II.18) SCF criteria, while in the closed-shell PPP CO case usually only five or six steps were needed. According to the detailed investigations, the number of necessary iteration steps depends strongly on the choice of the starting matrices $\mathbf{p}^{\eta\eta}(q)^{(0)}$ ($q = 0, \pm 1$).

III. Review of Results

A. Single Bases, Base Pairs, and Dinucleotides

The first calculation for the π-electron structure of the ground state of the single nucleotide bases has been performed by the Pullmans' (A. Pullman and B. Pullman, 1958; 1959) using the Hückel approximation. Among others, Hoffmann and Ladik (1964a) have executed the same calculation with the aid of somewhat different Hückel parameters. All these calculations have provided a rather realistic π-electron charge distribution of these compounds. On the basis of the molecular diagrams constructed with the aid of these charge distributions B. Pullman and A. Pullman (1963) were also able to interpret quite well the mechanisms of different chemical reactions of the bases. Their calculations have shown also that the purine bases A and G are better electron donors than the pyrimidine ones. On the other hand, A and C are better electron acceptors than G and T. These results are in good agreement with experiment.

Afterwards different authors have applied the PPP method to the ground state and excited states (in the latter case introducing CI) of the bases (Ladik, 1962; Veillard and Pullman, 1963; Nesbet, 1964; Ladik and Appel, 1966). For further references for calculations on the single bases in their normal and *in vivo* unusual tautomeric forms see the review paper of Pullman and Pullman in this series (A. Pullman and B. Pullman, 1968). PPP calculations have also been performed for the ground state of about 120 nucleotide base analogs (Ladik and Biczó, 1969, 1970). The ground-state PPP calculations have given charge distributions which agree quite well with each other and do not differ too much from the Hückel results of the Pullmans (A. Pullman and B. Pullman, 1958, 1959). The calculation of the singlet and triplet excited states together with the computation of the oscillator strength values of the different transitions has made possible quite good interpretation of the UV absorption spectra of the bases (for details and references see Section III.C).

As the next step semiempirical all-valence-electron calculations have been performed for the single bases. Jordan and Pullman (1968) performed an extended Hückel calculation (Hoffman, 1963, 1964) of the bases, while A. Pullman *et al.* (1968) and Rein *et al.* (1968b) have applied the iterative version (L. C. Cusachs and B. B. Cusachs, 1967) of this method. Further Giessner-Prettre and Pullman (1968) have used the CNDO/2 method (Pople *et al.* 1965; Pople and Segal, 1965, 1966) for the simultaneous study of the σ- and π-electrons of the bases. In a comparative study of the results of these calculations A. Pullman (1968) has concluded that the σ-electron distributions in all cases are rather similar to each other, including a refined version (Berthod and Pullman, 1965) of Del Re's method (Del Re, 1958), with the exception of the simple extended Hückel method which has provided exaggerated charge displacements. The same statement is nearly true for the π-electron distributions with the change that the results of the iterative extended Hückel method have also provided somewhat exaggerated charge displacements. Turning to the gross $(\sigma + \pi)$ charge densities, A. Pullman (1968) has shown that the extended Hückel method overemphasizes charge displacements, while the three other methods give rather similar charge distributions, the closest similarity being between the CNDO and PPP + Del Re (σ–π separation) charges. As usual, all the three mentioned all-valence-electron calculations resulted in a strong overlapping of the σ- and π-levels.

Finally it should be mentioned that recently Clementi *et al.* (1969) and Mely and Pullman (1969) have also performed an *ab initio* calculation of the single nucleotide bases using a rather small contracted Gaussian basis set. In both calculations they have obtained a strong intermingling between the σ- and π-levels. The second calculation (which was performed for A, T, and C only) usually gives somewhat larger charge displacements than the first one, phich is probably due to the application of a smaller basis set in the calculation of Mely and Pullman (1969). The orbital exponents and contraction coefficients applied in the two calculations are also rather different. Since these *ab initio* results are of rather preliminary nature, it does not seem worthwhile to compare the nonempirical and semiempirical all-valence-electron charge distributions in detail. We mention only that the signs of net charges usually agree and that the gross charge distribution obtained by the work using a somewhat larger basis set (Clementi *et al.*, 1969) on the one hand and the CNDO gross charge distribution of the bases on the other hand in most cases do not differ too much from each other. It should be further mentioned that A. Pullman *et al.* (1970) using their *ab initio* wave functions have also constructed probability density contour maps for A, T, and C. They have obtained the interesting result that their 0.01 probability curve taken in the plane of the bases coincides quite well with the van der Waals contour of these molecules constructed by drawing circles centered on each atom with the appropriate van der Waals radius (Pauling, 1945).

The first calculation of a nucleotide base pair treated as common delocalized π-systems was done again by the Pullmans (A. Pullman and B. Pullman, 1959) using the Hückel approximation. A similar calculation has been performed by Hoffmann and Ladik (1964a) using somewhat different parameter values. Both investigations have shown that the energy levels and ground-state charge distributions of the base pairs do not differ considerably from those of their constituent bases. On the other hand, some of the excited states are of the charge-transfer type, transporting nearly one elementary charge from one base to the other. In these cases the charge distribution of the excited base pairs are, of course, strongly changed as compared to the corresponding states of their constituents. Essentially the same conclusions have been reached in the PPP calculation of the ground state (Rein and Ladik, 1964) and of the excited states (Ladik and Appel, 1966) of the G–C base pair, showing that in its excited state 0.99*e* charge is transferred from G to C (for further details, see also Ladik, 1972).

In 1962 Löwdin raised the interesting idea that a tautomeric shift of the nucleotide bases which can lead, according to Watson and Crick (1953), to a point mutation, occurs through the rearrangement of the protons in the hydrogen bonds of the base pairs via tunneling. Since this theory was discussed in a series of papers of Löwdin (1963, 1964a,b, 1965, 1967) we do not enter into details here, but only give a very brief account of the calculations which were performed to work out Löwdin's theory.

To be able to find out the tunneling probability of the protons it was necessary to calculate the potential functions acting on them in the hydrogen bonds. (More precisely, if we consider the simultaneous motion of two protons we have to calculate a potential surface which is a function of the positions of both protons.) In the first calculation this author (Ladik, 1963) has used an electrostatic model for the middle N—H···N hydrogen bond of the G–C base pair. He has taken into account explicitly the four σ-electrons of the hydrogen bond, the whole π-electron system of G–C, and the eight σ-electrons of the other σ-bonds of the two nitrogen atoms at the two ends of the hydrogen bridge. The resulting potential function was highly asymmetric in the ground state and nearly completely symmetric in the first excited state of the π-electron system ($\Delta E = 2.7$ eV in the ground state and $\Delta E = 0.1$ eV in the first excited state, where ΔE is the energy difference between the two minima).

As next step Rein and Harris (1964, 1965a,b), taking into account the change with the different protonic positions of the distribution of the 24 π-electrons of G–C and that of the 4 σ-electrons of the hydrogen bonds have recalculated the potential function of the N—H···N hydrogen bond of G–C (Rein and Harris, 1964, 1965a) and the potential surface of both simultaneously moving protons of its N—H···N and O···H—N hydrogen bonds, respectively (Rein and Harris, 1965b). Applying the Born–Oppenheimer approximation they obtained the potential function or surface, respectively, calculating the total energy of the system using the PPP method for the π-electrons and the method of Wolfsberg and Helmholz (1952) for the σ-electrons for each protonic position separately. The calculations have been extended beyond the ground states to different excited and ionized states of the π-system of G–C. The potential surfaces of the two protons in the hydrogen bonds of A–T in its ground and different excited and ionized states have been calculated by Lunell and Sperber (1967). All these calculations have shown that though ΔE became less large ($\Delta E = 1.4$ eV) in the ground state of G–C (Rein and Harris, 1964), the potential functions or surfaces, respectively, remained asymmetric enough to make the normal tautomeric forms of the base pairs in their electronic or protonic ground state much more stable than the other tautomeric forms. These results seem to explain the experimentally well known stability of the genetic code. On the other hand, in some excited or ionized states the other positions of the protons became equally probable, or in a few cases more probable, than their normal positions. In this way we can get a possible interpretation of the well-known mutagenic effect of UV and ionizing radiation as it was suggested previously by this author (Ladik, 1964a), applying qualitative considerations to Löwdin's theory.

Using the simple method of Lippincott and Schroeder [1955, 1959; Schroeder and Lippincott (1957)], Biczó *et al.* (1966) have performed a model calculation for the potential functions of the N—H···N and O···N—H hydrogen bonds of G–C. This simple potential function had the advantage that it was quite easy to solve numerically with it the one-dimensional Schrödiger equation of the proton. Obtaining in this way the energy levels of the proton it was easy to calculate the tunnelling frequencies for the different levels and finally the probability of finding the proton in one well or the other. This calculation had the interesting result that due to the very small Boltzmann factors the probability is extremely small of getting the proton from its ground state to a tunneling level (the potential function obtained with the aid of the Lippincott–Schroeder method is valid only to the electronic ground state of the system). On the other hand, if the proton is already on a tunneling level, the probability is practically equal (0.521 versus 0.479) of finding it in one well or the other. Since the energy differences between the protonic ground states and the first tunneling levels fall in the infrared regions, one may expect that IR radiation could also have mutagenic effects. Of course, in considering such possibilities we have to investigate whether the lifetime of a protonic excited state is long enough to keep the proton on the tunneling level during the separation of the two constituents of a base pair.[6] Preliminary considerations (Hofacker, 1970), however, seem to indicate that this might not be the case.

Most recently Clementi *et al.* (1971) have performed an SCF LCAO MO *ab initio* calculation for the ground state of the G–C base pair, treating it as a common electron system with its 136 electrons. They have used seven s and three different p_x, p_y, and p_z per C, N, and O atoms and three s functions per H atom (7/3 set). They worked thus with 334 uncontracted Gaussians with fixed orbital exponents which they have contracted into 105 contracted Gaussian functions. They have performed the calculation for 7 positions of the proton in the O···H—N, for 8 positions of it in the N—H···N, and also for 8 positions of it in the N—H···N hydrogen bond of G–C, respectively. (In a series of calculations they have moved only one proton, the other two were kept in their experimental equilibrium positions. The positions of the heavy atoms were not changed either with the motion of the protons.) Altogether they had to compute 70×10^9 two-electron integrals over contracted Gaussians. To reach self-consistency in five figures of the LCAO coefficients they needed 10–15 iteration steps. For the whole calculation they used 8 × 24 hours on an IBM 360/195 computer.

According to their results there is a very strong overlapping of the σ- and π-levels. Comparing their energy levels of G–C with those of G and C (Clementi *et al*, 1969) it is apparent that the change of the original base levels in the base pair is much more pronounced than in previous semi-empirical π-electron calculations (Hoffmann and Ladik, 1964a; Rein and Ladik, 1964; Ladik and Appel, 1966).

The most striking result of this *ab initio* calculation of the G–C base pair is that Clementi and his co-workers have found only single-well

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[6] According to the detailed data (Biczó *et al.*, 1966) the tunneling frequency ν_T on the first tunneling levels is on the order of 10^6–10^7 sec^{-1}. Therefore the tautomeric rearrangement of a base pair via double proton tunneling, as Löwdin has pointed out (Löwdin, 1967), can lead to a remaining change of the tautomeric forms of the constituent bases, if all this happens in the unwinding zone of the DNA double helix. A further calculation of the G–C pair (Rai and Ladik, 1968) using the program of Rein and Harris (1964) has shown that the barrier between the two potential wells becomes considerably higher and broader when the distance between the end N atoms of the N–H···N hydrogen bonds is increased. Therefore the protons become localized with high probability in those wells where they were situated at the start of the breaking off of the base pair.

potentials for all the three hydrogen bonds, which seems to contradict to Löwdin's theory and the previous semiempirical calculations. In this connection it should be mentioned that in the case of a formic acid dimer, considering the simultaneous motion of both protons in the two hydrogen bonds of this system and using a larger 9/5 basis set, Clementi *et al.* (1971) report in the same paper the occurrence of a potential surface which has at certain intersections double wells. Therefore it seems rather probable that by considering the motion of both protons simultaneously and by using a larger basis set also in the G–C a double-well potential would occur. (The performation of such a calculation is at the moment for technical reasons not possible, but in a few years very probably it will be feasible.)

In connection with this *ab initio* calculation of such a large system as the G–C base pair a few further comments should be added. First of all, as is well known, Gaussian functions reproduce poorly the behavior of Slater functions at larger distances. Therefore the application of orbital exponents, contraction coefficients, and number of basis functions per atom, found satisfactory for smaller molecules, becomes questionable for big molecules. (Rather probably to obtain the same level of accuracy a larger number of Gaussians per atom is needed by a big molecule than by a smaller one.) For this reason for such large molecules the application of Slater basis seems to be more promising. Hopefully the advancement of integration techniques with Slater functions will make it possible to perform such calculations in the near future. Further, to obtain realistic *ab initio* results for the potential functions of the hydrogen bonds in G–C it is necessary to take into account the change of the geometry with the motion of the protons, at least of those atoms which are first neighbors of the end atoms of the hydrogen bonds (for instance, the C═O bond of guanine changes continuously to C—O—H as the proton of the O···N—H hydrogen bond moves from the nitrogen atom towards the oxygen; the increase of the C—O bond length is larger than 0.1 Å during this process).

As the next step of the systematic investigation of DNA the π-electrons of the dinucleotides and of two stacked base pairs were treated as common delocalized systems in the Hückel approximation (Hoffman and Ladik, 1964a; Ladik, 1964b). According to the detailed results the charge distributions in the ground state were rather similar to those of the constituent bases, while some excited states have shown again charge-transfer state properties. It was an interesting result that while the individual one-electron levels were much perturbed as compared to those of the single bases, the total energies of the composite systems (E_{AB}) were in all investigated cases exactly equal to the sums of the total energies of their constituents ($E_A + E_B$),

$$E_{AB} = E_A + E_B. \tag{III.1}$$

At the same time this phenomenon has not occurred for the previous Hückel approximation of the base pairs. Taking into account that in the Hückel approximation of the stacked systems no diagonal elements of the Hückel matrices were changed as compared to those of the Hückel matrices of the constituent systems, while in the case of the base pairs also diagonal Hückel matrix elements had to be changed to describe the delocalization of the π-electrons through the hydrogen bond, Biczó (1969) has given a general proof for Eq. (III.1).

The PPP investigation of the dinucleotides (Ladik and Sundaram, 1969) has given qualitatively the same results as the previous Hückel calculation with the exception that Eq. (III.1) no longer holds. The reason for this is that in the PPP method also the diagonal elements of the Fock matrix have to be changed as a consequence of the interaction of the stacked bases.

Finally it should be mentioned that different authors (see, for instance, De Voe and Tinoco, 1962; B. Pullman *et al.* 1966; Pollak and Rein, 1967; Rein *et al.*, 1968a, 1969) have treated the interaction between the constituent bases of the base pairs and between the stacked bases and base pairs, respectively, on the basis of different forms of the theory of van der Waals' forces. In this way they have tried to draw conclusions also about the conformation of these composite DNA constituents and about the interaction energies involved. Since this kind of treatment of the interbase interactions is in contradiction with our basic assumption about electron delocalization in DNA (see Section II.A), we do not discuss here these works, but refer to the paper of A. Pullman and B. Pullman in this series (1968), who review most of these calculations.

B. Periodic DNA Models

The band structures of the periodic DNA models obtained either with the aid of the simple tight-binding method or with the aid of the PPP CO method can be divided into two groups. The five homopolynucleotides (including also polyU) (Ladik and Appel, 1964; Ladik, *et al.* 1968a) and the poly(A–T) and poly(G–C) systems (Ladik and Biczó, 1965; Avery *et al.*, 1969) have rather broad bands in both approximations (the widths of the valence bands are 0.2–0.3 eV, those of the conduction bands ~0.1 eV, and the widths of the lowest filled bands are in all cases ~1 eV). On the other hand, we have obtained for the single-stranded heteropolynucleotides [for instance, poly(TC)] in the tight-binding approximation (Ladik and Biczó, 1965) and for the double-stranded $\mathrm{poly}\begin{pmatrix}\text{A–T}\\ \text{G–C}\end{pmatrix}$, etc., systems in both approximations (Ladik and Biczó, 1965, 1968; Rozsnyai *et al.*, 1970) very narrow bands (the widths of the valence bands are 0.01–0.03 eV, those of the conduction bands are usually ~0.01 eV and the widths of the lowest filled bands are ~0.1 eV). (For further details of the band structures of the different periodic DNA models we refer to the above-cited original papers.)

On the basis of perturbation theory it is easy to understand that if the same bases or base pairs are repeated [homopolynucleotides or the poly-(A–T), poly(G–C) systems] the splitting of the levels of the constituent single systems is much larger in the polymer than if different subsystems are alternating in it (as is the case in all periodic DNA models for which narrow bands have been obtained).

We can conclude on the basis of the obtained band structures that a delocalized, Bloch-type description is not very correct for the narrow-band periodic DNA models, and therefore the application of the hopping model seems to be more realistic. On the other hand, the Bloch picture is justified in the cases of periodic DNA models with broad bands.

In the case of the $\mathrm{poly}\begin{pmatrix}\text{A–T}\\ \text{G–C}\end{pmatrix}$ system the value of ~3.7 eV has been obtained for the width of the forbidden band between the valence and conduction bands in the simple LCAO CO (tight-binding) approximation (Ladik and Biczó, 1968). On the other hand, the PPP CO approximation resulted in a value of ~6.1 eV for the same system (Rozsnyai *et al.*, 1970)]. The value of ~3.7 eV seems to be realistic, because it was calculated on the basis of a band structure computed with the aid of parameter values which were fitted to reproduce the experimental ultraviolet absorption spectra of the single bases. Therefore, the PPP CO method has given a gap which seems to be high by ~2.4 eV. The reason for this difficulty is (for a detailed discussion, see Avery *et al.*, 1969) that in any closed-shell Hartree–Fock scheme (and thus also in the PPP scheme) the excitation energy is not just the difference of the corresponding one-electron energies (as it is in the Hückel case), but

$${}^{1}\Delta E_{i\to j} = \varepsilon_j(k) - \varepsilon_i(k) - J_{i,j}(k) + 2K_{i,j}(k). \qquad \text{(III.2)}$$

Here the $J_{i,j}(k)$ Coulomb and $K_{i,j}(k)$ exchange integrals disappear, if $N \to \infty$ (Avery *et al.*, 1969). [If we take into account all neighbors' interactions they disappear as ln N/N (Bierman and Ladik, 1969).] Therefore Eqs. (III.2) reduces to the difference of one-electron energies, giving too high results. The physical explanation of the problem is that using Eq. (III.2) we treat the motion of the promoted electron and the remaining hole as completely uncorrelated, which is not correct. To overcome this difficulty we have to take into account the correlation between them. The best way to do this is perhaps to take into account that an excitation also occurs primarily locally in a solid and so an appropriate form of the intermediate exciton theory could be used. Investigations along these lines are in progress.

As the first step in investigating the effect of impurities on the electron structure of DNA the band structure of poly(G–C) has been calculated in the simple tight-binding (Sklenar *et al.*, 1967) and in the PPP CO approximations (Rozsnyai and Ladik, 1970a), assuming that one or two water molecules are bound by hydrogen bonds to the NH_2 group of each cytosine molecule or/and to the C=O group of each guanine molecule. This means that it was assumed the H_2O molecules lie in the plane of the G–C base pair and thus each water molecule contributed an additional π-orbital (the π-orbital of oxygen) with two electrons to the delocalized π-system. According to the results obtained in both approximations (Sklenar *et al.*, 1967; Rozsnyai and Ladik, 1970a) the water molecules produced an extra π-band between the lowest filled bands, while the other bands (their position, widths, and therefore the gaps between them) remained practically unchanged.

As a further step in the investigation of the effect of impurities the band structures of poly(G–C) and of poly(A–T) were recalculated in the presence of Mg^{2+} ions using the PPP CO method (Rozsnyai and Ladik, 1970a,b). The ability of divalent metal ions to react with a variety of electron-donor sites of polynucleotide chains is well known from experiments and received considerable attention recently (see, for instance, Eichhorn and Shin, 1968; Cheng *et al.*, 1969, and references cited therein). For this model calculation the Mg^{2+} ion was chosen, because its effect on the different properties of DNA has been demonstrated and it is comparatively easy to handle it. The calculations have been performed for the poly(G–C) and poly(A–T) systems, with all possible types of Mg^{2+} attachments to the heterocyclic bases. We must distinguish here between two general cases, namely, when the ion is in and when it is out of the plane of the base pair. In the former case the Mg^{2+} ion contributes one additional π-orbital with two extra π-electrons to the system. This is the case when the attachment is to the electronegative N-7, N-3, O-11, and O-18 atoms of the G–C pair and to the N–7, O–17, and O–18 atoms of the A–T pair [for the numbering of the atoms in the base pairs, see Rozsnyai and Ladik (1970b)]. In all cases a distance of 2 Å has been assumed between the ion and the corresponding atom.

In the second case, when the Mg^{2+} is attached to an amino nitrogen, the ion is out of the plane of the base pair. In this case it has been assumed that the ion forms a covalent bond with two π-electrons of the amino group; consequently there is a tendency towards a tetrahedral structure corresponding to the (sp^3) hybridization, thereby partially destroying the planar structure of the amino group. This has the effect of removing the π-orbital of the amino group together with its two electrons from the rest of the systems. In this case again 2 Å was assumed for the N—Mg^{2+} distances, which means that the ion is located by 1.89 Å above the plane of the base pairs. Actually, in the course of the calculations it was assumed that the net positive charge is evenly distributed between the two atoms, using for the position of the point charge the half-distance between Mg^{2+} and N–19. This type of model has been used for the Mg^{2+} attachments to the amino nitrogens N–19 and N–10 of G–C and to the N–10 atom of A–T. In connection with these model calculations it should be mentioned that the atoms O–11 and N–19 in G–C and the atoms N–10 and O–18 in A–T are from obvious stereochemical reasons the most probable sites of ion attachments.

To take into account the effect of the charged ions on the π-electron systems of the base pairs the $\beta_{r,s}(0)$ and $\beta_{r,s}(\pm 1)$ core integrals of the PPP CO method have been modified as

$$\beta'_{r,s}(0) = \beta_{r,s}(0) - \tfrac{1}{2}z_I[\gamma_{r,N}(0) + \gamma_{s,N}(0) + \gamma_{r,N}(1) + \gamma_{sN}(1) + \gamma_{r,N}(-1) + \gamma_{s,N}(-1)]S_{r,s}(0), \quad \text{(III.3a)}$$

$$\beta'_{r,s}(\pm 1) = \beta_{r,s}(\pm 1) - \tfrac{1}{2}z_I[\gamma_{r,N}(0) + \gamma_{s,N}(0) + \gamma_{r,N}(1) + \gamma_{s,N}(1) + \gamma_{r,N}(-1) + \gamma_{s,N}(-1)]S_{r,s}(\pm 1). \quad \text{(III.3b)}$$

Here z_I is the net charge of the ion, the γ Coulomb integrals have been taken between the sites r or s, and the position N of the net charge and the $S_{r,s}(0)$ and $S_{r,s}(\pm 1)$ overlap integrals have been calculated using Slater orbitals (for further details, see Rozsnyai and Ladik, 1970a). It should be pointed out that the expressions (III.3a) and (III.3b) are consistent with the PPP method, if we apply for the occurring three-center integrals the Mulliken approximation.

The results obtained for poly(G–C) and poly(A–T) with a Mg^{2+} ion attachment to a given atom in each elementary cell indicate generally drastic changes of the band structures as compared to those of the unperturbed poly(G–C) and poly(A–T) systems, respectively. In the case of the Mg^{2+} "in the plane" models a very narrow practically completely localized extra Mg^{2+} band occurs at ~ -90 eV, which, of course, does not happen in the case of the "out of plane" models. Much more important is, however, that in all investigated cases the widths of the other π-bands are generally considerably larger than in the unperturbed systems (Rozsnyai and Ladik (1970a,b). For instance, in the case of poly($G–C–N_{19}\cdots Mg^{2+}$) the width of the valence band increases to $\sim$0.6 eV, that of the conduction band to $\sim$0.5 eV, and the lowest filled band is $\sim$2.0 eV broad.

The picture is not so simple in the case of the physically significant gap between the valence and conduction bands. In most of the investigated cases the Mg^{2+} attachment increases the gap, but not always. As we can see from Table I, the gap decreases very strongly to $\sim$2.0 eV if the Mg^{2+} ion is attached to N–19 of G–C and rather considerably if it is bound to the O–18 atom of A–T. At the same time we should not forget that both mentioned attachment sites are among the most probable ones. If we take into account that the PPP CO method gives for excitation energies values

TABLE I

ENERGY GAP BETWEEN THE HIGHEST FILLED AND LOWEST UNFILLED BANDS OF POLY(G–C) AND POLY(A–T) WITH Mg^{2+} AT THE MOST PROBABLE POSITIONS[a]

	E(eV)
Mg^{2+} at N-19 above the G–C plane[b]	1.996
Mg^{2+} at O–11[c]	8.654
Unperturbed poly(G–C)[d]	5.985
Mg^{2+} at N–10 above the A–T plane[e]	8.633
Mg^{2+} at O-18[f]	3.967
Unperturbed poly(A–T)[d]	6.473

[a] Rozsnyai and Ladik, 1970a, and b.

[b] The amino nitrogen of cytosine.

[c] The oxygen in the C=O group of guanine.

[d] Taken from Avery *et al.* (1969).

[e] The amino nitrogen of adenine.

[f] That oxygen of thymine which forms a hydrogen bond with the amino nitrogen of adenine.

too high by 2.0–2.5 eV (see above), we can conclude that this value may be very low or zero in the poly(G–C–$N_{19}\cdots Mg^{2+}$) system.

Concluding the discussion of this section, it seems rather probable that the band structure of real aperiodic DNA lies nearer to the narrow-band case than to the case of broad-band periodic models. On the other hand, from experimentally found nearest-neighbor frequencies of the nucleotide bases in DNA (Josse *et al.*, 1961) there is an indication of a preference to have the same base repeated. This fact together with the above-described band-broadening effect of charged impurities will increase at least in some segments of the macromolecule the delocalization of the π-electrons. For the description of the behavior of the electrons in the other parts of the DNA molecule the hopping model seems to be more correct.

C. Spectrum of DNA

To interpret the UV absorption spectra of the simple nucleotide bases several authors have performed PPP calculations for their singlet excited states. In their first calculation Ladik and Appel (1966) have performed only a very slight variation of the $\beta_{r,s}$ integrals and have taken into account only four singlet excited configurations in the CI performed for the excited states. In this way they have obtained in most cases an agreement within 0.5 eV between the first two calculated intensive transitions and the experimental absorption maxima available at the time of the preparation of the mentioned paper (DeVoe and Tinoco, 1962; Láng and Ladik, 1964). In the cases of uracil and thymine, however, the discrepancy was around 0.5 eV and 1 eV, respectively. Reexamining these theoretical results on the basis of the meanwhile published experimental findings of Clark and Tinoco (1965), which were obtained by the aid of more-refined methods, and those of the vapor-phase measurements of Clark *et al.* (1965), it has turned out that the discrepancy is also only 0.5 eV in the case of uracil; for the other nucleotide bases it is only 0.2–0.3 eV.

Afterwards Berthod *et al.* (1966) have carefully fitted the $\beta_{r,s}$ parameters of the PPP method to the ionization potentials, dipole moment, and singlet transition energies of some simpler reference compounds (pyridine, pyrimidine, pyrrole, aniline, formamide, etc.). Applying the $\beta_{r,s}$ values obtained in this way to the nucleotide bases and performing a CI calculation including all their singly excited π-electronic singlet excited configurations (Berthod *et al.*, 1967) they have obtained an agreement within 0.2 eV between theory and experiment for the first two transitions. It should be mentioned that in a later calculation Packer *et al.* (1969) without fitting the $\beta_{r,s}$ parameters to simpler compounds, but including the same amount of CI as Berthod *et al.* (1967) have obtained the same degree of agreement.

For the excitation energy of the first triplet state of the nucleotide bases, Kuprievich (1967) and A. Pullman (1967) have performed the first calculations using the PPP method with CI, including all singly excited triplet configurations. Kuprievich (1967) has also applied Roothaan's open-shell procedure (Roothaan, 1960) in its PPP form. More recently Packer *et al.* (1969) have performed the same calculations with the two mentioned methods and also with the aid of a UHF (DODS) PPP scheme (Dewar, 1963) annihilating the quintet component of the wave function.

Unfortunately there is only rather scarce experimental information about the triplet excitation energies of the nucleotide bases. Cohen and Goodman (1965) have given on the basis of their precise measurements the value of 3.05 eV for the first triplet excitation energy of adenine. This agrees quite well with the result of 3.0 eV of A. Pullman (1967) with PPP CI and with the results of Packer *et al.* (1969) obtained with the aid of the annihilated UHF and Roothaan's open-shell procedure (2.96 and 2.88 eV, respectively). All the theoretical calculations have also reproduced well the order of increasing triplet excitation energy $U < \mathrm{C} < \mathrm{G} < \mathrm{A}$ found by the experiments on energy transfer in dinucleotides (Hélène *et al.*, 1965). To close our brief discussion on the spectra of the single nucleotide bases [for numerical results and more detailed discussion, see the review paper of A. Pullman and Pullman (1968) and the paper of Packer *et al.*, (1969)], it seems that with the aid of the simple PPP method it is possible to describe fairly well the singlet and triplet excitations of these rather complicated heterocyclic molecules. The reasons why such a crude method, which was established to describe first of all the spectra of aromatic hydrocarbons, works so well also in these cases, is for the present author not clear.

The UV absorption spectrum of the whole DNA molecule has two main characteristic features: (1) The first intensive absorption maximum of the whole macromolecule is in the same region as those of the single bases and the whole extinction curve in this region has a close resemblance to the curve which we would obtain by superimposing the extinction curves of the single bases in a 1 : 1 : 1 : 1 ratio. (2) The oscillator strength value belonging to the absorption curve of the whole macromolecule is abut 40% smaller than that of the curve obtained by the mentioned superposition of the extinction curves of the single bases (hypochromicity) (see, for instance, Beaven *et al.*, 1955).

The interpretation of the first phenomenon seems to be quite easy.

The investigation of the base pairs and dinucleotides as common delocalized π-electron systems (Ladik and Appel, 1966; Ladik and Sundaram, 1969) has shown that besides excitations which correspond to excitations within the constituent bases ("intrabase excitations") there also occur charge-transfer type "interbase excitations." The calculation of the oscillator strength values of the latter excitations has proved, however, that they have intensities of two orders of magnitudes smaller than the "intrabase" excitations. Therefore these additional excitations, which do not occur in the spectra of the single bases, are so weak that the absorption bands corresponding to them are completely covered by the much more intense bands of the intraband excitations and therefore they could not be detected by the methods used for the investigation of the UV absorption spectrum of the whole DNA macromolecule.

To interpret the hypochromicity of DNA several authors have performed calculations on infinite DNA chains on the basis of the localized (Frenkel) exciton model (see, for instance, Tinoco, 1960, 1961; Rhodes 1961; DeVoe and Tinoco, 1962; Bradley *et al.*, 1963). All these calculations, which did not assume π-electron delocalization along the polynucleotide chains, have given reasonably good explanation for the experimentally known facts. As the first step of the interpretation of the hypochromicity of DNA on the basis of the delocalized description of the π-electrons of this macromolecule, Ladik and Sundaram (1969) have calculated the oscillator strength (f) values of different singlet transitions of the dinucleotides, treating them as common delocalized electron systems and introducing a limited CI. Subtracting in given spectral regions from the sum of the f values of the dinucleotides the sums of the f values of the constituent bases in the same region, we can define the hypochromicity as

$$\frac{\sum_i^{(R)} f_i^{\text{dinucl}} - \sum_i^{(R)} \left(f_i^{\text{base 1}} + f_i^{\text{base 2}}\right)}{\sum_i^{(R)} \left(f_i^{\text{base 1}} + f_i^{\text{base 2}}\right)} \times 100, \qquad \text{(III.4)}$$

where f_i^{dinucl} refers to the oscillator strength value of the ith transition of the dinucleotide in its spectral region R, while $f_i^{\text{base 1}}$ and $f_i^{\text{base 2}}$ are the same quantities for its constituent bases. According to the detailed results (Ladik and Sundaram, 1969) a hypochromicity (values between 21% and 3%) was found for the first intensive transition of the dinucleotides and in most cases they have found a hypochromicity also for the second intensive transition.

Finally, the problem of collective excited electronic states in DNA should be mentioned here. Energy loss experiments performed with electron beams on different organic solids have shown a very broad intense peak around 25 eV and a less intense one around 6 eV (see, for instance, Swansson and Powell, 1963). They were interpreted as collective excitations of all-valence electrons and that of the π-electrons alone, respectively. Therefore we can expect that collective excitations of biological macromolecules like DNA in these regions may play an important role in the primary effect of ionizing radiations on biomolecules. Using the π-electron band structures of different periodic DNA models obtained in the simple LCAO CO scheme (Ladik and Appel, 1964; Ladik and Biczó, 1965) their low-lying collective excited states were estimated by Jäger and Ladik (1968). In this estimation the expression

$$\omega^6 + \frac{\bar{\omega}_i{}^4}{\omega_{p\sigma}^2}\,\varepsilon_c\,\omega^4 - \frac{\bar{\omega}_i{}^4}{\omega_{p\sigma}^2}\,\omega_{p\pi}^2\,\omega^2 - \frac{\bar{\omega}_i{}^4}{\omega^{p\sigma}}\,\omega_{p\pi}^2 - \bar{\omega}_{kK}{}^2 = 0 \qquad \text{(III.5)}$$

was used, which can be derived from the dispersion relation for plasma oscillations (Pines, 1956) in a straightforward way (see Jäger and Ladik, 1968). Here ω is the frequency of the collective excitation ($\Delta E = \hbar\omega$), $\bar{\omega}_{kK}$ and $\bar{\omega}_i$ are the average π- and σ-electron one-electron excitation frequencies, $\omega_{p\pi}$ and $\omega_{p\sigma}$ are the plasma frequencies for free π- and σ-electrons, respectively,

$$\omega_{p\pi}^2 = \frac{4\pi e^2}{m} n_\pi, \qquad \omega_{p\sigma}^2 = \frac{4\pi e^2}{m} n_\sigma, \qquad \text{(III.6)}$$

(n_π and n_σ are the density of π- and σ-electrons, respectively), and finally

$$\varepsilon_c \approx 1 + \frac{\omega_{p\sigma}^2}{\bar{\omega}_i{}^2}$$

is the static dielectric constant for the core (σ) electrons. For $\hbar\omega_i$ the value of 9 eV ($\approx$140 nm) has been used; it was estimated on the basis of $\sigma \rightarrow \sigma^*$ transition energies (Rao, 1961) and for $\hbar\bar{\omega}_{kK}$ as first approximation the calculated band gaps of different periodic DNA models were used. To calculate the electron densities n_π and n_σ the geometry of DNA (Spencer, 1959) has been used (n_π values are between 2.7 and 4.0×10^{23} cm^{-3}, n_σ values between 6.2 and 8.7×10^{23} cm^{-3}).

In Table II we give for different periodic DNA models the energies of the π-electron collective excitations estimated on the basis of (III.5). [For more detailed data, see Jäger and Ladik (1968).] It is interesting to note that the values $\hbar\omega$ are in all cases (and in some further cases not shown in Table II) near to 6.0 eV, though there are considerable variations in the band structures of the different periodic DNA models. This seems to indicate that the energy of the π-electron collective excited state is quite

TABLE II

THE ENERGIES OF THE π-ELECTRON COLLECTIVE EXCITATION FOR DIFFERENT PERIODIC DNA MODELS (IN eV)

Periodic DNA Model	Gap ($h\bar{\omega}_{k\kappa}$)	$\hbar\omega$
PolyC	4.5	5.7
PolyT	4.9	6.1
PolyA	4.1	5.8
PolyG	4.6	6.0
Poly(A–T)	3.9	5.8
Poly(G–C)	4.1	5.8
$\mathrm{Poly}\begin{pmatrix}\text{A–T}\\ \text{G–C}\end{pmatrix}$	3.8	5.7
$\mathrm{Poly}\begin{pmatrix}\text{A–T}\\ \text{C–G}\end{pmatrix}$	3.8	5.7

insensitive to the finer details of the electron structure of different organic solids. Further it should be pointed out that the theoretical values for $\hbar\omega$ around 6 eV agree very well with the experimentally found $\hbar\omega$ values of the π-electron collective excited states of different hydrocarbon crystals. If the first collective excited state of DNA is also around 6 eV (which is probably the case, because also the experimentally found $\hbar\omega$ values are rather the same in different organic solids), we can expect a good agreement between theory and experiment also for DNA. Energy loss experiments have also been performed on DNA (C. D. Johnson and Rymer, 1967) and an intense peak around 25 eV has been found, but the investigated lowest value of energy loss was only about 10 eV. It would be rather interesting to see experimental results on DNA by smaller energies than this value. Finally it should be mentioned that for the interpretation of the experimentally found energy loss of DNA around 25 eV it seems to be necessary to extend this kind of investigation to all the valence electrons of nucleotide bases. Work along these lines is in progress.

D. Charge Transport in DNA

Conductivity measurements of DNA have been reported several times. Duchesne *et al.* (1960) have investigated the d.c. dark conductivity. They have assumed that in desiccated DNA the charge carriers are very probably mostly electrons and/or holes. In this case the well-known empirical relation

$$\sigma = \sigma_0 \exp(-w_{\text{act}}/2k_0T) \tag{III.7}$$

is valid for the specific conductivity σ, where w_{act} stands for the activation energy of conductivity, k_0 is the Boltzmann constant, and T the absolute temperature. Performing the measurement at different temperatures Duchesne *et al.* (1960) have found for w_{act} 1.60 eV. Afterwards Eley and Spivey (1962) have found 2.42 eV for w_{act} on the basis of their d.c. measurements on DNA, while the investigations of O'Konski and Shirai (1963) resulted in values of between 2.30 and 2.40 eV. O'Konski *et al.* (1964) have carefully investigated the dependence of the conductivity of DNA on its water content. They have found that with the increase of water content the conductivity of DNA increases by several orders of magnitude. They have observed further that by putting the desiccated DNA samples under electric potential difference, the current has reached a stationary value within a few seconds, while in the case of wet DNA samples this has occurred only after several hours.

Liang and Scalco (1963), and Snart (1963) have investigated the conductivity of DNA again with d.c. but in the presence of UV radiation. They have found that in this case w_{act} is about 2.20 eV, by ~0.2 eV smaller, than in the dark. They have also observed that as a result of the UV radiation the conductivity of desiccated DNA samples increases a considerable amount, while in the case of wet DNA samples the radiation did not cause a larger change. Finally, O'Konski *et al.* (1964) have measured the conductivity of different DNA samples with high frequency a.c. At the frequency of 10^9 sec^{-1} they have found for w_{act} the value of only 0.24 eV.

From all these experimental results we can draw the conclusions that most probably in desiccated DNA the charge transport is mostly electronic due to the delocalization of the π-electrons along the long axis of DNA (Ladik, 1960). [It should be mentioned that both Eley and Spivey (1962) and O'Konski (1963) accept this mechanism as the most probable explanation of the electronic conductivity.] On the other hand, in DNA samples with higher water content the charge carriers are predominantly ions. Further, since the w_{act} values for d.c. and a.c. are different by an order of magnitude, it seems very probable that the a.c. value refers to a single DNA macromolecule, while the reported ten times larger d.c. values are due to potential barriers between the macromolecules and between the macromolecules and the electrodes, respectively. That is, in a macroscopic DNA sample consisting of a lot of DNA molecules randomly oriented relative to each other, a direct current flows through all these barriers, while in the case of high-frequency a.c. the majority of charge carriers migrate only within the macromolecules. To prove the correctness of this interpretation it seemed to be interesting to investigate the d.c. and a.c. conductivity of oriented DNA fibers.

Such measurements have been performed by Rupprecht (1965) in the d.c. case and, as was expected, resulted in no asymmetry effect for w_{act}. On the other hand, by high-frequency a.c. we would expect a low value of w_{act}, if the field is parallel to the orientation of the DNA fibers and a high value if the field is perpendicular to the main axis of the DNA molecules. Unfortunately such experiments have not been performed.

To start with the theoretical interpretation of the conductivity of DNA, we have to assume that the activation energy of conductivity within a single macromolecule is $\sim$0.2 eV and the d.c. value of $\sim$2.4 eV can be interpreted as the sum of this quantity and a value of $\sim$2.2 eV due to intermacromolecular barriers. This point of view is supported also by the fact that irradiation of DNA by UV has decreased the d.c. w_{act} value only by $\sim$0.2 eV from $\sim$2.4 eV to $\sim$2.2 eV (Liang and Scalco, 1963; Snart, 1963).

Accepting this interpretation, there remains the difficult problem to explain of how can w_{act} be only $\sim$0.2 eV, while the energy necessary to promote an electron from the valence band to the conduction band requires, according to the calculations of the band structures of different periodic DNA models (described in Section III.B), energies of at least $\sim$4.0 eV. The recent results on poly(G–C–Mg^{2+}) (Rozsnyai and Ladik, 1970a) give a possible answer to this problem. As was described in Section III.B, the PPP CO calculation of poly(G–C) with a Mg^{2+} ion attached to each cytosine molecule by its amino group has resulted in a gap between the valence and conduction band of only $\sim$2.0 eV. Further, as we have seen, the PPP CO method gives band gaps which are by 2.0–2.5 eV higher than the energy of the first $\pi \rightarrow \pi^*$ transition. Our result therefore means that in the presence of Mg^{2+} ions the activation energy of conductivity may decrease to zero. Of course we do not claim that this is the only possible solution of the problem, but we feel that considering the effect of charged impurities, lattice imperfections, etc., the small value of w_{act} could be explained in a satisfactory manner.

The next question to discuss is the value of the constant σ_0 in (III.7). Recalculating its value from Eley's and Spivey's (1962) d.c. results we get 10^3 ohm^{-1}, while from O'Konski's and Shirai's (1963) d.c. data we obtain

$\sigma_0 = 10^7$ ohm^{-1} cm^{-1}. On the other hand, the high-frequency a.c. results of O'Konski's *et al.* (1964), in which case the small value of $w_{\text{act}} = 0.24$ eV has to be substituted into (III.10), provide a value of 10^{-3} ohm^{-1} cm^{-1}.

To calculate theoretically the value of $\sigma_0 = \sigma_{0e} \pm \sigma_{0h}$ as a first step the simple deformation potential approximation (Shockley, 1950) has been used for the mobilities. In the one-dimensional case it is possible to derive in this approximation (Beleznay *et al.*, 1965) the expressions for the contributions of the electrons and holes, respectively

$$\sigma_{0e} = \frac{2}{\pi} C_\perp \hbar e^2 \frac{1}{m_e{}^* \varepsilon_{1e}^2}, \tag{III.8a}$$

$$\sigma_{0h} = \frac{2}{\pi} C_\perp \hbar e^2 \frac{1}{m_h{}^* \varepsilon_{1h}^2}. \tag{III.8b}$$

Here $C_\perp$ is the elastic constant of the longitudinal acoustic waves [in the lack of the appropriate data for DNA the value of $C_\perp = 3.60 \times 10^{11}$ dyne/cm^2 found for graphite (Komatsu and Nagamya, 1951) has been applied], and $m_e{}^*$ and $m_h{}^*$ are the effective masses of the electron and the hole, respectively, which can be approximated by the expressions

$$m_e{}^* = \frac{\hbar^2 \pi^2}{2a^2 \Delta w_c}, \qquad m_h{}^* = \frac{\hbar^2 \pi^2}{2a^2 \Delta w_v}. \tag{III.9}$$

Here $a = 3.36$ Å is again the lattice constant of DNA, Δw_c and Δw_v are the widths of the conduction band and of the valence band, respectively. The deformation potentials of the electron (ε_{1e}) and of the positive hole (ε_{1h}) are defined by

$$\varepsilon_{1e} = \frac{\delta w_{c,l}}{\Delta}, \qquad \varepsilon_{1h} = \frac{\delta \Delta w_{v,u}}{\Delta}, \tag{III.10}$$

where $\delta w_{c,l}$ and $\delta w_{v,u}$, respectively, are the changes of the lower limit of the conduction band and of the upper limit of the valence band due to the longitudinal dilatation $\Delta = \delta a/a$ of the chain.

In the actual calculations simple tight-binding band structures of different periodic DNA models have been used and with the exception of polyA only the interaction with acoustic phonons have been taken into account assuming for δa an increase by $0.05a = 0.05 \times 3.36 = 0.17$ Å of the distance between the stacked bases. [In the case of polyA also the interaction with the bond-stretching vibration of the $\text{C–N}\langle^{(\text{H})}_{(\text{H})}$ bond (the bond between the ring carbon atom and the amino group of adenine) has been taken into account. This calculation, in which an interaction with optical phonons has been taken into account, has given in order of magnitude the same results as the calculations taking into account the interaction with acoustic phonons (Beleznay *et al.*, 1965). The change of the elements of the Hermitian complex matrix $\mathbf{C} = \mathbf{A} + \mathbf{B}e^{ika} + \mathbf{B}^{tr}e^{-ika}$ (whose eigenvalues give the band structure; see Section II.B) by the change of a to $a+$, δa has been estimated on the basis of the change of overlap integrals between the superimposed bases. Since the changes of all elements of **C** were very small, instead of redetermining the band structure by the changed geometry, only first-order perturbation theory was applied (Ladik *et al.*, 1966). In this way one obtains

$$\delta w_{c,l} = \mathbf{d}_c(k_{c,l})^+[\mathbf{A} + \Delta\mathbf{B}\exp(ik_{c,l}a) + (\Delta\mathbf{B})^{tr}\exp(-ik_{c,l}a)]\,\mathbf{d}_c(k_{c,l}) \tag{III.11}$$

and a similar expression holds for $\delta w_{v,u}$. Here $\Delta\mathbf{B} = \mathbf{B}(1.05a) - \mathbf{B}(a)$, and $\mathbf{d}_c(k_{c,l})$ and $k_{c,l}$ stand for the complex eigenvector and k value, respectively, belonging to the lower limit of the conduction band.

According to the results obtained in this way, the σ_0 values in the broad-band cases [homopolynucleotides and poly(A–T), poly(G–C)] were of the order of magnitude 10^3–10^4 ohm^{-1} cm^{-1} (σ_{0e} and σ_{0h} giving about equal contributions) (for details, see Ladik *et al.* 1966), while in the narrow-band cases (complicated periodic DNA models) the results were usually larger by one order of magnitude [$\sigma_0 \sim 10^5$ ohm^{-1} cm^{-1}; see Ladik *et al.*, 1968b).

This latter result, which is in contradiction to all physical expectations, clearly indicates that the simple deformation potential approximation breaks down in the case of very narrow bands. It should also be mentioned that in the broad-band case the order of magnitude of the calculated σ_0 values falls only into the region of σ_0 obtained experimentally by d.c. while they are by six or seven orders of magnitude larger than the σ_0 values obtained by the physically much more relevant high-frequency a.c. measurements.

To overcome the difficulties mentioned most recently Suhai (1972) has reinvestigated the problem of charge transport in periodic DNA models. Since in the case of narrow bands the band widths are comparable with the mean thermal energy, states in the band differring from the band limits will be populated by mobile charge carriers with a nonvanishing probability. Therefore he has taken into account: (1) transitions between arbitrary electronic states within the first Brillouin zone due to scatterings with the phonons, (2) Umklapp scattering processes, and (3) the inelasticity of electron–phonon scattering, because the energy of the absorbed or emitted phonon is not negligible compared to the band widths. Since the derivation of Suhai is rather complicated and needs special knowledge in the field of transport theory, we describe here only qualitatively his method of reasoning and refer for the mathematical formulation to the original paper (Suhai, 1972).

Using simple LCAO (tight-binding) CO's for the electrons he has directly calculated the electron–photon interaction matrix elements using the adiabatic approximation (Ziman, 1960). From these he has computed using time-dependent perturbation theory the probabilities of different transitions due to the electron–phonon scattering. Since, as is well known, in the case of inelastic scatterings the concept of general relaxation time does not exist any longer (Blatt, 1968), he had to define an approximate relaxation time $\tau_{\text{appr}}(k)$ which is still possible (Blatt, 1968).

From the latter quantity he has evaluated the mean free path of the charge carriers, averaging over the states of a band using Boltzmann statistics,

$$\tilde{\Lambda}^T = \frac{\int v(k)\tau_{\text{appr}}(k)\exp[-\varepsilon(k)/k_0T]\,dk}{\int \exp[-\varepsilon(k)/k_0T]\,dk}, \qquad \text{(III.12)}$$

where

$$v(k) = \frac{1}{\hbar}\frac{\partial\varepsilon(k)}{\partial k}.$$

Finally, changing the appropriate expressions for metals of the variational method of transport theory (Blatt, 1968) to nondegenerate semiconductors, he also calculated the specific conductivities σ and using the relation $\mu = \sigma/ne$ (n is the number of charge carriers) the mobilities μ for different periodic DNA models. In this calculation the interactions were taken again with the acoustic phonons.

In Table III we give in a few cases the band widths, the $\tilde{\Lambda}^T$ values, and the mobility values for 300°K found by Suhai (for further details, see Suhai, 1972). We can see from the Table III that in the so-called broad-band cases the mean-free path values are between 12 and 50 Å ($\sim 4a$–$\sim 15a$; $a = 3.36$ Å), which justifies the delocalized description. At the same time the $\tilde{\Lambda}$(300°K) values in the narrow-band cases are on the order of 1–2a, which makes questionable the band description for these cases.

The mobility values obtained for periodic DNA models with relatively

TABLE III

The Mean Free Path Values ($\tilde{\Lambda}$) and Mobility Values (μ) at $T = 300°K$ for a Few Periodic DNA Models[a]

Periodic DNA Model		Band width (eV)	$\tilde{\Lambda}$(300°K) (Å)	μ(300°K) ($cm^2 V^{-1} sec^{-1}$)
PolyT	Electron	0.072	12	30
	Hole	0.274	42	82
PolyA	Electron	0.244	32	65
	Hole	0.318	54	94
Poly(A–T)	Electron	0.268	25	40
	Hole	0.254	32	43
Poly$\begin{pmatrix}A\text{–}T\\G\text{–}C\end{pmatrix}$	Electron	0.046	8.5	7
	Hole	0.053	8	10
Poly$\begin{pmatrix}G\text{–}C\\C\text{–}G\end{pmatrix}$	Electron	0.027	5	4
	Hole	0.020	3.5	4

[a] Suhai (1972).

broader bands are 30–100 $cm^2V^{-1}sec^{-1}$, while in the narrow-band cases they are by one order of magnitude smaller. We can draw from these results the same conclusions as from the $\tilde{\Lambda}$ values. Mobilities much larger than 1 $cm^2V^{-1}sec^{-1}$ indicate delocalized motion while if the values of μ are comparable to 1 $cm^2V^{-1}sec^{-1}$ the band description may be problematic (Glarum, 1963). As we can see, the periodic DNA models with broader bands fall in the first category, the narrow-band models in the second one.

There are no direct experimental measurements on the mobilities of DNA. O'Konski *et al.* (1964), however, have observed a saturation of the conductivity at 10^8 cps. Assuming the average number of base pairs in a DNA double helix to be 10^6, on the basis of the relation

$$l = \mu F t \tag{III.13}$$

(l is the length of the chain, F the applied field strength, and t the period of the external field), using the data of O'Konski *et al.* (1964), Suhai (1972) has estimated the value of μ in DNA as on the order of 10^2 cm^2 V^{-1} sec^{-1}. This value is, of course, uncertain, first of all due to the uncertainty in l. (The number of base pairs in higher organisms is 10^8–10^9 but there may be lattice distortions which make the charge transport in certain regions impossible.)

Therefore the above given μ value can be accepted only for orientation. To clear up better the mechanisms of charge transport in DNA and to compare more seriously the experimental and theoretical results on both sides much more refined investigations have to be performed.

E. The Unwinding of DNA

According to the semiconservative duplication mechanism of DNA (Watson and Crick, 1953) the double helix starts to unwind at a certain point. After a few bases become free nucleotides of complementary bases coming from the cytoplasm will bind to them and in this way the formation of two new DNA helices starts. The finer details of this duplication mechanism are not completely clear yet, but it is generally accepted that the formation of the two new double helices proceeds parallel to the unwinding of the original DNA helix. In this way the energy released in the course of the formation of the bonds of the new double helices can break up further hydrogen bonds of the original double helix and so the duplication process can proceed.

There have been suggested different mechanisms for the details of DNA replication. For instance, the mechanism of Löwdin (1965) assumes the association of four nucleotide bases (two from the original double helix and two new complementary bases coming from the cytoplasma) in the replication plane which finally split to two new base pairs, each one containing one old and one new base. Energy calculations performed by Macintyre and Löwdin (1968) with the aid of the semiempirical SCF LCAO MO method have shown that if all four bases in the replication plane are in their normal (*in vivo* stable) tautomeric form, the system is much more stable than if two of them are in their "mutagenic" tautomeric form. (For further details of Löwdin's theory see the cited papers.)

All suggested duplication mechanisms have, however, one common feature; to start the process it is necessary to break up a few base pairs of the original double helix. Of course this requires some energy, the source of which is unknown. Several years ago Hoffmann and Ladik (1964a) suggested that the polarization in a strong local electric field of the π-electrons of the base pairs may induce the unwinding of the DNA double helix. It is obvious that this assumption may have a connection with the problems of growth and tumor development (for details, see Hoffmann and Ladik, 1964a; Ladik, 1972).

As a first step to testing this hypothesis Seprődi *et al.* (1969) have calculated the components of the permanent dipole moment ($\boldsymbol{\mu}$) and the elements of the polarizability tensor ($\boldsymbol{\alpha}$) for the nucleotide bases and base pairs (treating the latter ones as common delocalized π-systems). The calculation was restricted only to the π-electrons of these compounds, and their MO's obtained in the PPP approximation were used to calculate $\boldsymbol{\mu}$ and $\boldsymbol{\alpha}$. To be able to calculate also the off-diagonal elements of the tensor $\boldsymbol{\alpha}$ Seprődi *et al.* (1969) have generalized the perturbation treatment proposed by Hylleraas (1930) and by Hassé (1930) (see also Hirschfelder *et al.*, 1954). It should be mentioned that their expression agrees with that given in the book of Hirschfelder *et al.* (1954) for the diagonal elements of $\boldsymbol{\alpha}$ only, if some special conditions are fulfilled. [For further details and the derivation, see Seprődi *et al.* (1969).]

In the presence of a static and homogeneous electric field the total energy of a molecule is given by

$$E = E_0 - \boldsymbol{\mu}^+ \boldsymbol{\varepsilon} - \tfrac{1}{2}\boldsymbol{\varepsilon}^+ \boldsymbol{\alpha} \boldsymbol{\varepsilon} = E_0 + E', \tag{III.14}$$

where E_0 is the energy of the molecule in the absence of the field and $\boldsymbol{\varepsilon}$ stands for the electric field strength vector. If we calculate $\boldsymbol{\mu}$ and $\boldsymbol{\alpha}$ for a base pair and for its constituents and if

$$E_{x-y} > E_x + E_y \qquad \begin{matrix} x = G \text{ or } A, \\ y = C \text{ or } T. \end{matrix} \tag{III.15}$$

we can calculate the critical field strength at which the base pairs split. Namely, we can write

$$E_{x-y} - E_x{}' - E_y{}' = \Delta E^{(0)}_{x-y}, \tag{III.16}$$

where in the ground state of a base pair

$$\Delta E^{(0)}_{x-y} = \varepsilon_{\mathrm{deloc}} + k_{x-y}\varepsilon_{\mathrm{N-H\cdots O}} + \varepsilon_{\mathrm{N-H\cdots N}} = \begin{cases} 0.43 \text{ eV for G–C} \\ 0.34 \text{ eV for } A\text{–}T \end{cases}. \tag{III.17}$$

Here $\varepsilon_{\mathrm{deloc}}$ is the energy due to the delocalization of the π-electrons through the hydrogen bonds of the base pairs, $E_{\mathrm{N-H\cdots O}}$ and $\boldsymbol{\varepsilon}_{\mathrm{N-O\cdots N}}$ are the different hydrogen bond energies in the base pairs, and $k_{x-y} = 2$ for G–C and 1 for A–T, respectively. The values of the hydrogen bond energies and that of $\boldsymbol{\varepsilon}_{\mathrm{deloc}}$ were taken from B. Pullman and Pullman (1959), respectively.

Substituting into (III.16) the values of (III.17) and the expression (III.14) of E' the critical field strength which can cause the break up of a base pair was computed in their ground and in some of their excited and ionized states. The calculations have been performed in different directions of the field strength.

According to the results obtained (Seprődi *et al.*, 1969) in the ground state of G–C and A–T, respectively, in the presence of the field the separation of the two bases of a base pair is always energetically more favorable.

The critical field strength necessary to induce the split of a base pair is on the order of magnitude of 10^8 V/cm if the field lies in the planes of the base pair (its minimal value occurs then, if it points in the direction of the hydrogen bonds), while if its direction is perpendicular to the plane of the base pair the critical field strength is on the order of 10^9 V/cm. In some excited and ionized states the value of the critical field strength is somewhat smaller, but contrary to previous expectation (Hoffmann and Ladik, 1964a) not an order of magnitude smaller.

Homogeneous field strengths of order 10^8–10^9 V/cm of course are impossible to produce technically from outside. On the other hand, the inhomogeneous field produced by an elementary charge in a distance of 1 Å is on the order of magnitude of 10^9 V/cm. So due to some fluctuations of the ionic distributions or to the presence of a molecule with a strong dipole in the intimate neighborhood (in a microphysical sense) of the hydrogen bonds of the base pairs such strong local (again in the microphysical sense) field strengths may occur at the hydrogen bonds and induce their separation.

The other difficulty of the briefly described calculation is that by such extremely strong field strengths the σ–π separation completely breaks down (the σ- and π-orbitals will be distorted so strongly that they will not be orthogonal to each other).

Therefore Greguss *et al.* (1972) have repeated the calculation for the G–C base pair using the CNDO/2 method. They have performed a CNDO calculation for G and C separately and have taken into account only van der Waals interaction between them. The effect of the inhomogeneous electric field due to point charges situated in different positions in the immediate neighborhood of the hydrogen bonds was taken into account by the second order of the Raleigh–Schrödinger perturbation theory. They were unable to determine the value of the critical field strength, because they found a repulsive van der Waals interaction with an interaction energy already larger than ΔE°, in the absence of the field. This incorrect result is most probably due to the fact that the framework of the simple van der Waals interaction is not adequate for the description of the interaction of the bases. Therefore the base pairs should be treated in the future also in an all-valence-electron description as common delocalized systems. Nevertheless it was possible to see already from this calculation that at most point-charge positions the electric field causes additional repulsion between the bases and so a point charge may induce the starting of the unwinding of DNA.

Finally it should be mentioned that since DNA is a polyelectrolyte, by the assessment of the effect of an electric field on the unwinding of the double helix the mobile counterions of DNA have to play a very important role (probably a more important one than the polarization of the electrons). In this respect the interesting experiments of Neumann and Katchalsky (1971) should be mentioned. Applying short electric impulses up to 30 kV and of a duration of 1–5 μsec they have found that if the direction of the field strength is parallel to the main axis of an RNA-type triple helix the impulses cause the separation of the three helices. Obviously the same phenomenon should be expected also by DNA. Therefore it would be desirable to perform such calculations in the future which take into account both the polarization of the counterions due to an electric field and the change of field strength acting on the electrons of the nucleotides bases as a consequence of the change of the counterion distribution (see also Section IV). In our opinion only such much more refined calculations could lead to better established explanations of the starting of the unwinding.

IV. Study Program

In this section will be mentioned very briefly some problems of the electron structure of DNA which seem worthwhile to investigate in the next few years. There is no claim that these are necessarily the most important problems to be solved. They are, however, those which lie in the line of the investigations already performed by this author and therefore from a subjective point of view they seem to be the most interesting ones for him.

The first question to be cleared up better seems to be the question of *interaction* between the stacked bases and the constituents of a base pair. It seems probable that on the basis of semiempirical methods it will not be possible to decide whether a van der Waals description including higher order terms will be enough, or in all cases a delocalized treatment is always necessary. To settle this problem the single bases, two stacked bases together, and the base pairs should be treated with *ab initio* methods using possibly Slater functions as basis set. A new method proposed by Beleznay (1967) for the treatment of multicenter integrals of Slater functions can be very useful in this connection. Comparing then the interaction energies obtained by the delocalized treatment with those which one gets by sophisticated enough van der Waals treatment it will be possible to decide whether a van der Waals description should be used, or the delocalized one. It should be mentioned that to save computer time the question could be studied as a first step on appropriate model systems which contain the essential features of the nucleotide bases. For instance, following the suggestion of Csizmadia (1969), two formamide molecules at a distance of 3.36 Å between their parallel planes and one rotated by 36° in its plane with respect to the other could be used as a model for two stacked bases.

It seems probable that at least if bases of the same kind are stacked the delocalized description is needed. Therefore it would be interesting to perform as next steps of the investigation of "broad band" periodic DNA models *semiempirical all-valence-electron* (CNDO CO, MINDO CO, etc.) and later *ab initio* band structure calculations for the ground state of these systems using first-neighbor interactions. In connection with the *ab initio* CO methods versus the semiempirical CO methods it should be mentioned that Békássy *et al.* (1972) have performed a simple tight-binding treatment of the five homopolynucleotides taking into account intra and/or interbase overlap explicitly. According to their results the overlap integrals have a considerably larger effect on the band structure of a polymer than on the energy levels of the monomer.

To take into account the effect of the *further neighbors* one could study how much the band structures are influenced, taking van der Waals interactions with the second, third, etc., neighbors.

If it is possible to calculate *ab initio* band structures at least for the homopolynucleotides it would be interesting to repeat the calculations using different orbitals for different spins using the formalism of Biczó *et al.* (1972). On the basis of the experiences with molecules one would expect that in this way a considerable amount of the correlation energy of the polymer could be covered. At the same time it should be mentioned that this result is not to be expected if one performs a DODS calculation with the aid of some semiempirical CO method, because the parametrization of these methods already contains a certain (but unknown) amount of the correlation energy. A good demonstration of this situation was obtained by Kertész *et al.* (1972), who have performed a DODS PPP CO calculation for polyC. They have obtained for the total π-electron energy per unit cell 148.16 β in the DODS case and 148.33 β in the simple PPP CO case. Taking for β the Pariser–Parr (1953) value of -2.39 eV this means that the DODS treatment has lowered in polyC the total π-electron energy per unit cell only by the small amount of 0.39 eV.

For the treatment of the correlation energy in polymers like periodic DNA models, of course, the application of Green's function methods should also be considered (see, for instance, K. H. Johnson, 1968).

The correct description of the *excited states of a polymer* in the framework of the more sophisticated CO methods is, as we have seen in Section

III.B, also an unsolved problem. To take into account the correlation between the promoted electron and the remaining hole perhaps, as we have already mentioned, the intermediate exciton theory could be used. The problem of electron correlation in DNA is of course also in close connection with the occurrence of different *collective states* in this macromolecule [for instance, the possibility of superconductive-type enhanced conductivity in some regions of DNA on the basis of Little's mechanism (Little, 1964, 1967) cannot be excluded, according to Pearlstein (1968) and Ladik *et al.* (1969)].

To handle better the problem of charge transport in the more complicated periodic DNA models with very narrow bands in the future the *hopping model* should be used to describe better the probably rather uncorrelated motion of the charge carriers. At the same time, in addition to the effect of acoustic phonons also the interaction with the optical phonons (interbase vibrations) should be taken into account.

Of course, all the above-suggested investigations refer only to periodic models of chains consisting of the nucleotide bases only. If we want to extend the calculations towards the real DNA macromolecule we have to treat first of all the following three problems: (1) the aperiodicity of the base sequence in DNA, (2) the effect of different, especially charged, impurities, and (3) the effect of the nonzero resultant electric field due to the double layer of ions on the outer sides of the double helix and due to the dipole moments in the protein chain intermingled with the DNA double helix.

Besides the already mentioned perturbation treatment of the aperiodicity of DNA (Beleznay and Biczó, 1964) which applied the second order of conventional perturbation theory, nothing has been done yet to attack this difficult problem. In principle again Green's function methods (see K. H. Johnson, 1968) could be applied, but it seems that considerable work has to be done, before these methods could also handle our problem in practice. Another approach worked out by Del Re and Biczó (1972) to treat the problem of surface states may be promising also in the case of the aperiodicity problem. (Their method considers the effect of the surface of a half infinite linear chain as a perturbation in its infinite matrix **H** and treats this perturbation with the aid of the Brillouin–Wigner perturbation theory instead of the Raleigh–Schrödinger one.) It will probably be possible to treat on the basis of this method aperiodicity, lattice imperfections, impurities, and surface effects on the same footing.

After the very simple model calculations for water and Mg^{2+} ions described in Section III.B it would be necessary to perform calculations for periodic DNA models assuming given statistical distributions for the impurities. At the moment there seems to be the two ways for doing this. On the one hand, we could take, for instance for a homopolynucleotide, an enlarged elementary cell (for instance, five bases), assume a given amount of impurities (for instance, two Mg^{2+} ions per five bases) and construct all possible periodic models for the chosen elementary cell with a given amount of impurities (in our oversimplified example it is possible to construct only two different periodic models in this way). Then we can calculate the band structures of these different periodic DNA models in the usual way and add them by weighting each one according to the different probabilities of the different impurity distributions (Bierman, 1969). This method seems mathematically quite simple, but it would take very large computer times to simulate well the effect of statistically distributed impurities on the band structures of periodic DNA models in this way. Therefore it seems to be interesting to try to generalize to the many-band case the other method of Bierman (1970), which he has worked out to describe the effect of statistically distributed impurities on a single energy band. Since, however, this method is also mathematically quite involved in the case of a single band, it will not be easy to generalize it to the many-band case.

If one tries to approximate with the aid of quantum mechanical methods the electronic structure of a real DNA molecule, the effect of the ionic double layer surrounding it cannot be neglected. Since *in vivo* the K^+ ions are mostly dissociated from the negatively charged phosphate groups they will surround the DNA double helix from outside. In this way an electric double layer is formed with the positive ions outside and the negative ones inside on the outer part of both DNA helices. This double layer will cause at the nucleotide bases a resulting nonzero inhomogeneous electric field everywhere with the exception of the symmetry axis of the double helix. Until it becomes possible to take a whole nucleotide together with its sugar and phosphate residues as unit cell of the periodic DNA model, we can take into account the effect of the described electric double layer only in the point-charge approximation, putting negative and positive charges into suitably chosen positions in each elementary cell. Besides this, to take into account the also nonzero resulting field of the dipoles of the single protein chain intermingled with the DNA double helix, we can put a third point charge into each unit cell in such a position that its field should approximate well the resulting field of the protein chain. Having determined the positions of the point charges we can perform model calculations for the band structures of periodic DNA models in the presence of the electric double layer and of a protein chain. Very probably all these perturbations will cause considerable changes in the band structures. In this respect it should be mentioned that most recently Clementi (1971) has performed an *ab initio* band-structure calculation for polyethylene in the presence of point charges. He has found that by surrounding the polymer with positive or negative point charges the entire band system has raised or lowered its entire energy spectrum. He has found smaller changes when he has surrounded the polymer by alternate layers of point charges with different signs. On the basis of these results one might expect that the electric double layer will have a smaller effect on the band structure of the periodic DNA models than the resulting field of the protein chain. On the other hand, we have to be very cautious in drawing conclusions from these results on polyethylene on periodic DNA models, because in the latter case the unit cell is much larger and therefore the fact that the electric field is inhomogeneous may play a much more important role than in the case of polyethylene.

Finally, a few words should be said about some problems which are closely connected with the biological functions of DNA. In Section III.E we have discussed the mechanism of DNA unwinding from the point of view of the necessary energy to start this process. We have seen there also that an electric impulse will have the primary effect of changing the distribution of K^+ ions around DNA and thus it will also change the resulting field acting on the electrons of the nucleotide bases. Therefore to assess whether an electric field of given magnitude pointing in a given direction is able to split a base pair or not, rather intricate calculations have to be performed. To be able to perform such calculations first of all a model has to be constructed to describe the change of distribution of the K^+ ions due to a given electric impulse. On the basis of this it will be possible to perform later *ab initio* calculations on the electronic structure of a base pair and of its constituent bases in the presence of the changed field. In the assessment of whether a given electric impulse can induce the unwinding of DNA or not in addition to the effect of the changed ionic distribution on the electrons of the bases, of course, also the change of the direct interaction of the ions has to be taken into account.

Further, the possible effect of electric field on the unwinding of DNA may be important also from the point of view of information storage in the long-term memory. Namely, Ladik and Greguss (1971) have assumed a possible molecular mechanism which may lead from the electric impulse on the membrane of a brain cell finally to a change in the base sequence of the DNA molecules in the nucleus of the brain cell. An essential part of this hypothesis (which, of course, is only one of the many suggested possible mechanisms for information storage in the brain) is that the change of electric field strength at the cell membrane may be transferred to the DNA molecules of the cell nucleus and there they may cause the unwinding of DNA molecules. The final goal of the quantum mechanical investigation of DNA should of course be to contribute to the solution of the problem mentioned and of many other important biological problems. From the preceding discussion it is probably clear that to achieve this we have to travel along a long road on which we have done only the first few steps. Every long journey, however, starts with the first steps.

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