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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 or 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 or 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 describes it in terms of electronic wave patterns. It uses physical and chemical insight, sophisticated mathematics, and high-speed computing 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 which was previously unconceivable, 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 both for the expert and the nonexpert to follow the rapid development in this new borderline area.

The purpose of this series 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 almost overwhelming, and a second 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. Special thanks go to two of the great pioneers in the field, Professor Egil A. Hylleraas and Professor John C. Slater, as active as ever, who have taken the trouble to give us their personal views on two fundamental problems.

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 scientists 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.

*August, 1964* PER-OLOV LÖWDIN

# The Schrödinger Two-Electron Atomic Problem

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## I. Introduction

The present contribution to "Advances in Quantum Chemistry" is not intended to have the character of an encyclopedia article. Those who are interested in a complete treatment of the item should consult the thorough treatment given by Bethe and Salpeter (1957), which is complete up to the year of publication.

In the present article I take this opportunity of freedom to follow up some particularly interesting problems, more or less according to their historical development. This means, for instance, that we shall concentrate mainly upon the ground state problem, because of its ease of comparison with experimental data. From the point of view of quantum chemistry this is also a most important problem, since in the theory of chemical compounds one is mainly looking for ground states.

Because the field of research even within the atomic two-electron problem is so vast, a great number of investigations will be missing in the present article. This does not in any way mean that they are of secondary importance, but only that we are here considering those works which are necessary when talking freely of methods and results. Since a full report of works done in the field together with a documentation of their particular importance can be found in the above-mentioned encyclopedia article by Bethe and Salpeter, I consider this procedure legitimate.

## II. The Early State of the Helium Problem

### A. The Hydrogen and Helium Atoms in the Bohr Theory

1. *The Hydrogen Atom*

The natural frequency unit in atomic spectroscopy is the Rydberg constant $R$. The practical unit however is a reciprocal length $R/c$, which is usually also termed $R$. Because of the slight motion of the nucleus with respect to the electron-nucleus center of mass, the $R$ (or $R/c$) varies a little from atom to atom. For heavy atoms it converges toward a theoretical limit $R_\infty$. According to latest expert calculation (Cohen and Du Mond, 1957) the following values can be given:

$$\begin{aligned} R_\infty &= 109{,}737.309 \text{ cm}^{-1}, \\ R_{\mathrm{H}} &= 109{,}677.576 \text{ cm}^{-1}, \\ R_{\mathrm{He}^4} &= 109{,}722.26 \ \ \text{cm}^{-1}. \end{aligned} \tag{1}$$

The natural energy unit in atomic theory therefore becomes

$$Rh = \frac{m_0}{2}\left(\frac{e^2}{\hbar}\right)^2 = \frac{e^2}{2a_{\mathrm{H}}}, \qquad a_{\mathrm{H}} = \frac{\hbar^2}{m_0 e^2}, \tag{2}$$

where $\hbar = h/2\pi$ and $m_0$ and $e$ are mass and charge of the electron. This corresponds to the kinetic energy of an electron with velocity $c\alpha$, where

$$\alpha = \frac{e^2}{\hbar c} \simeq \frac{1}{137} \tag{3}$$

is the fine structure constant appearing in the Bohr–Sommerfeld relativistic theory of the hydrogen atom. It is also half the absolute value of the potential energy of an electron at a distance $a_{\mathrm{H}}$ from the hydrogen nucleus.

At the earliest stage of the Bohr theory, even in its primitive shape of circular electron orbit, a full set of energy levels was found,

$$E_n = -Rh/n^2. \tag{4}$$

When the theory was supplemented with the conception of elliptical orbit, as quantized even with respect to orientation in space, the energy formula remained unchanged. Among the triple of quantum numbers, now denoted by $n$, $l$, and $m$, i.e., principal, azimutal, and equatorial quantum numbers, only $n$ is significant for the energy. The degree of degeneration, i.e., the numbers of independent states belonging to the same energy level, is $n^2 = 1, 4, 9, \ldots$, just half the numbers $2n^2$ characteristic for the various groups of the periodic system of basic elements. The doubling has been explained by the existence of electron spin and the necessity to have it quantized by a double-valued quantum number.

If relativistic theory is applied, a separation of energy states with respect to the azimutal quantum number $l$ is produced. The separation is of the order of magnitude $\alpha^2 Rh$ and is correctly given by the famous Sommerfeld fine structure formula. A slight deviation called the Lamb effect was later found and must be thought of as a reaction from a virtual radiation field.

## 2. *The Helium Atom and Ion*

With this background of successful treatment of the hydrogen atom one must wonder that no numerical result of any value whatsoever could be obtained for the helium atom with its two electrons. This was caused by the well-known difficulties of many-body problems in classical mechanics. The Bohr rules for quantization of electron orbits

$$\oint p\,dq = nh \tag{5}$$

were inapplicable because the presupposed periodic or quasi-periodic character of the motion did not exist. The division of the procedure of quantization into two steps, solution of classical equations of motion followed by a selection of orbits by quantization rules, became fatal, and this could be mended only by an entirely new form of quantum theory, a true quantum mechanics.

The only state of the He atom which could at all be visualized in some tolerable form was the ground state. The states of the $\mathrm{He}^+$ ion with only one electron as well as the general one-electron atom (ion) with nuclear charge $Ze$ are as clear as those of the hydrogen atom, and their energy levels in nonrelativistic treatment are

$$E_n = -Z^2 Rh/n^2. \tag{6}$$

If the two electrons of the He atom are placed on either side of the nucleus, rotating in the same direction on the same circular orbit and with the same appropriate speed, it cannot be denied that they are moving periodically and according to classical mechanical laws. With this specialization, quantum rules can also be applied. The result must be an ionic energy for each electron corresponding to the effective nuclear charge

$Z = 2 - 0.25 = 1.75$, which gives a total energy $-6.125Rh$ and an ionization energy for the first electron

$$I_{\mathrm{He}} = 2.125Rh = 28.9\ \mathrm{eV}. \tag{7}$$

This energy is more than 4 eV too large.

From the viewpoint of wave mechanics this is due to a far too strong correlation between the motions of the two electrons which must be very much weakened in order that the configuration can exist.

## B. Simple Wave Mechanics of Two-Electron Atoms

### 1. *The Schrödinger Wave Equation in Atomic Units*

For a conservative mechanical system, the Schrödinger wave equation reads

$$H\psi = E\psi, \tag{8}$$

where $\psi$ represents a state and is called the wave function. It is a function of the coordinates of the system, and $H$ is the energy operator which is found from the classical Hamiltonian of the system in replacing momentum variables $p$ by differential operators $-i\hbar\partial/\partial q$. Hence the wave equation for the H atom is

$$\left(-\frac{\hbar^2}{2m_0}\nabla^2 + \frac{e^2}{r}\right)\psi = E\psi. \tag{9}$$

To simplify the equation it is tempting to apply atomic units, preferably the unit of length $a_{\mathrm{H}}$ of Eq. (9), which on dividing Eq. (9) by $e^2/a_{\mathrm{H}} = 2Rh$ yields the equation

$$\left(-\frac{1}{2}\nabla^2 + \frac{1}{r}\right)\psi = E\psi, \tag{10}$$

with coordinates measured in units $a_{\mathrm{H}}$ and the energy in double Rydberg units. This is seen to be equivalent to choosing $m_0$, $e$, and $\hbar$ for principal units of mass, charge, and action from which other units are obtained as secondary units. The velocity, for instance, is that of the electron velocity $e^2/\hbar$ on the first Bohr circular electron orbit of the hydrogen atom, which gives to the speed of light the numerical value $c = 137$.

Even though this is the most attractive and logical choice, there is another one which sometimes may be preferred on the basis that radial functions are of the confluent hypergeometric type which are most easily expressed by Laguerre functions, using for unit of length $\frac{1}{2}a_{\mathrm{H}}$. This system is obtained by changing the unit of mass into $2m_0$ with the effect that the energy unit becomes $4Rh$. If nevertheless the energy is measured in the conventional unit $Rh$, we must replace $E$ by $\frac{1}{4}E$ in the wave equation. Hence the hydrogen wave equation becomes

$$\left(-\nabla^2 + \frac{1}{r}\right)\psi = \tfrac{1}{4}E\psi. \tag{11}$$

Passing to the two-electron atom with nuclear charge $Ze$, the wave equation reads

$$\left\{-\nabla_1^2 - \nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right\}\psi = \tfrac{1}{4}E\psi, \tag{12}$$

$r_{12}$ denoting the interelectronic distance. From the point of view of perturbation theory we should rather use the equation

$$\left\{-\nabla_1^2 - \nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{Zr_{12}}\right\}\psi = \frac{E}{4Z^2}\psi \tag{13}$$

in changing to the unit of length $a_H/2Z$. In this equation $1/Z$ naturally appears as a perturbation parameter.

## 2. *Perturbation Energy*

Disregarding the perturbation function

$$V' = \frac{1}{Zr_{12}}, \tag{13a}$$

the unperturbed ground state wave function and energy are

$$\psi_0 = \frac{1}{8\pi}\exp[-\tfrac{1}{2}(r_1 + r_2)] \qquad \text{and} \qquad E_0 = -2Z^2, \tag{13b}$$

the latter being the energy of two one-electron atoms in the ground state. If the volume element is taken to be

$$d\tau = r_1^2 r_2^2 \sin\theta_1 \sin\theta_2 \, dr_1 \, dr_2 \, d\theta_1 \, d\theta_2 \, d\phi_1 \, d\phi_2, \tag{13c}$$

it means that $\psi_0$ is normalized to unity. Then the first-order perturbation energy is

$$E_1 = 4Z \int \frac{1}{r_{12}} \psi^2 \, d\tau. \tag{13d}$$

This is the potential energy of two spherically symmetric electric charges for which, in the expansion

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{r_1^l}{r_2^{l+1}} P_l(\cos\theta), \tag{14}$$

$$\cos\theta = \cos\theta_1 \cos\theta_2 + \sin_1\theta \sin\theta_2 \cos(\phi_2 - \phi_1),$$

we need consider only the first term. Hence, performing the integration in the angle variables and taking double the half-space integral, the result is

$$\begin{gathered} E_1 = 2Z \int_{r_2 > r_1} e^{-r_1 - r_2} \frac{d\tau'}{r_2} = \frac{5}{4} Z, \\ d\tau' = r_1^2 r_2^2 \, dr_1 \, dr_2 . \end{gathered} \tag{15}$$

The energy and ionization energy become

$$E = -2Z^2 + \tfrac{5}{4}Z, \qquad I = Z^2 - \tfrac{5}{4}Z. \tag{16}$$

This means that He has an ionization energy

$$I = 1.5Rh = 20.4 \text{ eV}, \tag{16a}$$

which is about as much too small as the artificial Bohr–Sommerfeld orbital ionization value was too large.

### 3. *Improved Perturbation Method*

If we take the perturbing function to be

$$V_1 = \frac{1}{Z}\left\{\frac{1}{r_{12}} - \frac{5}{16}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\right\}, \tag{17}$$

leaving for the unperturbed potential energy only

$$V_0 = -k\left(\frac{1}{r_1} + \frac{1}{r_2}\right), \qquad k = 1 - \frac{5}{16}\frac{1}{Z}, \tag{17a}$$

the perturbation energy becomes zero, because of the similarly simple shape $\exp[-k(r_1 + r_2)/2]$ of the unperturbed energy

$$E = -2Z^2k^2 = -2Z^2 + \frac{5}{4}Z - \frac{25}{128}. \tag{18}$$

This improves the ionization energy with approximately $\frac{1}{5}Rh$ or nearly 2.7 eV into $I = 23.06$ eV.

This, I think, was approximately the reasoning of Kellner (1927) in his first substantial improvement of the ground state energy of He on the basis of an effective nuclear charge, until in a private discussion Max Born pointed out that any effective nuclear charge $kZ = Z - \delta$ (above $\delta = 5/16$) might be introduced, its actual value having to be fixed by a minimum requirement for the energy.

### 4. *A Simple Form of the Variational Method: the Scale Factor k*

The wave equation can be derived from, and hence is equivalent to, the variational principle

$$\delta I = 0, \qquad I = \int \psi^* H \psi \, d\tau, \tag{19}$$

with the restriction

$$N = \int \psi^* \psi \, d\tau = 1. \tag{19a}$$

Alternatively, the variation $\delta\psi$ may be unrestricted and the variational principle be replaced by

$$\delta I - E \, \delta N = 0, \tag{19b}$$

or, finally, the energy may be defined as a stationary value of its mean or expectation value,

$$E = I/N, \tag{19c}$$

with the same free variation $\delta\psi$ of $\psi$.

Again we try a new transformation of the wave equation, choosing for independent variables

$$\mathbf{r}' = k\mathbf{r}, \tag{20}$$

i.e., changing again the unit of length by a scale parameter $k$. In such coordinates the two-electron wave equation reads

$$\{k^2 T + kV + kV'/Z\}\psi = (E/4Z^2)\psi, \tag{20a}$$

$$T = -\nabla_{12}^2 = -\nabla_1^2 - \nabla_2^2, \qquad V = -\left(\frac{1}{r_1} + \frac{1}{r_2}\right), \qquad V' = \frac{1}{r_{12}}, \tag{20b}$$

where, for simplicity, the primed coordinates have again been replaced by unprimed letters. The expectation energy value for real $\psi$ is now given by

$$(E/4Z^2)N = -k(L - L'/Z) + k^2 M,$$

$$N = \int \psi^2 \, d\tau, \qquad L = \int \left(\frac{1}{r_1} + \frac{1}{r_2}\right)\psi^2 \, d\tau, \qquad L' = \int \frac{1}{r_{12}} \psi^2 \, d\tau, \tag{21}$$

$$M = -\int \psi(\nabla_1^2 + \nabla_2^2)\psi \, d\tau = \int \{(\nabla_1\psi)^2 + (\nabla_2\psi)^2\} \, d\tau.$$

With the former wave function (13b), now expressed in the new coordinates, we have

$$N = 1, \qquad L = 1, \qquad L' = \frac{5}{16}, \qquad M = \frac{1}{2}. \tag{21a}$$

Minimizing the energy with respect to $k$ we have

$$E = -2Z^2k^2, \qquad k = 1 - \frac{5}{16}\frac{1}{Z}, \tag{21b}$$

giving exactly the already discussed energy value from the improved perturbation method of Eq. (18).

### 5. *The Virial Theorem*

The scaling method is one of highest general interest. Consider any system of charged particles interacting by Coulomb forces. If in a certain system its Hamiltonian is

$$H = T + V \tag{22}$$

and its expectation energy

$$E = M - L, \tag{22a}$$

where $T$ and $V$ are kinetic and potential energy operators and

$$M = \int \psi T \psi \, d\tau, \qquad L = -\int \psi V \psi \, d\tau, \qquad \text{with} \qquad \int \psi^2 \, d\tau = 1, \tag{22b}$$

are kinetic and potential expectation values, respectively. The corresponding result in the scaled system is

$$E = k^2 M - kL. \tag{22c}$$

If $\psi$ in the first system is the true wave function, then we have energy minimum at $k = 1$. On the other hand, from the minimum condition, $k = L/2M$, and the negative potential energy is numerically twice the kinetic energy. Not only for energy calculations but also for other purposes it is highly important to have the virial theorem fulfilled in this way.

## C. Para and Ortho States of Two-Electron Systems

### 1. *Symmetry Properties of Wave Functions*

Consider the many-electron atomic Hamiltonian

$$H = T + V + V', \tag{23}$$

$$T = \sum_{i=1}^{N} \frac{1}{2m_0} \mathbf{p}_i^2, \tag{23a}$$

$$V = -\sum_i \frac{Ze^2}{r_i}, \tag{23b}$$

$$V' = \sum_{i<k=1}^{N} \frac{e^2}{r_{ik}}, \tag{23c}$$

and its wave equation

$$H\psi = E\psi. \tag{24}$$

The Hamiltonian is symmetric in the electron coordinates and moments. Hence, introducing the permutation operator $P_{ik}$, meaning the interchange of variables $i$ and $k$,

$$P_{ik}H = H. \tag{24a}$$

Also

$$P_{ik}(H\psi) = (P_{ik}H)(P_{ik}\psi) = H(P_{ik}\psi). \tag{24b}$$

Hence, multiplying Eq. (24) by $P_{ik}$, we have

$$H(P_{ik}\psi) = E(P_{ik}\psi), \tag{25}$$

and $P_{ik}\psi$ is a solution of Eq. (24), belonging to the same energy value $E$ as $\psi$ itself.

Since $P_{ik}^2 = 1$, the eigenvalues of $P_{ik}$ are

$$P_{ik} = \pm 1. \tag{25a}$$

From Eq. (24b) it follows that $P_{ik}$ commutes with $H$ and hence is a constant of the motion. Its quantized values require either symmetric or antisymmetric wave functions with respect to the variables $i$ and $k$.

The permutation operators are not mutually commuting if one of the indices are common, as seen from

$$\begin{aligned} P_{12}P_{23}\psi(1, 2, 3) &= \psi(2, 3, 1), \\ P_{23}P_{12}\psi(1, 2, 3) &= \psi(3, 1, 2), \end{aligned} \tag{26}$$

the second representing cyclic and the first anticyclic permutation. Hence, in general permutation, operators cannot be quantized simultaneously. However, since $N!$ permutations are possible, the number of wave functions of different symmetry character is $N!$

For spatial wave functions, not all these types of symmetry are allowed. There will be one entirely antisymmetric, which is always allowed, and there will be one entirely symmetric, which is not allowed except in the case of $N = 2$.

### 2. *Restrictions Due to the Pauli Principle*

The Pauli principle states that no two or more electrons are allowed in the same state of quantization. This statement rests on the inadequate conception of single electronic states from which a wave function can be built up,

$$\psi = \psi_{n_1}(1)\psi_{n_2}(2) \cdots \psi_{n_N}(N), \tag{27}$$

the $n_i$ representing a full set of quantum numbers for the system.

The antisymmetric form, as produced from this function by permutations and linear combination, is

$$\Psi_a = \begin{vmatrix} \Psi_{n_1}(1)\Psi_{n_1}(2) \cdots \Psi_{n_1}(N) \\ \Psi_{n_2}(1)\Psi_{n_2}(2) \cdots \Psi_{n_2}(N) \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots \end{vmatrix} \tag{28}$$

Hence, if any two $n_i$ are identical the function vanishes, so they are all bound to be mutually different. The general form of the function is, however, not that of Eq. (28) but

$$\Psi_a = \psi(\overbrace{1, 2, \ldots N}), \tag{28a}$$

the brace denoting antisymmetry with respect to particle coordinates.

### 3. *Multielectron Spin Functions*

What breaks the requirement of full antisymmetry of spatial wave functions is the existence of electron spin, which may be represented by certain types of spin functions entering the total wave function. If single-electron spin functions are denoted by $\alpha(i)$, $\beta(i)$, it is convenient to write

$$\begin{aligned} A(1, 2, \dots m) &= \alpha(1)\alpha(2) \cdots \alpha(m), \\ B(m+1, \dots N) &= \beta(m+1) \cdots \beta(N) \end{aligned} \tag{29}$$

for composite functions of electron spin with the same spin orientation. The spin spinors are defined by

$$\sigma_z \alpha = \alpha, \qquad \sigma_z \beta = -\beta. \tag{29a}$$

Denoting the total electron spin by

$$\mathbf{S} = \boldsymbol{\sigma}_1 + \cdots + \boldsymbol{\sigma}_N, \tag{29b}$$

we have

$$S_z AB = (2m - N)AB. \tag{29c}$$

There is a high degree of degeneration present with respect to given quantized values, namely, all those functions arising from permutation between the positive and the negative group. However, these spin functions are all mutually orthogonal in the general quantum mechanical sense that $\alpha^2 = 1$, $\beta^2 = 1$, $\alpha\beta = 0$. Therefore, if we write

$$\Psi(\overbrace{1, \dots m}, \overbrace{m+1, \dots N}) = AB\psi(\overbrace{1, \dots m}, \overbrace{m+1, \dots N}) \tag{30}$$

as a part of the total wave function, $A$ and $B$ being the symmetric functions of Eq. (29), the $\psi$ function is bound to obey separately the nonrelativistic Schrödinger equation in which all spin interactions originating from relativistic theory have been omitted.

Hence, in nonrelativistic wave mechanics we always have to deal with wave functions which are antisymmetric within two definite groups of electrons, which may be characterized in such a way that all electrons within either group have positive or negative spin, respectively.

### 4. *Multiplet Structure of Spin and Spatial Wave Functions*

The spin function $A(1, 2, \dots N)$ belongs to the eigenvalues of total spin

$$\mathbf{S}^2 = N(N+2), \qquad S_z = N. \tag{31}$$

There are $N$ functions more belonging to the same total spin with $S_z$ ranging from $N-2$ to $-N$ by steps of two. They form multiplets of the order $N+1$ and are all symmetric, the second, for instance, obtainable by total symmetrization of $A(1, 2, \dots N-1)\beta(N)$.

We now should be aware of the existence of zero spin functions like

$$C(1,2)=\begin{vmatrix}\alpha(1) & \alpha(2)\\ \beta(1) & \beta(2)\end{vmatrix}. \tag{32}$$

Using the equation

$$\mathbf{S}^2=(S_x-iS_y)(S_x+iS_y)+S_z^2+2S_z \tag{32a}$$

in noting that $S_zC=0$ and

$$(S_x+iS_y)C=\begin{vmatrix}0 & 0\\ \beta(1) & \beta(2)\end{vmatrix}+2\begin{vmatrix}\alpha(1) & \alpha(2)\\ \alpha(1) & \alpha(2)\end{vmatrix}=0, \tag{32b}$$

the statement $\mathbf{S}^2C=0$ is proved.

Hence for $N$ electrons there is a spin function $C(1,2)A(3,\ldots N)$, antisymmetric in 1 and 2 and symmetric in all remaining electrons, having the spin values $\mathbf{S}^2=(N-2)N$, $S_z=N-2$. Together with other functions with $S_z$ ranging from $N-4$ to $-(N-2)$ it forms a $N-1$ multiplet. For $S_z=-(N-2)$ the function reads $C(1,2)B(3,\ldots N)$, and any of the functions have the general form

$$C(1,2)D(\overline{3,\ldots N}), \tag{32c}$$

the bar denoting symmetry in spin coordinates as obtained by symmetrization of any product of $\alpha$ and $\beta$ spinors.

For the highest multiplet, Eq. (31), the Schrödinger wave function is entirely antisymmetric and hence represents a highly excited state, usually of minor interest. In the next multiplet a symmetry in two electrons—representing what is called an electron pair—is allowed in the basic form

$$\psi=\psi(\overline{1,2},3,\ldots N). \tag{33}$$

Here two electrons are admitted in the same spatial quantum state, which means a lower degree of exitation and a lower total energy, i.e., a stronger binding as clearly effected by the electron pair, and this is the key to the understanding of chemical bonds by paired electrons.

However, writing the corresponding total wave functions as

$$\{\beta(1)A(2,\ldots N)-\beta(2)A(1,3,\ldots N)\}\psi(\overline{1,2},3,\ldots N) \tag{33a}$$

and inspecting the first product function, it is seen that, if we choose 1 to have negative and $2,\ldots N$ to have positive spin, our $\psi(1,2,3,\ldots N)$ must be antisymmetrized in the whole group $2,\ldots N$ to be accepted as a spatial wave function.

This means that electron 1 of negative spin is not paired with another definite electron, say 2, but only that it is paired with one of the electrons of positive spin.

In the case of even $N$, the lowest energy is obtained by pairing all electrons using the spin function $C(1,2)C(3,4)\cdots C(N-1,N)$ and correspondingly the spatial wave function

$$\psi = \psi(\overline{1,2}, \overline{3,4}, \ldots \overline{N-1,N}). \tag{33b}$$

Going back to the former conception of positive spin for the group $1, 3, \ldots N-1$ and negative spin for the other group, we shall have to antisymmetrize Eq. (33b) within each group before allowing it as an accepted solution of the wave equation. This possible symmetry, as well as all others we have mentioned, is forced upon the solutions by the Schrödinger wave equation itself, but some types of solutions like $\psi(\overline{1,2,\ldots N})$ of the highest symmetry are excluded by the Pauli principle. The highest admissible symmetry comes from Eq. (33b) and represents among others the ground state of the system.

### 5. *Application to the He Atom and He-Like Ions*

The preceding full theory is of course not strictly needed for the understanding of He atom and other two-electron configurations. The Schrödinger wave equation itself has, in this case, only two types of solutions, the symmetric and the antisymmetric ones (Heisenberg, 1926), $\psi(\overline{1,2})$ and $\psi(1,2)$, respectively. By means of the spin functions

$$\begin{gathered} C(1,2) = \alpha(1)\beta(2) - \beta(1)\alpha(2), \\ A(1,2) = \alpha(1)\alpha(2), \qquad D(\overline{1,2}) = \alpha(1)\beta(2) + \beta(1)\alpha(2), \\ B(1,2) = \beta(1)\beta(2), \end{gathered} \tag{34}$$

they are, however, most easily included in the general theory as a singlet $\psi(\overline{1,2})C(1,2)$, symmetric in space coordinates, and a corresponding triplet, antisymmetric in space. These are the famous *para* and *ortho* states of the He atom which at the era of the discovery of rare gases made the impression of two elements rather than one.

It is of course one of the greatest achievements of quantum mechanics that this peculiarity could be so easily explained by means of the conception of exchange integrals and symmetry properties and hence just at the decisive point remove the former impossibility of handling one- and many-electron systems by the same general theory.

A first-order approximation to the solution of the two-electron problem is afforded by simple perturbation theory, using solutions of the one-electron equations

$$\left\{\frac{\hbar^2}{2m_0} + \nabla_i^2 + E_{n_i} + \frac{Ze^2}{r_i}\right\}\psi_{n_i}(i) = 0, \qquad i = 1, 2. \tag{35}$$

In the zero-order approximation the *para* and *ortho* states can then be expressed by

$$\psi_{s,a} = 2^{-1/2}\{\psi_{n_1}(1)\psi_{n_2}(2) \pm \psi_{n_1}(2)\psi_{n_2}(1)\}, \tag{35a}$$

respectively, the one-electron wave functions being thought of as normalized to unity and in addition being mutually orthogonal if $n_1 \neq n_2$. In the case of $n_1 = n_2$ the *ortho* state drops out as nonexistent and the *para* state function is taken to be $\psi_s = \psi_n(1)\psi_n(2)$. In comparison to $n = 1$, the ground state, the doubly excited states for $n > 1$ are, of course, of secondary importance.

According to perturbation theory we find

$$E = E^0 + E', \tag{36}$$

$$E_0 = E_{n_1} + E_{n_2} = -Z^2Rh\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right), \tag{36a}$$

$$E'_{s,a} = \int \frac{e^2}{r_{12}}\,\psi_{s,a}^2\,d\tau = I_1 \pm I_2, \tag{36b}$$

$$I_1 = \int \frac{e^2}{r_{12}}\,\psi_{n_1}^2(1)\psi_{n_2}^2(2)\,d\tau, \qquad I_2 = \int \frac{e^2}{r_{12}}\,\psi_{n_1}(1)\psi_{n_2}(1)\psi_{n_1}(2)\psi_{n_2}(2)\,d\tau, \tag{36c}$$

where $I_1$ and $I_2$ are the well-known Coulomb and exchange integrals. As a general rule the energy of an *ortho* state, hence, is below that of the corresponding *para* state. Nevertheless, the lowest states are *para* states because of the elimination of *ortho* states for equal quantum numbers.

The main features of the He atomic states and the He spectral lines were first explained by Heisenberg (1926), using for either of the electrons the continuous unperturbed potential

$$\begin{aligned} V_i(r_i) &= -(Z-1)/r, \qquad && r > r_0 \\ &= -Z/r + 1/r_0, \qquad && r < r_0. \end{aligned} \tag{37}$$

The corresponding perturbing potential then becomes

$$\begin{aligned} V' &= \frac{1}{r_{12}} - \frac{1}{r_1} - \frac{1}{r_2}, && r_1, r_2 > r_0, \\ &= \frac{1}{r_{12}} - \frac{2}{r_0}, && r_1, r_2 < r_0, \\ &= \frac{1}{r_{12}} - \frac{1}{r_0} - \frac{1}{r_2}, && r_1 < r_0 < r_2. \end{aligned} \tag{37a}$$

By this procedure the calculated spectral terms come much nearer to the true ones than by the preceding simpler method, especially for singly excited states with energies $E = -(Z-1)^2 Rh/(n-\delta)^2$ for the outer electron with reasonable values for the Rydberg corrections $\delta$.

Another set of unperturbed wave functions has been used with considerable success by Hylleraas (1932), namely, for the outer electron solutions of the one-electron wave equation with potential function (Hylleraas, 1930b,c)

$$V(r) = -(Z-1)/r + \varepsilon(1-\varepsilon)/r^2. \tag{38}$$

## III. Advanced Methods in the Theory of Two-Electron Systems

While still in the first years of wave mechanics, Hartree (1927) invented his famous method of self-consistent field, which was later generalized by Fock (1930) to comprise exchange forces also. The reason for not entering this field in the present report is that its numerous applications have made it so familiar to quantum chemists that the short and primitive description which could be given here would be of very limited value.

### A. The Two-Electron Problem in Three Independent Variables

#### 1. *Elimination of Coordinates in the Ground State Problem*

Besides the energy there will be a certain number of dynamical variables, in principle corresponding to the degree of freedom of the atomic system, which are constants of the motion and hence quantizable quantities. For two electrons there are six dynamical variables, of which, besides the energy only two are easily handled, the square total angular momentum and a single of its components. The quantization of total angular momentum gives rise to the classification of energy states in the well-known way as $S$, $P$, $D$ states, etc., corresponding to the azimuthal quantum number $L = 0, 1, 2, \ldots$.

It was early observed (Hylleraas, 1928) that the ground state problem could be more easily handled by eliminating three angular coordinates, keeping, besides the nuclear distances $r_1$ and $r_2$ of the two electrons, only the angle $\theta_{12}$ or $\theta$ between the vectors $\mathrm{r}_1$ and $\mathrm{r}_2$. This means that the wave function depends only on the shape of the electron–nucleus triangle and not on its orientation in space. This is an entirely different conception than that of Bohr's theory, both for single- and many-electron systems.

This means, in fact, that the ground state is an $S$ state with zero angular momentum, as is easily seen in the following way. Consider total angular momentum operator

$$\mathbf{m} = \mathbf{m}_1 + \mathbf{m}_2, \qquad \mathbf{m}_i = \mathbf{r}_i \times \mathbf{p}_i. \tag{39}$$

The $\mathbf{m}_i$, $i = 1, 2$, commute with the $\mathbf{p}_i^2$ of the Hamiltonian, hence also with $\mathbf{r}_i^2$ and $1/r_i$ of the nuclear Coulomb energy. The component $m_z$ is most easily seen to commute with $\mathbf{r}_1\mathbf{r}_2 = x_1x_2 + y_1y_2 + z_1z_2$. Hence it commutes with $\mathbf{r}_{12}^2$ and with $1/r_{12}$. Since

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1r_2 \cos\theta, \tag{40}$$

$S$-state functions may be written in the alternative forms

$$\psi = \psi(r_1, r_2, \theta), \tag{40a}$$

$$\psi = \psi(r_1, r_2, r_{12}). \tag{40b}$$

2. *Properties of P and D States*

If angular momenta for the two electrons are quantized separately only in a formal way (Breit, 1930), we have for $P$ states the angular functions $\cos\theta_1$ and $\cos\theta_2$, if in addition the total $z$ component $m_z = 0$. For the $D$ states we have the corresponding functions $P_2(\cos\theta_1)$ and $P_2(\cos\theta_2)$, both giving total angular momenta $\mathbf{m}^2 = L(L+1)\hbar^2$, $L = 2$, and $m_z = 0$. There is a third function, however, corresponding to what is called a $(pp)$ state which is a doubly excited state. This function is most easily found by observing that

$$\mathbf{m}^2 z_1z_2 = 2\hbar^2(2z_1z_2 - x_1x_2 - y_1z_1) = 4\hbar^2(\tfrac{3}{2}z_1z_2 - \tfrac{1}{2}\mathbf{r}_1\mathbf{r}_2) \tag{41}$$

and that $\mathbf{m}^2\mathbf{r}_1\mathbf{r}_2 = 0$. Hence the function $\frac{3}{2}z_1z_2 - \frac{1}{2}\mathbf{r}_1\mathbf{r}_2$ has the square angular momentum $L(L+1)\hbar^2$, with $L = 2$.

The general forms of $P$ and $D$ wave functions therefore are

$$\psi_P = \psi(r_1, r_2, \cos\theta)\cos\theta_2 \pm \psi(r_2, r_1, \cos\theta)\cos\theta_1, \tag{41a}$$

$$\begin{aligned}\psi_D = {} & \psi(r_1, r_2, \cos\theta)P_2(\cos\theta_2) \pm \psi(r_2, r_1, \cos\theta)P_2(\cos\theta_1) \\ & + \{\Phi(r_1, r_2, \cos\theta) \pm \Phi(r_2, r_1, \cos\theta)\}(\tfrac{3}{2}\cos\theta_1\cos\theta_2 - \tfrac{1}{2}\cos\theta).\end{aligned} \tag{41b}$$

General formulas for any angular momentum wave function are obtainable, but the few of practical interest are easily found by simple reasoning like that above.

### 3. *Application to the Ground State*

The wave equation for $S$ states now reads

$$\begin{gathered}\left\{\nabla_1^2 + \nabla_2^2 + \frac{E}{4} + \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{Z}\frac{1}{r_{12}}\right\}\psi = 0, \\ \nabla_i^2 = \frac{1}{r_i^2}\frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i} + \frac{1}{r_i^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}.\end{gathered} \tag{42}$$

An appropriate functional system to be used by the variational method (Hylleraas, 1928) appears to be

$$\psi_{n_1n_2l} = R_{n_1l}(r_1)R_{n_2l}(r_2)P_l(\cos\theta) \tag{43}$$

with symmetrical combination of the $R$ functions.

For these functions it may be tempting to use hydrogen atomic functions, i.e., solutions of the equation

$$\left\{\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2} - \frac{1}{4n^2} + \frac{1}{r}\right\}R_{nl}(r) = 0 \tag{43a}$$

with or without the scaling parameter $k$. This means that the wave function is built up from simple hydrogenic or rather He-ionic discrete functions. The resulting ground state energy is then very inaccurate, and this of course is due to the incompleteness of the functional system, which entirely disregards the eigenfunctions of the continuous energy spectrum.

This particular defect is, however, easily removed by turning to $R$ functions defined by the equations

$$\left\{\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2} - \frac{1}{4} + \frac{n}{r}\right\}R_{nl}(r) = 0. \tag{43b}$$

The point is that by this transformation the eigenvalue spectrum $-1/4n^2$ is transformed into $n = 1, 2, \ldots \infty$, and hence with corresponding eigenfunctions forming a complete set in the coordinate region $0 \leqq r \leqq \infty$.

These functions also have more suitable orthogonality properties, being mutually orthogonal when multiplied by the density function $r$, whereas the hydrogen functions need the density function $r^2$. This is of considerable importance for the evaluation of the integral $L$ of Eq. (21) and is also useful for the evaluation of the normalization integral $N$, whereas the hydrogenic functions give simple results only for $N$.

Using the functions in Eq. (43b) (Hylleraas, 1928), one obtains by the variational method a fairly well-ordered secular determinant equation with only a few elements from $N$, $L$, and $M$ outside the diagonal, whereas, of course, all $L'$ elements are different from zero. In actual calculations, however, one is met with a new disappointment, namely according to calculations by Hylleraas, the energy parameter converges toward a value about $\frac{1}{10}$ eV above the experimental energy value. Whether this is a real stop, and hence the functional system used is really incomplete in the true mathematical sense, or it only means that the convergence is extremely slow, we need not decide about. The important thing is that a true and rapid convergence can be obtained in a much simpler way.

## B. Advanced Methods for *S* States

### 1. *The $r_{12}$ or s, t, u method*

When changing from the angular coordinate $\theta$ to the metric coordinate $r_{12}$ it is seen, from the equation

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1r_2 \cos\theta, \tag{44}$$

that in eliminating $\theta$ or $\cos\theta$ in Eq. (40a) this function becomes $\psi(r_1, r_1, r_{12}^2)$ rather than $\psi(r_1, r_2, r_{12})$ as in Eq. (40b). This is an essential difference because in expanding odd powers of $r_{12}$ in terms of $P_l$ (cos $\theta$) we have, for $r_{12}$ itself,

$$r_{12} = \sum_{l=0}^{\infty} \left[\frac{r_1^{l+2}}{(2l+3)r_2^{l+1}} - \frac{r_1^l}{(2l-1)r_2^{l-1}}\right] P_l(\cos\theta), \qquad r_2 > r_1, \tag{44a}$$

i.e., an expansion which, like the expansion for $1/r_{12}$, is different in the two half-spaces $r_1 \lesseqgtr r_2$. Remembering also that the other potential terms are $1/r_1$ and $1/r_2$, and that in the unperturbed wave function there is no discrimination between odd and even powers of $r_1$ and $r_2$, it is easy to infer from both arguments that odd powers of $r_{12}$ not only are necessary to ensure completeness properties of the functional system but also must have decisive effects upon practical calculations.

Changing to the metric coordinates $r_1, r_2, r_{12}$ the potential function is simplified, i.e., needs no expansion, whereas the Laplacians become more complex. From the equation

$$\nabla_1\psi = \hat{\mathbf{r}}_1 \frac{\partial\psi}{r_1} + \hat{\mathbf{r}}_{12} \frac{\partial\psi}{\partial r_{12}}, \qquad \hat{\mathbf{r}}_1 = \mathbf{r}_1/r_1, \quad \text{etc.,} \tag{45}$$

and the corresponding one for $\nabla_2\psi$, it is found that

$$\begin{aligned}(\nabla_1\psi)^2 + (\nabla_2\psi)^2 &= \left(\frac{\partial\psi}{\partial r_1}\right)^2 + \left(\frac{\partial\psi}{\partial r_2}\right)^2 + 2\left(\frac{\partial\psi}{\partial r_{12}}\right)^2 \\ &+ \frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}} \frac{\partial\psi}{\partial r_1}\frac{\partial\psi}{\partial r_{12}} + \frac{r_2^2 + r_{12}^2 - r_1^2}{r_2 r_{12}} \frac{\partial\psi}{\partial r_2}\frac{\partial\psi}{\partial r_{12}}\end{aligned} \tag{45a}$$

and also almost as easily that

$$\begin{aligned}\nabla_1^2\psi + \nabla_2^2\psi &= \frac{\partial^2\psi}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial\psi}{\partial r_1} + \frac{\partial^2\psi}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial\psi}{\partial r_2} + 2\frac{\partial^2\psi}{\partial r_{12}^2} + \frac{4}{r_{12}}\frac{\partial\psi}{\partial r_{12}} \\ &+ \frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}} \frac{\partial^2\psi}{\partial r_1\,\partial r_{12}} + \frac{r_2^2 + r_{12}^2 - r_1^2}{r_2 r_{12}} \frac{\partial^2\psi}{\partial r_2\,\partial r_{12}}.\end{aligned} \tag{45b}$$

On comparison it is found that, in order for the following equation to be true

$$\int \{(\nabla_1\psi)^2 + (\nabla_2\psi)^2\}\, d\tau = -\int \psi(\nabla_1^2 + \nabla_2^2)\psi\, d\tau, \tag{45c}$$

the volume element to be used is

$$d\tau = r_1 r_2 r_{12}\, dr_1\, dr_2\, dr_{12} = r_1^2 r_2^2 \sin\theta\, dr_1\, dr_2\, d\theta. \tag{45d}$$

The same result is obtained by calculating directly both square gradients and Laplacians in the coordinate system $r_1$, $r_2$, $\theta$ and proves that a detailed study of the deleted angular coordinates determining the space orientation of the electron-nucleus triangle is superfluous.

Particularly for the ground state (Hylleraas, 1929) but also for the lowest *ortho* $S$ state, the following coordinates,

$$s = r_1 + r_2, \qquad t = -r_1 + r_2, \qquad u = r_{12}, \tag{46}$$

are even more appropriate than the triple $r_1$, $r_2$, $r_{12}$. The volume element becomes

$$dt = \tfrac{1}{8}u(s^2 - t^2)\, ds\, dt\, du, \tag{46a}$$

and from Eq. (45a) one fairly easily obtains

$$\begin{aligned}\tfrac{1}{2}u(s^2 - t^2)\{(\nabla_1\psi)^2 + (\nabla_2\psi)^2\} &= u(s^2 - t^2)\left\{\left(\frac{\partial\psi}{\partial s}\right)^2 + \left(\frac{\partial\psi}{\partial t}\right)^2 + \left(\frac{\partial\psi}{\partial u}\right)^2\right\} \\ &\quad + 2s(u^2 - t^2)\frac{\partial\psi}{\partial s}\frac{\partial\psi}{\partial u} + 2t(s^2 - u^2)\frac{\partial\psi}{\partial t}\frac{\partial\psi}{\partial u}.\end{aligned} \tag{46b}$$

For the evaluation of the kinetic integral $M$ this square gradient formula is usually to be preferred over the Laplacian formula, which is therefore omitted. Another reason for using (46b) is that, on writing

$$\psi = \psi_0\Psi, \qquad \psi_0 = e^{-\frac{1}{2}s}, \tag{47}$$

we obtain the very useful formula

$$M = L - 2N + M', \qquad M' = \int e^{-s}\{(\nabla_1\Psi)^2 + (\nabla_2\Psi)^2\}\, d\tau, \tag{47a}$$

if $N$ is redefined as

$$N = \tfrac{1}{4}\int \psi^2\, d\tau, \tag{47b}$$

and hence

$$\begin{gathered}N = \tfrac{1}{4}\int e^{-s}\,\Psi^2\, d\tau, \qquad L = \int e^{-s}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\Psi^2\, d\tau, \\ L' = \int e^{-s}\frac{1}{r_{12}}\,\Psi^2\, d\tau.\end{gathered} \tag{47c}$$

This is because we have the general formula

$$\begin{aligned}\int \{(\nabla_1\psi_0\Psi)^2 + (\nabla_2\psi_0\Psi)^2\}\, d\tau &= \int \Psi_0^2\{(\nabla_1\Psi)^2 + (\nabla_2\Psi)^2\}\, d\tau \\ &\quad - \int \Psi^2\psi_0(\nabla_1^2 + \nabla_2^2)\psi_0\, d\tau.\end{aligned} \tag{47d}$$

The energy formula with a scale factor $k$ now becomes

$$NE = -k(L - L'/Z) + k^2M, \tag{48}$$

leading by the variational method to the secular determinant equation

$$|k(L - L'/Z) - k^2M + NE| = 0 \tag{48a}$$

with the understanding that the elements of the determinant are the coefficients of the quadratic forms in Eq. (48) if the wave function is expanded in linear terms

$$\psi = \sum_n c_n\psi_n \tag{48b}$$

or more definitely

$$\psi = e^{-s/2} \sum_{nlm} c_{nlm}\Psi_{nlm}, \qquad \Psi_{nlm} = s^n t^l u^m. \tag{49}$$

The integrals of Eqs. (47), whether in square or product form with respect to different $\psi$ are easily obtained and can be given in explicit form (Hylleraas, 1930d).

Using only the three terms in $\Psi$, namely 1, $u$, $t^2$, the result is

$$E = -1.45122 \tag{49a}$$

as compared with recent very accurate calculations and also with the observed value

$$E = -1.45186. \tag{49b}$$

The discrepancy hence is

$$0.00064.4Rh \simeq 0.035 \text{ eV}, \tag{49c}$$

and adding the terms $s$, $s^2$, $u^2$ it is reduced to

$$0.00024.4Rh \simeq 0.013 \text{ eV}. \tag{49d}$$

Hence, in comparison with the $(r_1, r_2, \theta)$ method with about double the number of terms as expressed in the coordinates $r_1$, $r_2$, $\theta$, or $r_1$, $r_2$, $r_{12}^2$, the discrepancy has been reduced by a factor of 1/10 (Hylleraas, 1929; Chandrasekhar *et al.*, 1953, 1955; Hart and Herzberg, 1957).

### 2. *The Kinoshita Method*

Some doubt may be cast upon even the $s$, $t$, $u$ method with respect to its completeness properties. This is because a formal solution of the wave equation cannot be expressed in terms of positive powers of $s$, $t$, $u$. A clarification of this point has been given by Fock (1954) and Hylleraas

(1960) in studying formal solutions, and also independently by Kinoshita (1957) using terms of the general type

$$\Psi_{ik} = s^i\left(\frac{u}{s}\right)^k\left(\frac{t}{u}\right)^l = s^{i-k}u^{k-l}t^l \tag{50}$$

with positive $i$ and $k$ and even positive $l$, i.e., with negative powers of $s$ and $u$ permitted.

In the evaluation of necessary integrals there is no essential difference from the conventional $s$, $t$, $u$ method, therefore, the same explicit formulas can be applied.

Kinoshita's method has given extremely accurate energy values in the 39th and 80th approximation (Kinoshita, 1957, 1959), and he has also proved the ability of his functional system to express formal solutions of the wave equation.

### 3. *The Pekeris Method*

A very exciting and powerful method of handling the lowest $S$ states was invented some years ago by Pekeris (1958, 1959, 1962), using perimetric coordinates

$$\begin{aligned} x &= \tfrac{1}{2}(r_{12} + r_1 - r_2) = \tfrac{1}{2}(u - t),\\ y &= \tfrac{1}{2}(r_{12} - r_1 + r_2) = \tfrac{1}{2}(u + t),\\ z &= r_1 + r_2 - r_{12} = s - u. \end{aligned} \tag{51}$$

From the inverse formulas

$$r_1 = x + \tfrac{1}{2}z, \qquad r_2 = y + \tfrac{1}{2}z, \qquad r_{12} = x + y, \tag{51a}$$

$$s = x + y + z, \qquad u = x + y, \qquad t = y - x \tag{51b}$$

and the functional determinant

$$\frac{\partial(r_1, r_2, r_{12})}{\partial(x, y, z)} = \begin{vmatrix} 1 & 0 & \frac{1}{2} \\ 0 & 1 & \frac{1}{2} \\ 1 & 1 & 0 \end{vmatrix} = -1, \tag{51c}$$

we find the volume element

$$d\tau = (x + \tfrac{1}{2}z)(y + \tfrac{1}{2}z)(x + y)\, dx\, dy\, dz \tag{51d}$$

with common domain of integration $0 \leqq x, y, z \leqq \infty$ for all three coordinates.

The square gradient sum in these coordinates is given by

$$\begin{aligned}(x+\tfrac{1}{2}z)(y+\tfrac{1}{2}z)(x+y)\{(\nabla_1\psi)^2+(\nabla_2\psi)^2\}\\ &= \{2(x^2+y^2)+(x+y)z\}z\left(\frac{\partial\psi}{\partial z}\right)^2\\ &\quad+\{(x+y)(y+z)+\tfrac{1}{2}z^2\}x\left(\frac{\partial\psi}{\partial x}\right)^2\\ &\quad+\{(x+y)(x+z)+\tfrac{1}{2}z^2\}y\left(\frac{\partial\psi}{\partial y}\right)^2\\ &\quad-(2x+z)xz\frac{\partial\psi}{\partial x}\frac{\partial\psi}{\partial z}-(2y+z)yz\frac{\partial\psi}{\partial y}\frac{\partial\psi}{\partial z}. \qquad (52)\end{aligned}$$

The point is that, in this system, using for trial functions products of simple Laguerre polynomials

$$\Psi_{lmn}=L_l(x)L_m(y)L_n(z), \qquad (53)$$

the matrix elements will all be zero outside a certain range consisting of the main diagonal and a number of neighboring diagonals of the secular determinant. Moreover the Laguerre functional system $e^{-\frac{1}{2}x}L_n(x)$ is not only an orthogonal system but also normalized to unity.

In the $L$ and $L'$ integrals the integrands will be products of Laguerre functions multiplied by $(x+y+z)(x+y)$ and $(x+\frac{1}{2}z)(y+\frac{1}{2}z)$, respectively; the distribution of nonzero matrix elements outside the diagonal can be found fairly easily using the general recurrence formula,

$$xL_n=-(n+1)L_{n+1}+(2n+1)L_n-nL_{n-1}. \qquad (54)$$

The factors above contain the separate terms $x^2+y^2$, $xy$, $(x+y)z$, and $z^2$ which for each function in Eq. (53) gives the maximum number eighteen nonzero combination integrals or nine on either side of the diagonal by a well-ordered arrangement of the functions. Of these only seven are common, the remaining two both belonging to either $L$ or $L'$.

In $M'$ we have the same number of nonzero elements, i.e., the same eighteen combinations or nine on either side. In the $N$ integral however the number rises to forty-two or twenty-one on either side.

To avoid the latter complication, Pekeris chose a bound value of the scale factor

$$k=\varepsilon=\sqrt{-E/2}, \qquad (55)$$

the energy parameter. On dividing the equations by $k = \varepsilon$ his secular determinant equation may be written formally as

$$|L - L'/Z - \varepsilon(L + M')| = 0. \tag{55a}$$

In the long run, the number of nonzero matrix elements grows only linearly with the number of functional terms, and this allows the use of an exceptionally large number of terms. In Pekeris's second publication (1959) this number is over one thousand, and the numerical values obtained are very accurate.

On the other hand the convergence is comparatively slow, probably due partly to the bound $k$ and partly to the use of terms equivalent to the conventional $s, t, u$ method.

## 4. *Other Possible Ways of Orthogonalization*

The author has repeatedly tried to construct some useful orthogonalization of $s, t, u$ terms, but the degree of simplification has been too small to be of any use in the region of twenty- to thirty-term functions. Still the possibilities may be briefly mentioned. Using the coordinate triple

$$s, \qquad \eta = \frac{u}{s}, \qquad \xi = \frac{t}{u}, \tag{56}$$

one might try to express the wave function in terms of Laguerre functions of $s$ and hypergeometric functions of $\xi$ and $\eta$.

Another way would be to use

$$z = s - u, \qquad u, \qquad \xi = \frac{t}{u}, \tag{57}$$

which in reality means the same as using $z, u, t$, except with independent regions for $z$ and $u$, $0 \leqq z, u \leqq \infty$. The volume element becomes

$$d\tau = \tfrac{1}{8}\{z(z + 2u) + u^2 - t^2\}u\, dz\, du\, dt \tag{58}$$

and the gradient square sum is given by

$$\begin{aligned}
\tfrac{1}{2}\{z(z + 2u) + u^2 - t^2\}\{(\nabla_1\psi)^2 + (\nabla_2\psi)^2\}& \\
= 2z\{(z + u)u + t^2\}\frac{\partial\psi}{\partial z}\left(\frac{\partial\psi}{\partial z} - \frac{\partial\psi}{\partial u}\right)& \\
+ \{z(z + 2u) + u^2 - t^2\}\left\{\left(\frac{\partial\psi}{\partial u}\right)^2 + \left(\frac{\partial\psi}{\partial t}\right)^2\right\}& \\
+ 2tz(z + 2u)\frac{\partial\psi}{\partial t}\left(\frac{\partial\psi}{\partial u} - \frac{\partial\psi}{\partial z}\right).&
\end{aligned} \tag{58a}$$

The functional system to be used,

$$\Psi_{lmn} = P_l\left(\frac{t}{u}\right)u^l L^{2l+1}_{2l+1+m}(u)L_n(z), \tag{58b}$$

is in principle related to the Pekeris terms in Eq. (53) in a simple way. However, in practice the expansion coefficients are fairly complex, so that the number of nonzero matrix elements is not easily found in that indirect way.

The number can however be estimated directly, in a manner similar to the Pekeris method. The result is that for $L$ only five, while for $L'$ eleven, neighboring diagonals on either side are needed. The corresponding number for $N$ is eighteen.

As to the number of nondiagonal elements this alternative procedure is almost at the point of competing with Pekeris's method, whether with or without a bound $k$. In simplicity, however, it cannot compete. If, on the other hand, one tries to improve the convergence for instance by means of different exponentials in the $z$ and $u$ functions and in addition leaves $k$ free, the improved covergence probably will not pay for the relatively greater number and complication of matrix elements. In the long run, probably only the Kinoshita or some similar method is able to produce a sensibly better convergence.

## C. Some Numerical Examples

### 1. *The He Atom*

According to the calculations by Pekeris, the most accurate thus far, the nonrelativistic ground state energy for He—without mass polarization —is

$$\begin{aligned} E &= -2.9037\,24376 \text{ a.u.} \\ &= -5.8074\,48752Rh^{1} \\ &= -1.451862.4Rh. \end{aligned} \tag{59}$$

The simple perturbation method gave

$$E = -1.375 \tag{59a}$$

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[1] The value $-5.80749$ given by Hylleraas (1930d), which is too low, is due to a mistake in a prepared matrix element (row 2, column 7) in his system, which should be $-0.07557$ instead of $-0.09557$.

in $Z^2Rh$ units, and the scale factor method with $k = 1—5/16Z$ gave

$$E = -1.423828. \tag{59b}$$

It may be of some interest to study the effect of some simple improved functions which may be thought of as resulting from the point of view of some physical considerations. For instance the partly normalized function

$$\Psi = (1-\alpha)^{5/2} e^{\frac{1}{2}\alpha u} \tag{60}$$

is likely to express the greater probability of the electrons to keep apart rather than to come close to each other. It will represent a correlation of the motion of the electrons somewhere between the entirely noncorrelated case of $\psi = 1$ and the excessive correlation of opposite position of the electrons on either side of the nucleus as was tried in the Bohr–Sommerfeld picture. In suitable normalization

$$d\tau = r_1^2 r_2^2 \, dr_1 \, dr_2 \, \tfrac{1}{2} \sin \theta \, d\theta, \tag{60a}$$

the result is

$$\begin{aligned} 4N &= 2 + 1.5(1-\alpha) + 0.5(1-\alpha)^2, \\ L &= 3(1-\alpha) + (1-\alpha)^2, \\ M &= L - 2(1-\alpha^2)N, \\ L' &= 0.5(1-\alpha) + 0.5(1-\alpha)^2 + 0.25(1-\alpha)^3. \end{aligned} \tag{60b}$$

Very simple calculations for $\alpha = 0$, 0.1, and 0.2 fix the minimum approximately to $\alpha = 0.14$, for which

$$\begin{gathered} 4N = 3.6598, \qquad L = 3.3196, \\ M = 1.525566, \qquad \tfrac{1}{2}L' = 0.479407, \\ E = -1.444800. \end{gathered} \tag{60c}$$

Another point of view is that, apart from exchange of their roles, one of the electrons will be outside the other and hence partly shielded from the nuclear attraction. This is to some extent expressed by the function

$$\Psi = (1-\beta^2)^{\frac{1}{2}} \cosh \tfrac{1}{2}\beta t, \tag{61}$$

giving

$$\begin{aligned} 4N &= 2 + 2(1-\beta^2)^3 = L, \\ M &= 2N + \beta^2\{1 - (1-\beta^2)^3\}, \\ L' &= \tfrac{1}{2}(1-\beta^2) + \tfrac{1}{8}(1-\beta^2)^2 + \tfrac{5}{8}(1-\beta^2)^3, \end{aligned} \tag{61a}$$

with $\beta^2$ rather than $\beta$ as variational parameter. For $\beta^2 = 0.1$ we readily find

$$\begin{gathered} 4N = L + 3.458, \qquad M = 1.7561, \qquad \tfrac{1}{2}L' = 0.503437, \\ E = -1.437515, \end{gathered} \tag{61b}$$

which is near to the minimum $E = -1.4377$ at $\beta^2 = 0.09$. A combination of the two methods

$$\Psi = e^{\frac{1}{2}\alpha u} \cosh \tfrac{1}{2}\beta t \tag{62}$$

gives

$$E = -1.4497. \tag{62a}$$

This we should now compare with the results from the simple three-term function

$$\Psi = 1 + c_1 u + c_2 t^2 \tag{63}$$

with the much more convenient linear variational parameters. In this case we have the formulas

$$\begin{array}{llll} N = 4 + 2\cdot 17.5c_1 + 2\cdot 24c_2 & & L = \phantom{0.62}4 + 2\cdot 15c_1 + 2\cdot 24c_2 & \\ \quad + 96c_1^2 \quad + 2\cdot 154c_1c_2 & & \qquad\qquad + 72c_1^2 \quad + 2\cdot 140c_1c_2 & \\ \qquad\qquad + 576c_2^2, & & \qquad\qquad\qquad\quad + 576c_2^2, & \\ M = 2 + 2\cdot 6.25c_1 + 2\cdot 12c_2 & & \tfrac{1}{2}L' = 0.625 + 2\cdot 2c_1 \quad + 2\cdot 2.25c_2 & (63a) \\ \quad + 32c_1^2 \quad + 2\cdot 73c_1c_2 & & \qquad\qquad + 8\cdot 75c_1^2 + 2\cdot 12c_1c_2 & \\ \qquad\qquad + 480c_2^2, & & \qquad\qquad\qquad\quad + 39c_2^2, & \end{array}$$

which as above have to be used in connection with the scale parameter

$$k = \frac{L - L'/Z}{2M} \qquad \text{from which} \qquad E = -\frac{(L - L'/Z)^2}{4MN} \tag{63b}$$

In varying only one parameter the result is

$$c_1 = 0.1, \qquad E = -1.4456, \tag{63c}$$

$$c_2 = 0.012, \qquad E = -1.4384, \tag{63d}$$

and varying both of them

$$c_1 = 0.08, \qquad c_2 = 0.01, \qquad E = -1.4512. \tag{63e}$$

In all cases in Eqs. (63c,d, and e) the results are sensibly ahead of the corresponding Eqs. (60c), (61b), and (62a). This demonstrates clearly the somewhat surprising superiority of the less intuitive though more easily applicable method of linear parameters.

Adding three more terms, $s$, $s^2$, $u^2$, as was first done by Hylleraas (1929), the result was

$$E = -1.45162 \tag{63f}$$

with a discrepancy of only $0.97 \times 10^{-3} Rh = 0.013$ eV, which is ten times smaller than that afforded by the $(r_1, r_2, \theta)$ system in the highest approximation.

### 2. *The Negative Hydrogen Ion*

Putting $Z = 1$ for the ground state of $H^-$ (Bethe, 1929; Hylleraas, 1930a) and using only one variational parameter we find

$$c_1 = 0.3, \qquad E = -1.0176, \tag{64}$$

$$c_2 = 0.06, \qquad E = -1.0238, \tag{64a}$$

with $E$ now in $Rh$ units. Both results ensure the existence of the stable $H^-$ ion. A peculiarity should be noted, however, namely that, between the terms $u$ and $t^2$, $t^2$ has now become the more prominent, in contrast to the situation for He and ions of larger $Z$. Varying both of them, a surprisingly large improvement was obtained,

$$c_1 = 0.2, \qquad c_2 = 0.05, \qquad E = -1.0506. \tag{64b}$$

An extension to six parameters (Hylleraas, 1929) gave $E = -1.05$ and to eleven parameters (Hylleraas, 1930d) gave

$$E = -1.05284. \tag{64c}$$

This result again was considerably improved by S. Chandrasekhar (1944) and particularly by Henrich (1944) to

$$E = -1.05512, \tag{64d}$$

and finally we have the Pekeris result (1959),

$$E = -1.055502. \tag{64e}$$

### 3. *The Isoionic Series $Z = 1, 2, \ldots \infty$*

The possibility of including a number of experimental results for positive ions in the theory of two-electron configurations was created by B. Edlén in his excellent works in the late twenties and following years (see various articles referred to in "Handbuch der Physik"). For the purpose of better judgment of both theoretical and experimental values, Hylleraas put up the general interpolation formula for the ground state energies

$$E = -2Z^2 + \tfrac{5}{4}Z + \varepsilon_2 + \varepsilon_3 Z^{-1} + \cdots, \tag{65}$$

where as $Z \to \infty$ the calculations are simplified, and gave (Hylleraas, 1930d)

$$\varepsilon_2 = -0.31488. \tag{65a}$$

Interpolation by means of carefully calculated energies for He and $H^-$, $Z = 2, 1$, gave the theoretical formula

$$E = -2Z^2 + \tfrac{5}{4}Z - 0.31488 + 0.01752Z^{-1} - 0.00548Z^{-2}. \tag{65b}$$

More recently it has been extended and improved by Hylleraas and Midtdal (1956, 1958), who in particular in several steps improved the constant term $\varepsilon_2$, ending up at

$$\varepsilon_2 = -0.315315. \tag{65c}$$

As we shall see later on, a great number of the coefficients $\varepsilon_n$ have been calculated directly (Scherr and Knight, 1963) and in particular even $\varepsilon_2$ could still be improved up to

$$\varepsilon_2 = -0.3153328 \tag{65d}$$

with still one or two correct decimals more.

Unfortunately the calculations are not so easily compared with experimental data for higher $Z$ values owing to the rapid growth of relativistic and related effects. For He, however, those effects are small enough to be handled safely by the present state of relativistic treatment and appear to agree excellently with the finest spectroscopic measurements. (Hart and Herzberg, 1957).

### 4. *The Hylleraas Perturbation Method*

Consider a Hamiltonian with a perturbing term $\varepsilon H'$ and write the wave equation and its solution as

$$\begin{aligned} &(H^0 - E + \varepsilon H')\psi = 0, \\ &\psi = \psi_0 + \varepsilon\psi_1 + \varepsilon^2\psi_2 + \cdots, \\ &E = E_0 + \varepsilon E_1 + \varepsilon^2 E_2 + \cdots . \end{aligned} \tag{66}$$

The following equations have to be satisfied separately (Hylleraas, 1930d):

$$\begin{aligned} (H^0 - E_0)\psi_0 &= 0, \\ (H^0 - E_0)\psi_1 + (H' - E_1)\psi_0 &= 0, \\ (H^0 - E_0)\psi_2 + (H' - E_1)\psi_1 - E_2\psi_0 &= 0, \\ &\cdots \\ (H^0 - E_0)\psi_n + (H' - E_1)\psi_{n-1} - E_2\psi_{n-2} - \cdots - E_n\psi_0 &= 0. \end{aligned} \tag{66a}$$

If in this way the wave function has been found up to the approximation $\varepsilon^n$, the energy parameter is determined up to $\varepsilon^{2n+1}$, i.e., up to $E_{2n}$ and $E_{2n+1}$.

Applying the variational principle we have

$$\int \psi(H^0 - E + \varepsilon H')\psi \, d\tau = 0 \tag{67}$$

separately for any power of $\varepsilon$. Introducing for brevity

$$H_{ik}^{0} = \int \psi_i H^0 \psi_k \, d\tau, \qquad H'_{ik} = \int \psi_i H' \psi_k \, d\tau, \qquad N_{ik} = \int \psi_i \psi_k \, d\tau, \tag{67a}$$

with $N_{00} = 1$, i.e., normalized $\psi_0$, and collecting terms of $\varepsilon^{2n+1}$, one finds

$$\begin{aligned} E_{2n+1} = H'_{mn} &- E_1 N_{nn} - E_2(N_{n(n-1)} + N_{(n-1)n}) - \cdots \\ &- E_n(N_{n1} + N_{(n-1)2} + \cdots + N_{2(n-1)} + N_{1n}) - \cdots \\ &- E_{2n-1}(N_{20} + N_{11} + N_{02}) - E_{2n}(N_{10} + N_{10}). \end{aligned} \tag{68}$$

Adding in the next approximation $\varepsilon^{n+1}\psi_{n+1}$ to the wave function, there will be additional terms

$$2\int \psi_{n+1}\{(H^0 - E_0)\psi_n + (H' - E_1)\psi_{n-1} - E_2\psi_{n-2} - \cdots - E_n\psi_0\} \, d\tau = 0. \tag{68a}$$

in virtue of the last one of Eqs. (66a). Similarly, adding $\varepsilon^{n+2}\psi_{n+2}$ does not alter the $E_{2n+1}$ value, and so on, in virtue of the remaining Eqs. (66a).

In the corresponding calculation of $E_{2n}$ we have to include the term

$$\int \psi_n(H^0 - E_0)\psi_n \, d\tau = -\{H'_{n(n-1)} - E_1 N_{n(n-1)} - E_2 N_{n(n-2)} - \cdots\} \tag{69}$$

which cancels with half of the terms connected with $\psi_n$. The result is

$$\begin{aligned} E_{2n} = H'_{n(n-1)} &- E_1 N_{n(n-1)} - E_2[N_{(n-1)(n-1)} + N_{(n-2)n}] \\ &- \cdots \\ &- E_n[N_{(n-1)1} + N_{(n-2)2} + \cdots + N_{1(n-1)} + N_{0n}] \\ &- E_{n+1}[N_{(n-1)0} + \cdots + N_{0(n-1)}] - \cdots \\ &- E_{2n-2}[N_{20} + N_{11} + N_{02}] - E_{2n-1}[N_{10} + N_{01}]. \end{aligned} \tag{69a}$$

Again addition of $\varepsilon^{n+1}\psi_{n+1}$ and higher terms to the wave function does not alter the result.

Since the solution $\psi_0$ of the homogeneous first equation can be added to any $\psi_n$, it is possible to orthogonalize all $\psi_n$ with respect to $\psi_0$. This removes all $N_{0n} = 0$ from the formulas and gives

$$\begin{aligned} E_{2n+1} = H'_{nn} &- E_1 N_{nn} - E_2[N_{n(n-1)} + N_{(n-1)n}] - \cdots \\ &- E_n(N_{n1} + \cdots + N_{1n}) - \cdots \\ &- E_{n+1}[N_{(n-1)1} + \cdots + N_{1(n-1)}] - \cdots \\ &- E_{2n-1}N_{11}, \end{aligned} \tag{69b}$$

$$\begin{aligned} E_{2n} = H'_{n(n-1)} &- E_1 N_{n(n-1)} - E_2[N_{(n-1)(n-1)} + N_{(n-2)n}] - \cdots \\ &- E_n[N_{(n-1)1} + \cdots + N_{1(n-1)}] \\ &- E_{n+1}[N_{(n-2)1} + \cdots + N_{1(n-2)}] - \cdots \\ &- E_{2n-2}N_{11}. \end{aligned} \tag{69c}$$

The result is simple enough to be easily kept in mind and simplifies the deduction of conventional perturbation theory.

### 5. *The Scherr–Knight Method*

The above principal method was thought of as a theoretical guide to be used for interpolation purposes except for the constant term of the energy formula of the ground state. Even the $Z^{-1}$ term as determined by the first-order perturbation of the wave function appeared doubtful from a practical point of view.

A great achievement has been made by Knight and Scherr (1962a,b, 1963; Scherr and Knight, 1963) in considering the method literally as a working program and exploiting it to the highest degree. In our notation their energy formula reads

$$E = -2\left\{Z^2 - \tfrac{5}{8}Z + \sum_{n=2}^{\infty} \varepsilon_n Z^{2-n}\right\} \tag{70}$$

and is obtained by successive determination of the terms in the expansion of the wave function

$$\psi = \sum_{n=0}^{\infty} \psi_n Z^{-n}. \tag{70a}$$

The functions used to express the $\psi_n$ are Kinoshita terms, as it appears, with preference for terms of lowest degree like

$$r, \quad s, \quad u, \quad t^2/s, \quad t^2/u, \quad u^2/s, \quad ut^2/s^2, \quad \text{etc.} \tag{70b}$$

The number of terms is of the order of one hundred as compared with the eighty Kinoshita term functions and the ten times more numerous Pekeris terms.

The wave function has been determined up to the degree of $Z^{-6}$ and correspondingly the last energy term is $\varepsilon_{13}$. We shall be satisfied by giving their energy terms in comparison with those very few as given by Hylleraas and Midtdal, which are very inaccurate except for $\varepsilon_2$ (Table I).

Also some of the ion energies are given in atomic units compared with those obtained by Pekeris (see Table II).

TABLE I

| $n$ | $\varepsilon_n$ (Scherr–Knight) | $\varepsilon_n$ (Hylleraas–Midtdal) |
|---|---|---|
| 2 | 0.15766 6405 | 0.157 6575 |
| 3 | −0.00869 8991 | −0.008 535 |
| 4 | 0.00088 8587 | 0.00034 |
| 5 | 0.00103 6372 | 0.00082 |
| 6 | 0.00061 2917 | 0.00244 |
| 7 | 0.00037 2187 | — |
| 8 | 0.00024 2872 | — |
| 9 | 0.00016 5651 | — |
| 10 | 0.00011 6157 | — |
| 11 | 0.00008 3281 | — |
| 12 | 0.00006 0866 | — |
| 13 | 0.00004 5213 | — |

TABLE II

| $Z$ | $E$ (Scherr–Knight) | $E$ (Pekeris) |
|---|---|---|
| 1 | −0.5275 9152 | −0.5277 50962 |
| 2 | −2.9037 2433 | −2.9037 24376 |
| 3 | −7.2799 1339 | −7.2799 13386 |
| 4 | −13.6555 6622 | −13.6555 66210 |
| 5 | −22.0309 7156 | −22.0309 71550 |

Except for $H^-$ and He the values are as good as those given by Pekeris, and by extrapolation of the coefficient series, approximately as a geometric series, the He value becomes very accurate and even the $H^-$ value fairly good.

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# Energy Band Calculations by the Augmented Plane Wave Method*

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## I. The Method and Its Development

In 1937 the present writer (Slater, 1937) suggested a method for solving the problem of the motion of an electron in a periodic potential resembling that found in a crystal. This potential in its simplest form is spherically symmetrical in nonoverlapping spheres surrounding each nucleus in the crystal, and is constant in the region between spheres. The wave function in the region between spheres was expanded in a finite series of plane waves, of the form $\exp i(\mathbf{k} + \mathbf{K})\cdot\mathbf{r}$, where $\mathbf{k}$ is the reduced wave vector and $\mathbf{K}$ one of the vectors of the reciprocal lattice, so that the expansion automatically has the proper symmetry behavior under translation of the lattice through the vector from one unit cell to another. Inside a sphere, the wave function was expanded in a series of functions each of which is a spherical harmonic of angle times a function of $r$. The function of $r$ is a solution of the radial Schrödinger equation for the potential actually found within the sphere, regular at the origin, computed for an energy which is chosen at the end of the calculation to be the actual energy of the solution. Each plane wave $\exp i(\mathbf{k} + \mathbf{K})\cdot\mathbf{r}$ is made continuous with a series of spherical solutions at the surface of the sphere, but in general the normal derivative of the function will be discontinuous if we choose only one plane wave and its associated spherical functions. By superposing a number of such

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plane waves in the region outside the spheres, with the corresponding spherical solutions inside, one can get a very good approximation to the true solution of Schrödinger's equation for the assumed potential. At the same time that the accuracy of the solution is improved by adding terms, the discontinuity in first derivative of the function, over the surface of the spheres, is reduced.

To carry out the calculation in a practical fashion, one derives a secular equation connecting the various plane waves, each supplemented by its spherical part inside the spheres; it is now customary to refer to such a function as an augmented plane wave (abbreviated APW). In the paper cited above, the matrix elements entering into this secular equation are worked out. The energy enters the secular equation in two ways. First, it is found, as always in a secular equation, in an explicit fashion. Second, the spherical solutions within the spheres are computed by numerical solution of Schrödinger's equation in this spherical region, and this solution must be carried out for a definite energy parameter. This energy parameter is carried as a variable quantity until the last part of the calculation, when it is set equal to the eigenvalue of the secular problem. To accomplish this in a practical fashion, one computes the determinant, which must be set equal to zero to get the secular equation, as a function of the energy parameter, which enters both explicitly and implicitly in determining the radial solutions, and then one looks for the zeros of this determinant. When the calculation is completed, we have an exact solution of Schrödinger's equation within the spheres, and a good approximation in the region between, the excellence of the approximation depending only on the number of plane waves retained.

Soon after this method was proposed, a calculation for the copper crystal was carried out by Chodorow (1939a,b), using a desk computer, and finding the energy at only a few symmetry points in the Brillouin zone. The method proved to be difficult, but by no means impossible, for numerical calculation. Soon after the method was suggested, the orthogonalized plane wave (OPW) method was proposed by Herring (1940), and was used by Herring and Hill (1940) for calculations on beryllium. The war intervened, after which the OPW method was applied to diamond and germanium by Herman and co-workers (Herman, 1952, 1954; Herman and Callaway, 1953). At about this same time, the APW method was used by Trlifaj (1952) for magnesium and by Antoncik (1953) for aluminium. The present writer encouraged his students to re-examine the method with a view to using bitfurther. Their impression was that it was difficult, and the writer (Slater, 1953), together with M. M. Saffren (Saffren and Slater, 1953), proposed a modification which was essentially equivalent, but seemed perhaps easier to program for a digital computer. This scheme, to which the name augmented plane wave method was first applied, was used by Howarth (1955) for calculations on copper, which apparently must have contained some error since his results do not agree with those found later by the same method. The method was studied about this time by Leigh (1956). Saffren (1959) investigated the programming of the revised method, and also of the original 1937 method, and concluded that in fact the earlier method was more practical. Consequently in more recent work we have gone back to that, and have applied the term augmented plane wave method to it.

Saffren programmed the method for the Whirlwind Computer at M.I.T., and made some calculations (Saffren, 1959) for sodium in connection with his doctor's thesis. J. H. Wood then programmed the method for the IBM 704 computer, later modifying the program for the 709 or 7090, and he used it in working out the energy bands of the iron crystal (Wood, 1960, 1962). Since that time, the method has been used at M.I.T. for a considerable number of calculations on a wide variety of types of crystals, as will be described in Section IV. Since many of these results are so far unpublished, it seems worthwhile listing them in this review article, so that the reader will realize the many results which are now being obtained by the method. In the meantime a modification of the method has been introduced by Schlosser and Marcus (1963).

Wood has reduced the program to an entirely practical form. Its convergence is adequate for the type of crystal we have handled. One needs some forty to eighty plane waves to get an accurate expansion of the wave function between spheres. Inside a sphere, while in principle one has a series of spherical harmonics extending over all $l$ values, one needs in practice to retain terms up to about $l = 12$. The calculation can be handled on the machine retaining as many terms as this. One finds that convergence of energy is achieved, since addition of further terms makes a negligible change in the eigenvalues. Calculation of course is much simpler at symmetry points of the Brillouin zone, but calculations at general points are practical. It is not unduly difficult to program the method for a new crystal symmetry. We have made calculations for the face-centered and body-centered cubic structures, hexagonal close-packed, sodium chloride and cesium chloride, and the structure of gallium, with four atoms per unit cell. We have programs also for the diamond and zinc blende structures, and L. F. Mattheiss has programmed the $\beta$-wolfram structure. The major part of the work connected with these structures is encountered simply in setting up the irreducible representations of the space group.

In addition to the program for the direct solution of Schrödinger's equation, we have programs for determining the potential, by methods to be described later, and for evaluating some properties of the final wave function, in particular for finding the amount of electronic charge inside each of the spheres, a quantity needed in determining the self-consistency of the solution. These programs have been the work of Wood, Mattheiss, and A. C. Switendick. G. W. Pratt, Jr., and his student L. E. Johnson have been incorporating the spin-orbit interaction and the relativistic effects into the calculation, on a perturbation basis, and are now able to handle crystals containing heavy atoms on a relativistic basis. We are working on the problem of self-consistency, and on the inclusion of crystal-field terms in the potential, that is, terms involving departures from the assumption that the potential is spherically symmetrical within the spheres and constant outside. These departures will be handled by including diagonal and non-diagonal matrix elements of the perturbing potential in the secular equation.

## II. The Accuracy of the Method, and Comparison with Other Methods

We have every reason to believe that the method yields solutions of as good accuracy as desired for the assumed Schrödinger equation. Part of this reason comes from the convergence which the solution shows as the number of terms is increased. Part of it is a result of agreement of calculations by Burdick (1961, 1963) on copper with the calculations of Chodorow (1939a,b), mentioned earlier, and particularly with calculations on copper by Segall (1961b, 1962) using the Green's function method of Kohn and Rostocker (1954), which is equivalent to the method of Korringa (1947). The Kohn–Rostocker method, described in detail by Ham and Segall (1961), is adapted to a solution of Schrödinger's equation with precisely the same type of potential which we use with the APW method, using the same expansion for the wave function, but the steps are entirely different. Burdick, working at M.I.T., and Segall, working at the General Electric Company, have made calculations using the same potential assumed by Chodorow for purpose of check. They agree with each other to within the estimated errors of each calculation, and at the few points computed by Chodorow they also check his results. It is very gratifying, as pointed out by Segall and by Burdick in the papers cited above, that the calculations for copper give energy bands in excellent agreement with experimental results for this metal, which has been studied by a variety of methods.

The APW method has closer resemblance to the cellular method than to any other. If the cellular method is used for the same type of potential assumed in the APW method, we should try to expand the solution throughout the interior of the Wigner–Seitz cell as a series of spherical harmonics of angle times radial solutions of Schrödinger's equation. That is, we should extend the solution, which in the APW method is used only within the nonoverlapping spheres, out into the region between spheres. We should then run into the well-known difficulty found with the cellular method, that of matching boundary conditions over the surface of the cell. In the APW method the matching problem is thrown into the much more convenient form of matching over the surfaces of the spheres. It was to obtain this more convenient procedure, and to get an automatic agreement with the Empty Lattice Test, that the writer suggested the APW method (Slater, 1937), just at the time when Shockley (1937) was pointing out that the cellular method as then used, with only a few terms, failed rather badly to satisfy the Empty Lattice Test.

More recently, however, it has been pointed out by both Ham (1954, 1962) and Saffren (1959) that we should not expect the cellular method even in principle to be correct. For if we consider the Wigner–Seitz cells, which fit together to fill all space, and if we set up a sphere surrounding the center of one cell whose radius is large enough so that the sphere extends into neighboring cells, then in general the potential will no longer be spherical within the parts of the sphere which extend into neighboring cells, and we cannot expect an expansion of the type used in the cellular method to be convergent in this region. It is only inside the sphere inscribed in the Wigner–Seitz cell that we must expect convergence, and this is just the region in which we use the radial expansion in the APW method, as also in the Green's function method. Hence it is felt that the APW and Green's function methods have a very definite logical advantage over the cellular method, as well as being more convenient to apply. In the present writer's view, the cellular method should no longer be used in energy band calculations.

As compared with the OPW method, the APW method has the great advantage that it gives an exact solution of Schrödinger's equation, while the OPW method approximates by using a more limited basis set. In practice the OPW method is good for such cases as silicon or germanium, but is not well adapted for crystals containing transition elements. The reason is that the OPW method generally makes up a wave function out of a sum of Bloch combinations of atomic orbitals which are concentrated enough around the atoms to be nonoverlapping plus a certain number of plane waves. To build up a band having the properties of a 3*d* state, for instance, out of such a basis set is rather impractical, for the atomic 3*d* functions are extended enough so that they would overlap, and one does not use them in the basis set, so that one is reduced to trying to expand them in plane waves, a very slowly convergent expansion.

This does not seem to be permanently a difficulty with the OPW method. One could in principle use a larger basis set of atomic orbitals, some extending out far enough to overlap orbitals on neighboring atoms, and combined as Bloch sums so as to form functions of proper symmetry. One could supplement these with a number of plane waves. If one set up all the nondiagonal as well as diagonal matrix elements of the Hamiltonian and the overlap matrix between these functions, and used a Roothaan method, one could obtain results of any desired accuracy from such an extended OPW calculation. It would, however, demand three- and four-center integrals of a type which have not been conveniently available previously but which are now rapidly becoming practicable. The writer forsees future usefulness of the OPW method if defined in this way, but it is not clear that it would be any simpler than the APW method. For such uses, the OPW method would stand to the APW method in something the same relationship that the analytic approximation to an atomic orbital stands to the determination of the orbital as a numerical table of values. Both methods, as we are now aware from the atomic case, have their uses. But it is essential that the OPW method be handled with the accuracy which we have described to compare with the APW method, and so far this has very seldom been done.

There are a number of features of the calculation which have to be specially taken care of with the OPW or tight-binding methods (the latter being equivalent to our interpretation of the OPW method, if we omit any plane waves from the basis functions) but which are automatic with the APW method. For instance, there is a good deal of discussion in the literature of how to build up hybrid orbitals on various atoms using *s* and *p* orbitals, or *s*, *p*, and *d*, or even including *f* orbitals, so as to get bonds in different directions. Such orbitals would then be used as equivalent orbitals in a tight-binding calculation to build up an energy band function. But in the APW method, far from limiting ourselves to *s*, *p*, *d*, or *f* orbitals, with $l = 0, 1, 2$, or 3, all the series go up to $l$ of the order of magnitude of 12. In other words, all of these characteristics of the wave functions are automatically included, without any arbitrariness. Or again, one can be considering such a case as a transition element in which some energy bands have the characteristics of 3*d* bands, others of 4*s* and $4p$. In a tight-binding or OPW calculation, we might first handle the $3d$ band separately from the others, then consider their interaction. In the APW method this again is quite automatic, on account of the inclusion of all $l$ values. These illustrations show how some features of the other approximations, which make difficulties, do not have to be considered at all with the APW method, which effectively leads to an exact solution of the problem.

## III. The Determination of the Potential

The periodic potential which one wishes to use for determination of energy bands will be in some sense a self-consistent potential. It is not at all obvious, however, that it should be literally a Hartree–Fock potential, and hence different for each occupied spin orbital. This is a matter on which there has been a good deal of loose thinking. The Hartree–Fock method will lead to a total energy for a determinantal wave function which is lower than that found for any other determinantal wave function. Consequently the correlation energy, the correction to the energy of the determinantal function required to get the correct energy (suitable attention being paid to relativistic corrections), will be numerically as small as possible for this wave function. If one wishes to compare the correlation energy with that found in isolated atoms, or in molecules, as has been discussed by Clementi (1963) and others, then one should find the energy of a determinantal function formed from energy band spin orbitals. This would be needed for a really proper calculation of the binding or cohesive energy of the crystal, of which a classic example is Löwdin's (1947, 1956) calculation of the cohesive energy of the alkali halides, for which essentially this method was used.

More often, however, the object of calculating energy bands is to compare them with the rapidly expanding set of experimental facts which can be described in terms of a one-electron picture of the crystal. We are thinking here of such simple things as the use of Fermi statistics for describing the properties of a semiconductor or the electronic specific heat of a metal, and such phenomena as cyclotron resonance, the de Haas–van Alphen effect, magnetic interband transitions, and a host of other developed experimental methods of studying solids, as described for instance in "The Fermi Surface" (Harrison and Webb, 1960). The empirical fact is that a one-electron picture works for these properties better than some physicists think it should. In particular, it is well-known that the Hartree–Fock method, applied to the simple model of a free-electron gas, leads to a dependence of exchange energy on wave vector which is entirely contrary to experiment. This is described for instance by Raimes (1954). The reason is that the Hartree–Fock method leads to a much greater lowering of the energy on account of exchange for the lower, occupied energy levels of a system than for the upper, empty levels, and there is an almost discontinuous variation of the exchange in the neighborhood of the Fermi level, which would completely vitiate the simple free-electron picture of the energy levels. Yet is is known that the free-electron picture works quite well. H. V. Bohm and Pines have supplied part of the explanation of this phenomenon, in terms of their theory of plasma oscillations of an electron gas, described for instance by Pines (1955).

Perhaps however we do not have to look so far for the reason why the Hartree–Fock method is not a very suitable starting point. The use of Fermi statistics in solid-state problems is based on the assumption that one can write the energy of the whole system as a sum of one-electron energies. It is of course a familiar fact that the total energy of a Hartree–Fock system is not the sum of the one-electron energies of that system; there are additional terms which enter, which cannot be explained away. Almost the only case which has been worked out in which we can check the solution of a many-electron problem against the type of simplification postulated in the Fermi statistics is the calculation of the hexagonal ring of six hydrogen atoms by Mattheiss (1961), which has been discussed by the present writer (Slater, 1963) from the point of view of its relation to the Fermi statistics. Mattheiss has used configuration interaction methods to solve a very extensive secular equation for this problem, finding the energies of a great many multiplets. The present writer has shown that one can set up one-electron energies for the six energy levels of the problem, associated with quantum numbers which may be described as $m = 0, \pm 1, \pm 2, 3$, such that the sum of the one-electron energies agrees quite well with the weighted mean of the multiplets arising from the corresponding assignment of electrons to states. Thus, the lowest states are for $m = 0$ and $\pm 1$, and in the ground state of the system we may assume each of these is doubly occupied. Then if for instance one electron is excited from state 1 to state 2, there can be a number of multiplets, depending on the spin of the excited electron. If we find the average energy of these excited states, we may compare it to the energy difference between the one-electron energies of states 1 and 2. As just mentioned, the writer has found that one can set up one-electron energies for states $0, \pm 1, \pm 2$, and 3 which are capable of describing all the excited states with quite good accuracy.

Thus in this case, which has the property of a one-dimensional chain of hydrogen atoms or a one-dimensional crystal with only six atoms in the repeating length, it is found empirically that the additivity of one-electron energies to get excited energy levels required for the application of the Fermi statistics actually holds to a considerably better accuracy than one has any reason to expect. The accuracy is a result of approximate cancellation of complicated combinations of exchange integrals. But it is significant that the one-electron energies which must be used do not show the properties of those found by the Hartree-Fock method. We do not start with the ground state of the system, with the six electrons in states 0 and ±1 and with states ±2 and 3 empty, to find the one-electron energies to use. Instead, we start with a state in which each of the states 0, ±1, ±2, and 3 has one electron, all of the same spin. This corresponds to a single determinantal function, with the maximum multiplicity found in the system. In this case, the exchange is much more nearly the same for each of the states. We do not have the depression of the one-electron energies of states 0 and ±1 compared to ±2 and 3 which we should have found from the ground state. If we use the one-electron energies found from the ground state, we have nothing comparable to the accurate agreement between sum of one-electron energies and actual energies of the excited states which we have mentioned above.

Here, then, is a case in which one can actually check the applicability of the method used in Fermi statistics and in conventional one-electron theory. The method proves to be surprisingly good, provided one forgets about the feature of dependence of exchange energy on the wave vector **k**, which is such a characteristic feature of the Hartree–Fock method. It is very strongly suggested by this that we shall have best results if we use a periodic potential which is only a function of position, not of wave vector. This conclusion has also been reached, for somewhat different but related reasons, by Segall (1961a).

Such a potential was suggested by the present writer a number of years ago (Slater, 1953a), which can be described as follows. We take the true wave function of the problem, assume that one electron is at a particular point of space, and find the distribution of all other electrons under this condition. We find the potential of these other electrons and the nuclei, at the location of the first electron, and use this potential as the appropriate one if the first electron is at this particular point. This potential has various good features as compared with the Hartree–Fock potential, one being that it takes account of the static polarization of all other electrons, static dielectric effects, electric images, and so on. Löwdin (1955) has shown that the wave function satisfying Schrödinger's equation, using this potential, is a natural spin orbital. This potential, we note, has the desired property that it is a function only of position, not of **k**. A simpler potential which has the same property is the other one suggested by the present writer (Slater 1951a), formed from the complete Coulomb potential of all electrons and nuclei, corrected by an exchange correction which is the average of all Hartree–Fock potentials at the given point of space, averaged over the occupied orbitals, or, even more crudely, which is proportional to the 1/3 power of the electron density.

The potentials which are currently being used for the energy band calculations are based on this last approximation. We have programs, worked out by Wood, Mattheiss, and Switendick, to find the Coulomb potential arising from a superposition of the atomic charge densities of the various atoms forming the crystal, and to correct it by the $\rho^{1/3}$ exchange correction, finally forming a spherical average over the interior of the spheres and finding an average over the region between the spheres. This is the potential which has been used so far. It does not pretend to be self-consistent, except as the original atomic charge densities are self-consistent. For the latter, we are using charge densities determined by the atomic program of Herman and Skillman (1963), which also assumes the $\rho^{1/3}$ exchange correction, and which has very kindly been supplied to us by F. Herman. The question comes up, in using this method, whether the atomic charge densities for neutral atoms or for ions should be used. So far, we have made merely the obvious assumptions: that in a metal we use neutral atoms, and in a crystal like NaCl we use the ionic cases $Na^+$ and $Cl^-$.

We are in the process, however, of going beyond this simple assumption. We are setting up programs by which we can take the wave functions determined by the APW method and find how much charge actually is located in each sphere and how much in the region between spheres. This will then be compared with the corresponding initially assumed charge distribution, and the potentials will be modified to work in the direction of self-consistency. In the cases where this has so far been checked, the initial assumption was fairly close to self-consistency. But there will be cases in which such a check is necessary, for instance in such a crystal as ZnS where it is not at all clear whether we should start with $Zn^{2+}S^{2-}$, with neutral atoms, or with something in between.

The general argument which we have given in the present section should serve to show that the proper potential to use is almost certainly not exactly a Hartree–Fock potential and to justify us in using the much simpler form of potential which is a function only of position. To go beyond this, however, we must appeal to further knowledge which we do not really have.

In the case of $H_6$, where we had a solution of the many-particle problem, we could justify the use of one-electron methods. In a crystal where a solution of the many-electron problem is impracticable, this cannot be done. Hence the present writer is inclined to think that, at the present stage of development of the theory, we had better consider the one-electron method to be a partially empirical procedure. If it appears that the prescription which we are using for finding the potential leads to results in agreement with experiment, then it is well justified.

In this connection it is an interesting fact that various modifications which we, and other workers in the field, have made in the potential seem to have the effect of moving one energy band up or down with respect to another, but not of making much change in the details of each energy band. In such a case it seems reasonable at present to make empirical changes in the potential so as to get the bands in the relation to each other indicated by experiment. When this is done, by variation of some simple feature of the potential (such as, in our case, the constant value of the potential in the region between the spheres), there then seems to be good reason for thinking that the great detail found in the structure of the bands will have a good deal of resemblance to the experimentally determined bands. This at least seems a sufficiently promising line of attack to deserve a good deal of attention.

## IV. Results of Augmented Plane Wave (APW) Calculations

In the present section we shall describe some of the energy band calculations which have been made so far at M.I.T. A few of these have been published, but a number of them are still in a preliminary stage, and the description given here is not intended to do more than indicate in a general way the type of result found. First we have the calculation on iron carried out by Wood (1960, 1962). We show the energy bands in Fig. 1. The characteristic here is of course the bands of $3d$ character interposed in the middle of the $4s$-like band. Wood's calculations are made for a nonmagnetic potential; that is, the same potential is used for electrons of both spin. However, Wood has also estimated the effect of using different potentials for the two spins, to give an energy band description of ferromagnetism. By using two different $\rho^{1/3}$ exchange potentials, that of each spin being derived from the charge density of electrons of the corresponding spin, as proposed by the present author (Slater 1951b), one brings about a separation of the energy bands for the electrons of the two spins. A common Fermi level then leads to having more electrons of one spin than of the other. The indications are that one can in this way get a consistent description of the ferromagnetism of the iron group elements, similar to that used by the present writer many years ago (Slater, 1936) using the crude energy bands available at that time. However, Wood has not yet carried through a complete discussion of the ferromagnetism of iron on this basis.

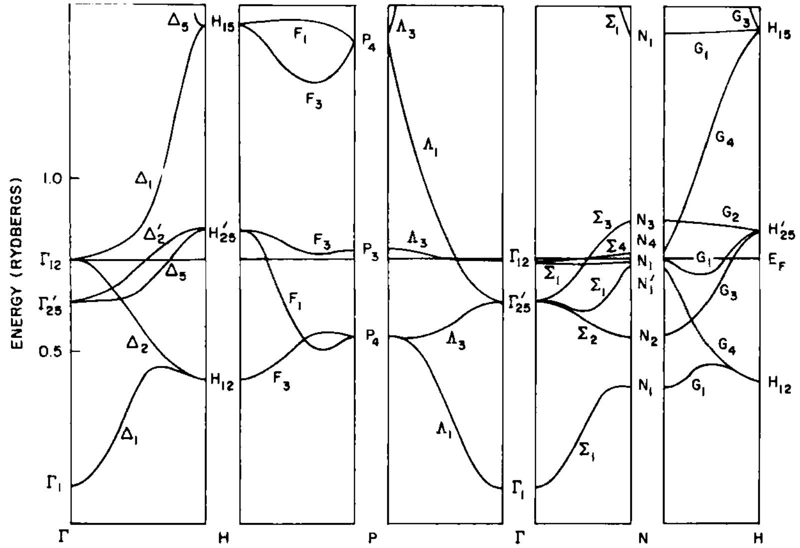

**Fig. 1.** Energy bands of body-centered cubic (bcc) iron from Wood (1962). The bands starting from states of symmetry $\Gamma_{12}$ and $\Gamma'_{25}$ are of *d*-like character.

The next similar calculation is that on copper by Burdick (1961, 1963), mentioned earlier. These energy bands are shown in Fig. 2, from Burdick's paper (1963). As in iron, the 3*d* bands are introduced midway in the 4*s* band, but here, in contrast to iron, the Fermi level lies high enough so that the 3*d* bands are entirely occupied. Mattheiss (1963), in work so far not published in detail, has carried the study of the transition elements far beyond these two cases of iron and copper. Hanus (1961) had earlier carried out calculations for nickel, and had shown that the relative positions of the 3*d* and 4*s* bands were quite sensitive to the details of the assumed potential, though the shapes of the individual bands were not. Mattheiss settled on a definite method of finding the potential, and carried through calculations for elements all the way from argon, before the start

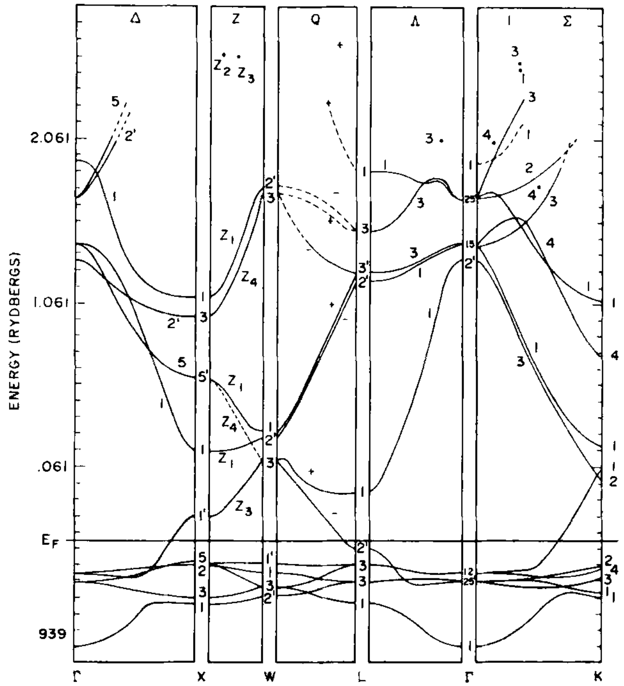

Fig. 2. Energy bands of copper, from Burdick (1963).

of the $3d$ transition series, to zinc. Mattheiss's procedure was essentially as we have described in Section III, superposing the charge densities of the neutral atoms, finding an exchange correction from the 1/3 power of the total charge, and carrying out spherical averages through the spheres and an average through the region between the spheres. With these potentials, he obtained energy bands for argon, as shown in Fig. 3, and energy bands for the whole series of elements, shown for one particular direction of propagation in Fig. 4, so as to exhibit the behavior as we go through the transition series.

First, in argon, the energy bands shown in Fig. 4 are the excited ones arising from the $4s$, $4p$, and $3d$ type of atomic behavior. The valence band, of $3s$ and $3p$ type, lies below the bottom of the figure in Fig. 4 but is shown in Fig. 3. The energy gap found between the valence and conduction bands agrees well with that observed in solid argon. At the time the figure was made, calculations had not been carried out for potassium, calcium, and scandium. Furthermore, calculations were not made for the complicated crystal structure of manganese. The other elements, from titanium

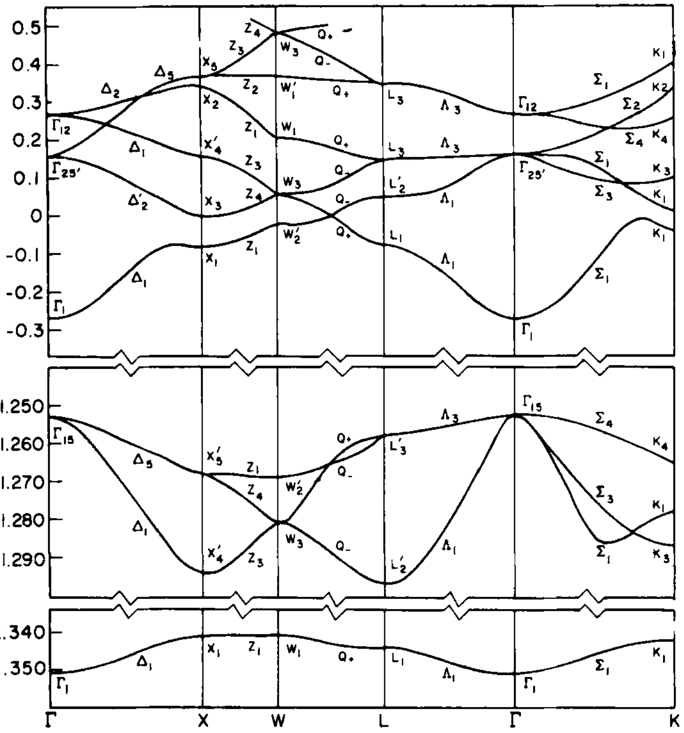

Fig. 3. Energy bands of solid argon, from Mattheiss (1964).

to zinc, are all included. The iron, nickel, and copper calculations in Fig. 4 are not those of Wood, Hanus, and Burdick, respectively, but are recomputed using the method just described for finding the potential. They agree well, however, with the work of Wood, Hanus, and Burdick.

A number of interesting features may be seen in Fig. 4. In the first place, we see of course the changes in type of band in going from one crystal structure to another. In particular, the hexagonal close-packed cases, particularly titanium, are much more complicated than the cubic cases. We see the evidence of the 3*d* band, however, in each case from argon to copper. The breadth of this band—the energy separation between lowest and highest states of 3*d* type of symmetry—decreases as we go from argon to copper, as would be expected. The height of the 3*d* band above the bottom of the 4*s* band does not change much until we reach zinc, in which the 3*d* band has fallen below the bottom of the 4*s* band and is not shown in the figure. The 3*d* is even lower in the next element, gallium, which we shall

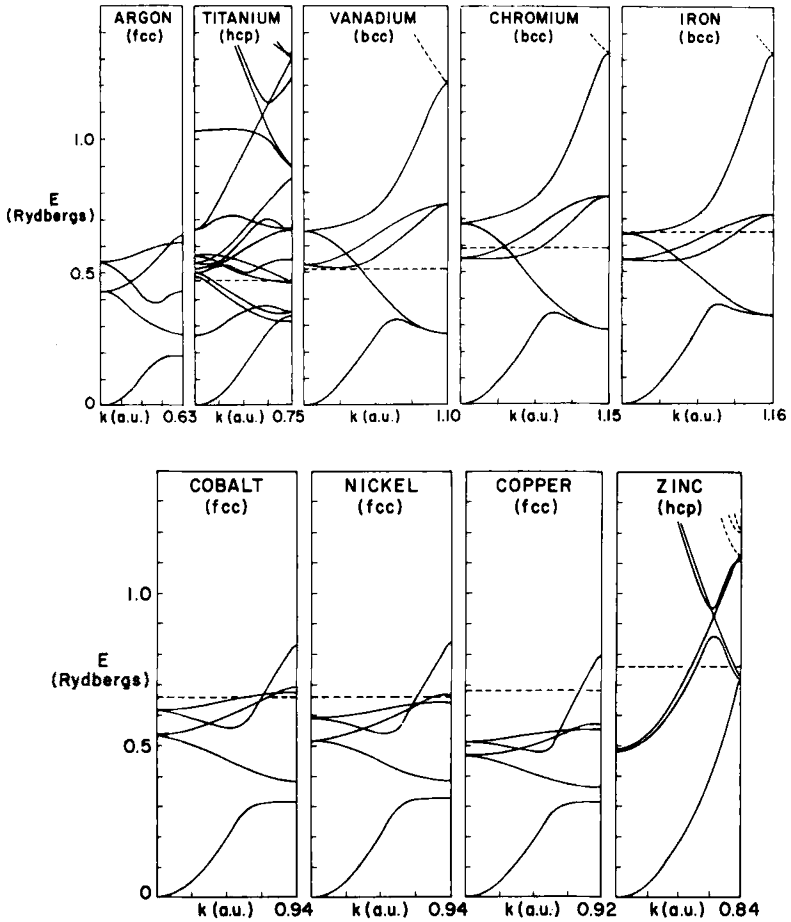

**Fig. 4.** Energy bands of 3*d* transition elements, from Mattheiss (1963).

describe later. Another interesting feature is the similarity in energy bands between the three body-centered cubic elements vandium, chromium, and iron and between the four face-centered cubic elements argon, cobalt, nickel, and copper, except of course for the way in which the Fermi level rises with increasing number of electrons. This verifies the so-called rigid band approximation which has so often been used for discussing these elements and which was presupposed in the discussion of ferromagnetism by the present author mentioned earlier (Slater, 1936).

Mattheiss, in unpublished work, has studied the ferromagnetic nature of nickel in the way previously discussed for iron, and has shown that here too we get a good picture of the ferromagnetism from these energy bands. Conclusions regarding the ferromagnetism of nickel, the antiferromagnetism of chromium, and various features of the energy bands of these transition elements have been discussed by various writers from other institutions, including Lomer (1962), Phillips (1964), and Ehrenreich *et al.* (1963), on the basis of earlier versions of the energy bands as derived at M.I.T. Switendick is engaged in a calculation of the antiferromagnetic structure of chromium, using different exchange potentials for the two spins.

One interesting study which Mattheiss (1963) has made is the effect of the assumed potential on the energy bands. For the case of vanadium, he has used two separate atomic configurations as starting points, namely $3d^3 4s^2$ and $3d^4 4s$. These of course correspond to somewhat different charge densities. With the potentials arising from these charge distributions, he has found the two sets of energy bands given in Fig. 5. As we see, the general appearance of these energy bands is the same in the two cases, but the $3d$ bands lie higher in comparison to the $4s$ in the case $3d^4 4s$ than in $3d^3 4s^2$. From this example we see the sort of displacement of the bands which is

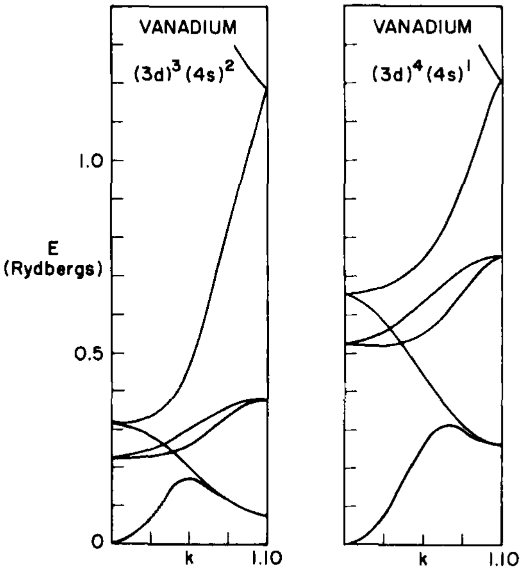

**Fig. 5.** Energy bands of vanadium, from Mattheiss (1963), computed from potentials derived from two different configurations of the vanadium atom.

to be expected if the initial potential was not self-consistent. Presumably the self-consistent field in this case would give results somewhere between these two cases.

In addition to this series of transition elements, Wood (1963) has been working on the energy bands of gallium, the next element beyond zinc. Results of this calculation are shown in Fig. 6. This case is considerably

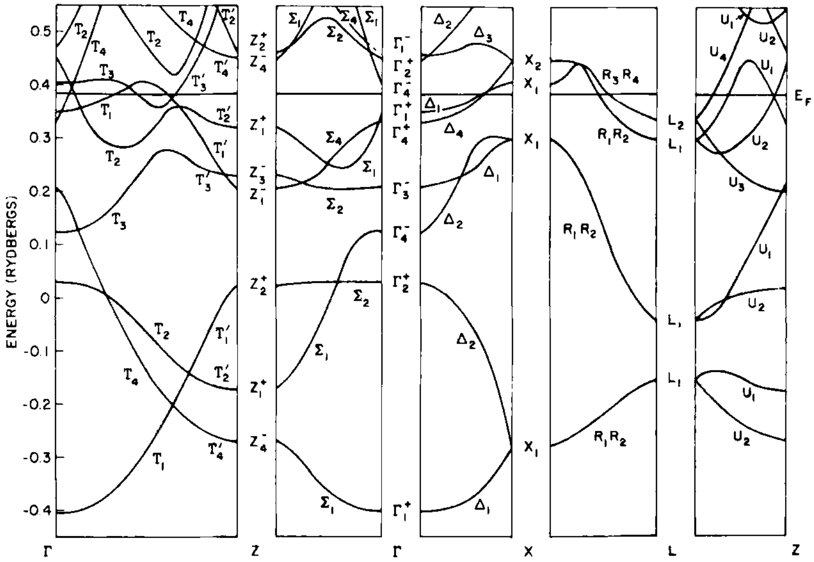

**Fig. 6.** Energy bands of gallium, from Wood (1963).

more complicated than the others that have been discussed, for two reasons. In the first place, there are four atoms per unit cell, whereas in the other elements so far considered we do not have more than two. Second, there is much more empty space in the crystal between the spheres, so that a much larger part of the wave function must be expanded in plane waves. This leads to fairly slow convergence of the series of augmented plane waves, but still not slow enough to prevent the use of the method. In gallium, one has a very complicated case of a substance like a semimetal; that is, there are several different energy bands which just barely cut above the Fermi level, or just barely cut below it, so that it is hard from calculations at a finite grid of points to be sure just how much of the bands are occupied with electrons or holes as the case may be. The various experimental results on gallium, such as those of Roberts (1961) and Reed and Marcus (1962, 1963), are difficult to interpret, and we are hoping that these results of Wood may be a help to the experimenters in interpreting their results.

This concludes the list of elements which have been studied at M.I.T., except for a little work by Saffren on sodium, L. C. Allen on potassium, Johnson on lithium, and Mattheiss on beryllium and magnesium which verified the energy band structure which had been found for these elements by other methods. Matthesis's beryllium work has been carried through to a complete energy band determination by J. H. Terrell, a graduate student at Brandeis University, who has been working with the group at M.I.T. We expect to carry through further calculations on elements. It must be remembered also that a number of calculations for elements have been made by the Green's function method at other institutions, and these are essentially comparable in accuracy to the APW calculations reported in this article. These include lithium, by Kohn and Rostocker (1954); germanium, by Segall (1959); aluminium, by Segall (1961a); copper, by Segall (1962); and alkali metals, by Ham (1962).

In addition to this work on elements, we have carried out, or are carrying out, work on several compounds. The first of these is NiO, which has been studied by Switendick (1963). This crystal has the sodium chloride structure, and its interesting physical feature is that it is antiferromagnetic and an insulator. The nickel ions are known to have magnetic moments of two Bohr magnetons, as if the crystal were formed as $Ni^{2+}O^{2-}$, the nickel ions being in their lowest state, with parallel spins for the two unpaired electrons. The spins of adjacent nickel ions are oriented in opposite directions. To handle this problem by the energy band method, one would have to use different exchange potentials for the two orientations of spin, as was proposed by the present writer some time ago (Slater 1951b). Switendick did not use the type of potential appropriate for an antiferromagnetic case, but rather that for a hypothetical ferromagnetic form. His results, very preliminary, suggest that an energy band treatment of this crystal may form a first approximation to its behavior. However, we must remember that in such a case, in which the interaction between the spins in a single ion are of primary importance, the many-electron aspect is so important that one cannot expect to get far with a one-electron picture.

A second compound which we have so far worked on is PbTe, which is being studied by G. W. Pratt, Jr., together with J. B. Conklin, L. E. Johnson, and Switendick (see Johnson *et al.*, 1963a, b). This compound also has the sodium chloride structure, and does not have the complicat-

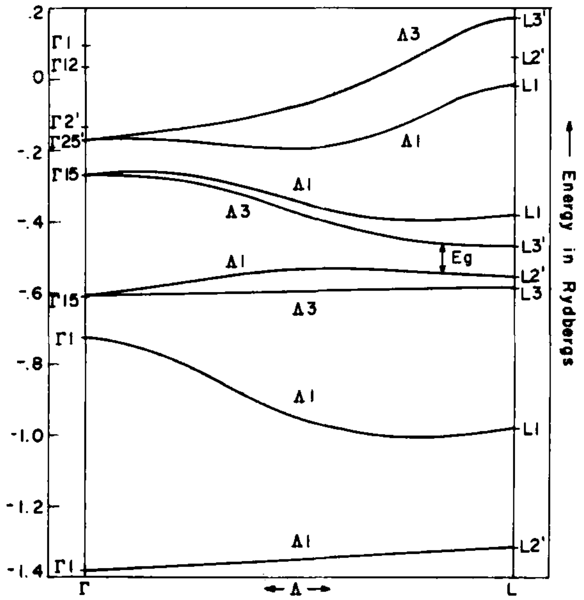

**Fig. 7.** Energy bands of lead telluride, along [111] direction, from Johnson *et al.* (1963b).

ing feature of antiferromagnetism. It does, however, have one characteristic which is of great importance: the atoms are so heavy that the relativistic corrections are necessary to get even a qualitatively correct result. In Fig. 7 we show energy bands, computed nonrelativistically, for propagation in the [111] direction. In Fig. 8 we show the effect at the point $L$, the extremity of the [111] direction, first of the spin orbit correction alone, then of the complete relativistic correction. It is here that the energy gap occurs, between the states $L_{2'}$ and $L_{3'}$ in the notation used without spin orbit interaction, or between the two states $L_6^-$ in the notation of the double group with spin orbit interaction. One sees that the energy gap without any relativistic or spin orbit corrections is about 0.11 Rydberg, which is reduced by the relativistic corrections to about 0.032 Rydberg, bringing it much more nearly into agreement with the experimental value of about 0.022 Rydberg.

A further compound on which calculations are being made is AgCl, which is being studied by P. Scop, the work being as yet unpublished. Preliminary results on the energy bands of this compound are shown in Fig. 9. Scop will probably study AgBr as well. On account of the great importance of these substances in the photographic process, the accurate

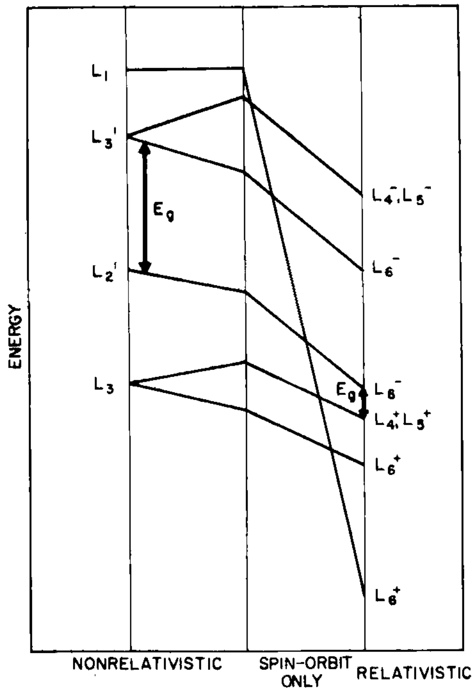

**Fig. 8.** Effect of spin orbit interaction and complete relativistic treatment on energy bands of lead telluride at point *L*, from Johnson *et al.* (1963b).

energy bands which we expect to get in this way should be of great importance in helping to interpret the experimental results. Various other compounds are under investigation by members of the group, including KCl by P. DeCicco, and work is planned on 3–5 compounds. Mattheiss, now at the Bell Telephone Laboratories, Inc., is working on certain compounds having the $\beta$-wolfram structure. The method is as well adapted to the investigation of compounds as of elements, and the limited number of results obtained so far is only an indication of the limited amount of manpower which we have available for the study.

The general conclusion which we come to about the APW method is that it shares with the Green's function method the distinction of being the most accurate procedure available for calculating energy bands in the type of periodic potential found in a solid. We feel, as Segall (1961a) does, that the errors involved in the use of the particular type of potential assumed, namely one which is spherically symmetrical in spheres surround-

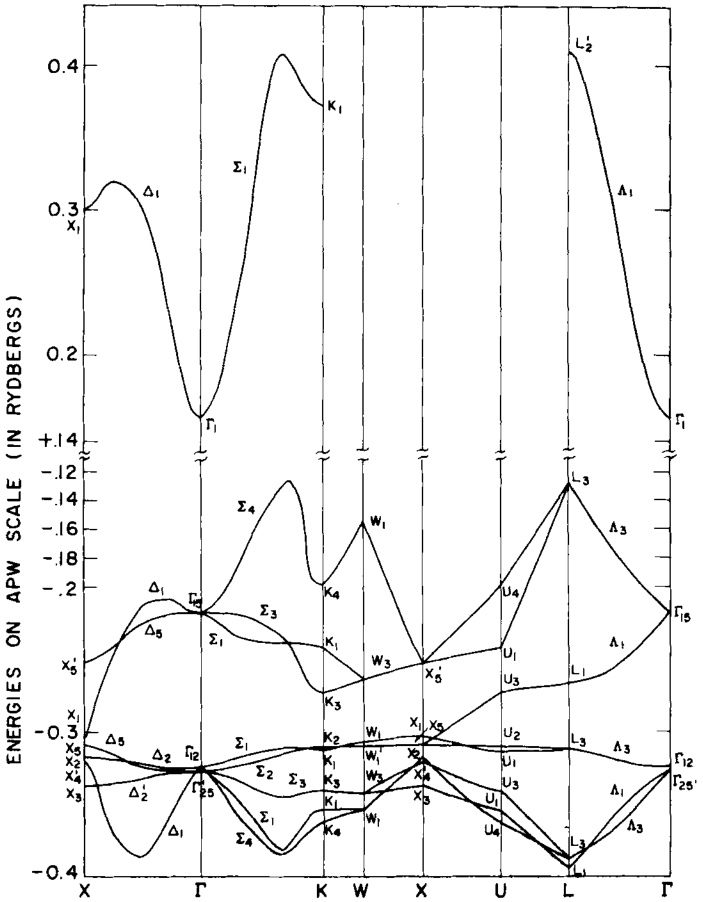

Fig. 9. Energy bands of silver chloride, from Scop (1963).

ing each atom and constant between, are small. We are planning the same type of investigation regarding the magnitude of these errors which he has made; in particular, DeCicco is planning to include terms representing the departure from this type of potential in his study of KCl. We expect the errors arising from the approximation to be of the order of magnitude of a few hundredths of a Rydberg. The success which has so far attended the attempts to correlate the results of APW and Green's function calculations with experiment leads us to hope that these will turn into valuable methods for the guidance of experiment in cases with complicated energy band structure. It seems, in other words, to be a promising field for a great deal of future work.

I should like, finally, to give full credit to the various present and past members of the Solid-State and Molecular Theory Group at M.I.T. who have contributed to the program and who have been mentioned in this report. It is their cooperative effort which has made possible the progress which we have achieved so far in the development of the method. We wish also to give full credit to Professor M. P. Barnett and the staff of the Cooperative Computing Laboratory at M.I.T., without whose efficient operation these results could not have been obtained. Finally we are grateful for financial support from the National Science Foundation, the Office of Naval Research, and the Lincoln Laboratory, supported by the Air Force, Army, and Navy.

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# Spin-Free Quantum Chemistry

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> *A picture of reality drawn with a few sharp lines cannot be expected to be adequate to the variety of all its shades. Yet even so the draftsman must have courage to draw the lines firm.*
>
> H. Weyl in *Philosophy of Mathematics and Natural Science*

# I. Introduction

The quantum mechanics of a polyelectronic system with a spin-free Hamiltonian can be formulated independently of spin functions or spin operators. Each concept in the conventional spin formulation is replaced by a corresponding concept in the spin-free formulation. The spin state is replaced by the permutation (symmetry) state. The spin quantum number is replaced by the pair number. The Hund rule that states of highest multiplicity (i.e., highest spin) lie the lowest is replaced by the rule that states of lowest pair number lie the lowest. The concept of spin correlation is replaced by the concept of permutation correlation. The intercombination rule that electric dipole transitions between different spin states are forbidden is replaced by the rule that electric dipole transitions between different permutation states are forbidden. The equivalents of the exclusion principle and the spin branching diagram occur in the spin-free formulation. It should be pointed out that a spin-free formulation of quantum chemistry does not constitute a denial of the existence of spin.

The core of the spin-free formulation is the pair operator, a linear combination of permutation operators, constructed on a Young tableau. Each pair operator provides an operator representation of a particular pair (bond) diagram. The pair operator projects a pair (bond) function out of an arbitrary spin-free primitive function. A set of linearly independent pair functions is a basis for a representation of a spin-free Hamiltonian. In Section III we discuss the pair operator and formulate the rules mentioned above.

A spin-free formulation depends upon the permutational symmetry of the spin-free Hamiltonian. The effect of permutational symmetry is quite analogous to the effects of other symmetries. The general problem of symmetry in quantum mechanics can be conveniently handled by the group algebra as outlined in Section IV. In Section V we discuss the permutation algebra and present the theoretical justification for the formulation presented in Section III.

In Section VI we present the conventional antisymmetric spin formulation. We use the language of the permutation algebra to facilitate the comparison of the results with those of Section III. It should be noted that spin, through the Dirac identity and the antisymmetry principle, imposes both a twoness property and a permutational symmetry upon the space wave function. It is the permutational symmetry which is responsible for the so-called spin effects for a spin-free Hamiltonian. The classical spin formulation obscures the role played by the permutational symmetry. The fact that spin is so intimately involved in the conventional formulation often leads the beginner to assign to spin a role it does not possess. One encounters statements like "electrons with parallel spin repel one another" or "an electron pair bond is formed because the spins are paired."

In Section II we attempt to fit the spin-free formulation into the historical development of the concept of chemical structure. We note that the concept of chemical structure is a topological one which involves points and tie lines. The spin-free formulation is capable of mapping, by means of the pair operator, the structure topology onto an arbitrary spin-free function space. The principle references for Sections III, IV, and V are Rutherford (1948) and Matsen (1962a,b).

I am indebted to members of both the Texas and Wisconsin Theoretical Chemistry Groups and particularly to C. H. Carlisle and R. D. Poshuta of the former group. I wish also to acknowledge financial support from the Welch Foundation of Houston and the National Aeronautical and Space Administration.

## II. The Concept of Chemical Structure

### A. Introduction

In Section II we shall develop the concepts of chemical structure from its origins to current views. The sequence is not quite the historical one, but one in which the simpler concepts are developed first. We use the term "chemical structure" in place of the more common "electronic structure" because a number of important ideas predate the discovery of the electron.

We begin with the Kekulé pair (bond) diagram. A pair diagram is a topological construction consisting of a group of points tied into sets, no set containing more than two points. This latter property we call the twoness property of a point. Certain of the diagrams (the canonical diagrams) are representations of basis vectors (pure valence states) which span a structure vector space. The chemical structure of a molecule is a vector in the structure space. It is a "superposition" or "resonance hybrid" of pure valence states. The structure basis vector can also be represented by algebraic expressions or by linear combinations of permutation operators called pair operators. Now the permutation operators can be taken as representations of basis vectors in a "permutation" space. The pair operators span a "structure" subspace of the permutation space. The relative magnitudes of certain scalar products in this space can often be inferred from experiment. Then inferences can be drawn about the chemical structure vector itself.

The permutation operators acting on an arbitrary "primitive" function yield pair functions which also span a structure space. The well-known exclusion principle obtains in this space.

With the discovery of the electron the point becomes the electron and the twoness of the point becomes the twoness of the electron. The discovery of spin provides a rationale for the twoness property. With spin and the antisymmetry principle, one can construct antisymmetric pair functions which span the structure space. These pair functions can be taken as the basis for the calculation of the energy of the molecule. However, for most chemical problems, the dynamic influence of spin may be disregarded so that spin-free functions provide an equivalent basis for computation.

### B. The Pair Diagram

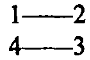
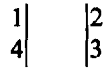
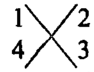
The earliest representation of chemical structure was the pair (bond) diagram developed by Kekulé (1857) and others in the middle of the last century. We take the pair diagram to consist of $N$ numbered points arranged in clockwise order around a circle with $p$ tie lines connecting pairs of points. We denote a pair diagram by the symbol $D_\kappa^p$ where $\kappa$ is used to distinguish different pair diagrams with the same number of pairs. The number of unpaired points is called the valence of a pair diagram and is designated by $v$:

$$v = N - 2p. \tag{1}$$

One or several points may be assigned to a single atom. The pair diagram does not specify the spatial arrangements of the atoms. We arbitrarily set $\kappa = \text{I}$ for the pair diagram which pairs point one with point two, etc.

Historically, the chemist has preferred the so-called canonical pair diagrams, pair diagrams with uncrossed tie lines.

For $N = 4, p = 2$,

| $\kappa =$ | I | II | III |
|---|---|---|---|
| $D_\kappa^p =$ |  |  |  |
| Classification: | Canonical | Canonical | Noncanonical |

We present an aufbau procedure which produces only canonical pair diagrams and we extend the meaning of the word canonical to all pair diagrams constructed by the aufbau technique. We begin with $N = 1$ and add one point at a time. If a tie line is to be added, we add it by tying the

*N*th point to the point of the largest unpaired integer. The number of canonical pair diagrams for a given $N$ and $p$ is

$$f_N^p = N!(N - 2p + 1)/p!(N - p + 1)!. \tag{2}$$

We present the aufbau to $N = 4$ in Figure 1.

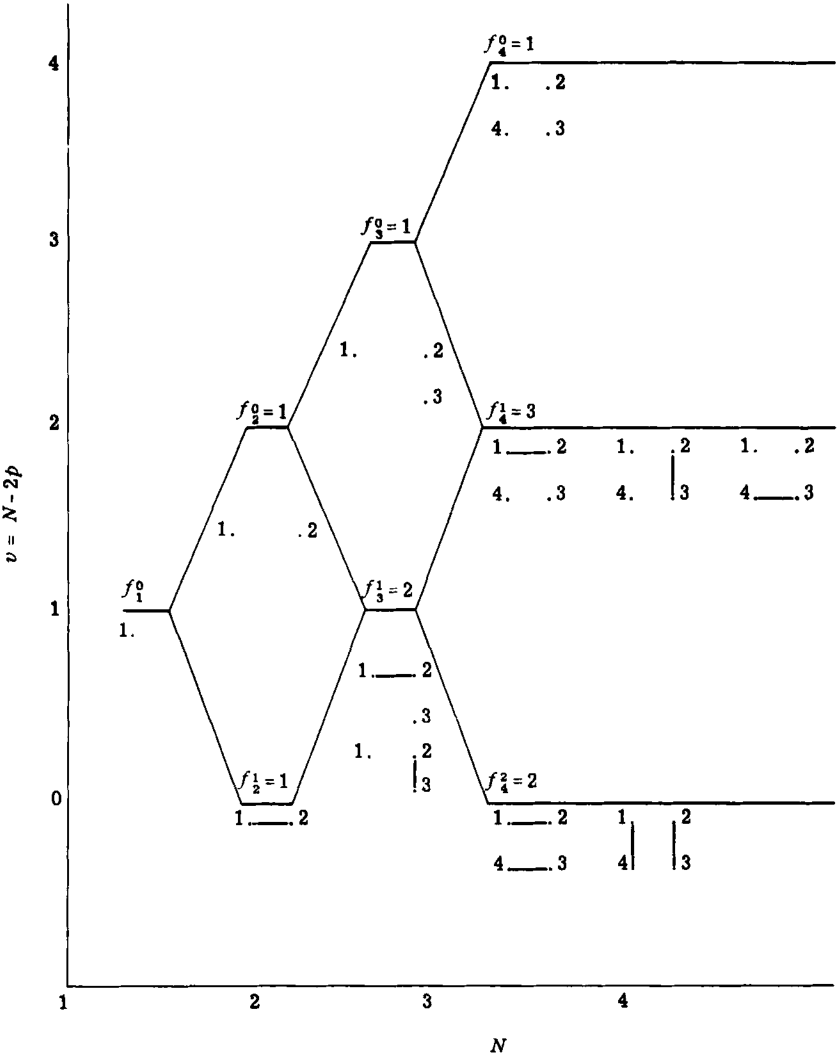
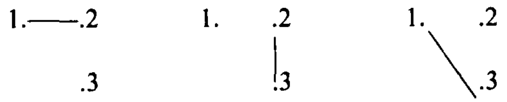


Fig. 1. Aufbau of canonical pair diagram ($f_N^p$ is the number of canonical pair diagrams for a given $N$ and $p$).

Pair diagrams for $N = 3$, $p = 1$, $f_N^p = 2$ are:

$\kappa =$ I II III

$D_\kappa^p =$



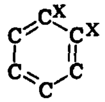
Classification: Canonical Canonical Noncanonical

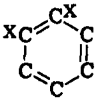
As examples we take the ground states of the following systems:

| $\kappa =$ | I | II | III |
|---|---|---|---|
| (*i*) Allyl radical | $C = C - \dot{C}$ | $\dot{C} - C = C$ | $C - \dot{C} - C$ |
| (*ii*) Three colinear hydrogen atoms | $H - H \quad \dot{H}$ | $\dot{H} \quad H - H$ | $H \quad \dot{H} \quad H$ |
| (*iii*) Lithium atom | $(1s1s')2s$ | $(1s'2s)1s$ | $(1s2s)1s'$ |

The pair diagrams are a simple topology of points and tie lines. The exclusion of diagrams which tie more than two points is called the twoness property of the points.

Pair diagrams were found to provide excellent models for many molecules. However, a few molecules were found which could not be adequately described by single pair diagrams. Kekulé noted in 1872 the nonexistence of two isomers of orthodisubstituted benzene:





Arndt *et al.* (1924), Ingold and Ingold (1926), and others suggested that benzene possesses a chemical structure intermediate between several pair diagrams. Such a concept is conveniently described in terms of a structure vector space. We discuss this concept in the following section.

## C. The Structure Vector Space

We postulate a vector space, called the *p*th structure vector space, spanned by $f_N^p$ basis vectors $|\kappa\rangle$ which lie in one-to-one correspondence with the $f_N^p$ canonical pair diagrams $D_\kappa^p$. Vectors corresponding to a noncanonical pair diagram are expressed as a linear combination of the basis vectors. The basis vectors are called pure valence states. The chemical structure of a molecule is represented by a vector

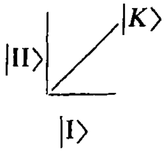
$$|K\rangle = \sum_{\kappa}^{f_N^p} b_{\kappa K}|\kappa\rangle \qquad (3)$$

where $b_{\kappa K}$ is a numerical coefficient. The chemical structure $|K\rangle$ is a "superposition" or "resonance hybrid" of pure valence states.

For $N = 3$, $p = 1$, $f_N^p = 2$,

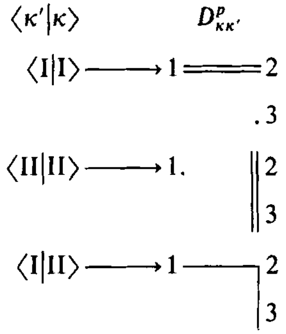
$$|K\rangle = b_{\mathrm{I}K}|\mathrm{I}\rangle + b_{\mathrm{II}K}|\mathrm{II}\rangle.$$

A graphical representation of $|K\rangle$ is

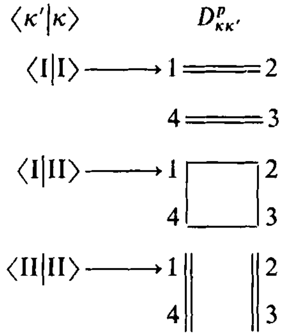


Associated with $|\kappa\rangle$ is a dual vector $\langle\kappa|$ defined with respect to $|\kappa\rangle$ by the scalar product $\langle\kappa|\kappa\rangle$. The scalar product $\langle\kappa'|\kappa\rangle$ is represented by the superposition $D_{\kappa\kappa'}^p$ of two-pair $D_{\kappa'}^p$ and $D_\kappa^p$.

For $N = 3$, $p = 1$,



For $N = 4$, $p = 2$,



Let $H$ be the energy operator on the vector space. The form of $H$ need not be specified here. The scalar products $\langle\kappa'|H|\kappa\rangle$, $\kappa,\kappa' = \mathrm{I}$ to $f_N^p$ constitute a matrix representation of $H$. The element $\langle\kappa|H|\kappa\rangle$ is the energy of the pure valence state of $|\kappa\rangle$. To obtain the coefficient $b_{\kappa K}$ one formally solves the equations

$$\sum_{\kappa}^{f_N^p} b_{\kappa K}\{\langle\kappa'|H|\kappa\rangle - E\langle\kappa'|\kappa\rangle\} = 0, \qquad \kappa' = 1 \text{ to } f_N^p. \tag{4}$$

For $N = 3$, $p = 1$, the determinant from Eq. (4) is

$$\begin{vmatrix} \langle\mathrm{I}|H|\mathrm{I}\rangle - E & \langle\mathrm{I}|H|\mathrm{II}\rangle - E\langle\mathrm{I}|\mathrm{II}\rangle \\ \langle\mathrm{II}|H|\mathrm{I}\rangle - E\langle\mathrm{II}|\mathrm{I}\rangle & \langle\mathrm{II}|H|\mathrm{II}\rangle - E \end{vmatrix} = 0,$$

$$E_K = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A},$$

$$A = 1 - (\langle\mathrm{I}|\mathrm{II}\rangle)^2,$$

$$B = \langle\mathrm{I}|H|\mathrm{I}\rangle + \langle\mathrm{II}|H|\mathrm{II}\rangle - 2\langle\mathrm{I}|H|\mathrm{II}\rangle\langle\mathrm{I}|\mathrm{II}\rangle,$$

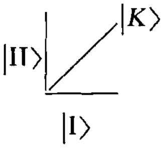
$$C = \langle\mathrm{I}|H|\mathrm{I}\rangle\langle\mathrm{II}|H|\mathrm{II}\rangle - (\langle\mathrm{I}|H|\mathrm{II}\rangle)^2.$$

*Case* 1.

$$\langle\mathrm{I}|H|\mathrm{I}\rangle = \langle\mathrm{II}|H|\mathrm{II}\rangle \quad \text{and} \quad \langle\mathrm{I}|\mathrm{I}\rangle = \langle\mathrm{II}|\mathrm{II}\rangle = 1,$$

then

$$b_{\mathrm{I}K}/b_{\mathrm{II}K} = \pm 1,$$



*Case* 2.

$$(\langle\mathrm{I}|H|\mathrm{I}\rangle)^2 \gg (\langle\mathrm{II}|H|\mathrm{II}\rangle)^2, (\langle\mathrm{I}|H|\mathrm{II}\rangle)^2$$

and

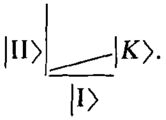
$$1 \gg (\langle\mathrm{I}|\mathrm{II}\rangle)^2,$$

then

$$E_K \cong \langle\mathrm{I}|H|\mathrm{I}\rangle,$$

and

$$b_{\mathrm{I}K} \cong 1, \qquad b_{\mathrm{II}K} \sim 0,$$



*Case* 3.

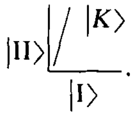
$$(\langle \mathrm{II}|H|\mathrm{II}\rangle)^2 \gg (\langle \mathrm{I}|H|\mathrm{I}\rangle)^2, (\langle \mathrm{I}|H|\mathrm{II}\rangle)^2,$$

and

$$1 \gg (\langle \mathrm{I}|\mathrm{II}\rangle)^2,$$

$$E_K \simeq \langle \mathrm{II}|H|\mathrm{II}\rangle,$$

$$b_{\mathrm{II}K} \simeq 1, \qquad b_{\mathrm{I}K} \sim 0,$$



The relative magnitudes of the energies of the several valence states can often be inferred from symmetry arguments and from experiment. When these relative magnitudes can be inferred, the relative magnitudes of the coefficients $b_{\kappa K}$ can be inferred.

For the three examples:

(*i*) the allyl radical is case 1;
(*ii*) in the course of the reaction

$$H_2 + H \rightarrow H + H_2$$

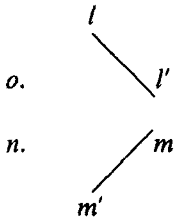
the vector moves from case 2 to case 3 passing through case 1;
(*iii*) the lithium atom is case 2.

We have developed the concept of pure valence states based on canonical pair diagrams. There exist alternate nongeometrical representations of canonical pair diagrams which give insight into the structure vector space. These are developed in the following sections.

## D. An Algebraic Representation

Sylvester (1878) proposed an algebraic representation of pair diagrams in a classical paper entitled "On an Application of the New Atomic Theory to the Graphical Representation of the Invariants and Covariants of Binary Quantics." He introduced his paper with the sentence, "By the new Atomic Theory, I mean that sublime invention of Kekulé which stands to the old in a somewhat similar relation as the Astronomy of Kepler to Ptolemy or the System of Nature of Darwin to that of Linnaeus—like the latter it lies outside of the immediate sphere of energetics basing its laws on pure relations of form and like the former as perfected by Newton, these laws admit exact arithmetical definition." Clearly, Sylvester regarded the pair diagram as a topological concept.

A simple binary quantic for (an algebraic representation of) a pair diagram was proposed by Weyl (1931; see also Rumer *et al.*, 1931; Rumer, 1932). For the pair diagram



the algebraic expression is

$$\kappa^p = [ll'][mm'][n][o]. \tag{5}$$

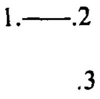
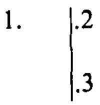
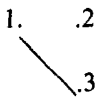
Here

$$[ll'] = l_+l'_- - l_-l'_+ \tag{6}$$

is the algebraic expression for pairing between points $l$ and $l'$. Here $l_+$ and $l_-$ represent two "states" of the same integer. For an unpaired point we write

$$[o] = o_+. \tag{7}$$

For $N = 3$, $p = 1$, $f_N^p = 2$,

| $\kappa$ | $D_\kappa^p$ | Classification | $\kappa^p$ |
|---|---|---|---|
| I |  | Canonical | $\mathrm{I}^p = [12][3] = 1_+2_-3_+ - 1_-2_+3_+$ |
| II |  | Canonical | $\mathrm{II}^p = [23][1] = 1_+2_+3_- - 1_+2_-3_+$ |
| III |  | Noncanonical | $\mathrm{III}^p = [13][2] = 1_+2_+3_- - 1_-2_+3_+$ |

Note that

$$\mathrm{III}^p = \mathrm{I}^p + \mathrm{II}^p.$$

For $N = 4$, $p = 2$, $f_N^p = 2$,

| $\kappa$ | Classification | $\kappa^p$ |
|---|---|---|
| I | Canonical | $\mathrm{I}^p = [12][34] = 1_+2_-3_+4_- - 1_-2_+3_+4_-$<br>$- 1_+2_-3_-4_+ + 1_-2_+3_-4_+$ |
| II | Canonical | $\mathrm{II}^p = [14][23] = 1_+4_-2_+3_- - 1_-4_+2_+3_-$<br>$- 1_+4_-2_-3_+ + 1_-4_+2_-3_+$ |
| III | Noncanonical | $\mathrm{III}^p = [13][24] = 1_+3_-2_+4_- - 1_-3_+2_+4_-$<br>$- 1_+3_-2_-4_+ + 1_-3_+2_-4_+$ |

Note that

$$\mathrm{III}^p = \mathrm{I}^p + \mathrm{II}^p.$$

The algebraic expression for the noncanonical diagrams can be expressed in terms of the $f_N^p$ algebraic expressions for the canonical diagrams. This provides a mathematical rationale for the structure vector space spanned by $f_N^p$ basis vectors. It also provides a mathematical rationale for the chemists' intuitive rejection of noncanonical pair diagrams.

Initially, chemists, e.g., Mallet (1878) and Frankland (1878), expressed considerable interest in the algebraic representation of chemical structure. However, in the absence of dynamical laws by which to determine the binding forces, the chemists abandoned the algebraic representation and stuck to the graphical one.

### E. The Pair Operator Representation

Young (1900) introduced a mathematical construction by means of which one can obtain pair operators which are representations of the pair diagrams. The pair operator for pair diagram $D_\kappa^p$ is written

$$\kappa^p = \sum_c \kappa_c^p P_c \tag{8}$$

where $\kappa_c^p$ is a numercial coefficient and $P_c$ is one of the $N!$ permutations on the $N$ objects. The detail of this formulation is given in Section III.

For $N = 3$, $p = 1$, $f_N^p = 2$,

$$\begin{aligned}
\mathrm{I}^p &= \mathscr{I} - (13) + (12) - (123),\\
\mathrm{II}^p &= -\mathscr{I} + (13) - (23) + (132),\\
\mathrm{III}^p &= -(23) + (12) - (123) + (132).
\end{aligned}$$

Note that

$$\mathrm{III}^p = \mathrm{I}^p + \mathrm{II}^p.$$

The pair operators for canonical diagrams $D_\kappa^p$ are representations of the basis vectors of the $p$th structure vector space. Considered as vectors, the canonical pair operators span a subspace of a larger space, the permutation vector space.

### F. The Permutation Vector Space

The permutation vector space is a vector space spanned by $N!$ vectors $|P_c\rangle$ which lie in one-to-one correspondence with the $N!$ permutations $P_c$. The dual of $|P_c\rangle$ is $\langle P_c|$. A scalar product is

$$\begin{aligned} \langle P_{c'}|P_c\rangle &= \langle P_c^{-1}P_{c'}|\mathscr{I}\rangle \\ &= \langle P_d|\mathscr{I}\rangle \end{aligned} \tag{9}$$

where $P_d = P_c^{-1}P_{c'}$. The pair operator is treated as a vector in this space,

$$|\kappa\rangle = \sum_c \kappa_c|P_c\rangle. \tag{10}$$

The $f_N^p$ canonical pair operators span the $p$th structure space, a subspace of the permutation space.

We can express the scalar products of the structure space in terms of scalar products in the permutation space. Thus by Eq. (39)

$$\begin{aligned} \langle\kappa'|\kappa\rangle &= \sum_c \sum_c \kappa_{c'}^{\prime p}\kappa_c^p\langle P_{c'}|P_c\rangle \\ &\equiv C^p \sum_d [P_d]_{\kappa'\kappa} P\langle_d|\mathscr{I}\rangle \end{aligned} \tag{11}$$

and

$$\langle\kappa'|H|\kappa\rangle = C^p \sum_d [P_d]_{\kappa'\kappa}\langle P_d|H|\mathscr{I}\rangle \tag{12}$$

where $C^p = 2^p(N-p)!p!$.

For $N = 3$, $p = 1$,

| $P_d =$ | $\mathscr{I}$ | (12) | (13) | (23) | (123) | (132) |
|---|---|---|---|---|---|---|
| $[P_d]_{\mathrm{I\,I}} =$ | 1 | 1 | $-1/2$ | $-1/2$ | $-1/2$ | $-1/2$ |
| $[P_d]_{\mathrm{II\,II}} =$ | 1 | $-1/2$ | $-1/2$ | 1 | $-1/2$ | $-1/2$ |
| $[P_d]_{\mathrm{I\,II}} =$ | $-1/2$ | $-1/2$ | 1 | $-1/2$ | $-1/2$ | 1 |

Note that

$$\langle(123)|\mathscr{I}\rangle = \langle\mathscr{I}|(123)\rangle = \langle\mathscr{I}|(132)\rangle = \langle(132)|\mathscr{I}\rangle.$$

We shall consider several cases.

(*a*) Let

$$\langle P_c|H|\mathscr{I}\rangle = \text{constant for all } P_c,$$

then,

$$\langle \mathrm{I}|H|\mathrm{I}\rangle = \langle \mathrm{II}|H|\mathrm{II}\rangle = \langle \mathrm{I}|H|\mathrm{II}\rangle = 0.$$

This is an exclusion principle for matrix elements.

(*b*) Let

$$\langle (12)|H|\mathscr{I}\rangle = \langle (23)|H|\mathscr{I}\rangle,$$

then

$$\langle \mathrm{I}|H|\mathrm{I}\rangle = \langle \mathrm{II}|H|\mathrm{II}\rangle, \qquad \text{Case 1.}$$

(*c*) Let

$$\langle \mathscr{I}|H|\mathscr{I}\rangle = Q,$$

$$\langle (12)|H|\mathscr{I}\rangle = (ab),$$

$$\langle (13)|H|\mathscr{I}\rangle = (ac),$$

$$\langle (23)|H|\mathscr{I}\rangle = (bc),$$

$$\langle (123)|H|\mathscr{I}\rangle = \langle (132)|H|\mathscr{I}\rangle = 0,$$

then

$$\langle \mathrm{I}|H|\mathrm{I}\rangle = 4[Q + (ab) - (1/2)(ac) - (1/2)(bc)],$$

$$\langle \mathrm{II}|H|\mathrm{II}\rangle = 4[Q + (bc) - (1/2)(ac) - (1/2)(ab)],$$

$$\langle \mathrm{I}|H|\mathrm{II}\rangle = 4[-(1/2)Q + (ac) - (1/2)(ab) - (1/2)(bc)].$$

(*d*) Let

$$\langle (12)|\mathscr{I}\rangle = \langle (13)|\mathscr{I}\rangle = \langle (23)|\mathscr{I}\rangle = \langle (123)|\mathscr{I}\rangle = \langle (132)|\mathscr{I}\rangle = 0,$$

$$(ab) = \alpha, \qquad (bc) = \beta, \qquad (ac) = \gamma,$$

then

$$E = Q \pm (1/\sqrt{2})\sqrt{(\alpha - \beta)^2 + (\alpha - \gamma)^2 + (\beta - \gamma)^2}.$$

Compare with Eyring *et al.* (1944).

The coefficients $[P_a]_{\kappa'\kappa}$ for $P_a = \mathscr{I}$ or $(ef)$ and for $p = (N-\delta)/2$ ($\delta = 0$ or 1 for $N$ even or odd) can be obtained by a scheme due to Pauling (1933). We form for $N + \delta$ the composite pattern $D^p_{\kappa'\kappa}$ for the scalar product $\langle \kappa'|\kappa\rangle$. We call a closed polygon an island and designate their number by $i$.

Let $q = (N + \delta)/2 - i$. Then

$[\mathscr{I}]_{\kappa'\kappa} - (1/2)^q$,

$[(ef)]_{\kappa'\kappa} = (1/2)^q$, if $e$ and $f$ are in the same island and connected by an odd number of tie lines,

$= -(1/2)^{q-1}$, if $e$ and $f$ are in the same island and separated by an even number of tie lines,

$= -(1/2)^{q+1}$, if $e$ and $f$ are in different islands.

$[P_a]^p_{\kappa'\kappa}$ for $N = 4$(or 3) and $p = 2$ (or 1):

| | | | | | $P_a$ | | | |
|---|---|---|---|---|---|---|---|---|
| $\kappa'$ | $\kappa$ | $D^p_{\kappa\kappa'}$ | $i$ | $q$ | $\mathscr{I}$ | (12) | (13) | (23) |
| I | I | 1 ═ 2<br>4 ═ 3 | 2 | 0 | 1 | 1 | −1/2 | −1/2 |
| II | II | 1‖ ‖2<br>4‖ ‖3 | 1 | 0 | 1 | −1/2 | −1/2 | 1 |
| I | II | 1┌─┐2<br>4└─┘3 | 1 | 1 | 1/2 | 1/2 | −1 | 1/2 |

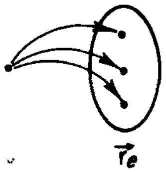
To a trivial phase factor these are the same as the $[P_a]^p_{\kappa'\kappa}$ given above.

### G. The Function Representation

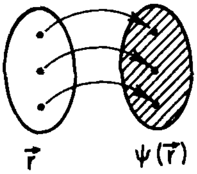
A pair function representation of a pair diagram is obtained by projection with a pair operator on an arbitrary function, a "primitive" function. Let the primitive function be

$$\Psi = \Psi(\mathbf{r}) \tag{13}$$

where $\mathbf{r} = \{\mathbf{r}_1 \ldots \mathbf{r}_e \ldots \mathbf{r}_N\}$ and $\mathbf{r}_e$ is a freely varying vector for point $e$ in Euclidian three-space. The assignment of the vector $\mathbf{r}_e$ to the point $e$ maps (delocalizes, smears out) point $e$ onto Euclidean three-space:



The function $\Psi(\mathbf{r})$ maps each point of Euclidean three-space, one-to-one, onto a function space[1]:



Thus $\Psi(\mathbf{r})$ affects a delocalization, a smearing out, of the $N$ points onto a function space. The pair function for $D_\kappa^p$ is, by Eq. (8),

$$\Psi_\kappa^p = \kappa^p \Psi(\mathbf{r})$$

$$= \sum_c \kappa_c^p \Psi(P_c \mathbf{r}). \tag{14}$$

For $N = 3$, $p = 1$, and $\Psi = a(1)\, b(2)\, c(3) = abc$,

$$\Psi_{\mathrm{I}}^p = abc - cba + bac - bca,$$

$$\Psi_{\mathrm{II}}^p = -abc + cba - acb + cab,$$

$$\Psi_{\mathrm{III}}^p = -acb + bac - bca + cab.$$

Note that

$$\Psi_{\mathrm{III}}^p = \Psi_{\mathrm{I}}^p + \Psi_{\mathrm{II}}^p.$$

If $D_\kappa^p$ pairs $l$ and $l'$ then

$$(\overline{ll'})\Psi_\kappa^p = \Psi_\kappa^p. \tag{15}$$

Here the $(\overline{ll'})$ indicates a permutation on the function space:

$$(\overline{12})\Psi_{\mathrm{I}}^p = \quad bac - bca + abc - cba = \Psi_{\mathrm{I}}^p,$$

$$(\overline{23})\Psi_{\mathrm{II}}^p = -acb + cab - abc + cba = \Psi_{\mathrm{II}}^p,$$

$$(\overline{13})\Psi_{\mathrm{III}}^p = -bca + cab - acb + bac = \Psi_{\mathrm{III}}^p.$$

Thus in the function representation $\Psi_\kappa^p$ of pair diagram $D_\kappa^p$, the paired points are distributed identically over the function space. The pair operator maps the pair diagram onto the function space.

---

[1] Our usage of the term "function space" follows Altmann (1962).

If the primitive function is invariant under the group of permutations on any three indices, then

$$\Psi_{\kappa}^{p} = 0.$$

Let $a = b = c$. Then

$$\Psi_{\mathrm{I}}^{p} = \Psi_{\mathrm{II}}^{p} = \Psi_{\mathrm{III}}^{p} = 0.$$

Such a primitive function is excluded as a source of a function representation of a pair diagram.

It should be noted that up to this point we have used only the canonical pair diagrams and the corresponding pair operators. We have used no property of the electron other than its twoness, nor have we used an explicit form for the Hamiltonian or the primitive function. Nevertheless, we have been able to formulate matrix elements and an exclusion principle. Such a formulation could be called an electron-free quantum chemistry.

### H. The Electron, the Hamiltonian and Spin

Lewis (1916) and Langmuir (1919) showed that a point in a pair diagram is to be identified with an electron and that the twoness property of a point is the twoness property of an electron. In 1925 the electron was found to have an intrinsic angular momentum, called spin, for which two values are possible. In addition, the electron was found to possess an intrinsic or spin magnetic moment. By 1926 an explicit dynamical form of the Hamiltonian (the energy operator) was obtained. The spin magnetic moment was found to make only small contributions to the energy. Consequently, for conventional chemistry, spin is not a dynamical variable and the Hamiltonian is essentially spin-free. The principal contribution of spin to quantum chemistry is the proprety of twoness which it bestows on the electron (Pauli, 1925). An accurate solution to the one-electron atomic problem shows the electron to be delocalized. These solutions provide orbital forms with which to construct primitive functions for polyelectronic problems.

Since the spin-free Hamiltonian possesses permutational symmetry, it was clear that group theoretical methods would apply. The major work in the field is Weyl (1928). Slater (1953), in speaking of this early application of the permutation algebra to polyelectronic problems, said it was "complicated, but not fruitful. Those engaged in it became immersed in their mathematics and failed to make connections with the theory of complex spectra already so well developed from the vector model point of view." Weyl (1928) said, "It is rumored that the group pest is gradually being cut out of quantum physics. It does indeed seem possible to avoid [the use of the permutation group] with the aid of the Pauli exclusion principle."

### I. The Antisymmetric Space-Spin Representations

The development to which Weyl referred is the antisymmetric space-spin formulation outlined in Section VI. If the space primitive function is a product of space orbitals, an antisymmetric space-spin function is obtained by forming a Slater determinant. Pair functions are linear combinations of the Slater determinants.

With an explicit form for the energy operator and good primitive functions, the matrix elements over pair functions can be evaluated and the eigenvalues and eigenvectors determined. This method has been tremendously successful. It has supported and extended all earlier concepts of chemical structure and has permitted the precise prediction of the properties of simple atoms and molecules.

### J. Spin-Free Quantum Chemistry

Following the early developments, Serber (1934*a*,b,), Yamanouchi (1938), and Kotani *et al.* (1955) made important contributions to the application of permutation group theory to quantum chemistry and, in consequence, to the development of a spin-free quantum chemistry. The application of the techniques elaborated in these papers required, or appeared to require, considerable knowledge of group theory. These approaches appeared almost as formidable as the earlier ones.

It was noted above that the pair operators provide a means for obtaining pair functions which are faithful representations of pair diagrams. The canonical pair functions are a suitable basis for quantum chemical computation. While the applicability of pair operators rests on group theory, the construction and use of pair operators require no knowledge of group theory. With the pair operators, a spin-free formulation appears to be as simple as the Slater formulation. Thus the spin-free formulation provides simplicity in methodology and in concept.

## III. The Spin-Free Formulation of Quantum Chemistry

### A. Construction of Pair Operators

The first step in the spin-free formulation of quantum chemistry is the construction of a pair (projection) operator. We begin by specifying the number $N$ of electrons and the number $p$ of electron pairs. The pair number $p$ identifies the $p$th permutation state and is related to the total spin quantum number $S$ by

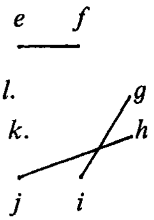
$$p = N/2 - S. \tag{16}$$

Consider $N = 3$, $p = 1$. Examples are the ground states of:

(*i*) the $\pi$ electrons of the allyl radical,
(*ii*) three hydrogen atoms;
(*iii*) the lithium atom.

We next form a pair diagram by arranging the first $N$ integers in a circle and forming $p$ integer pairs with $p$ tie lines. We designate by $D^p_\kappa$ a pair diagram containing $p$ pairs where $\kappa$ is used to distinguish pair diagrams which differ only in the way integers are paired. Thus

$D^p_\kappa =$

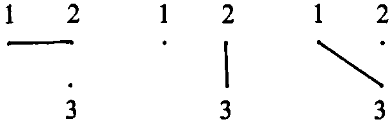


We arbitrarily set $\kappa = \mathrm{I}$ for the diagram in which one is paired with two, three with four, etc.

For $N = 3$, $p = 1$,

$\kappa =$ I II III

$D^p_\kappa =$



Next, for each $D^p_\kappa$ we arrange the first $N$ integers into two columns of lengths $N - p$ and $p$, respectively, so that the paired integers lie in the same row, with the smaller first. We call this array a tableau and label it $T^p_\kappa$. Thus

$$T^p_\kappa = \begin{array}{|c|c|}\hline e & f \\ \hline g & i \\ \hline h & j \\ \hline k \\ \cline{1-1} l \\ \cline{1-1}\end{array}$$

For $N = 3$, $p = 1$

$$\begin{array}{cccc} \kappa = & \mathrm{I} & \mathrm{II} & \mathrm{III} \\ T^p_\kappa = & \begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 \\ \cline{1-1}\end{array} & \begin{array}{|c|c|}\hline 2 & 3 \\ \hline 1 \\ \cline{1-1}\end{array} & \begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 \\ \cline{1-1}\end{array} \end{array}$$

For each $T_\kappa^p$ there exists a permutation $\sigma_{I\kappa}$ which rearranges the integers in $T_I^p$ so as to convert it into $T_\kappa^p$. Thus

$$T_\kappa^p = \sigma_{I\kappa} T_I^p . \tag{17}$$

| $\kappa =$ | I | II | III |
|---|---|---|---|
| $\sigma_{I\kappa} =$ | $\mathscr{I}$ | (132) | (23) |
| Classification: | Even | Even | Odd |
| $\varepsilon(\sigma_{I\kappa}) =$ | +1 | +1 | −1 |

For $T_\kappa^p$ we define a row operator

$$P_\kappa^p = \sum_a \pi_{\kappa a}^p . \tag{18}$$

The sum extends over the identity operator and the permutations of integers along rows in $T_\kappa^p$. We define a column operator

$$N_\kappa^p = \sum_b \varepsilon_g v_b^p . \tag{19}$$

The sum extends over the identity operator and the permutations of integers down columns in $T_\kappa^p$. The symbol $\varepsilon_b = \pm 1$ for $v_b^p$ an even or odd permutation.

For $T_I^p$

$$P_I^p = \mathscr{I} + (12),$$

$$N_I^p = \mathscr{I} - (13).$$

Finally for a pair diagram $D_\kappa^p$ we define a pair operator[2]

$$\begin{aligned} \kappa^p &= \varepsilon(\sigma_{I\kappa}) N_I^p P_I^p \sigma_{I\kappa} \\ &\equiv \sum_c \kappa_c^p P_c . \end{aligned} \tag{20}$$

The operator $N_I^p P_I^p \sigma_{I\kappa}$ is a Young operator. The properties of Young operators are discussed in more detail in Section V.

Of all possible pair operators only

$$f_N^p = N!(N - 2p + 1)/p!(N - p + 1)! \tag{21}$$

are linearly independent. The $f_N^p$ pair operators for the $f_N^p$ canonical diagrams are linearly independent and span the $p$th structure vector space.

---

[2] The factor $\varepsilon(\sigma_{I\kappa})$ is a phase factor which was included to yield the same phase relations as in Section VI. It can be omitted.

For $N = 3, p = 1, f_N^p = 2$,

$$\begin{aligned} \mathrm{I}^p &= (+1)N_\mathrm{I}^p P_\mathrm{I}^p = [\mathscr{I} - (13)][\mathscr{I} + (12)] \\ &= \mathscr{I} - (13) + (12) - (123), \end{aligned}$$

$$\begin{aligned} \mathrm{II}^p &= (+1)N_\mathrm{I}^p P_\mathrm{I}^p(132) = [\mathscr{I} - (13) + (12) - (123)](132) \\ &= -\mathscr{I} + (13) - (23) + (132), \end{aligned}$$

$$\begin{aligned} \mathrm{III}^p &= (-1)N_\mathrm{I}^p P_\mathrm{I}^p(23) = -[\mathscr{I} - (13) + (12) - (123)](23) \\ &= -(23) + (12) - (123) + (132). \end{aligned}$$

Note that

$$\mathrm{III}^p = \mathrm{I}^p + \mathrm{II}^p.$$

For $N = 3, p = 0, f_N^p = 1$,

$$D_\mathrm{I}^p = \begin{array}{lr} 1. & .2 \\ & \\ 3. & \end{array} \qquad T_\mathrm{I}^p = \begin{array}{|c|}\hline 1 \\ \hline 2 \\ \hline 3 \\ \hline \end{array}$$

$$P_\mathrm{I}^p = \mathscr{I},$$

$$N_\mathrm{I}^p = \mathscr{I} - (12) - (13) - (23) + (123) + (132),$$

$$\mathrm{I}^p = N_\mathrm{I}^p P_\mathrm{I}^p = \mathscr{I} - (12) - (13) - (23) + (123) + (132).$$

## B. Construction of Spin-Free Pair Functions

We begin by selecting an arbitrary "primitive" function

$$\Psi = \Psi(\mathbf{r}). \tag{22}$$

Here $\mathbf{r} = \{\mathbf{r}_1, \ldots \mathbf{r}_e, \ldots \mathbf{r}_N\}$, where $\mathbf{r}_e$ represents the coordinates of the $e$th electron in Euclidean three-space. The primitive function distributes, in some particular way, arbitrarily numbered electrons in the physical space of the system. Its choice depends upon the motivation, experience, and computing facilities of the investigator. A frequent choice of primitive function is the orbital product.

$$\Psi = a(1)b(2)c(3) \cdots \equiv abc \cdots \tag{23}$$

where $a(1) = a(\mathbf{r}_1)$ is a function only of the coordinate $\mathbf{r}_1$. When the electron designation is omitted, the orbital in the first position is assigned electron one, etc. For an orbital product primitive function, the pair diagram expresses pairing between orbitals. For orbitals localized on separate atoms, the pair diagram expresses pairing between atoms.

For $N = 3$ we take $\Psi = a(1)b(2)c(3) \equiv abc$. The examples are as follows:

(*i*) *Allyl radical.* $a$, $b$, and $c$, are $\pi$ orbitals localized on carbon atoms $a$, $b$, and $c$.

$$\begin{array}{llll} \kappa = & \text{I} & \text{II} & \text{III} \\ D^p_\kappa = & \text{C}_a = \text{C}_b\text{—}\dot{\text{C}}_c & \dot{\text{C}}_a\text{—}\text{C}_b = \text{C}_c & \overline{\text{C}_a\text{—}\dot{\text{C}}_b\text{—}\text{C}_c} \end{array}$$

(*ii*) *Three hydrogen atoms.* $a$, $b$, and $c$ are $1s$ orbitals on atoms, $a$, $b$, and $c$. For a colinear configuration,

$$\begin{array}{llll} \kappa = & \text{I} & \text{II} & \text{III} \\ D^p_\kappa = & \text{H}_a\text{—H}_b \quad \text{H}_c & \text{H}_a \quad \text{H}_b\text{—H}_c & \overline{\text{H}_a \quad \dot{\text{H}}_b \quad \text{H}_c} \end{array}$$

(*iii*) *The lithium atom.* $a$, $b$, and $c$ are $1s$, $1s'$, and $2s$ orbitals. Primed and unprimed orbitals differ in their orbital exponents.

$$\begin{array}{llll} \kappa = & \text{I} & \text{II} & \text{III} \\ D^p_\kappa = & (1s1s')2s & (1s'2s)1s & (1s2s)1s' \end{array}$$

The parentheses represent paired orbitals.

We now define the operation

$$P_a\Psi(\mathbf{r}) \equiv \Psi(P_a\mathbf{r}). \tag{24}$$

We consider in this section only those primitive functions for which the functions $P_a\Psi(q)$, $a = 1$ to $N!$, are independent.

For $\Psi = a(1)b(2)c(3) = abc$ and $P_a = (123)$ we have

$$(123)a(1)b(2)c(3) = a(3)b(1)c(2) = bca.$$

A pair function for pair diagram $D^p_\kappa$ is projected out of a primitive function $\Psi(q)$ by the pair operator $\kappa^p_\kappa$. That is

$$\begin{aligned} \Psi^p_\kappa &= \kappa^p\Psi(\mathbf{r}) \\ &= \sum_a \kappa^p_a P_a\Psi(\mathbf{r}) \\ &= \sum_a \kappa^p_a\Psi(P_a\mathbf{r}). \end{aligned} \tag{25}$$

For $p = 1, f_N^p = 2$,

$$\begin{aligned}
\Psi_{\mathrm{I}}^p &= a(1)b(2)c(3) - a(3)b(2)c(1) + a(2)b(1)c(3) - a(3)b(1)c(2) \\
&= abc - cba + bac - bca, \\
\Psi_{\mathrm{II}}^p &= -a(1)b(2)c(3) + a(3)b(2)c(1) - a(1)b(3)c(2) + a(2)b(3)c(1) \\
&= -abc + cba - acb + cab, \\
\Psi_{\mathrm{III}}^p &= -a(1)b(3)c(2) + a(2)b(1)c(3) - a(3)b(1)c(2) + a(2)b(3)c(1) \\
&= -acb + bac - bca + cab.
\end{aligned}$$

Note that

$$\Psi_{\mathrm{III}}^p = \Psi_{\mathrm{I}}^p + \Psi_{\mathrm{II}}^p.$$

For $p = 0, f_N^p = 1$,

$$\begin{aligned}
\Psi_{\mathrm{I}}^p &= a(1)b(2)c(3) - a(2)b(1)c(3) - a(3)b(2)c(1) = a(1)b(3)c(2) \\
&\qquad + a(2)b(3)c(1) \\
&= abc - bac - cba + acb + bca + cab.
\end{aligned}$$

We now write

$$\Psi(\mathbf{r}) = |\mathscr{S}\rangle \tag{26}$$

and for a particular $p$

$$\Psi_\kappa^p = \kappa|\mathscr{S}\rangle = |\kappa\rangle. \tag{27}$$

The eigenfunction relative to a given primitive function is

$$|K\rangle = \sum_{\kappa}^{f^p} b_{\kappa K}|\kappa\rangle. \tag{28}$$

The coefficients $b_{\kappa K}$ are obtained in the usual manner from the equation

$$\sum_{\kappa} b_{\kappa K}[\langle\kappa'|H|\kappa\rangle - E\langle\kappa'|\kappa\rangle] = 0 \tag{29}$$

where

$$\langle\kappa'|H|\kappa\rangle = \int \Psi_\kappa^{p'*} H \Psi_\kappa^p \, d\tau. \tag{30}$$

For $N = 3$, $p = 1, f_N^p = 2$,

$$|K\rangle = b_{\mathrm{I}K}|\mathrm{I}\rangle + b_{\mathrm{II}K}|\mathrm{II}\rangle$$

$$\begin{vmatrix} \langle\mathrm{I}|H|\mathrm{I}\rangle - E\langle\mathrm{I}|\mathrm{I}\rangle & \langle\mathrm{I}|H|\mathrm{II}\rangle - E\langle\mathrm{I}|\mathrm{II}\rangle \\ \langle\mathrm{II}|H|\mathrm{I}\rangle - E\langle\mathrm{II}|\mathrm{I}\rangle & \langle\mathrm{II}|H|\mathrm{II}\rangle - E\langle\mathrm{II}|\mathrm{II}\rangle \end{vmatrix} = 0.$$

### C. Matrix Elements

Let $Q$ be a spin-free Hermitian operator that commutes with every permutation operator. The matrix element for $Q$ over pair functions $\Psi_{\kappa'}^{p'}$ and $\Psi_{\kappa}^{p}$ is

$$\begin{aligned}\langle\kappa'|Q|\kappa\rangle &= \int \Psi_{\kappa'}^{p'*} Q \Psi_{\kappa}^{p}\, d\tau \\ &= \int \kappa'^{p'}\Psi^{*} Q \kappa^{p}\Psi\, d\tau \\ &= \int \bar{\kappa}^{p}\kappa'^{p'}\Psi^{*} Q\Psi\, d\tau. \end{aligned} \tag{31}$$

Here

$$\begin{aligned}\bar{\kappa}^{p} &= \sum_{c} \kappa_{c}(P_{c})^{-1} \\ &= \varepsilon(\sigma_{\mathrm{I}\kappa})\sigma_{\kappa\mathrm{I}} P_{\mathrm{I}}^{p} N_{\mathrm{I}}^{p}.\end{aligned} \tag{32}$$

By Eqs. (32) and (20), and (138) and (158),

$$\begin{aligned}\bar{\kappa}^{p}\kappa'^{p'} &= \delta^{pp'}\varepsilon(\sigma_{\kappa\kappa'}) m^{p} P_{\kappa}^{p} N_{\kappa}^{p} P_{\kappa}^{p} \sigma_{\kappa\kappa'} \\ &\equiv \delta^{pp'} C^{p} \sum_{e} [P_{e}]_{\kappa'\kappa}^{p} P_{e}\end{aligned} \tag{33}$$

where $C^{p} = 2^{p}(N-p)!p!$.

For $N = 3$, $p = 1$,

$$\begin{aligned}\bar{\mathrm{I}}^{p}\mathrm{I}^{p} &= 2[\mathscr{I} + (12)][\mathscr{I} - (13)][\mathscr{I} + (12)] \\ &= 4[\mathscr{I} + (12) - (1/2)(13) - (1/2)(23) - (1/2)(123) - (1/2)(132)], \\ \overline{\mathrm{II}}^{p}\mathrm{II}^{p} &= 2[\mathscr{I} + (23)][\mathscr{I} - (12)][\mathscr{I} + (23)] \\ &= 4[\mathscr{I} + (23) - (1/2)(12) - (1/2)(13) - (1/2)(123) - (1/2)(132)], \\ \bar{\mathrm{I}}\,\mathrm{II}^{p} &= \bar{\mathrm{I}}^{p}\mathrm{I}^{p}(132) = 4[-(1/2)\mathscr{I} - (1/2)(12) - (13) - (1/2)(123) - (132)]\end{aligned}$$

| $P_a$ = | $\mathscr{I}$ | (12) | (13) | (23) | (123) | (132), |
|---|---|---|---|---|---|---|
| $[P_a]_{\mathrm{I\,I}}$ = | 1 | 1 | −1/2 | −1/2 | −1/2 | −1/2, |
| $[P_a]_{\mathrm{I\,II}}$ = | −1/2 | −1/2 | 1 | −1/2 | −1/2 | 1, |
| $[P_a]_{\mathrm{II\,II}}$ = | 1 | −1/2 | −1/2 | 1 | −1/2 | −1/2. |

We substitute Eq. (33) into Eq. (31) to obtain

$$\langle\kappa'|Q|\kappa\rangle = \delta^{pp'} C^{p} \sum_{e} [P_{e}]_{\kappa'\kappa}^{p} \langle P_{e}|Q|\mathscr{I}\rangle \tag{34}$$

where

$$\langle P_e|Q|\mathscr{I}\rangle = \int P_e\Psi^* Q\Psi \, d\tau. \tag{35}$$

The Hamiltonian operator contains one- and two-electron operators only. If $\Psi$ is taken to be a product of distinct orthonormal orbital then

$$\langle P_e|H|\mathscr{I}\rangle = 0 \qquad \text{for } P_e \neq \mathscr{I} \text{ or a transposition.} \tag{36}$$

We set

$$\langle \mathscr{I}|H|\mathscr{I}\rangle \equiv Q, \tag{37}$$

$$(ab) \equiv \int (ba)^* Hab \, d\tau. \tag{38}$$

For $N = 3$, $p = 1$,

$$\langle \mathrm{I}|H|\mathrm{I}\rangle = 4[Q + (ab) - (1/2)(ac) - (1/2)(bc)],$$
$$\langle \mathrm{II}|H|\mathrm{II}\rangle = 4[Q + (bc) - (1/2)(ab) - (1/2)(ac)],$$
$$\langle \mathrm{I}|H|\mathrm{II}\rangle = 4[(-1/2)Q + (ac) - (1/2)(ab) - (1/2)(bc)].$$

The off-diagonal matrix elements $[P_a]^p_{\kappa'\kappa}$ may be obtained from the diagonal elements $[P_a]^p_{\kappa\kappa}$. Thus

$$\begin{aligned} \bar{\kappa}^p\kappa'^{p'} &= \delta^{pp'}\varepsilon(\sigma_{\kappa\kappa'})\bar{\kappa}^p\kappa^p\sigma_{\kappa\kappa'} \\ &= \delta^{pp'}\varepsilon(\sigma_{\kappa\kappa'})C^p\sum_a [P_a]^p_{\kappa\kappa}P_a\sigma_{\kappa\kappa'}. \end{aligned} \tag{39}$$

Let

$$P_b = P_a\sigma_{\kappa\kappa'}, \tag{40}$$

then

$$P_a = P_b\sigma_{\kappa'\kappa}, \tag{41}$$

so

$$\bar{\kappa}^p\kappa'^{p'} = \delta^{pp'}\varepsilon(\sigma_{\kappa\kappa'})C^p\sum_b [P_b\sigma_{\kappa'\kappa}]^p_{\kappa\kappa}P_b, \tag{42}$$

thus

$$[P_a]^p_{\kappa'\kappa} = [P_a\sigma_{\kappa'\kappa}]^p_{\kappa\kappa}. \tag{43}$$

For $N = 3$, $p = 1$, $\sigma_{\mathrm{II\,I}} = (123)$,

$$\begin{array}{rlccccc}
P_a & = \mathscr{I} & (12) & (13) & (23) & (123) & (132), \\
P_a(123) & = (123) & (23) & (12) & (13) & (132) & \mathscr{I}, \\
[P_a]_{\mathrm{I\,II}} = [P_a\sigma_{\mathrm{I\,II}}]_{\mathrm{I\,I}} & = -1/2 & -1/2 & 1 & -1/2 & -1/2 & 1.
\end{array}$$

For systems with $N \leqslant 6$ and $p = (N - \delta)/2$, where $\delta = 0$ or 1, we can with the help of Eq. (43) obtain all $[P_a]^p_{\kappa'\kappa}$ from a table of the diagonal values $[P_a]^p_{\kappa\kappa}$ developed by Kotani (1958, 1961). See Appendix, p. 112.

The diagonal elements $[P_a]_{\kappa\kappa}$ are obtained directly from the Kotani table for any pair function $\Psi^p_\kappa$. We obtain off-diagonal elements $[P_a]^p_{\kappa'\kappa}$ between $\Psi^p_\kappa$ and $\Psi^p_{\kappa'}$ as follows:

(*i*) form $D^p_{\kappa'}$ and $T^p_{\kappa'}$ for $\Psi^p_{\kappa'}$,

(*ii*) choose a permutation $\sigma_{\kappa\kappa'}$ such that

$$T^p_{\kappa'} = \sigma_{\kappa'\kappa} T^p_\kappa ,$$

(*iii*) form the products

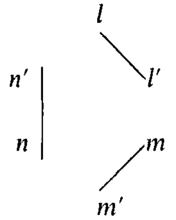
$$P_a \sigma_{\kappa'\kappa} ,$$

(*iv*) set

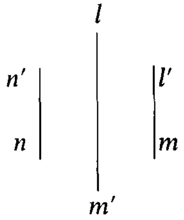
$$[P_a \sigma_{\kappa'\kappa}]^p_{\kappa\kappa} = [P_a]^p_{\kappa'\kappa} .$$

For example, let

$D^p_\kappa =$



$D^p_{\kappa'} =$



$$T^p_\kappa = \begin{array}{|c|c|} \hline l & l' \\ \hline m & m' \\ \hline n & n' \\ \hline \end{array} \qquad T^p_{\kappa'} = \begin{array}{|c|c|} \hline l & m' \\ \hline l' & m \\ \hline n & n' \\ \hline \end{array}$$

$$\sigma_{\kappa'\kappa} = (m'ml'),$$

$$(mm')\sigma_{\kappa'\kappa} = (mm')(m'ml') = (ml'),$$

$$[(mm')]^p_{\kappa'\kappa} = [(ml')]^p_{\kappa\kappa} = -1/2.$$

## D. The Pairing Concept

We wish now to examine the concept of pairing in the spin-free formulation. We consider a permutation which acts on the function space rather than on the coordinate space (see Altmann, 1962). We designate such a permutation by

$$\bar{P}_a \Psi(\mathbf{r}) = \bar{\Psi}(\mathbf{r}). \tag{44}$$

For $\Psi = a(1)b(2)c(3)$,

$$\overline{(123)}\Psi = \overline{(123)}a(1)b(2)c(3) = c(1)a(2)b(3) = cab.$$

Note that $\overline{(123)}\Psi \neq (123)\Psi$.

If we permute both the function space and the coordinate space, the function remains unchanged. Thus

$$\Psi(\mathbf{r}) = \bar{P}_a\Psi(P_a\mathbf{r})$$

or

$$(\bar{P}_a)^{-1}\Psi(\mathbf{r}) = \Psi(P_a\mathbf{r}) = P_a\Psi. \tag{45}$$

Consequently

$$\bar{P}_a = P_a^{-1}. \tag{46}$$

For $\Psi = a(1)b(2)c(3)$,

$$\overline{(123)}a(1)b(2)c(3) = c(1)a(2)b(3) = cab,$$
$$[(123)]^{-1}a(1)b(2)c(3) = (132)a(1)b(2)c(3) = a(2)b(3)c(1) = cab.$$

We denote by a bar an operator on the function space. Thus

$$\bar{\kappa}^p = \sum_c \kappa_c \bar{P}_c. \tag{47}$$

By Eq. (46) we can express $\bar{\kappa}^p$ in terms of operators on the coordinate space. Thus

$$\bar{\kappa}^p = \sum_c \kappa_c^p (P_c)^{-1}. \tag{48}$$

Conversely an operator on the coordinate space can be expressed in terms of operators on the function space. Thus

$$\kappa^p = \sum_c \kappa_c (\bar{P}_c)^{-1}. \tag{49}$$

By Eqs. (20), (18) and (19),

$$\kappa^p = \varepsilon(\sigma_{\mathrm{I}\kappa}) \sum_b \sum_a \nu_{\mathrm{I}b}^p \pi_{\mathrm{I}a}^p \sigma_{\mathrm{I}\kappa} \tag{50}$$

By Eq. (46),

$$\begin{aligned} \nu_{\mathrm{I}a}^p \pi_{\mathrm{I}b}^p \sigma_{\mathrm{I}\kappa} &= (\bar{\nu}_{\mathrm{I}b}^p \bar{\pi}_{\mathrm{I}a}^p \bar{\sigma}_{\mathrm{I}\kappa})^{-1} \\ &= (\bar{\sigma}_{\mathrm{I}\kappa})^{-1}(\bar{\pi}_{\mathrm{I}a}^p)^{-1}(\bar{\nu}_{\mathrm{I}b}^p)^{-1}. \end{aligned} \tag{51}$$

Each of the sets of operators $(\bar{\pi}_{\mathrm{I}a}^p)$ and $(\bar{\nu}_{\mathrm{I}b}^p)$ constitutes a group so that each set contains its own inverses. Also

$$(\bar{\sigma}_{\mathrm{I}\kappa})^{-1} = \bar{\sigma}_{\kappa\mathrm{I}}. \tag{52}$$

By Eq. (114),

$$\begin{aligned}\kappa^p &= \varepsilon(\sigma_{\kappa\mathrm{I}})\bar{\sigma}_{\kappa\mathrm{I}}\bar{P}^p_{\mathrm{I}}\bar{N}^p_{\mathrm{I}} \\ &= \varepsilon(\sigma_{\kappa\mathrm{I}})\bar{P}^p_{\kappa}\bar{N}^p_{\kappa}\bar{\sigma}_{\kappa\mathrm{I}}. \end{aligned} \tag{53}$$

Note that if integers *l and l′* are paired

$$(1/2)[\mathscr{I} + (\overline{ll'})]P^p_{\kappa} = P^p_{\kappa} \tag{54}$$

so that

$$\begin{aligned}(\overline{ll'})\kappa^p &= (\overline{ll'})(1/2)[\mathscr{I} + (\overline{ll'})]\kappa^p \\ &= \kappa^p\end{aligned} \tag{55}$$

and

$$(\overline{ll'})\Psi^p_{\kappa} = \Psi^p_{\kappa}. \tag{56}$$

$$\begin{aligned}(\overline{12})\Psi^p_{\mathrm{I}} &= bac - bca + abc - cba = \Psi^p_{\mathrm{I}}, \\ (\overline{23})\Psi^p_{\mathrm{II}} &= -acb + cab - abc + cba = \Psi^p_{\mathrm{II}}, \\ (\overline{13})\Psi^p_{\mathrm{III}} &= -bca + cab - acb + bac = \Psi^p_{\mathrm{III}}.\end{aligned}$$

Note that

$$\begin{aligned}(12)\Psi^p_{\mathrm{I}} &= a(2)b(1)c(3) - a(2)b(3)c(1) + a(1)b(2)c(3) - a(3)b(2)c(1) \\ &= bac - cab + abc - cba \neq \Psi^p_{\mathrm{I}}.\end{aligned}$$

Here one should remember that Eq. (56) is interpreted as the interchange of the symbols in the first and second positions irrespective of the integers in those positions.

By Eq. (56) two electrons $l$ and $l'$ are paired in a pair function if the pair function is invariant under the transposition $(\overline{ll'})$ on the function space. Thus the pair function distributes electrons $l$ and $l'$ identically in the physical space of the system.

## E. An Exclusion Principle

A spin-free exclusion principle arises when we consider a primitive function $\Psi^\alpha_r$ which is invariant under a subgroup $G^\alpha_r = \{\pi^\alpha_{ra}\}$ of order $n^\alpha$, a subgroup of the permutation group. The subgroup $\{\pi^\alpha_{ra}\}$ contains the identity operator and the operators that permute the integers along the rows in tableau $T^\alpha_r$. Thus

$$\bar{\pi}^\alpha_{ra}\Psi^\alpha_r = \Psi^\alpha_r \tag{57}$$

and

$$\bar{E}^{\alpha}_{r}\Psi^{\alpha}_{r} = \Psi^{\alpha}_{r} \tag{58}$$

where

$$\begin{aligned}\bar{E}^{\alpha}_{r} &= (1/n^{\alpha})\bar{P}^{\alpha}_{r}\\ &= (1/n^{\alpha})\sum_{a}^{n^{\alpha}} \bar{\pi}^{\alpha}_{ra}.\end{aligned} \tag{59}$$

For $N = 3$,

| $\Psi^{\alpha}_{r}$ | $T^{\alpha}_{r}$ | $n^{\alpha}$ | $\{\pi^{\alpha}_{ra}\}$ | $E^{\alpha}_{r}$ |
|---|---|---|---|---|
| *abc* | $\begin{array}{\|c\|}\hline 1\\\hline 2\\\hline 3\\\hline\end{array}$ | 1 | $\{\mathscr{I}\}$ | $\mathscr{I}$ |
| *aab* | $\begin{array}{\|c\|c\|}\hline 1 & 2\\\hline 3 \\\cline{1-1}\end{array}$ | 2 | $\{\mathscr{I}, (12)\}$ | $(1/2)[\mathscr{I} + (12)]$ |
| *aba* | $\begin{array}{\|c\|c\|}\hline 1 & 3\\\hline 2 \\\cline{1-1}\end{array}$ | 2 | $\{\mathscr{I}, (13)\}$ | $(1/2)[\mathscr{I} + (13)]$ |
| *abb* | $\begin{array}{\|c\|c\|}\hline 2 & 3\\\hline 1 \\\cline{1-1}\end{array}$ | 2 | $\{\mathscr{I}, (23)\}$ | $(1/2)[\mathscr{I} + (23)]$ |
| *aaa* | $\begin{array}{\|c\|c\|c\|}\hline 1 & 2 & 3\\\hline\end{array}$ | 6 | $\{\mathscr{I}, (12), (13), (23), (123), (132)\}$ | $(1/6)[\mathscr{I} + (12)$<br>$+ (13) + (23)$<br>$+ (123) + (132)]$ |

*Theorem* (the spin-free exclusion principle). If $T^{\alpha}_{r}$ contains a pair of integers in a row that $T^{p}_{1}$ contains in a column,

$$\kappa^{p}\Psi^{\alpha}_{r} = 0. \tag{60}$$

If $T^{\alpha}_{r}$ contains $e$ and $f$ in a row, we have by Eq. (57)

$$\Psi^{\alpha}_{r} = (1/2)[\mathscr{I} + (\overline{ef})]\Psi^{\alpha}_{r}. \tag{61}$$

If $T^{p}_{1}$ contains $e$ and $f$ in a column, we have by Eq. (53)

$$\kappa^{p} = \kappa^{p}(1/2)[\mathscr{I} - (\overline{ef})]. \tag{62}$$

Consequently,

$$\begin{aligned}\kappa^{p}\Psi^{\alpha}_{r} &= \kappa^{p}(1/2)[\mathscr{I} - (\overline{ef})](1/2)[\mathscr{I} + (\overline{ef})]\Psi^{\alpha}_{r}\\ &= 0.\end{aligned} \tag{63}$$

For $N = 3$, $p = 1$,

$$T_{\mathrm{I}}^{p} = \begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 \\ \cline{1-1}\end{array},$$

$$\Psi_r^\alpha = aab, \qquad T_r^\alpha = \begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 \\ \cline{1-1}\end{array},$$

$$\Psi_{\mathrm{I}}^{p} = aab - baa + aab - aba = 2aab - baa - aba,$$

$$\Psi_r^\alpha = aba, \qquad T_r^\alpha = \begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 \\ \cline{1-1}\end{array},$$

$$\Psi_{\mathrm{I}}^{p} = aba - aba + baa - baa = 0,$$

$$\Psi_r^\alpha = baa, \qquad T_r^\alpha = \begin{array}{|c|c|}\hline 2 & 3 \\ \hline 1 \\ \cline{1-1}\end{array},$$

$$\Psi_{\mathrm{I}}^{p} = baa - aab + aba - aab = -2aab + baa + aba.$$

*Corollary.* If $\Psi_r^\alpha$ is invariant under $m > p$ transpositions,

$$\kappa^p \Psi_r^\alpha = 0. \tag{64}$$

$$\Psi = aab, \qquad (\overline{12})\Psi = \Psi, \qquad m = 1.$$

For $p = 0$,

$$\Psi_{\mathrm{I}}^{p} = aab - aab - baa - aba + aba + baa = 0.$$

*Corollary.* If $T_r^\alpha$ contains more than two columns,

$$\kappa^p \Psi_r^\alpha = 0$$

for all $p$.

If $\Psi_r^\alpha$ is an orbital product, no more than two electrons may be assigned to the same orbital.

For $\Psi_r^\alpha = aaa$, $T_r^\alpha = \begin{array}{|c|c|c|}\hline 1 & 2 & 3 \\ \hline\end{array}$,

$p = 1$,

$$\Psi_{\mathrm{I}}^{p} = \Psi_{\mathrm{II}}^{p} = \Psi_{\mathrm{III}}^{p} = 0;$$

$p = 0$,

$$\Psi_{\mathrm{I}}^{p} = 0.$$

## F. Two Useful Rules

The rules derived in this section are analogous to the rules obtained in the conventional spin formulation.

### 1. *The Intercombination Rule*

Electric dipole transitions between different permutation states are forbidden.

The electric dipole moment operator for $N$ electrons is

$$R = \sum_e \mathbf{r}_e \tag{65}$$

where $\mathbf{r}_e$ is the position vector for the $e$th electron. But $R$ commutes with every element in the permutation group. Then by Eq. (34),

$$\int \Psi_\kappa^{p*} R \Psi_{\kappa'}^{p'}\, d\tau = 0 \qquad \text{for } p \neq p'. \tag{66}$$

The above rule replaces the rule that electric dipole transitions between different spin states (different multiplicities) are forbidden.

### 2. *The Hund Rule*

The mean energy of the state of lowest permutation quantum number lies the lowest.

The Hund (1925) rule applies to those systems and those states that are well-described with a primitive function which is a product of distinct orthonormal orbitals. The mean energy of the $p$th permutation state is

$$\bar{E}^p = \sum_m E_m / f^p. \tag{67}$$

By Eq. (126),

$$\bar{E}^p = Q - [p^2 - p(N+1) + N(N-1)/2]\bar{K}. \tag{68}$$

$\bar{K}$ is the mean exchange integral, which is normally positive.

| $N$ | $p$ | $E^p$ |
|---|---|---|
| 2 | 0 | $Q - \bar{K}$ |
| | 1 | $Q + \bar{K}$ |
| 3 | 0 | $Q - 3\bar{K}$ |
| | 1 | $Q$ |
| 4 | 0 | $Q - 6\bar{K}$ |
| | 1 | $Q - 2\bar{K}$ |
| | 2 | $Q$ |

We see that the state of lowest $p$ lies the lowest. The above rule replaces the classical rule that the state of highest $S$ (highest multiplicity) lies the lowest.

The classical interpretation of the Hund rule is that in the state of highest $S$ the electrons are kept apart by spin correlation which reduces the net repulsion of the electrons. In the spin-free interpretation we say that $p$ specifies the number of pairs, i.e., the number of sets of two electrons in which both electrons occupy identically the physical space of the system. Hence paired electrons increase the net repulsion. Consequently, the fewer the pairs, the lower the energy. Unpaired electrons are said to possess permutation correlation.

## IV. Finite Group Algebras and Quantum Mechanics

### A. An Introduction to Finite Group Algebras

The spin-free formulation of quantum chemistry presented in Section III depends upon the permutational symmetry of the spin-free Hamiltonian. The effect of the permutational symmetry on the quantum mechanical description is quite analogous to the effects of other symmetry groups. We treat the general symmetry problem by means of the group algebra. The contents of this section apply to any finite group including the permutation group $\pi_N$ on $N$ integers. We use the permutation group $\pi_3$ as an example.

We consider a finite group $G$ of order $n$,

$$G = \{R_1, \ldots R_e \ldots R_n\}. \tag{69}$$

For $\pi_3$

$$G = \{\mathscr{I}, (12), (13), (23), (123), (132)\}.$$

The multiplication table is

| | $\mathscr{I}$ | (12) | (13) | (23) | (123) | (132) |
|---|---|---|---|---|---|---|
| $\mathscr{I}$ | $\mathscr{I}$ | (12) | (13) | (23) | (123) | (132) |
| (12) | (12) | $\mathscr{I}$ | (132) | (123) | (23) | (13) |
| (13) | (13) | (123) | $\mathscr{I}$ | (132) | (12) | (23) |
| (23) | (23) | (132) | (123) | $\mathscr{I}$ | (13) | (12) |
| (123) | (123) | (13) | (23) | (12) | (132) | $\mathscr{I}$ |
| (132) | (132) | (23) | (12) | (13) | $\mathscr{I}$ | (123) |

A class is indexed by the symbol $\rho$ and contains $n_\rho$ elements. Thus

$$\{\rho\} = \{R_1^\rho, \ldots R_a^\rho, \ldots R_{n_\rho}^\rho\}. \tag{70}$$

$R_a^\rho$ and $R_b^\rho$ belong to $\rho$ if, and only if, there is at least one $R_c \in G$, such that

$$R_b^\rho = R_c R_a^\rho R_c^{-1}. \tag{71}$$

For $\pi_3$

| $\rho$ | $n_\rho$ | $\{\rho\}$ |
|---|---|---|
| 1 | 1 | $\{\mathscr{I}\}$ |
| 2 | 3 | $\{(12), (13), (23)\}$ |
| 3 | 2 | $\{(123), (132)\}$ |

An algebra $A$ on group $G$ is the set of all linear combinations of the elements of $G$. The order of the algebra is the order of the group. An element of $A$ is

$$X = \sum_a (X)_a R_a \tag{72}$$

where $(X)_a$ is from the complex number field.

A basis $\{\eta\}$ of an algebra of order $n$ is a set of $n$ linearly independent elements in terms of which any element of $A$ can be expressed. The elements of $G$ constitute a basis called the regular basis. Thus

$$\{\eta\}^r = \{R_1, \ldots R_a, \ldots R_n\}. \tag{73}$$

For $\pi_3$

$$\{\eta\}^r = \{\mathscr{I}, (12), (13), (23), (123), (132)\}.$$

A finite group algebra has a matric basis[3]

$$\{\eta\}^m = \{\ldots e_{rs}^\alpha, \ldots\}, \qquad \alpha = 1 \text{ to } M, \qquad r, s = 1 \text{ to } f^\alpha. \tag{74}$$

For $\pi_3$, $n = 6$,

$$M = 3; \qquad f^\alpha : f^1 = 1, \qquad f^2 = 2, \qquad f^3 = 1; \qquad 1^2 + 2^2 + 1^2 = 6;$$

$$\{\eta\}^r = \{e_{11}^1, e_{11}^2, e_{12}^2, e_{21}^2, e_{22}^2, e_{11}^3\}.$$

The matric basis $\{\eta\}^m$ and the regular basis $\{\eta\}^r$ are related by

$$e_{rs}^\alpha = (1/\Theta^\alpha) \sum_a^n [R_a^{-1}]_{sr}^\alpha R_a \tag{75}$$

and

$$R_a = \sum_\alpha^M \sum_r^{f^\alpha} \sum_s^{f^\alpha} [R_a]_{rs}^\alpha e_{rs}^\alpha. \tag{76}$$

---

[3] The proof that a finite group algebra has a matric basis was first given by Frobenius. For references and the proof, see Littlewood (1950), p. 42 ff. The word matric is used because the doubly subscripted elements resemble matrix elements and because of their close relation to matrix representation theory.

Here

$$\Theta^\alpha = n/f^\alpha \tag{77}$$

and the coefficient $[R_a]^\alpha_{rs}$ is the element from the $r$th row and $s$th column of the $f^\alpha$ dimensional matrix $[R_a]^\alpha$ representing $R_a$ in the irreducible representation $\Gamma^\alpha$ of the group. The coefficients satisfy the orthogonality relations

$$\sum_a^n [R_a]^\alpha_{rs}[R_a]^\beta_{ut} = \delta^{\alpha\beta}\delta_{rt}\delta_{su}\Theta^\alpha. \tag{78}$$

The representation of the identity element is a unit matrix. It follows from this fact and from Eq. (76) that

$$\mathscr{I} = \sum_\alpha^M \sum_r^{f^\alpha} e^\alpha_{rr}. \tag{79}$$

For $\pi_3$

| $\alpha$ | $f^\alpha$ | $\mathscr{I}$ | (12) | (13) | (23) | (123) | (132) |
|---|---|---|---|---|---|---|---|
| 1 | 1 | $[1]$ | $[-1]$ | $[-1]$ | $[-1]$ | $[1]$ | $[l]$ |
| 2 | 2 | $\begin{vmatrix}1 & 0\\ 0 & 1\end{vmatrix}$ | $\begin{vmatrix}1 & 0\\ 0 & -1\end{vmatrix}$ | $\begin{vmatrix}-a & b\\ b & a\end{vmatrix}$ | $\begin{vmatrix}-a & -b\\ -b & a\end{vmatrix}$ | $\begin{vmatrix}-a & -b\\ b & -a\end{vmatrix}$ | $\begin{vmatrix}-a & b\\ -b & -a\end{vmatrix}$ |
| 3 | 1 | $[1]$ | $[1]$ | $[1]$ | $[1]$ | $[1]$ | $[1]$ |

$$a = 1/2, \quad b = \sqrt{3}/2.$$

From Eq. (75)

$$e^2_{21} = (1/3)[0\mathscr{I} + 0(12) + b(13) - b(23) + b(123) - b(132)].$$

From Eq. (76),

$$(23) = -e^1_{11} - ae^2_{11} - be^2_{12} - be^2_{21} + ae^2_{22} + e^3_{11}.$$

From Eq. (79),

$$\mathscr{I} = e^1_{11} + e^2_{11} + e^2_{22} + e^3_{11}.$$

The matrix basis elements multiply according to

$$e^\alpha_{rs}e^\beta_{tu} = \delta^{\alpha\beta}\delta_{st}e^\alpha_{ru}. \tag{80}$$

For $\pi_3$

| | $e^1_{11}$ | $e^2_{11}$ | $e^2_{12}$ | $e^2_{21}$ | $e^2_{22}$ | $e^3_{11}$ |
|---|---|---|---|---|---|---|
| $e^1_{11}$ | $e^1_{11}$ | 0 | 0 | 0 | 0 | 0 |
| $e^2_{11}$ | 0 | $e^2_{11}$ | $e^2_{12}$ | 0 | 0 | 0 |
| $e^2_{12}$ | 0 | 0 | 0 | $e^2_{11}$ | $e^2_{12}$ | 0 |
| $e^2_{21}$ | 0 | $e^2_{21}$ | $e^2_{22}$ | 0 | 0 | 0 |
| $e^2_{22}$ | 0 | 0 | 0 | $e^2_{21}$ | $e^2_{22}$ | 0 |
| $e^3_{11}$ | 0 | 0 | 0 | 0 | 0 | $e^3_{11}$ |

From Eqs. (76) and (80) we see that

$$R_a e^\alpha_{rs} = \sum_u [R_a]^\alpha_{us} e^\alpha_{us}. \tag{81}$$

A general element in the matric basis is

$$X = \sum_\alpha^M \sum_r^{f^\alpha} \sum_s^{f^\alpha} [X]^\alpha_{rs} e^\alpha_{rs}. \tag{82}$$

The coefficients in Eqs. (82) and (72) are related by

$$[X]^\alpha_{rs} = \sum_a (X)_a [R_a]^\alpha_{rs}. \tag{83}$$

## B. The Matric Projector

We now define an element called the matric projector:

$$e^\alpha = \sum_n^{f^\alpha} e^\alpha_{rr} \tag{84}$$

$$= (1/\Theta^\alpha) \sum_r^{f^\alpha} \sum_a^n [R_a^{-1}]^\alpha_{rr} R_a \tag{85}$$

$$= (1/\Theta^\alpha) \sum_a^n \chi^\alpha(R_a^{-1}) R_a.$$

Here $\chi^\alpha(R_a)$ is a number called the character of $R_a$ in $\Gamma^\alpha$. The characters of elements of a class are equal and so we define

$$\chi^\alpha_\rho = \chi^\alpha(R_a), \qquad R_a \in \rho \tag{86}$$

to be the character of elements of the $\rho$th class in $\Gamma^\alpha$. We define the class operator

$$K_\rho = \sum_a^{n_\rho} R^\rho_a, \tag{87}$$

then

$$e^\alpha = (1/\Theta^\alpha) \sum_\rho^M \chi^\alpha_{\bar\rho} K_\rho. \tag{88}$$

For $\pi_3$

$$\begin{aligned} &K_1 = \mathscr{I}, \quad K_2 = (12) + (13) + (23), \quad K_3 = (123) + (132), \\ &e^1 = (1/6)(K_1 - K_2 + K_3), \\ &e^2 = (1/3)(2K_1 - K_2), \\ &e^3 = (1/6)(K_1 + K_2 + K_3). \end{aligned}$$

Note that

$$\mathscr{I} = e^1 + e^2 + e^3.$$

By Eqs. (84) and (79),

$$\mathscr{I} = \sum_{\alpha}^{M} e^{\alpha}. \tag{89}$$

By Eqs. (84) and (80),

$$e^{\alpha}e^{\beta} = \delta^{\alpha\beta}e^{\alpha}. \tag{90}$$

By Eq. (89),

$$\begin{aligned} X &= \mathscr{I}X \\ &= \sum_{\alpha}^{M} X^{\alpha} \end{aligned} \tag{91}$$

where

$$\begin{aligned} X^{\alpha} &= e^{\alpha}X = Xe^{\alpha} \\ &= \sum_{r}^{f^{\alpha}} \sum_{s}^{f^{\alpha}} [X]^{\alpha}_{rs} e^{\alpha}_{rs}. \end{aligned} \tag{92}$$

The element $X^{\alpha}$ is an element in a subalgebra $A^{\alpha}$ of order $(f^{\alpha})^2$ called a matric subalgebra of the group algebra. It has a basis

$$\{\eta\}^{m\alpha} = \{e^{\alpha}_{11}, \dots e^{\alpha}_{rs}, \dots e^{\alpha}_{gg}\}, \qquad g = f^{\alpha}. \tag{93}$$

In Eq. (88) we expressed $e^{\alpha}$ in terms of the class operators $K_{\rho}$. Conversely, we can express the class operators in terms of the matric projectors. Thus

$$K_{\rho} = \sum_{\alpha}^{M} K^{\alpha}_{\rho} e^{\alpha} \tag{94}$$

where

$$K^{\alpha}_{\rho} = n_{\rho}\chi^{\alpha}_{\rho}/f^{\alpha}. \tag{95}$$

From Eqs. (92) and (94),

$$K_{\rho}X^{\alpha} = K^{\alpha}_{\rho}X^{\alpha}, \qquad \rho = 1 \text{ to } M. \tag{96}$$

That is, any element $X^{\alpha}$ in $A^{\alpha}$ is an eigenelement to the $M$ class operators with class eigenvalues which serve to identify the matric subalgebra $A^{\alpha}$ to which it belongs.

### C. Application to Quantum Mechanics

Consider a system with a Hamiltonian $H$ that commutes with the operators in $G$. Its eigenfunctions $|\alpha rK\rangle$ are divided among $M$ symmetry states indexed by $\alpha$ where $M$ is the number of classes. For a given symmetry state each eigenfunction is characterized by a degeneracy index $r$ and an eigenstate index $K$. Now

$$K_\rho|\alpha r K\rangle = K_\rho^\alpha|\alpha r K\rangle, \qquad \rho = 1 \text{ to } M \tag{97}$$

where

$$K_\rho = n_\rho \chi_\rho^\alpha / f^\alpha \tag{98}$$

and

$$R_a|\alpha r k\rangle = \sum_w [R_a]^\alpha_{wr}|\alpha r k\rangle. \tag{99}$$

The eigenfunction can be expressed in the form

$$|\alpha r K\rangle = \sum_s b_{sK}|\alpha r s\rangle \tag{100}$$

where

$$|\alpha r s\rangle = e^\alpha_{rs}|\mathscr{I}\rangle. \tag{101}$$

Here $|\mathscr{I}\rangle$ represents a primitive function. We note by Eqs. (101), (96), and (81) that

$$K_\rho|\alpha r s\rangle = K_\rho^\alpha|\alpha r s\rangle, \tag{102}$$

$$R_a|\alpha r s\rangle = \sum_w^{f^\alpha} [R_a]^\alpha_{wr}|\alpha w s\rangle. \tag{103}$$

Consequently, Eq. (100) satisfies Eqs. (97) and (99). The coefficients $b_{sK}$, Eq. (100), are determined in the usual manner from solutions of the equation

$$\sum_s b_{sK}|\langle \alpha r s|H|\beta t u\rangle - E\langle \alpha r s|\beta t u\rangle| = 0. \tag{104}$$

If $\Gamma^\alpha$ is unitary,

$$\langle \alpha r s|H|\beta t u\rangle = \delta^{\alpha\beta}\delta_{rt}\langle \alpha u s|H|\mathscr{I}\rangle. \tag{105}$$

Here

$$\langle \alpha u s|H|\mathscr{I}\rangle = (f^\alpha/n)\sum_e [P_e]^\alpha_{us}\langle P_e|H|\mathscr{I}\rangle \tag{106}$$

where

$$\langle P_e|H|\mathscr{I}\rangle \equiv \int P_e\Psi^* H \Psi \, d\tau. \tag{107}$$

As a consequence of Eqs. (105) and (103) the eigenfunctions $|\alpha r K\rangle$, $r = 1$ to $f^\alpha$, are $f^\alpha$-fold degenerate.

If $|\mathscr{I}\rangle = a(1)b(2)c(3)$ and if

$$\langle a|b\rangle = \delta_{ab}, \qquad \text{etc.}$$

For $\alpha = 1$,

$$6\langle 111|H|111\rangle = Q - (ab) - (ac) - (bc).$$

For $\alpha = 2$, the nonzero elements are

$$3\langle 221|H|221\rangle = 3\langle 211|H|211\rangle = Q + (ab) - (1/2)(ac) - (1/2)(bc),$$

$$3\langle 222|H|221\rangle = 3\langle 212|H|211\rangle = (\sqrt{3}/2)[-(ac) + (bc)],$$

$$3\langle 222|H|222\rangle = 3\langle 212|H|212\rangle = Q - (ab) + (1/2)(ac) + (1/2)(bc).$$

## V. The Permutation Algebra

### A. The Young Operators

Each matric subalgebra $A^{\alpha}$ of the permutation algebra $A$ is indexed by a partition of $N$ into $k$ integers:

$$\alpha = \{\alpha^1, \alpha^2, \ldots \alpha^i, \ldots \alpha^k\}, \qquad a^1 \geqslant \alpha^2 \geqslant \text{etc.} \tag{108}$$

where

$$\sum_{i=1}^{k} \alpha^i = N. \tag{109}$$

The partition has a condensed form

$$\alpha = \{\ldots g^{\alpha_g}, \ldots 2^{\alpha_2}, 1^{\alpha_1}\} \tag{110}$$

where

$$\sum_g g\alpha_g = N. \tag{111}$$

We designate the number[4] of partitions by $M$.

For $N = 6$, $M = 11$,

$$\alpha = \{1^6\}, \{2, 1^4\}, \{2^2, 1^2\}, \{2^3\}, \{3, 1^3\}, \{3, 2, 1\}, \{3^2\}, \{4, 1^2\}, \{4, 2\}, \{5, 1\}, \{6\}.$$

For a partition $\alpha$ we construct a matric projector $e^{\alpha}$, the projector for the matric subalgebra $A^{\alpha}$. We begin by forming a shape $S^{\alpha}$, an array of squares in $k$ rows with the $i$th row containing $\alpha^i$ squares. If the rows and columns of $S^{\alpha}$ are interchanged, the conjugate shape $S^{\tilde{\alpha}}$ is obtained. $\tilde{\alpha}$ is the partition for $S^{\alpha}$. If $S^{\tilde{\alpha}} = S^{\tilde{\alpha}}$ the shape is self-conjugate.

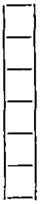
---

[4] A method for the computation of $M$ is given by Littlewood (1950), p. 59.

For $N = 6$,

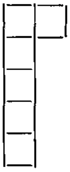
$S^\alpha$

$\{1^6\} = \{\widetilde{6}\}$

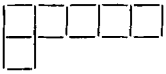


$\{6\} = \{\widetilde{1^6}\}$

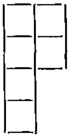
$\{2, 1^4\} = \{\widetilde{5, 1}\}$



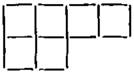
$\{5, 1\} = \{\widetilde{2, 1^4}\}$



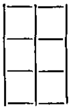
$\{2^2, 1^2\} = \{\widetilde{4, 2}\}$



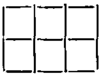
$\{4, 2\} = \{\widetilde{2^2, 1^2}\}$



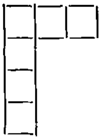
$\{2^3\} = \{\widetilde{3^2}\}$



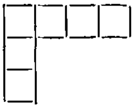
$\{3\}^2 = \{\widetilde{2^3}\}$



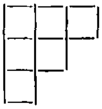
$\{3, 1^3\} = \{\widetilde{4, 1^2}\}$



$\{4, 1^2\} = \{\widetilde{3, 1^3}\}$



$\{3, 2, 1\} = \{\widetilde{3, 2, 1}\}$



(self-conjugate)

From a shape $S^\alpha$ we construct a tableau $T_r^\alpha$ by placing the first $N$ integers in arbitrary order in the squares of the shape. Those tableaux for which the integers lie in ascending order along the rows and down the columns are standard tableaux. The number of standard tableau for partition $\alpha$ is denoted by $f_N^\alpha$.

For $N = 6$, $\alpha = \{2^3\}$, the standard tableaux are

$$T_1^\alpha = \begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & 4 \\ \hline 5 & 6 \\ \hline \end{array}; \quad T_2^\alpha = \begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 & 4 \\ \hline 5 & 6 \\ \hline \end{array}; \quad T_3^\alpha = \begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 & 5 \\ \hline 4 & 6 \\ \hline \end{array}; \quad T_4^\alpha = \begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & 5 \\ \hline 4 & 6 \\ \hline \end{array}:$$

$$T_5^\alpha = \begin{array}{|c|c|}\hline 1 & 4 \\ \hline 2 & 5 \\ \hline 3 & 6 \\ \hline \end{array}.$$

The number of standard tableaux is given by the expression

$$f_N^\alpha = N! \prod_{i<j\leqslant k} (x_i - x_j) / \prod_i x_i! \tag{112}$$

where

$$x_i = \alpha^i + k - i.$$

For $N = 6$, $\alpha = \{2^3\}$, $k = 3$, $\alpha^1 = \alpha^2 = \alpha^3 = 2$,

$$x_1 = 4, \qquad x_2 = 3, \qquad x_3 = 2,$$

$$f_N^\alpha = \frac{6!(x_1 - x_2)(x_1 - x_3)(x_2 - x_3)}{x_1!x_2!x_3!} = 5.$$

We note that

$$\sum_\alpha f_N^\alpha = N!. \tag{113}$$

For $N = 6$,

$$\begin{array}{lccccccccccc} \alpha = & \{1^6\} & \{2,1^4\} & \{2^2,1^2\} & \{2^3\} & \{3,1^3\} & \{3,2,1\} & \{3^2\} & \{4,1^2\} & \{4,2\} & \{5,1\} & \{6\}, \\ f^\alpha = & 1 & 5 & 9 & 5 & 10 & 16 & 5 & 10 & 9 & 5 & 1, \end{array}$$

$$(1)^2+(5)^2+(9)^2+(5)^2+(10)^2+(16)^2+(5)^2+(10)^2+(9)^2+(5)^2+(1)^2 = 720.$$

For each pair of tableaux $T_r^\alpha$ and $T_s^\alpha$ we construct a Young operator

$$\begin{aligned} E_{rs}^\alpha &= N_r^\alpha \sigma_{rs} P_s^\alpha \\ &= \sigma_{rs} E_s^\alpha \\ &= E_r^\alpha \sigma_{rs}. \end{aligned} \tag{114}$$

If the two subscripts are the same, one is suppressed. Here $N_r^\alpha$ and $P_s^\alpha$ are the row and column operators described in Section III.

A matric projector for the matric subalgebra $A^\alpha$ is

$$e^\alpha = \sum_{r}^{f_N^\alpha} E_r^\alpha. \tag{115}$$

The sum extends over the Young operators for the standard tableaux.

The classes of the permutation operators are also characterized by partitions. We designate a permutation operator by

$$P_a = (efg)(hi)\cdots . \tag{116}$$

Here $(efg)$ is a cycle of length three, $(hi)$ is a cycle of length two, etc. The set of integers

$$\rho = \{\rho^1, \rho^2, \ldots \rho^i, \ldots \rho^k\} = \{g^{\rho_g}, 2^{\rho_2}, 1^{\rho_1}\} \tag{117}$$

where $\rho^i$ is the length of the $i$th cycle is called the cycle structure of $P_a$. Elements with the same cycle structure lie in the same class. The number of elements in the $\rho$th class is

$$n_\rho = \frac{N!}{\prod_g g^{\rho_g} \rho_g!}. \tag{118}$$

For $\pi_3$, $M = 3$,

| $\rho$ | $n_\rho$ | $\{\rho\}$ |
|---|---|---|
| $\{1^3\}$ | 1 | $\{(1)(2)(3)\} = \{\mathscr{I}\}$ |
| $\{2, 1\}$ | 3 | $\{(12)(3), (13)(2), (23)(1)\} = \{(12), (13), (23)\}$ |
| $\{3\}$ | 2 | $\{(123), (132)\}$ |

The number $M$ of classes of $\pi_N$ is equal to the number of partitions of $N$.

## B. Application to Quantum Mechanics

Consider a system of $N$ identical particles. The Hamiltonian for this system commutes with the $N!$ permutation operators in $\pi_N$. The eigenfunctions are divided into $M$ permutation states indexed by $\alpha$ where $M$ is the number of classes (or partitions).

The systems of identical particles in which we are interested are the fermions, electrons, or nucleons. For those we construct a spin-free Hamiltonian which commutes with the permutations of the space coordinates. For these systems not all of the $M$ space permutation states obtained from the solution of the spin-free Hamiltonian are observed in nature.

*Spin-Free Exclusion Principle for Fermions*

We exclude those permutation states for which the shapes $S^\alpha$ contain more columns than the number of individual fermion spin states. This number is two for electrons and four for nucleons.

This exclusion principle is obtained from the application of the antisymmetry principle to a space-spin primitive function. For electrons the allowed partitions are

$$\alpha = \{2^p, 1^{N-2p}\}, \qquad 0 \leqslant p \leqslant N/2, \tag{119}$$

then Eq. (112) becomes

$$f^p = N!(N - 2p + 1)/p!(N - p + 1)!. \tag{120}$$

We could proceed with the quantum mechanical application as outlined in Section IV by forming matric basis functions

$$|\alpha rs\rangle = e^\alpha_{rs}|\mathscr{I}\rangle. \tag{121}$$

To obtain the Hund rule described in Section III,F we take $\Psi$ to be a product of distinct orthonormal orbital products as in Eq. (36). Then with Eqs. (121) and (105) the secular equation for the $\alpha$th permutation state is

$$|\Theta^\alpha\langle\alpha us|H|\mathscr{I}\rangle - \delta_{us}E| = 0 \tag{122}$$

with roots $E_m$, $m = 1$ to $f^\alpha$. The average energy of the $\alpha$th permutation state is by (106) and (36)

$$\begin{aligned} E &= \Theta^\alpha \sum_m^{f^\alpha_N} E_m/f^\alpha_N \\ &= \Theta^\alpha \sum_r^{f^\alpha_N} \langle\alpha rr|H|\mathscr{I}\rangle/f^\alpha_N \\ &= \Theta^\alpha \int \sum_r^{f^\alpha_N} e^\alpha_{rr}\Psi^* H\Psi \, d\tau/f^\alpha_N \\ &= \Theta^\alpha \int e^\alpha \Psi^* H\Psi \, d\tau/f^\alpha_N \\ &= \sum_\rho^M \chi^\alpha_\rho \int K_\rho \Psi^* H\Psi \, d\tau/f^\alpha_N. \end{aligned} \tag{123}$$

For $\{\rho\} = \{1^N\}$, $\qquad \chi^\rho_\alpha/f = 1.$

For $\{\rho\} = \{2, 1^{N-2}\}$,[5]

$$K^{\alpha}_{\rho} = N(N-1)\chi^{\alpha}_{\rho}/2f^{\alpha} = (1/2)[\alpha^1(\alpha^1 - 1) + \alpha^2(\alpha^2 - 3) + \alpha^3(\alpha^3 - 5) + \cdots]; \tag{124}$$

and for $\{\alpha\} = \{2^p, 1^{N-2p}\}$, $\{\tilde{\alpha}\} = \{N-p,\ p\}$,

$$K^{\alpha}_{\rho} = -K^{\tilde{\alpha}}_{\rho} = -[p^2 - p(N+1) + N(N-1)/2]. \tag{125}$$

Now let

$$\int K_{\rho}\Psi^{*}H\Psi\, d\tau = \sum_{e<f} \int (ef)\Psi^{*}H\Psi\, d\tau$$

$$= N(N-1)\bar{K}/2.$$

Then

$$\bar{E}^{\alpha} = Q - [p^2 - p(N+1) + N(N-1)/2]\bar{K}. \tag{126}$$

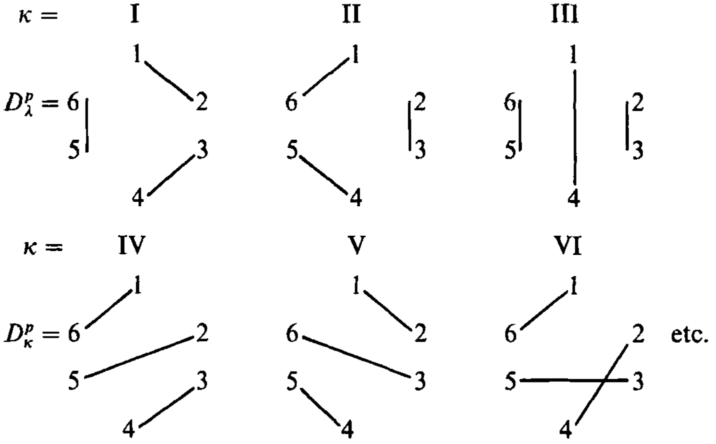
In Section III we employed pair functions rather than matric functions for the polyelectronic problem. These have two advantages over the matric basis functions: (*i*) their formulation does not require a knowledge of the irreducible representations, and (*ii*) they lie in one-to-one correspondence with the widely used pair diagrams.

Pair functions are projected from primitive functions by pair operators. The latter are discussed in the following section.

## C. The Pair Operator

We begin by specifying the number of electrons $N$, the number of electron pairs $p$, and the pair diagram $D^p_\kappa$.

For $N = 6$, $p = 3$, $f^p_N = 5$



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[5] F. Hund, see Wigner (1937).

We next form pair tableaux $T_\kappa^p$ by arranging the $N$ integers in two columns with $p$ rows. The paired integers are placed in the same row with the smaller integer first. The remaining integers fill out the remaining $N$-$p$ spaces in the first column.

For $N = 6$, $p = 3$,

$$\begin{array}{cccccccl}
\kappa = & \mathrm{I} & \mathrm{II} & \mathrm{III} & \mathrm{IV} & \mathrm{V} & \mathrm{VI} & \\
r = & 1 & 4 & 2 & 5 & 3 & 5 & \text{last number sequence} \\
T_\kappa^p = &
\begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & 4 \\ \hline 5 & 6 \\ \hline \end{array} &
\begin{array}{|c|c|}\hline 1 & 6 \\ \hline 2 & 3 \\ \hline 4 & 5 \\ \hline \end{array} &
\begin{array}{|c|c|}\hline 1 & 4 \\ \hline 2 & 3 \\ \hline 5 & 6 \\ \hline \end{array} &
\begin{array}{|c|c|}\hline 1 & 6 \\ \hline 2 & 5 \\ \hline 3 & 4 \\ \hline \end{array} &
\begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & 6 \\ \hline 4 & 5 \\ \hline \end{array} &
\begin{array}{|c|c|}\hline 1 & 6 \\ \hline 2 & 4 \\ \hline 3 & 5 \\ \hline \end{array} & \text{etc.} \\
 & & & & & & & \text{discard}
\end{array}$$

Of the possible bond tableaux for a given $N$ and $p$ we retain only the $f_N^p$ canonical tableaux, those that correspond to canonical pair diagrams. The canonical tableaux contain different sets of integers in their first columns. Now a two-columned standard tableau is completely determined by the integers in its first column. The first columns of standard tableaux contain the same sets of integers as do the canonical tableaux, so the number of tableaux in a standard set and a basis set is the same. Then by Eq. (120) the number of canonical tableaux is

$$f^p = N!(N - 2p + 1)/p!(N - p + 1)!. \tag{127}$$

The canonical tableaux can be arranged in a first column–last number sequence, in which a tableau with $N$ in the last row of the first column comes before one with $N - 1$ in the last row, etc. For $s > r$ in the last number sequence, $T_s^p$ contains a pair of integers (say $e$ and $f$) in a column that $T_r^p$ contains in a row.

The pair operator for $D_\kappa^p$ is, by Eq. (20),

$$\begin{aligned} \kappa^p &= \varepsilon(\sigma_{\mathrm{I}\kappa}) N_{\mathrm{I}}^p P_{\mathrm{I}}^p \sigma_{\mathrm{I}\kappa}\,. \\ &\equiv \kappa_r^p. \end{aligned} \tag{128}$$

Here $r$ designates the position of $T_\kappa^p$ in the last number sequence.

*Theorem.* For $s > r$ in the last number sequence

$$\kappa_r^p \kappa_s^p = 0. \tag{129}$$

For $s > r$

$$\kappa_r^p = \kappa_r^p (1/2)[\mathscr{I} + (ef)],$$

$$\kappa_s^p = (1/2)[\mathscr{I} - (ef)]\kappa_s^p.$$

Hence

$$\kappa_r^p\kappa_s^p = \kappa_r^p(1/2)[\mathscr{I} + (ef)](1/2)[\mathscr{I} - (ef)]\kappa_s^p. \tag{130}$$

*Theorem.* The pair operators corresponding to the canonical tableaux are linearly independent.

We assume the opposite. Then there exists a set of coefficients $a_r$, not all zero, such that

$$\sum_r^{f^p} a_r\kappa_r^p = 0. \tag{131}$$

We multiply from the right by $\kappa_g^p$, where $g = f_N^p$, the last member in the last number sequence. Since

$$\kappa_r^p\kappa_g^p = 0 \qquad \text{for } r \neq g$$

it follows that

$$a_g\kappa_g = 0. \tag{132}$$

Now $\kappa_g^p \neq 0$ so $a_g = 0$. Hence

$$\sum_r^{g-1} a_r\kappa_r^p = 0. \tag{133}$$

We multiply from the right by $\kappa_{g-1}^p$ and show that

$$a_{g-1} = 0 \tag{134}$$

etc. Hence

$$a_r = 0 \qquad \text{for } r = 1 \text{ to } g = f^p \tag{135}$$

and we have a contradiction.

The operators $\kappa^p$ and $\bar{\kappa}^p$ are elements in the matric subalgebra $A^\alpha$ where $\alpha = \{2^p, 1^{N-2p}\}$. Then

$$\kappa^p = e^\alpha\kappa^p = \kappa^p e^\alpha \tag{136}$$

and

$$\bar{\kappa}^p = e^\alpha\bar{\kappa}^p = \bar{\kappa}^p e^\alpha. \tag{137}$$

Then by

$$\bar{\kappa}^{p'}\kappa^p = 0 \qquad \text{for } p \neq p'. \tag{138}$$

The pair operators can be expressed in terms of a set of matric basis elements

$$1^p = \sum_s^{f_N^p} d_s e_{1s}^\alpha \tag{139}$$

where $d_s$ is a scalar quantity. Further,

$$\begin{aligned}\kappa^p &= \varepsilon(\sigma_{\mathrm{I}\kappa})I^\kappa\sigma_{1\kappa}\\ &= \varepsilon(\sigma_{\mathrm{I}\kappa})\sum_s d_s e_{1s}^\alpha \sigma_{\mathrm{I}\kappa}\\ &= \varepsilon(\sigma_{\mathrm{I}\kappa})\sum_s\sum_t d_s[\sigma_{\mathrm{I}\kappa}]_{st}^\alpha e_{1t}^\alpha .\end{aligned} \tag{140}$$

The $e_{1t}^\alpha$, $t = 1$ to $f_N^\alpha$, are linearly independent and span a subspace of the permutation space, the $p$th structure space. It follows that, since the $f_N^p(=f_N^\alpha)$ canonical pair operators are linearly independent, they span the $p$th structure space also.

## D. The Structure Matric Basis

In Section VI we shall present, in the language of group algebra, the conventional formulation of quantum chemistry. For this development we choose a particular matric basis called the structure matric basis. The diagonal elements in this basis are

$$e_{11}^\alpha = (1/n^\alpha\Theta^\alpha)P_{\mathrm{I}}^\alpha N_{\mathrm{I}}^\alpha P_{\mathrm{I}}^\alpha \tag{141}$$

and

$$e_{rr}^\alpha = (1/n^\alpha\Theta^\alpha)N_r^\alpha P_r^\alpha N_r^\alpha \tag{142}$$

for $r = 2$ to $f_N^\alpha$ in the last number sequence of standard tableaux. These $f_N^\alpha$ elements are idempotent and linearly independent.

For $\pi_3$, $p = 1$, $f_N^\alpha = 2$, $\Theta^\alpha = 6/2 = 3$,

$$e_{11}^\alpha = (1/3)[\mathscr{I} + (12) - (1/2)(13) - (1/2)(23) - (1/2)(123) - (1/2)(132)]$$

$$e_{22}^\alpha = (1/3)[\mathscr{I} - (12) + (1/2)(13) + (1/2)(23) + (1/2)(123) + (1/2)(132)]$$

We have the following relations:

$$P_{\mathrm{I}}^\alpha P_{\mathrm{I}}^\alpha = n^\alpha P_{\mathrm{I}}^\alpha, \tag{143}$$

$$E_{\mathrm{I}}^\alpha = (1/n^\alpha)P_{\mathrm{I}}^\alpha, \tag{144}$$

$$N_{\mathrm{I}}^\alpha N_{\mathrm{I}}^\alpha = m^\alpha N_{\mathrm{I}}^\alpha, \tag{145}$$

$$e_{11}^\alpha e_{rr}^\alpha = e_{rr}^\alpha e_{11}^\alpha = 0 \qquad \text{for } r \neq 1, \tag{146}$$

$$e_{11}^\alpha E^{\mathrm{I}} = E^{\mathrm{I}} e_{11}^\alpha = e_{11}^\alpha, \tag{147}$$

$$e_{sr}^\alpha E^{\mathrm{I}} = E^{\mathrm{I}} e_{rs}^\alpha = 0 \qquad \text{for } r \neq 1. \tag{148}$$

By analogy to Eq. (81) we conclude that

$$[E^{\mathrm{I}}]_{rs}^\alpha = \delta_{1r}\delta_{1s}. \tag{149}$$

The representations on this basis are said to be canonical to $E_{\mathrm{I}}$. That is $\Gamma^{\alpha} = \Gamma^{\alpha}_{\mathrm{I}}$.

The representation of $\pi_3$, $p = 1$, given in Section III is $\Gamma^{\alpha}_{\mathrm{I}}$,

$$[E^{\mathrm{I}}]^{\alpha} = 1/2([\mathscr{I}]^{\alpha} + [(12)]^{\alpha}) = (1/2)\left(\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix} + \begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}\right)$$
$$= \begin{bmatrix}1 & 0\\ 0 & 0\end{bmatrix}.$$

By Eqs. (144), (147), (148) and (143),

$$P^{\alpha}_{\mathrm{I}} e^{\alpha}_{uv} P^{\alpha}_{\mathrm{I}} = \delta_{u1}\delta_{v1}(n^{\alpha})^2 e^{\alpha}_{11}. \tag{150}$$

We now develop an explicit relation needed in Section VI.
By Eqs. (81), (150), (141), and (145),

$$\begin{aligned} P^{\alpha}_{\mathrm{I}} N^{\alpha}_{\mathrm{I}} e^{\alpha}_{gg} N^{\alpha}_{\mathrm{I}} P^{\alpha}_{\mathrm{I}} &= \sum_{u}^{f^{\alpha}} \sum_{v}^{f^{\alpha}} [N^{\alpha}_{\mathrm{I}}]^{\alpha}_{ug} [N^{\alpha}_{\mathrm{I}}]_{gv} P^{\alpha}_{\mathrm{I}} e^{\alpha}_{uv} P^{\alpha}_{\mathrm{I}} \\ &= (n^{\alpha})^2 [N^{\alpha}_{\mathrm{I}}]^{\alpha}_{1g} [N^{\alpha}_{\mathrm{I}}]^{\alpha}_{g1} e^{\alpha}_{11} \\ &= (n^{\alpha}/\Theta^{\alpha}) [N^{\alpha}_{\mathrm{I}}]^{\alpha}_{1g} [N^{\alpha}_{\mathrm{I}}]^{\alpha}_{g1} P^{\alpha}_{\mathrm{I}} N^{\alpha}_{\mathrm{I}} P^{\alpha}_{\mathrm{I}} \\ &= B^{\alpha} P^{\alpha}_{\mathrm{I}} N^{\alpha}_{\mathrm{I}} N^{\alpha}_{\mathrm{I}} P^{\alpha}_{\mathrm{I}} \end{aligned} \tag{151}$$

where

$$B^{\alpha} = (n^{\alpha}/m^{\alpha}\Theta^{\alpha}) [N^{\alpha}_{\mathrm{I}}]^{\alpha}_{1g} [N^{\alpha}_{\mathrm{I}}]^{\alpha}_{g1}. \tag{152}$$

By Eqs. (20), (32), and (151),

$$\begin{aligned} \bar{\kappa}^{p} e^{\alpha}_{gg} \kappa'^{p} &= \varepsilon(\sigma_{\kappa\kappa'}) \sigma_{\kappa\mathrm{I}} P^{\alpha}_{\mathrm{I}} N^{\alpha}_{\mathrm{I}} e^{\alpha}_{gg} N^{\alpha}_{\mathrm{I}} P^{\alpha}_{\mathrm{I}} \sigma_{\mathrm{I}\kappa'} \\ &= B^{\alpha} \varepsilon(\sigma_{\kappa\kappa'}) \sigma_{\kappa\mathrm{I}} P^{\alpha}_{\mathrm{I}} N^{\alpha}_{\mathrm{I}} N^{\alpha}_{\mathrm{I}} P^{\alpha}_{\mathrm{I}} \sigma_{\mathrm{I}\kappa'} \\ &= B^{\alpha} \varepsilon(\sigma_{\kappa\kappa'}) \bar{\kappa}^{p} \kappa'^{p}. \end{aligned} \tag{153}$$

### E. The Antisymmetrizer

The conventional formulation requires the use of products of space and spin functions. It requires further that the total wave function be antisymmetric under the permutation of space and spin coordinates. The algebraic formulation requires the antisymmetrizer, a linear combination of direct products of permutation operators. We begin by defining a representation $\Gamma^{\bar{\alpha}}$ which is conjugate to $\Gamma^{\alpha}$

$$[P_a]^{\bar{\alpha}}_{rs} = \varepsilon_a [P_a]^{\alpha}_{rs}. \tag{154}$$

If $\alpha \neq \tilde{\alpha}$, $\bar{\alpha} = \tilde{\alpha}$.

For $N = 3$ the irreducible conjugate representations of $\pi_3$ are

| $\alpha P_a$ | | (12) | (13) | (23) | (123) | (132) |
|---|---|---|---|---|---|---|
| $\{1^3\}, \{\bar{3}\}$ | $[1]$ | $[-1]$ | $[1]$ | $[-1]$ | $[1]$ | $[1]$ |
| $\{2, 1\}$ | $\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$ | $\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$ | $\begin{bmatrix} -a & b \\ b & a \end{bmatrix}$ | $\begin{bmatrix} -a & -b \\ -b & a \end{bmatrix}$ | $\begin{bmatrix} -a & b \\ -b & -a \end{bmatrix}$ | $\begin{bmatrix} -a & -b \\ b & -a \end{bmatrix}$ |
| $\{2, \overline{1}\}$ | $\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$ | $\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$ | $\begin{bmatrix} a & -b \\ -b & -a \end{bmatrix}$ | $\begin{bmatrix} a & b \\ a & -a \end{bmatrix}$ | $\begin{bmatrix} -a & b \\ -b & -a \end{bmatrix}$ | $\begin{bmatrix} -a & -b \\ b & -a \end{bmatrix}$ |
| $\{3\}, \{\overline{1^3}\}$ | $[1]$ | $[1]$ | $[1]$ | $[1]$ | $[1]$ | $[1]$ |

$$a = 1/2, \qquad b = \sqrt{3}/2.$$

Equation (154) defines a conjugate matric basis

$$e^{\bar{\alpha}}_{rs} = (1/\Theta^{\bar{\alpha}}) \sum_a [P_a^{-1}]^{\bar{\alpha}}_{sr} P_a. \tag{155}$$

We can express a permutation in terms of a conjugate matric basis

$$P_a = \sum_{\bar{\alpha}}^{M} \sum_{t}^{f^{\bar{\alpha}}} \sum_{u}^{f^{\bar{\alpha}}} [P_a]^{\bar{\alpha}}_{tu} e^{\bar{\alpha}}_{tu}. \tag{156}$$

For the algebraic development of the conventional formulation we define the antisymmetrizer,

$$\mathscr{A} = (1/N!) \sum_a \varepsilon_a (P_a \times P_a). \tag{157}$$

Here the cross denotes the direct product. Note that

$$\mathscr{A}(\mathscr{I} \times P_b) = \varepsilon_b \mathscr{A}(P_b^{-1} \times \mathscr{I}). \tag{158}$$

We substitute Eqs. (76) and (156) for the first and second factors, respectively, in the direct product in Eq. (157):

$$\mathscr{A} = (1/N!) \sum_{\alpha}^{M} \sum_{r}^{f^{\alpha}} \sum_{s}^{f^{\alpha}} \sum_{\bar{\beta}}^{M} \sum_{t}^{f^{\bar{\beta}}} \sum_{u}^{f^{\bar{\beta}}} (e^{\alpha}_{rs} \times e^{\bar{\beta}}_{tu}) \times \sum_a \varepsilon_a [P_a]^{\alpha}_{rs} [P_a]^{\bar{\beta}}_{tu}. \tag{159}$$

By Eqs. (154) and (78),

$$\begin{aligned} \sum_a \varepsilon_a [P_a]^{\alpha}_{rs} [P_a]^{\bar{\beta}}_{tu} &= \sum_a [P_a]^{\alpha}_{rs} [P_a]^{\beta}_{tu} \\ &= \delta^{\alpha\beta} \delta_{rt} \delta_{su} \Theta^{\alpha}. \end{aligned} \tag{160}$$

Consequently

$$\mathscr{A} = \sum_{\alpha} \mathscr{A}^{\alpha} \tag{161}$$

where

$$\mathscr{A}^{\alpha} = (1/f^{\alpha}) \sum_{r}^{f^{\alpha}} \sum_{s}^{f^{\alpha}} (e^{\alpha}_{rs} \times e^{\bar{\alpha}}_{rs}). \tag{162}$$

It should be noted that Eq. (162) is the algebraic analog of the analysis of a Slater determinant $\Psi^0$ into a linear combination of spin functions (Löwdin, 1955). Thus

$$e^{\alpha}\mathscr{A} = \mathscr{A}^{\alpha} \tag{163}$$

is equivalent to

$${}^{2S+1}\Phi\,\Psi_0 = {}^{2S+1}\Psi \tag{164}$$

where

$${}^{2S+1}\Phi = \prod_{k \neq S} \frac{S^2 - k(k+1)}{S(S+1) - k(k+1)}. \tag{165}$$

If we choose $\Gamma^{\alpha} = \Gamma^{\alpha}_{1}$, then $\Gamma^{\bar{\alpha}} = \Gamma^{\bar{\alpha}}_{1}$, where

$$[E^1]^{\bar{\alpha}}_{rs} = \delta_{rg}\delta_{sg} \qquad \text{where } g = f^{\alpha}. \tag{166}$$

For $N = 3$, $p = 1$, $f^{\alpha} = 1$,

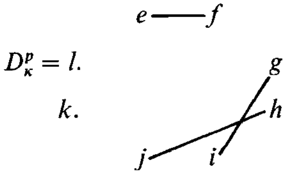
$$\begin{aligned} [E^1]^{\bar{\alpha}} &= (1/2)([\mathscr{I}]^{\bar{\alpha}} + [(12)]^{\bar{\alpha}}) \\ &= (1/2)\left(\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}\right) \\ &= \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}. \end{aligned}$$

## VI. The Conventional Formulation

### A. The Construction of Antisymmetric Space-Spin Pair Functions

In this section we present the conventional formulation of quantum chemistry. In this formulation we construct pair functions which are antisymmetric under permutation of space and spin coordinates. We carry out the construction in the language of the permutation algebra to facilitate a comparison with the spin-free formulation of Section III.

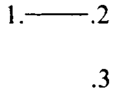
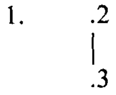
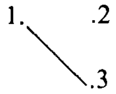
We begin by forming a spin primitive function $\Theta_{\kappa}$ relative to the pair diagram



by assigning $\alpha$ spin to the smaller integer and $\beta$ spin to the larger integer in each pair and $\alpha$ to the unpaired integers:

$$\Theta_{\kappa} = \alpha(e)\beta(f)\alpha(g)\beta(i)\alpha(h)\beta(j)\alpha(k)\alpha(l)\ldots \tag{167}$$

For $N = 3, p = 1$,

| $\kappa$ | $D_\kappa^p$ | $\Theta_\kappa$ |
|---|---|---|
| I |  | $\alpha(1)\beta(2)\alpha(3)$ |
| II |  | $\alpha(2)\beta(3)\alpha(1) = \alpha(1)\alpha(2)\beta(3)$ |
| III |  | $\alpha(1)\beta(3)\alpha(2) = \alpha(1)\alpha(2)\beta(3)$ |

From $\Theta_\kappa$ we construct a tableau consisting of two rows. The first row contains the integers assigned $\alpha$ spins and the second row contains the integers assigned $\beta$ spins arranged so as to put paired integers in the same column. Thus

$$T_\kappa^{\bar{\alpha}} = \begin{array}{|c|c|c|c|c|c|c|c|}\hline \cdot & e & g & h & k & l & \cdot & \cdot \\ \hline \cdot & f & i & j \\ \cline{1-4}\end{array}. \qquad (168)$$

The partition for $T_p^{\bar{\alpha}}$ is

$$\bar{\alpha} = \{N\text{-}p, p\}. \qquad (169)$$

The conjugate tableau is

$$T_\kappa^{\alpha} = \begin{array}{|c|c|}\hline \cdot & \cdot \\ \hline e & f \\ \hline g & i \\ \hline h & j \\ \hline k \\ \cline{1-1} l \\ \cline{1-1} \cdot \\ \cline{1-1}\end{array} \qquad (170)$$

and the conjugate partition is

$$\alpha = \{2^p, 1N^{-2p}\}. \qquad (171)$$

For $N = 3, p = 1,$

| $\kappa$ | $T_\kappa^{\bar{\alpha}}$ | $T_\kappa^{\alpha}$ |
|---|---|---|
| I | $\ytableaushort{13,2}$ | $\ytableaushort{12,3}$ |
| II | $\ytableaushort{21,3}$ | $\ytableaushort{23,1}$ |
| III | $\ytableaushort{12,3}$ | $\ytableaushort{13,2}$ |

Let $\sigma_{\mathrm{I}\kappa}$ be a permutation such that

$$\sigma_{\mathrm{I}\kappa} T_\kappa^{\bar{\alpha}} = T_{\mathrm{I}}^{\bar{\alpha}}, \tag{172}$$

then

$$\sigma_{\mathrm{I}\kappa} \Theta_\kappa = \Theta_{\mathrm{I}}. \tag{173}$$

For $N = 3,\ p = 1,$

| $\kappa =$ | I | II | III |
|---|---|---|---|
| $\sigma_{\mathrm{I}\kappa} =$ | $\mathscr{I}$ | (132) | (23) |
| $\sigma_{\mathrm{I}\kappa}\Theta_\kappa =$ | $\alpha(1)\beta(2)\alpha(3)$ | $\alpha(1)\beta(2)\alpha(3)$ | $\alpha(1)\beta(2)\alpha(3)$ |

For $\Theta_\kappa$ there exists an idempotent

$$E_\kappa^{\bar{\alpha}} = (1/n^{\bar{\alpha}}) P_\kappa^{\bar{\alpha}} \tag{174}$$

where

$$n^{\bar{\alpha}} = (N - p)!\,p! \tag{175}$$

and $P_\kappa^{\bar{\alpha}}$ is the row operator for $T_\kappa^{\bar{\alpha}}$, such that

$$\Theta_\kappa = E_\kappa^{\bar{\alpha}} \Theta_\kappa . \tag{176}$$

For $N = 3, p = 1,$

| $\kappa$ | $E_\kappa^{\bar{\alpha}}$ |
|---|---|
| I | $(1/2)[\mathscr{I} + (13)]$ |
| II | $(1/2)[\mathscr{I} + (12)]$ |
| III | $(1/2)[\mathscr{I} + (12)]$ |

From the space primitive function $\Psi$ and the spin primitive function $\Theta_\kappa$ we form an antisymmetric space-spin function:

$$\phi_\kappa = \sqrt{N!}\,\mathscr{A}\Psi\Theta_\kappa. \tag{177}$$

Here the factor $\sqrt{N!}$ yields the conventional normalization of $\phi_\kappa$ and $\mathscr{A}$ is the antisymmetrizer in which the first and second permutations in the direct product operate on the space and the spin primitive functions, respectively. If the space primitive function is an orbital product, $\phi_\kappa$ can be written as a Slater determinant:

$$\phi_\kappa = \begin{pmatrix} ab\cdots \\ \alpha\beta\cdots \end{pmatrix}$$

$$= (1/\sqrt{N!}) \begin{vmatrix} a(1)\alpha(1) & b(1)\beta(1) & \cdots \\ \cdots & \cdots & \cdots \\ a(N)\alpha(N) & b(N)\beta(N) & \cdots \end{vmatrix} \tag{178}$$

For $N = 3, p = 1$,

$$\phi_{\mathrm{I}} = \begin{pmatrix} abc \\ \alpha\beta\alpha \end{pmatrix} = (1/\sqrt{3!}) \begin{vmatrix} a(1)\alpha(1) & b(1)\beta(1) & c(1)\alpha(1) \\ a(2)\alpha(2) & b(2)\beta(2) & c(2)\alpha(2) \\ a(3)\alpha(3) & b(3)\beta(3) & c(3)\alpha(3) \end{vmatrix}$$

$$\phi_{\mathrm{II}} = \phi_{\mathrm{III}} = \begin{pmatrix} abc \\ \alpha\alpha\beta \end{pmatrix} = (1/\sqrt{3!}) \begin{vmatrix} a(1)\alpha(1) & b(1)\alpha(1) & c(1)\beta(1) \\ a(2)\alpha(2) & b(2)\alpha(2) & c(2)\beta(2) \\ a(3)\alpha(3) & b(3)\alpha(3) & c(3)\beta(3) \end{vmatrix}$$

We now define a spin function

$$\Theta_{\kappa a} = \bar{v}^{\bar{a}}_{\kappa a}\Theta_\kappa \tag{179}$$

where $\bar{v}^{\bar{a}}_{\kappa a}$ is a permutation on $\Theta_\kappa$ which reverses the spin assignment in one or more pairs and which permutes integers in the columns of $T^{\bar{a}}_\kappa$. From $\Theta_{\kappa a}$ we form the antisymmetric functions

$$\phi_{\kappa a} = \sqrt{N!}\mathscr{A}(\mathscr{S} \times \bar{v}^{\bar{a}}_{\kappa a})\Psi\Theta_\kappa . \tag{180}$$

An antisymmetric pair function for pair diagram $D^p_\kappa$ is a linear combination of the $\phi_{\kappa a}$ with coefficients $(-1)^{R_a} = \varepsilon_a$, where $R_a$ is the number of spin reversals in $\Theta_{\kappa a}$ relative to $\Theta_\kappa$. Thus

$$\Omega^p_\kappa = \sqrt{N!}\mathscr{A}\Big(\mathscr{S} \times \sum_a \varepsilon_a \bar{v}^{\bar{a}}_{\kappa a}\Big)\Psi\Theta_\kappa . \tag{181}$$

We now obtain an expression which contains the space pair operator $\kappa^p$. From Eq. (181) and (176),

$$\begin{aligned}\Omega_\kappa^p &= \sqrt{N!}\mathscr{A}(\mathscr{I} \times \bar{N}_\kappa^\alpha)\Psi\Theta_\kappa \\ &= n^p(\sqrt{N!}/n^{\bar{\alpha}})\mathscr{A}(\mathscr{I} \times \bar{N}_\kappa^{\bar{\alpha}}P_\kappa^{\bar{\alpha}}\sigma_{\kappa\mathrm{I}})\Psi\Theta_\mathrm{I} \\ &= n^p\varepsilon(\sigma_{\kappa\mathrm{I}})(\sqrt{N!}/n^{\bar{\alpha}})\mathscr{A}(\sigma_{\kappa\mathrm{I}}N_\kappa^\alpha P_\kappa^\alpha \times \mathscr{I})\Psi\Theta_\mathrm{I} \\ &= n^p(\sqrt{N!}/n^{\bar{\alpha}})\mathscr{A}(\kappa^\alpha \times \mathscr{I})\Psi\Theta_\mathrm{I}. \end{aligned} \tag{182}$$

For $N = 3, p = 1$,

$$\Omega_\mathrm{I}^p = \begin{pmatrix} abc \\ \alpha\beta\alpha \end{pmatrix} - \begin{pmatrix} abc \\ \beta\alpha\alpha \end{pmatrix} = \begin{pmatrix} abc \\ \alpha\beta\alpha \end{pmatrix} + \begin{pmatrix} bac \\ \alpha\beta\alpha \end{pmatrix},$$

$$\Omega_\mathrm{II}^p = \begin{pmatrix} abc \\ \alpha\alpha\beta \end{pmatrix} - \begin{pmatrix} abc \\ \alpha\beta\alpha \end{pmatrix} = -\begin{pmatrix} acb \\ \alpha\beta\alpha \end{pmatrix} - \begin{pmatrix} abc \\ \alpha\beta\alpha \end{pmatrix},$$

$$\Omega_\mathrm{III}^p = \begin{pmatrix} abc \\ \alpha\alpha\beta \end{pmatrix} - \begin{pmatrix} abc \\ \beta\alpha\alpha \end{pmatrix} = -\begin{pmatrix} acb \\ \alpha\beta\alpha \end{pmatrix} + \begin{pmatrix} bac \\ \alpha\beta\alpha \end{pmatrix}.$$

Note that

$$\Omega_\mathrm{III}^p = \Omega_\mathrm{I}^p + \Omega_\mathrm{II}^p.$$

From Eqs. (161) and (162)

$$\mathscr{A} = \sum_\alpha \mathscr{A}^\alpha \tag{183}$$

where

$$\mathscr{A}^\alpha = (1/f^\alpha)\sum_r\sum_s (e_{rs}^\alpha \times e_{rs}^{\bar{\alpha}}). \tag{184}$$

Then, since $\kappa^p$ is an element in the matric subalgebra $A^\alpha$, $\alpha = \{2^p, 1^{N-2p}\}$,

$$\begin{aligned}\mathscr{A}(\kappa^p \times \mathscr{I}) &= \mathscr{A}^\alpha(\kappa^p \times \mathscr{I}) \\ &= \sum_r\sum_s (e_{rs}^\alpha\kappa^p \times e_{rs}^{\bar{\alpha}}). \end{aligned} \tag{185}$$

We now show that

$$S^2\Omega_\kappa^p = S(S+1)\Omega_\kappa^p \tag{186}$$

where

$$S = N/2 - p. \tag{187}$$

By the Dirac equation

$$S^2 = [(4N - N^2)/4]K_1 + K_2 \tag{188}$$

where

$$K_1 = \mathscr{I} \tag{189}$$

and

$$K_2 = \sum_{e<f} (ef). \tag{190}$$

By Eqs. (187) and (96),

$$S^2 e_{rs}^{\bar{\alpha}} = \{[(4N - N^2)/4]K_1^{\bar{\alpha}} + K_2^{\bar{\alpha}}\} e_{rs}^{\bar{\alpha}}. \tag{191}$$

By Eq. (124)

$$K_1^{\bar{\alpha}} = 1,$$

$$K_2^{\bar{\alpha}} = \left[p^2 - p(N+1) + \frac{N(N-1)}{2}\right]. \tag{192}$$

Consequently

$$S^2 e_{rs}^{\bar{\alpha}} = S(S+1) e_{rs}^{\bar{\alpha}} \tag{193}$$

and

$$S^2 \Omega_\kappa^p = S(S+1)\Omega_\kappa^p. \tag{194}$$

### B. Matrix Elements

The matrix elements in a pair function basis for a spin-free operator $Q$ that commutes with the permutations on the space coordinates are evaluated as follows:

$$\begin{aligned} \langle\kappa|Q|\kappa'\rangle = [N!/(f^\alpha)^2] \sum_r \sum_{r'} \sum_s \sum_{s'} \\ \times \int e_{rs}^{\alpha} \kappa^p \Psi^* Q e_{r's'}^{\alpha} \kappa'^p \Psi \, d\tau \\ \times \int e_{rs}^{\bar{\alpha}} \Theta_1 e_{r's'}^{\bar{\alpha}} \Theta_1 \, d\tau. \end{aligned} \tag{195}$$

We evaluate first the integral over the spin coordinates. By Eqs. (174) and (148),

$$\begin{aligned} \int e_{rs}^{\bar{\alpha}} \Theta_1 e_{r's'}^{\bar{\alpha}} \Theta_1 \, d\tau &= \delta_{sg}\delta_{s'g} \int e_{rg}^{\bar{\alpha}} \Theta_1 e_{r'g}^{\bar{\alpha}} \Theta_1 \, d\tau \\ &= \delta_{rr'}\delta_{sg}\delta_{s'g}\, \Delta^\alpha \end{aligned} \tag{196}$$

where

$$\Delta_g^\alpha = \int e_{gg}^{\bar{\alpha}} \Theta_1 \Theta_1 \, d\tau. \tag{197}$$

Then by Eq. (153),

$$\begin{aligned}\langle\kappa|Q|\kappa'\rangle &= (N!\,\Delta^\alpha/f^\alpha)\int e^\alpha_{gg}\kappa^p\Psi^*Q\kappa'^p\Psi\,d\tau\\ &= (N!\,\Delta^\alpha/f^\alpha)\int \bar{\kappa}'^p e^\alpha_{gg}\kappa^p\Psi^*Q\Psi\,d\tau\\ &= B^\alpha\varepsilon(\sigma_{\kappa\kappa'})\int \bar{\kappa}'^p\kappa^p\Psi^*Q\Psi\,d\tau. \qquad (198)\end{aligned}$$

We see that, to a multiplicative constant which depends only on the pair number $p$, the matrix elements over antisymmetric space-spin bond functions are identical to the matrix elements over the spin-free bond functions. This constitutes the final justification of the procedure outlined in Section III.

## Appendix:

## Types of Permutation $P_a$ and Diagonal Values $(P_a)^p_{\kappa\kappa}$

| Permutation, $P_a$ | No. of permutations of this type | $(P_a)^p_{\kappa\kappa}$ | Permutation, $P_a$ | No. of permutations of this type | $(P_a)^p_{\kappa\kappa}$ |
|---|---|---|---|---|---|
| $E$ | 1 | 1 | $(ll'mm')$, $(lmm')(nn')$ | $12+12=24$ | $-1/2$ |
| $(ll')$ | 3 | 1 | | | |
| $(lm)$ | 12 | $-1/2$ | $(lml'm')$, $(lml'm')(nn')$ | $6+6=12$ | 1 |
| $(ll')(mm')$ | 3 | 1 | | | |
| $(lm)(l'm')$ | 6 | 1 | $(ll'mn)$ | 48 | $1/4$ |
| $(ll')(mm')(nn')$ | 1 | 1 | $(lml'n)$ | 24 | $1/4$ |
| $(ll')(mn)$ | 12 | $-1/2$ | $(ll'mn)(m'n')$ | 48 | $-1/2$ |
| $(lm)(l'n)$ | 24 | $1/4$ | $(lml'n)(m'n')$ | 24 | $1/4$ |
| $(lm)(l'n)(m'n')$ | 8 | $1/4$ | $(ll'mm'n)$ | 48 | $1/4$ |
| $(lm)(l'm')(nn')$ | 6 | 1 | $(ll'mnm')$ | 48 | $1/4$ |
| $(ll'm)$, $(ll'm)(nn')$ | $24+24=48$ | $-1/2$ | $(lml'm'n)$ | 48 | $-1/2$ |
| $(lmn)$ | 16 | $1/4$ | $(ll'mm'nn')$ | 16 | $1/4$ |
| $(lmn)(l'm')$ | 48 | $-1/2$ | $(ll'mnm'n')$ | 48 | $-1/2$ |
| $(ll'm)(m'n)$ | 48 | $1/4$ | $(lmnl'm'n')$ | 8 | 1 |
| $(ll'm)(m'nn')$ | 24 | $1/4$ | $(lmnm'l'n')$ | 24 | $1/4$ |
| $(lmn)(l'm'n')$ | 8 | 1 | $(ll'mnn'm')$ | 24 | $1/4$ |
| $(lmn)(l'n'm')$ | 8 | $1/4$ | | | |
| | | | Total | 720 | |

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# On the Basis of the Main Methods of Calculating Molecular Electronic Wave Functions*

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## I. Some Mathematical Requirements

### A. Mathematical Properties of Exact Solutions

Let us denote by $\phi\ (q_1, q_2, \dots q_n;\ Q_1,\ Q_2, \dots\ Q_p)$ a spatial wave function associated with a given stationary state of a certain molecule. The $q$'s

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* This paper is based on my course of lectures during the last International Summer Institute in Menton (July 1963), and a review of the main ideas which form the basis of the usual methods of calculating electronic wave functions, especially for large molecules. Some recent advances are very briefly presented, particularly those which have resulted from work done at the Centre de Mécanique Ondulatoire Appliquée.

denote the coordinates of points associated with the various electrons and the $Q$'s correspond to the nuclei.

$\phi$ is a solution of a certain Schrödinger equation:

$$H_T\phi = W_T\phi, \tag{1}$$

where $H_T$ represents the Hamiltonian operator and $W_T$ the energy corresponding to $\phi$.

As is well known, the Born–Oppenheimer procedure helps us to develop $\phi$ in a basis of products of electronic wave functions and nuclear wave functions. We are led to the calculation of electronic wave functions which represent the motion of electrons in the field of "fixed nuclei." If $\Phi$ denotes such an electronic wave function, it will be a solution of another equation:

$$H\Phi = W\Phi \tag{2}$$

where $H$ differs from $H_T$ by the omission of the kinetic energy operator of the nuclei.

Let $W_a$ be a given eigenvalue of Eq. (2) and $\Phi_a^b$, $b = 1, \ldots,$ be the set of corresponding eigenfunctions. It is well known that *this set of functions is a basis for a certain representation (usually irreducible) of any groups of operators which commute with H.* Among these groups are the permutation group $S_n$ of the $n$ coordinates $q_i$ and the symmetry group $G$ of the operations which permute the nuclei of identical nature. To introduce the spin we must transform the $\Phi$'s to functions $\psi$ containing the spin coordinates. The $\psi$'s must be:

(*a*) antisymmetrical with respect to a simultaneous exchange of the spin and space coordinates associated with two given electrons;

(*b*) eigenfunctions of the spin operators $S^2$ and $S_z$.

To obtain the $\psi$'s we can use the formula

$$\psi = \sum_P (-1)^P P\Phi\sigma, \tag{3}$$

where $\sigma$ is an eigenfunction of $S^2$ and $S_z$ and $P$ is an operator which permutes simultaneously the space electronic coordinates in $\Phi$ and the spin coordinates in $\sigma$, the sign $(-1)^P$ being positive or negative according to the parity of the permutation. It is easy to see that the $\psi$'s built using formula (3) either vanish or fulfill the necessary requirements. When the $\psi$'s corresponding to a certain $W_i$ and to a certain $\sigma$ vanish, we must conclude that the corresponding energy cannot be associated with the spin state represented by $\sigma$. If the $\psi$'s associated with a given $W_i$ vanish for every possible $\sigma$, the corresponding energy has no physical meaning.

## B. Bases of the Main Methods for Calculating Approximate Solutions

It is well-known that the Schrödinger equation

$$H\Phi = W\Phi \tag{4}$$

is equivalent to the variational equation

$$\delta \int \Phi^*(H - W)\Phi \, dv = 0 \tag{5}$$

$$\Phi \in \mathscr{H} \tag{6}$$

where expression (6) indicates that the variation is allowed in all the Hilbert space $\mathscr{H}$.

Evidently this variational equation, like the Schrödinger equation, cannot be solved rigorously except in very simple cases. The problem is to find some approximate solutions. The main method to obtain such solutions is to replace Eq. (6) by

$$\Phi \in D \tag{7}$$

where $D$ is a limited part of $\mathscr{H}$. Physical intuition is required to make precise the form of $D$. This important question will be discussed in Section II. If $D$ is a linear subspace $\Phi$ may be represented in a basis made of a limited set of function $\Upsilon_1, \Upsilon_2, \ldots \Upsilon_k$.

In this case we shall write

$$\Phi_{\mathrm{ap}} = \sum_i c_i \Upsilon_i . \tag{8}$$

The problem now is to calculate the values of the $c_1$'s for which $\Phi$ satisfies Eq. (5). This is a trivial variational problem. The $c_i$'s are the nonzero solutions of the *secular system*:

$$\sum_i c_i \left[ \int \Upsilon_p^* H \Upsilon_i \, dv - W \int \Upsilon_p^* \Upsilon_i \, dv \right] = 0. \tag{9}$$

$$p = 1, 2, \ldots k.$$

These nonzero solutions exist only if the determinant of the brackets in Eq. (9) is zero:

$$\det \left[ \int \Upsilon_p^* H \Upsilon_i \, dv - W \int \Upsilon_p^* \Upsilon_i \, dv \right] = 0. \tag{10}$$

Equation (10) is called the *secular equation* of the problem. MacDonald's theorem shows that the values of $W$ which satisfy this equation are upper limits to the various electronic levels of the molecule. If we introduce one of the obtained values of $W$ in the secular *system*, Eq. (9), the corresponding set of $c_i$ determines a function $\Phi_{\mathrm{ap}}$, which may be considered as an approximation to the electronic wave function for that level. This linear variational method just described is the basis for all *configuration interaction methods*. When $D$ is not a linear subspace the problem must usually be solved by iterations; it has the mathematical structure of the *self-consistent field methods*.

To go further we have to remember that the rigrous Φ's would usually be a basis for an irreducible representation of a certain symmetry group $G$. If we start from a set of *fixed functions*:

$$\Upsilon_1, \Upsilon_2, \dots, \Upsilon_n$$

we are therefore interested in transforming them to such a basis. This transformation may be achieved by using the metric operators associated with the various irreducible representations of the group. Let us denote by

$$K^j_{u,k}$$

the $k$th element of the basis obtained from the action on $\Upsilon_j$ of the metric operators $\rho_{u,k}$ associated with the representation $u$:

$$K^j_{u,k} = \rho_{u,k}\Upsilon_j. \tag{11}$$

All the products

$$K^j_{u,k}\sigma$$

derived from the same $\Upsilon^j$ are said to be belong to the same *configuration*. In other words, the linear subspace built on all these products is called a *configuration*.[1] A function like

$$\phi^j_m = \sum_P (-1)^p P K^j_{u,k}\sigma \tag{12}$$

where $m$ denotes a certain choice of $u$, $k$ and $\sigma$, has (with the exact solution Φ) the following properties:

(*a*) It conforms to the Pauli principle.
(*b*) It is an element of a basis of an irreducible representation of $G$.
(*c*) It is an eigenfunction of $S^2$ and of $S_z$.

Therefore it is reasonable to search for a approximate function to Φ in a family of functions such as

$$\Phi_{\mathrm{ap}} = \sum_{j=1}^{j=n} \sum_m c^j_m \phi^j_m. \tag{13}$$

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[1] This is an extreme generalization of the word. Usually this word is used when the Υ's are products of monoelectronic functions with a more restricted meaning.

We recognize the linear variational problem analyzed recently. The functions in Eq. (13) are linear combinations of configurations, and the calculation of $c_m^j$ leads to a secular equation and to a secular system. This method *is the configuration interaction method.*

The calculation of the roots of the secular equation requires the computation of matrix elements such as

$$\int \phi_m^{j*} H \phi_{m'}^{j'}\, dv.$$

Following a well-known result of group theory, such a matrix element will vanish unless $\Phi_m^j$ and $\Phi_{m'}^{j'}$ belong to the same irreducible representation of $G$ and also to the same irreducible representation of $S_n$. Therefore this matrix element will vanish unless $\Phi_m^j$ and $\Phi_{m'}^{j'}$ correspond to the same representation $u$ and the same eigenfunction of $S^2$ and $S_z$. This result shows the great simplification obtained when we start from functions which form bases for the irreducible representations of the groups involved. A direct consequence will be that, in a given approximate function $\Phi_{\text{ap}}$ there will be from each configuration only the terms corresponding to a given eigenvalue of $S^2$ and of $S_z$ and to a given irreducible representation of $G$.

An alternative method is to start from one configuration only. We have

$$\Phi_{\text{ap}} = \sum_m c_m^j \phi_m^j . \tag{14}$$

Now $\Upsilon_j$ will *not* be considered as a given function, but as a function belonging to a certain nonlinear family of functions,

$$\Upsilon^j \in D.$$

We will be led to a non-linear variational problem. That is the generalized *self-consistent field method.*[2]

Evidently it will be possible to introduce an intermediate procedure, taking $\Phi_{\text{ap}}$ as in Eq. (8) but considering now that the various $\Upsilon_j$'s are not fixed functions but functions belonging to various families:

$$\Upsilon_l \in D_j$$

## II. Physical Aspects of the Problem

From the last section it appears that the main problem is to select a certain set of functions $\Upsilon_j$, that is to say, a region of the Hilbert space

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[2] This is also an extreme generalization of the term.

which will be explored by purely mathematical procedures with the hope that it will be possible to find in this region some good approximations for the unknown solutions of the Schrödinger equation. Physical intuition is the main guide to the choice of the *generating functions* $\Upsilon_j$ and, as may easily be anticipated, the kinds of convenient generating functions depend on the kind of molecule studied or, more precisely, on the nature of the chemical bonds which form the molecule. The choice of the generating functions may also depend on the nature of the properties of the molecule to be investigated (namely, energy levels, dipole moment, rate of reaction, equilibrium constant, etc.).

### A. Some Aspects of Atomic and Molecular Structure: Notion of Loge and Difference Density Function

A simple geometrical picture of the electronic clouds of atoms and molecules is a good starting point. Let us consider, as an example, the first excited state of the helium atom. In the old theory of Bohr this state would correspond to one *K* electron in a certain circular orbit and an *L* electron in another one. From the wave mechanical point of view the situation is rather different, but we can nevertheless obtain a geometrical picture in the following way. Let us consider a sphere of radius *R* with its center at the nucleus. With the help of the electronic wave functions we may evaluate the probability *P* of finding one electron and one only in this sphere. When *R* is very small this probability is also very small because the sphere is generally empty. When *R* is very large, *P* again will be very small because now the sphere will generally contain both electrons. Thus, intuitively, we must anticipate that *P* will possess a maximum for at least one value of the radius *R*. The curve of Fig. 1 (Daudel *et al.*, 1955) shows that this is the case. The calculation has been done starting from a Hylleraas

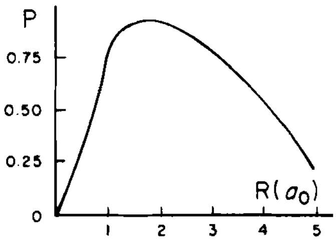


**Fig. 1.** The probability *P* expressed as a function of *R* for the first excited state of helium.

wave function. The maximum of $P$ is very large (0.93), and is observed for $R = 1.7a_0$. We can summarize the situation saying that, in the case of the first excited state of helium, the sphere of radius $R = 1.7a_0$ corresponds to the best decomposition into spherical *loges* and that the probability of finding one and only one electron in this sphere is 93%. Evidently the probability of finding one and only one electron outside of this sphere is also 93%. We are thus quite naturally led to associate the sphere of radius $1.7a_0$ with the $K$ shell and the rest of the space with the $L$ shell.

These results can be extended (Odiot, 1957). The space associated with an atom (in its ground state) can be cut up into spherical shells all concentric with the nucleus, one built on the other, in such a way that there is a high probability of finding two electrons of opposite spin in the first loge, eight in the second (four of each spin), and so on. If the volume of a given loge is divided by the number of electrons which it usually contains, we obtain a certain volume $v$ which gives an idea of the space associated with one electron in the loge. We can also evaluate the average value $P$ of the electronic potential which is exerted in the loge.

The following relation is observed for all atoms and all shells (Odiot and Daudel, 1954):

$$P^{3/2}v = \text{constant}. \tag{15}$$

*A kind of Boyle–Mariotte Law exists between the "electric pressure" P and the volume v associated with one electron in an atomic loge.*

Another important feature in the geometrical description of atoms arises from the Pauli principle or, more exactly, from the symmetry of the electronic wave functions. This symmetry, as is well-known, leads to the conclusion that the probability of finding two electrons at the same point with the same spin is zero. From this, it is can be deduced that, in addition to Coulomb repulsion, there is a further tendency for two electrons of the same spin to avoid being in the same small region of space. This will become clear in studying the most probable configuration of the electrons of atoms. The most probable configuration is the electronic configuration of an atom which has the highest probability density. For beryllium in its $^3P$ state, the most probable configuration corresponds to two electrons of opposite spin at the nucleus and two electrons of the same spin at $2.7a_0$ from the nucleus, the angle formed by these two electrons and the nucleus being 180° (Fig. 2). In the most probable configuration of boron in its $^4P$ state, two electrons of opposite spin are found at the nucleus and three electrons of the same spin are found $2.45a_0$ from the nucleus at the vertices of an equilateral triangle (Fig. 2) (Linnett and Poe, 1951). *It is observed*

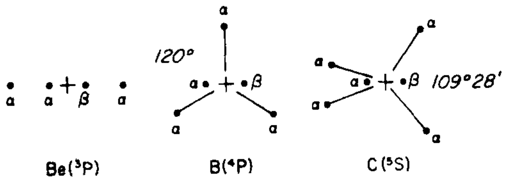


**Fig. 2.** The most probable configuration of small atoms.

*that in a given shell the electrons of the same spin tend to form the largest possible angles with the nucleus.*

It is useful to extend to molecules the kind of discussion we have given for atoms. In a good decomposition of a molecule into loges some of the loges, which are representative of atoms before bonding, will be found again in the molecule (with only small modifications). They can be called the *loges of the cores* while the others make up the *loges of the bond(s)*.

In the case of the lithium molecule, for example, we can consider the decomposition in loges formed by two spheres with their centers, respectively, on each nucleus and a radius equal to $R$. The value of $R$ corresponding to the highest value of the probability $P$ of finding two electrons (and two only) of opposite spin in one of the spheres is found to be $R = 1.53a_0$ if the Coulson and Duncanson (1944) wave function is used. The corresponding value of the probability $P$ is about 0.96. This shows that the distribution of the electrons symbolized by Fig. 3 has a very high probability (Daudel *et al.*, 1955).

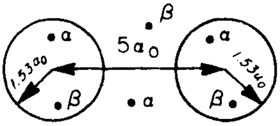


**Fig. 3.** A good decomposition into loges for the lithium molecule.

Another approach to a geometrical picture of chemical bonds is the use of the difference density function. This function is given by the relation

$$\delta(M) = \rho(M) - \rho^f(M), \tag{16}$$

where $\rho(M)$ is the actual electronic density at a given point $M$ of a molecule, and $\rho^f(M)$ is the electronic density which would occur at this point if the density in the molecule were the simple sum of the densities in the free atoms. At a point where $\delta$ is positive there is an increase in the electronic density as a result of chemical binding. Where the function is negative the reverse is true.

Figure 4 shows the result (Roux *et al.*, 1956) of such a study based on the James and Coolidge wave function. It is seen that between the nuclei the $\delta$ function is always positive and large. In agreement with chemical intuition the chemical binding leads in this case to an important increase of electronic density between the nuclei.

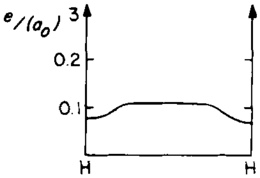


**Fig. 4.** The function $\delta$ calculated for $H_2$ along the molecular axis.

Let us take now the case of the oxygen molecule. In Fig. 5 (Bratoz *et al.*, 1960) the regions where $\delta$ is positive are designated by crosses. Outside of these regions $\delta$ is negative. One observes that now $\delta$ is negative along the molecular axis but positive in an annular region centered on the axis. The $O_2$ bond is therefore annular in some sense. The fact that there is no increase of electronic density along the internuclear line is probably due to the presence of four electrons (two of each spin) in the vicinity of the axis. *The repulsion between electrons of the same spin tends to place them outside of the small space surrounding the axis.* In conclusion we can say that

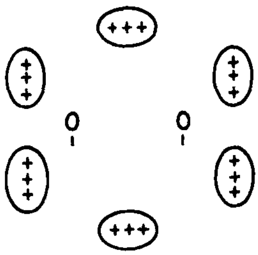


**Fig. 5.** The function $\delta$ calculated for $O_2$ in a plane passing through the molecular axis. The regions where $\delta$ is positive are designated by crosses.

*near the line connecting two nuclei (of small atoms) and between the cores of these atoms there is only room for two electrons of opposite spin.*

## B. Localized and Delocalized Bonds

Therefore, when, in a molecule (in its ground state), *the number of electrons is exactly twice the number of pairs of neighboring cores*, we can anticipate that there will be a high probability of finding two electrons with opposite spin between each pair of neighboring cores. In other words, between two neighboring cores it will be possible to find a good loge for two electrons of opposite spin. When such a situation occurs it is said that there is between the two cores a *localized bond.* A molecule containing only localized bonds is said to be *saturated.*

It is reasonable to associate with the loge of such a localized bond a bielectronic function $B(1, 2)$. If we take the example of methane, made of the $K$ core of a carbon atom and four localized CH bonds, we should be led to consider as starting functions those of the form

$$\Upsilon = C(1, 2)B_1(3, 4)B_2(5, 6)B_3(7, 8)B_4(9, 10), \qquad (17)$$

where $C$ is associated with the cores and the $B_i$'s with the various CH bonds.

But it is easy to see that in certain cases it will not be possible to localize between two neighboring cores a region in which there is a high probability of finding a given number of electrons with a certain organization of the spins. Let us consider diborane. The geometrical arrangement of the cores of this molecule is given in Fig. 6. The double arrows represent the pairs of neighboring cores, which are eight in number. However, twelve electrons are available for bonding. Therefore it is not possible to associate two electrons with each pair of neighboring cores. From the measurements of the bond lengths it appears that the four outer BH bonds are normal simple bonds, that is to say, two-electron localized bonds. There remain four electrons to be distributed around the four central cores. Figures 7(*a*) and (*b*) give two possible configurations for these electrons. The probabilities of these two configurations are obviously identical. Therefore the probability of finding one electron with a given spin between a given

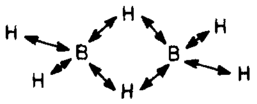
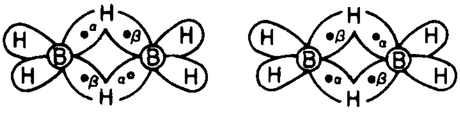


**Fig. 6.** Geometrical structure of diborane.

boron atom and a given central H is certainly not greater than 0.5. There is no good loge for one electron between B and a central H.



(a) (b)

**Fig. 7.** One-electron bonds in diborane.

If, now, we divide the space of the central BH between two three-center loges, as in Fig. 8, this kind of difficulty disappears. There is no a priori reason to believe that it is impossible to find such good loges, but as they are now extended over three cores we shall say that they correspond to a *two-electron bond delocalized over three centers* (two B and one H).

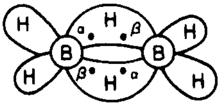


**Fig. 8.** A better decomposition into loges for diborane.

Finally, when we are not able to find a good loge between a pair of neighboring cores we will have to extend the loge over more than two cores, and we will be led to consider that the corresponding bond is delocalized.

Figure 9 gives an example[2a] for which the various possible situations are

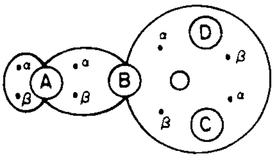


**Fig. 9.** A typical example of decomposition into loges.

encountered in the same molecule. On atom A there is a lone pair, between A and B a two-electron localized bond, and between B, C, and D a four-

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[2a] This example is an extrapolation of the previous results as no exact calculations of the best decomposition in loges have been made for complex molecules.

electron delocalized bond. For such a molecule, if all the cores are $K$ shells, it will be natural to start from a function like

$$\Upsilon = K_A(1,2)K_B(3,4)K_C(5,6)K_D(7,8) \times L_A(9,10)B_{AB}(11,12)B_{BCD}(13,14,15,16) \tag{18}$$

where the $K_i$'s denote the functions associated with the cores, $L_A$ corresponds to the lone pair, $B_{AB}$ represents the localized bond, and $B_{BCD}$ the delocalized one.

Finally we see that the knowledge of a good decomposition into loges suggests a form for a generating funcion $\Upsilon$. But because a knowledge of the wave function is necessary to obtain a precise decomposition into loges, we seem to be in a vicious circle. Happily this is not the case, because we need to know only the qualitative aspects of a good decomposition into loges, and we have seen, in the cases of methane and diborane, that some general principles help is to obtain such information directly. Experimental data, previous calculations on similar molecules, and chemical intuition are also helpful in deciding what would be, for a given molecule, the qualitative aspects of a good decomposition into loges.

However the work is not at its end when the general form, as in Eq. (18), is obtained. In principle, it would be possible to introduce $\Upsilon$ in the generalized self-consistent field formalism described in Section I,B. But for technical reasons the use of polyelectronic functions is extremely tedious. Furthermore, if the configuration interaction method is used, the precise form of the $\Upsilon$'s must be known. For these various reasons, new approximations are necessary, and it is usual to express the various functions encountered in this section in terms of monoelectronic or (in some cases) bielectronic functions called orbitals and biorbitals (or geminals).

## III. Orbitals and Biorbitals (or Geminals)

### A. The Independent Electron Model: Monoelectronic Orbitals

As is well known, the idea of orbital is based on the noninteracting electron (or independent electron) model. Furthermore, this model will give a first example of an application of the mathematical formalism described in Section I.

In this model the interaction between the electrons is neglected in such a way that the new Hamiltonian $H^0$ can be written

$$H^0 = H - \sum_{i<j} \frac{e^2}{r_{ij}} \tag{19}$$

where $r_{ij}$ denotes the interatomic distance between the points associated with electrons $i$ and $j$. Therefore $H^0$ is just the sum of Hamiltonians $h_i$ representing the motion of the $i^{\text{th}}$ electron in the field of the nuclei of the molecule.

We are led to consider the equation

$$h_i\varphi_k(i) = \mathscr{E}_k\varphi_k(i), \tag{20}$$

and it is easy to see that any product of $n$ functions $\varphi_k$

$$\Phi_l^0 = \varphi_k(1) \cdots \varphi_{k+n-1}(n) \tag{21}$$

is a rigorous solution of the equation

$$H^0\Phi^0 = W^0\Phi^0 \tag{22}$$

with

$$W^0 = \mathscr{E}_k + \mathscr{E}_{k+1} + \cdots + \mathscr{E}_{k+n-1}. \tag{23}$$

The functions $\varphi$ *are the orbitals* of the noninteracting model. They form a basis for the representations (usually irreducible) of the group $G$ associated with $H^0$ or $H$. Therefore the effect of the metric operators of $G$ on such an orbital will be to transform it into a linear combination of orbitals. If the product

$$\Upsilon_l = \Phi_l^0 = \varphi_k(1) \cdots \varphi_{k+n-1}(n) \tag{24}$$

is taken as a generating function $\Upsilon$, the effect of the metric operator will be to transform it to a linear combination of such products. We shall have

$$\rho\Upsilon_l = K = \sum_l c_l\Upsilon_l, \tag{25}$$

and the corresponding wave function will be

$$\phi = \sum_P (-1)^P \sum_l c_l\Upsilon_l\sigma \tag{26}$$

if we take account of Eq. (12).

But as the spin function $\sigma$ is also a linear combination of products of monoelectronic spin functions,

$$\sigma = \sum_m s_m\sigma_m \qquad \text{with} \qquad \sigma_m = \sigma_p(1) \cdots \sigma_{p+n-1}(n) \cdots, \tag{27}$$

we can write

$$\phi = \sum_l \sum_m c_l s_m \sum_P (-1)^P P\Upsilon_l\sigma_m. \tag{28}$$

As obviously

$$\sum_P (-1)^P P\Upsilon_l\sigma_m = \det \varphi_k(1)\sigma_p(1)\varphi_{k+1}(2)\sigma_{p+1}(2) \cdots \varphi_{k+n-1}(n)\sigma_{p+n-1}(n), \tag{29}$$

the formalism of Section I leads to the well-known conclusion that the $\phi$'s constituting the configurations and therefore the physical solutions of the independent electron model are linear combinations of Slater determinants.

Starting from a given product of orbitals, $\Upsilon_l$, corresponding to a certain energy $W_l^0$, it is possible to generate various functions $\phi$ which belong to the same configuration and correspond to various states of the system. The energies of these states are identical, and they differ by the symmetry properties of their wave functions.

It is very important to note that we cannot introduce in $\Upsilon_l$ the same orbital more than twice. Otherwise the corresponding determinant will have at least two identical columns (as there are only two different monoelectronic spin functions $\alpha$ and $\beta$) and will be zero. Therefore, as the energy $W^\circ$ is the sum of the energies $\mathscr{E}$ associated with the orbitals included in the product, to represent the fundamental states we must use each orbital of lowest energy twice if there is an even number of electrons.

Now we have to go from that model to the actual molecule. The fact that products of monoelectronic functions are exact solutions of the problem when the interelectronic repulsion is neglected suggests that perhaps such products exist which give at least approximate solutions when this interaction is included. Therefore we are led to use as generating functions, $\Upsilon$, products of unknown monoelectronic functions and to calculate the best one following the self-consistent field method. We have to solve the variational equation

$$\delta \int \Phi_{\mathrm{ap}}^*(H - W)\Phi_{\mathrm{ap}}\, dv = 0 \tag{30}$$

where $\Phi_{\mathrm{ap}}$ is a linear combination of Slater determinants. Another procedure is to consider a limited number of configurations of the noninteracting electron model as a basis, and to apply the configuration interaction method. An intermediate method is to improve the configurations by a variational procedure before introducing the configuration interaction.

But, from the technical point of view none of these methods can be used without supplementary approximations. But before discussing that point we shall present another interesting model.

### B. The Independent Pair Model: Bielectronic Orbital (Biorbitals or Geminals)

Let us consider a molecule with an even number $2p$ of electrons in a state where $S_z = 0$. If we measure the spin of each electron at a given instant we shall find $p$ electrons with the $z$ spin component $+\frac{1}{2}\, h/2\pi$ and $p$ electrons with the $z$ spin component $-\frac{1}{2}h/2\pi$. We know that two electrons with the same spin tend to stay far apart but that two electrons with opposite spin may be found in the same small region of space. A simplified picture of the molecule is obtained by assuming that it consists of a set of pairs of interacting electrons (with opposite spin) but that there is no coulombic interaction between the pairs.

The simplified total Hamiltonian of the problem may be written as the sum of $p$ Hamiltonians, $h_{ij}$ representing the motion of one isolated pair $ij$, and we are led to consider an equation like

$$h_{ij}\chi_k(i, j) = \mathscr{E}_k\chi_k(i, j). \tag{31}$$

The $\chi$ may be called the *bielectronic orbitals* (or geminals or biorbitals) of the independent pair model, and it is easy to see that a product of $p$ functions $\chi$ is a rigorous solution for this model.

We can easily reproduce on this basis the various discussions we had starting from the independent electron model. The only difference is that the formalism does not now introduce determinants, and it is therefore possible to introduce products of functions $\chi$ containing an arbitrary number of identical $\chi$'s. Usually however the $\chi$'s introduced in the generating functions are all different (see, for example, Parks and Parr, 1958). But the generating function

$$\Upsilon = \chi(1, 2)\chi(3, 4) \cdots \chi(n-1, n), \tag{32}$$

where all the $\chi$'s are identical, can also be used. If we assume, to simplify the discussion, that the group $G$ contains only the identity, we will have

$$K = \Upsilon, \tag{33}$$

and consequently

$$\phi = \sum_P (-1)^P P\chi(1, 2)\chi(3, 4) \cdots \chi(n-1, n)\sigma. \tag{34}$$

These are the functions constituting the configurations in this particular case. Durand and Daudel (in press) has shown that, if $\chi$ is assumed to be antisymmetric with respect to a permutation of the coordinates, these functions lead to

$$\Phi_{\mathrm{ap}} = \sum_P (-1)^P P\eta(1, 2)\eta(3, 4) \cdots \eta(n-1, n), \tag{35}$$

where

$$\eta(i, j) = \chi(i, j)[\alpha(i)\beta(j) - \beta(i)\alpha(j)] \tag{36}$$

follows from the condition

$$S^2\Phi_{\mathrm{ap}} = S_z\Phi_{\mathrm{ap}} = 0. \tag{37}$$

This is exactly the wave function proposed by Bratoz (1963).

### C. Representation of the Cores: the AO (Atomic Orbital) Approximation

We saw that, near the nuclei of a molecule, core regions exist in which the electronic density is about the same as that in the free atom. In order to represent these parts of the molecule it is normal to take in first approximation the same functions as are used in the free atoms. Atoms may be considered as monocentric molecules; therefore, the orbitals formalism is applicable to atoms. The solutions of the self-consistent field problem in the special case where each orbital is used twice (when possible) has been extensively calculated, mainly by Hartree (see for instance Hartree, 1957). In the case of a state for which a representation by a unique determinant like[3]

$$\Phi_{\mathrm{ap}} = \det \varphi_1(1)\overline{\varphi_1(2)}\varphi_2(3)\overline{\varphi_2(4)} \cdots \varphi_{n/2}(n-1)\overline{\varphi_{n/2}(n)} \tag{38}$$

is possible, the self-consistent field method leads to the well known Hartree–Fock equation

$$h^N\varphi_i + \sum_j (2J_j - K_j)\varphi_i = \sum_k \mathcal{E}_{ki}\varphi_k \tag{39}$$

where the operators $J_j$ and $K_j$ are such that

$$J_j\varphi_i(1) = \left(\int \varphi_j^2(2)\frac{1}{r_{12}}\,dv_2\right)\varphi_i(1) \tag{40}$$

and

$$K_j\varphi_i(1) = \left(\int \varphi_j(2)\varphi_i(2)\frac{1}{r_{12}}\,dv_2\right)\varphi_j(1) \tag{41}$$

and where $h^N$ is the sum of the kinetic energy operator associated with an electron and of the potential energy operator due to the nucleus.

It is easy to see that when a set of orbitals is obtained the effect of any unitary transformation $T$ leads to another set of orbitals $\zeta$ given by

$$\zeta_i = \sum_j T_{ij}\varphi_j \tag{42}$$

in such a way that

$$\det \varphi_1(1) \cdots \bar{\varphi}_{n/2}(n) = \det \zeta_1(1) \cdots \bar{\zeta}_{n/2}(n) = \Phi_{\mathrm{ap}}. \tag{43}$$

There is a particular transformation for which

$$\mathcal{E}_{ki} = \delta_{ki}\mathcal{E}_{ii}. \tag{44}$$

---

[3] For simplicity $\varphi(i)$ is written for $\varphi(i)\alpha(i)$ and $\overline{\varphi(i)}$ for $\varphi(i)\beta(i)$.

The corresponding orbitals $\psi_i$ are the solutions of the equations

$$h^N\psi_i + \sum_j (2J_j - K_j)\psi_i = \mathscr{E}_{ii}\psi_i. \tag{45}$$

It has been shown (see for instance Roothaan, 1951) that these equations may be solved in such a way that the solutions form a basis for the irreducible representations of the group $G$. It is usually under this form that the Hartree–Fock equations are solved and the corresponding $\psi$'s are tabulated for many atoms and ions.

These *particular* atomic orbitals are almost localized in the loge corresponding to their shell (see for instance Daudel, 1956). For instance, in the case of $Rb^+$ the radii of the various spheres limiting the loges $K$, $L$, and $M$ are, respectively, 0.06, 0.265, and 1.055 (in atomic units). The corresponding orbitals 1*s*, 2*s*, and 3*s* are such that

$$\int_0^{0.06} (1s)^2\, dv = 0.81, \tag{46}$$

$$\int_{0.06}^{0.265} (2s)^2\, dv = 0.85, \tag{47}$$

$$\int_{0.265}^{1.055} (3s)^2\, dv = 0.92. \tag{48}$$

The main part of 1*s* is in the loge $K$, the main part of 2*s* is in the loge $L$, and so on. So, we can take the orbitals corresponding to the shells of the core to build the core contribution to the generating function $\Upsilon$.

As an example, let us take the case of propane in its ground state. Figure 10 gives an idea of a good decomposition into loges for this molecule.

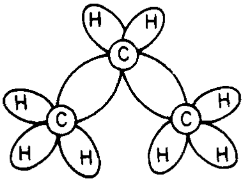

**Fig. 10.** Decomposition into loges for propane.

In such a case, the cores will consist of the $K$ shells of the three carbon atoms. From the study of the free carbon atoms we know that each core may be represented by two identical 1*s* atomic orbitals. The core part of the $\Upsilon$ function will be

$$C = 1s_1(1)1s_1(2)1s_2(3)1s_2(4)1s_3(5)1s_3(6) \tag{49}$$

if $1s_j$ denotes the 1*s* function associated with the *j*th carbon atom.

### D. Representation of the Localized Bonds: the BO (Bond Orbital) and the LCAO (Linear Combination of Atomic Orbital) Approximations

To represent a *q*-electron localized bond we have to introduce a certain function *B* depending on *q* points. This function may be called a *q-electronic bond orbital* or simply a *bond q orbital.* In the case of propane the number of electrons available for bonding is obviously twice the number of pairs of neighboring cores. From that we said in Section II we are not surprised to learn that there are many reasons to consider that this molecule is made of two-electron localized bonds CH and CC. We shall be led to associate with each bond a biorbital (or geminal) as shown in the following tabulation.

| Function | Associated with: | Function | Associated with: |
|---|---|---|---|
| $B_1$ | $C_1H_1$ | $B_6$ | $C_2H_6$ |
| $B_2$ | $C_1H_2$ | $B_7$ | $C_2H_7$ |
| $B_3$ | $C_1H_3$ | $B_8$ | $C_2H_8$ |
| $B_4$ | $C_2H_4$ | $\mathscr{B}$ | $C_1C_2$ |
| $B_5$ | $C_2H_5$ | $\mathscr{B}'$ | $C_2C_3$ |

The contribution of the bonds to $\Upsilon$ will be

$$D = B_1(7, 8)B_2(9, 10) \cdots B_8(21, 22)\mathscr{B}(23, 24)\mathscr{B}'(25, 26) \tag{50}$$

and $\Upsilon$ will be

$$\Upsilon = C \cdot D. \tag{51}$$

To represent the ground state, for which $S^2\Phi_{\text{ap}} = 0$, $S_z\Phi_{\text{ap}} = 0$, in using the formalism of Section I we are led to the function[4]

$$\Phi_{\text{ap}} = \sum (-1)^p P 1s_1(1)\overline{1s_1}(2) \cdots \overline{1s_3}(5)1s_3(6)B_1(7, 8)[\alpha(7)\beta(8) - \alpha(8)\beta(7)]$$
$$\cdots \mathscr{B}'(25, 26)[\alpha(25)\beta(26) - \alpha(26)\beta(25)]. \tag{52}$$

---

[4] Here $1s(i)$ denotes $1s(i)\alpha(i)$ and $\overline{1s}(i)$ denotes $1s(i)\beta(i)$.

Usually each bond function is approximated by a product of two identical monoelectronic functions (called monoelectronic bond orbitals or simply bond orbitals). In this case

$$B_1(7, 8) \quad = b_1(7)b_1(8) \tag{53}$$

$$\dots$$

$$B_8(21, 22) = b_8(21)b_8(22) \tag{54}$$

$$\mathscr{B}(23, 24) \ = b(23)b(24) \tag{55}$$

$$\mathscr{B}'(25, 26) = b'(25)b'(26) \tag{56}$$

and the function $\Phi_{\mathrm{ap}}$ becomes

$$\Phi_{\mathrm{ap}} = \det 1_{s1}(1)\overline{1s_1(2)} \cdots 1s_3(5)\overline{1s_3(6)}b_1(7)\overline{b_1(8)} \cdots b_8(21)\overline{b_8(22)}b(23)\overline{b(24)}b'(25)\overline{b'(26)}. \tag{57}$$

As in the atomic case this function may be written in another form:

$$\Phi_{\mathrm{ap}} = \det \varphi_1(1)\bar{\varphi}_1(2) \cdots \varphi_{13}(25)\bar{\varphi}_{13}(26), \tag{58}$$

where the $\varphi$'s are related to the previous orbitals by an unitary transformation

$$\varphi_j = \sum_i T_{ij} b_i, \tag{59}$$

where $b_i$ denotes any of the previous orbitals.

In this form the method is called the LCBO method because the new orbitals are linear combinations of bond orbitals. The previous orbitals (in the case of molecules possessing a certain symmetry) are localized and may be classified in sets of *equivalent orbitals*. For example, here $b$ is equivalent to $b'$, $b_4$ is equivalent to $b_5 \cdots$.

Among the new orbitals, as in the atomic case, there is a particular set which diagonalizes the self-consistent field operator and forms a basis for the irreducible representation of the group $G$ (Lennard-Jones, 1949, Lennard-Jones and Pople, 1950; Hall and Lennard-Jones, 1950, 1951). These particular orbitals are called *molecular orbitals*. If we consider, for instance, a molecule possessing a center of symmetry, for a nondegenerate level a molecular orbital will be symmetric or antisymmetric with respect to this center. Therefore, if this orbital has an important absolute value at an extremity of the molecule, it will have the same absolute value at the other symmetrical extremity. Usually the molecular orbitals will be completely delocalized over all the molecule.

Finally we are led to the conclusion that an approximate *convenient wave function representing localized bonds can be arbitrarily expressed in terms of localized or delocalized orbitals, the two expressions being completely identical.* This result shows that we have to be extremely careful in going from the notion of orbital to the physical properties of a molecule. We shall come back to this point.

In the function $\Phi_{\text{ap}}$ the $1s$ functions are known, and the only problem is to calculate the bond orbitals. In principle the self-consistent field method could be used, but in practice the calculations are not possible.

Even with these simple functions a new approximation is necessary. The most usual one consists of expressing the bond orbitals as linear combinations of some of the atomic orbitals of the valence shells of the atoms involved in the bond. That is the LCAO approximation. In order to represent a given localized bond we must try to organize the atomic orbitals available in order to obtain a function localized in the region of the bond. One common way of doing this is to make linear combinations of the atomic orbitals of one of the atoms in order to obtain a function as large as possible in the direction of the other atom. This is the well-known method of *hybrid atomic orbitals* (Pauling, 1944).

In the case of our propane molecule the available orbitals are, for each carbon atom, $2s$, $2p_x$, $2p_y$, and $2p_z$. The various bonds starting from a given carbon are separated by the tetrahedral angle of 109°28′. The following linear combinations of atomic orbitals:

$$te_1 = \tfrac{1}{2}(2s + 2p_x + 2p_y + 2p_z), \tag{60}$$

$$te_2 = \tfrac{1}{2}(2s + 2p_x - 2p_y - p_z), \tag{61}$$

$$te_3 = \tfrac{1}{2}(2s - 2p_x + 2p_y - 2p_z), \tag{62}$$

$$te_4 = \tfrac{1}{2}(2s - 2p_x - 2p_y + 2p_z), \tag{63}$$

are functions pointing in four directions separated by angles of 109°28′. They are called tetrahedral hybrids, and they may be used in building bond orbitals. For example a CH bond will be represented by a linear combination of the $1s$ orbital of the hydrogen and a tetrahedral hybrid $te$ associated with the carbon and pointing in the direction of the hydrogen. We will put for example

$$b_1 = \lambda_1 te_1 + \mu_1 1s_1 \tag{64}$$

and the problem will now be to calculate the various coefficients $\lambda$ and $\mu$ thereby introduced into the function $\Phi_{\text{ap}}$.

When the self-consistent field method is used to solve this problem we are led to the Roothaan equations. Usually they cannot be solved rigorously because they contain polycentric integrals which are very tedious to calculate. The integrals are usually approximated.

### E. The Completely Delocalized Representation

In some cases the use of a decomposition into loges or of an equivalent model can be avoided. This occurs if the generating function $\Upsilon$ is a product of monoelectronic orbitals, with each orbital $\varphi$ expanded over all the atomic orbitals $\psi$ of the occupied shells in the ground states of the free atoms constituting the molecule. In that case we shall have for instance

$$\Upsilon = \varphi_1(1)\bar{\varphi}_1(2)\bar{\varphi}_2(4) \cdots \varphi_{n/2}(n-1)\bar{\varphi}_{n/2}(n) \tag{65}$$

with

$$\varphi_i = \sum_j a_{ij}\psi_j . \tag{66}$$

If we introduce this function into the formalism of the self-consistent field method and if we add as a requirement the condition that the $\varphi$'s form a basis for the irreducible representations of the group $G$, we obtain the Roothaan equations (Roothaan, 1951):

$$\sum_q h_{pq}^{\mathrm{SCF}} a_{iq} = \mathscr{E}_{ii} a_{ip} \tag{67}$$

where

$$h_{pq}^{\mathrm{SCF}} = \beta_{pq}^N + \sum_i \sum_{r,s} a_{ir} a_{is} [2(pq/rs) - (pr/qs)] \tag{68}$$

and

$$\beta_{pq}^N = \int \psi_p h^N \psi_q \, dv. \tag{69}$$

$$(pq/rs) = \int \psi_p(1)\psi_q(1) \frac{e^2}{r_{12}} \psi_r(2)\psi_s(2) \, dv_1 \, dv_2 \tag{70}$$

The more difficult case where the orbitals $\varphi$ are not all doubly occupied has been discussed by various authors (Lefebvre, 1955, 1959; MacWeeny, 1956, 1957; Roothaan, 1960; Masse, 1962). The electronic computers make it possible to use this method easily for small molecules, and it has been widely used for diatomic and even triatomic molecules.

For these small molecules various improvements have been introduced. For instance, the molecular orbitals can be expanded on a larger basis than the set of the occupied orbitals in the ground state of the free atom.

Lefebvre-Brion *et al.* (1961) have, for example, calculated the self-consistent field wave function of the ground state of carbon monoxide taking as a basis the atomic orbitals of the *K*, *L*, and *M* shells of C and O.

For larger molecules the calculation becomes very tedious. Kaplan (1957) has treated the case of $NH_3$. This size molecule is near the limit of capability of the present state of the technique. For other molecules it becomes necessary to introduce the approximations discussed in Sections III, C and III, D.

It is interesting to compare the results of the complete delocalized representation with the representation based upon the notions of cores and of localized bonds. In the case of methane, for instance, the molecular orbitals of the complete delocalized representation take the form

$$s = 1s + \xi 2s + \eta(a + b + c + d), \tag{71}$$

$$s' = \zeta 1s + 2s + \lambda(a + b + c + d), \tag{72}$$

$$t_x = 2p_x + \mu(a + b - c - d), \tag{73}$$

$$t_y = 2p_y + \mu(-a + b + c - d), \tag{74}$$

$$t_z = 2p_z + \mu(-a + b - c + d), \tag{75}$$

where $a$, $b$, $c$, and $d$ represent, respectively, the $1s$ orbitals of the four hydrogen atoms and $1s$, $2s$, $2p_x$, $2p_y$, and $2p_z$ the orbitals of the carbon atoms (Fig. 11). $\xi$, $\eta$, and $\zeta$ are found to be small and can be neglected for our purpose. In this case a unitary transformation permits us to transform

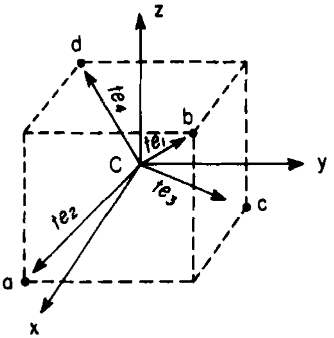

**Fig. 11.** Notation of the orbitals of methane.

these molecular orbitals into the following equivalent orbitals (Coulson, 1950):

$$A = s' + t_x - t_y - t_z, \tag{76}$$

$$B = s' + t_x + t_y + t_z, \tag{77}$$

$$C = s' - t_x + t_y - t_z, \tag{78}$$

$$D = s' - t_x - t_y + t_z, \tag{79}$$

the $s$ orbital staying unchanged.

The orbital $B$, for instance, can be more explicitly written:

$$B = 2s + 2p_x + 2p_y + 2p_z + (\lambda + 3\mu)b + (\lambda - \mu)(a + c + d). \tag{80}$$

The first four terms are the hybrid $te_1$, Eq. (60), of the carbon atom pointing in the direction of the orbital $b$. The first five terms are exactly of the form given by Eq. (64). The only difference between the localized representation of methane and the complete delocalization of methane lies in the last term in Eq. (80):

$$(\lambda - \mu)(a + c + d).$$

As $\lambda - \mu$ is found to be rather small, the difference is not very important.

### F. Representation of Delocalized Bonds: the Pariser and Parr Approximation and the Naive Methods

It is trivial to say that in benzene there is a delocalized bond extended over the six carbon cores. These cores are $K$ loges and the six CH bonds are localized two-electron bonds. (Fig. 12). As the nuclei about a carbon atom

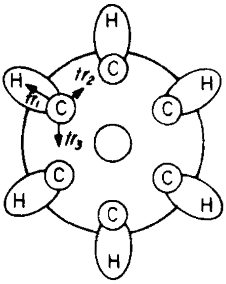

**Fig. 12.** Decomposition into loges for benzene.

make angles with it of approximately 120° we are led to represent the CH bond by a linear combination of the hydrogen 1*s* orbital and a trigonal hybrid orbital $tr_1$ of the carbon atom. This hybrid is chosen to point in the direction of the hydrogen.

If the plane of the figure contains the $x$ and $y$ axes, and if $0x$ lies along the CH bond under consideration, the hybrid $tr_1$ is

$$tr_1 = \frac{1}{\sqrt{3}}\, s + \frac{\sqrt{2}}{\sqrt{3}}\, p_x . \tag{81}$$

The other hybrids

$$tr_2 = \frac{1}{\sqrt{3}}\, s - \frac{1}{\sqrt{6}}\, p_x + \frac{1}{\sqrt{2}}\, p_y \tag{82}$$

and

$$tr_3 = \frac{1}{\sqrt{3}}\, s - \frac{1}{\sqrt{6}}\, p_x - \frac{1}{\sqrt{2}}\, p_y \tag{83}$$

and the orbital $p_z$ are not engaged in the localized bond.

As the situation is the same for each carbon atom we are led to represent the delocalized bond by a product of orbitals $\varphi$ expanded over all the orbitals $tr_2$, $tr_3$, and $p_z$.

It is obvious that $tr_2$ and $tr_3$ are symmetric with respect to the plane of the figure. On the contrary, the $p_z$'s are antisymmetric. Therefore $p_z$ and the $tr$'s do not belong to the same irreducible representation of the group $G$.

Roothaan (1951) has shown that, when solving the Roothaan equations, if we start from functions making a basis for an irreducible representation of $G$, the solutions of the corresponding iteration are a basis for this representation. So we can manage the calculation in such a way as to produce two kinds of molecular orbitals associated with the delocalized bond: those containing the $tr$'s which are called $\sigma$ orbitals, and those containing the $p_z$ called $\pi$ orbitals:

$$\sigma_j = \sum_i (a_{ij} tr_{2i} + b_{ij} tr_{3i}), \tag{84}$$

$$\pi_j = \sum_i c_{ij} p_{zi} . \tag{85}$$

As the energies associated with the $\pi$ orbitals are found to be smaller than those of the $\sigma$ orbitals, the properties of the molecule corresponding to small changes in the total energy may be considered as mainly due to a change in the $\pi$ orbitals. For this reason the $\sigma$ orbitals are very often grouped with the core in many calculations. But from the geometrical point of view there are regions of the space of the molecule where $\sigma$ and $\pi$ orbitals both take important values (Coulson *et al.*, 1952) and it is not possible to decompose the space into good $\sigma$ and $\pi$ loges (Daudel *et al.*, 1955).

If we call $h^c$ the self-consistent field operator including the core and the $\sigma$ orbitals, the matrix elements [Eq. (68)] of the Roothaan equations become

$$h_{pq}^{\mathrm{SCF}} = \beta_{pq}^{c} + \sum_{i} \sum_{r,s} a_{ir} a_{is} [2(pq/rs) - (pr/qs)] \tag{86}$$

where

$$\beta_{pq}^{c} = \int \psi_p h^c \psi_q \, dv \tag{87}$$

and where $p$, $q$, $r$, and $s$ are only the $p_z$ orbitals.

As we have said it is extremely difficult to calculate an integral like

$$(pr/qs)$$

when $p \neq r$ or $q \neq s$. For this reason Pariser and Parr (1953) have suggested neglecting this kind of integral. Furthermore they estimate the $\beta^c$ empirically.

There is an elegant way to understand why this apparently drastic approximation is successful (Löwdin, 1955; MacWeeny, 1955; Hall, 1954 Peradejordi, 1956). It consists of expanding the molecular orbitals in a basis of Löwdin's orthogonalized orbitals (Löwdin, 1950). Each Löwdin orbital is a linear combination of atomic orbitals containing one main term coming from one carbon atom and a small amount of the others in order to ensure the orthogonality.

**TABLE I**

VALUES OF INTEGRALS

| Löwdin orbitals | (eV) | Atomic orbitals | (eV) |
|---|---|---|---|
| $\overline{aa}/\overline{aa}$ | 17.28 | $aa/aa$ | 16.92 |
| $\overline{bb}/\overline{bb}$ | 17.57 | $bb/bb$ | 16.92 |
| $\overline{aa}/\overline{bb}$ | 9.01 | $aa/bb$ | 9.23 |
| $\overline{bb}/\overline{cc}$ | 8.63 | $bb/cc$ | 8.69 |
| $\overline{aa}/\overline{ab}$ | −0.06 | $aa/ab$ | 3.60 |
| $\overline{bb}/\overline{ab}$ | −0.08 | $bb/ab$ | 3.60 |
| $\overline{ab}/\overline{bc}$ | +0.007 | $ab/bc$ | 0.63 |
| $\overline{ab}/\overline{cd}$ | −0.006 | $ab/cd$ | 0.46 |

Table I coming from a work of Peradejordi (1964) compares some values of the integrals on the normal $p_z$ atomic orbitals (denoted $a$, $b$, $c$, and $d$) and the values of the corresponding integrals on the Löwdin's orbitals $\bar{a}$, $\bar{b}$, $\bar{c}$, and $\bar{d}$, in the case of trans-butadiene.

It is clearly seen that the bicentric integrals do not change very much when passing from the normal basis to the Löwdin basis but that the tri- and tetracentric integrals neglected by Pariser and Parr are not negligible in the basis of the atomic orbitals but are negligible in the Löwdin basis. Finally, in the Löwdin basis the Pariser and Parr approximation is convenient. But in estimating the parameters and in interpreting the coefficients of the orbitals it is important to remember that the basis is not made of atomic orbitals. A new change of basis is necessary to come back to these atomic orbitals. In a recent work Leroy (1963) has shown that the standard Pariser and Parr method and the complete and correct use of the Löwdin basis lead to very similar results in the case of alternant hydrocarbons. The agreement is not so good for heteromolecules like pyridine or pyrrole. A more serious discrepancy appears for nonalternant hydrocarbons. The discrepancies are usually larger for the properties directly depending on the coefficients $c_{ij}$ (such as the electronic charges, bond orders, etc.) than for the energies.

As is well-known, the so-called naive methods (e.g., the Hückel approximation) can be considered as resulting from a simplification of the Pariser and Parr procedure. For example, when penetration integrals are neglected in the Pariser and Parr procedure we obtain, for alternant hydrocarbons,

$$\beta_{ik} = \beta_{ik}^{c} - \tfrac{1}{2} p_{ik}(ii/kk) \tag{88}$$

and

$$\alpha_i = \beta_{ii} = W_{2p} - \tfrac{1}{2}(ii/ii), \tag{89}$$

where $p_{ik}$ is the mobile bond order between the atoms $i$ and $j$ and $W2p$ the energy associated with a $p_z$ orbital in a carbon atom in the convenient valence state. Therefore, all the $\alpha$'s will be constant as assumed by Hückel, and the nature of the other hypothesis made by Hückel concerning the equality of the $\beta$'s is clearly shown by formula (88).

## G. Ionized and Excited States

A priori, a special complete self-consistent field calculation is needed for each particular state of a molecule. However, as Koopmans (1933) has shown that the various energies $\mathscr{E}$ associated with the molecular orbitals are good approximations of the ionization energies,[6] products of all but one of the orbitals of the ground state of a molecule are often used as a generating function $\Upsilon$ to represent the positive ion. Several estimates have been made of the error due to this approximation. Lorquet and Lefebvre-Brion (1960), for instance, have discussed the case of the ion $NH_3^+$. They found that Koopman's theorem leads to the value of 14 eV for the ionization energy (the experimental value is 10.2 eV). A new self-consistent field calculation of the ion leads to the better value of 12.1 eV.

Furthermore, the distribution of the electronic density coming from this new calculation is significantly different and probably better than that which results from the application of Koopmans' representation.

Hoyland and Goodman (1962) have obtained analogous results for large molecules when the Pariser and Parr approximation is used.

When the self-consistent field operator of the ground state of a molecule is explicitly known and considered as a fixed operator, there are other eigenfunctions than the occupied orbitals. These unoccupied orbitals are called *virtual orbitals.*

By generalization of what happens in the case of the independent electron model, products of occupied orbitals and of virtual orbitals of the ground state are used to build *new configurations* in the configuration interaction method, and to represent *excited states.* The error introduced by this approximation in the calculation of excited energy can be important Bertheuil (1963) has observed, for instance, that when the Pariser and Parr approximation is used in the case of benzyl radical the method of virtual orbitals leads to the value of 4.6 eV for transition $^2A_2 \leftarrow {}^2B_2$. A new SCF (self-consistent field) calculation of the excited state leads to 2.8 eV for this same energy. The experimental value is 2.73.

## IV. Concluding Remarks

To conclude this chapter we shall come back to the notion of orbital. In studying the independent electron model, an orbital is defined as the solution of Eq. (20):

$$h_i\varphi_k(i) = \mathscr{E}_k\varphi_k(i). \tag{90}$$

In this case the orbital represents the wave function associated with an *isolated* electron in the field of the nuclei of the molecule.

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[6] In fact, Koopmans has discussed the case of atoms, and Hall and Lennard-Jones (1950) have reported on the case of molecules.

But when more than one electron is considered the notion of orbital loses its simple physical character. In the independent electron model the wave function associated with two electrons in a state with $S_z = h/2\pi$ will be

$$\Phi(1, 2) = \sum (-1)^P P\varphi_1(1)\varphi_2(2)\alpha(1)\alpha(2) \tag{91}$$

$$= \begin{vmatrix} \varphi_1(1) & \varphi_2(1) \\ \varphi_1(2) & \varphi_2(2) \end{vmatrix} \alpha(1)\alpha(2),$$

and the probability of finding electron 1 in a small volume $dv_1$ surrounding point $M$ will be given by

$$dP = dv_1 \int |\Phi(M, 2)|^2 \, dv_2 . \tag{92}$$

If the $\varphi$'s are orthonormalized, it is readily seen that

$$dP = \tfrac{1}{2}[\varphi_1^2(M) + \varphi_2^2(M)] \, dv_1 . \tag{93}$$

It is thus clearly seen that the probability of finding electron 1 in volume $dv_1$ depends on both $\varphi_1$ and $\varphi_2$. *"The motion" of a given electron depends on all the occupied orbitals.* There is no unambiguous relation between one orbital and one electron.

When the self-consistent field approach is used we saw that there is an infinite number of sets of orbitals corresponding to exactly the same total wave function. *The notion of orbital is not invariant.* Some sets are particularly interesting. The set which diagonalizes the self-consistent field operator corresponds, in the case of atoms, to orbitals localized in the various loges associated with the various shells. The energies of these orbitals are approximations of the ionization energies. In the case of molecules the corresponding set is called the set of molecular orbitals. The associated energies are also approximations of the ionization energies in such a way that *the electronic distribution in an orbital gives a rough idea of the hole of electronic density which occurs when the molecule loses an electron.* The limitation of this picture has been underlined.

Furthermore, *the molecular orbitals are usually largely delocalized and do not correspond to the localized bonds.* A particular unitary transformation permits us to pass from these orbitals to a set of orbitals which corresponds to the loges of the localized bonds when such bonds exist.

Finally, group theory permits us to separate the molecular orbitals between various classes (like $\sigma$ and $\pi$ orbitals) which can occupy the same loge.

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# Theory of Solvent Effects on Molecular Electronic Spectra

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## I. Introduction

The frequency of a molecular electronic absorption band is generally displaced when a molecule is immersed in a solvent medium such as a liquid or a foreign gas. These shifts are usually towards longer wavelengths although the opposite is sometimes true. In 1878, Kundt concluded that the absorption maximum of a solute is shifted towards the longer wavelength side with increasing dispersion of the solvent. Sheppard (1942) proposed a formula

$$\Delta v_m = a\left(1 - \frac{1}{D}\right) \tag{1}$$

where $\Delta v_m$ is the increase of the wave number of the absorption maximum, $D$ is the dielectric constant of the solvent, and $a$ is a constant. Brooker and Sprague's study of the solvent effect on the electronic spectra of phenol blue (1941) indicates that the frequency shift increases in the order of solvent dielectric constant. The more extensive study of Le Rosen and Reid (1952) shows that there is no correlation with dielectric constant, but the shifts induced by the hydrocarbon and aryl halide solvents vary regularly with solvent refractive index. Le Rosen and Reid found no correlation of the shifts induced by other solvents with any of the solvent macroscopic properties or a combination of such properties. Similar observations have been made by Sheppard on cyanine dyes (1942). The attempt to correlate solvent shift with dielectric constant arose from the concept that, as the light absorption is associated with the separation of electronic charges in a molecule, the energy change should be proportional to $1/Dr$ ($D$ is the dielectric constant of the solvent and $r$ is the distance through which the charges move during excitation). This idea is basically wrong because the electrons and the nuclei of a molecule in solution cannot be considered as imbedded in a continuous dielectric.

In the recent years, considerable progress has been made in understanding the effect of solvent on various spectral characteristics of a solute using quantum mechanical methods. When a molecule absorbs or emits light undergoing an electronic transition from one state to another, it is important to realize that both the energy and the electronic charge distribution in the molecule change. Let us consider an isolated molecule of the substance under investigation. This molecule can be in one of the two electronic energy states: the ground ($g$) or excited ($e$) states, having energies $\mathscr{E}_g$ and $\mathscr{E}_e$, respectively. In the absorption or emission of a quantum of frequency $\nu = (\mathscr{E}_e - \mathscr{E}_g)/h$, a redistribution of electron density in the molecule takes place. In the first case the permanent dipole moment $\mu$ of the solute molecule changes from $\mu_g$ to $\mu_e$ and in the second from $\mu_e$ to $\mu_g$. When the molecule under investigation is mixed with the solvent it interacts with the entire set of surrounding solvent molecules. This changes a number of its electrical and optical properties; especially, the solvent–solute interaction energy (also called the stabilization energy) in the ground and in the excited states of the solute is different because of the difference in dipole moments of the two states. The energy levels of the solute will therefore be shifted due to solvent–solute interaction by the stabilization energy $W_i$ of the particular state $i$ as compared to its value in the gaseous state. If the excited and ground states are stabilized to the same extent then the transition involving these two levels will show no solvent shift. If, however, the two states are differently stabilized then the solvent shift will be given by the difference in the stabilization energies of the two states, i.e.,

$$\Delta\nu^a = \frac{\langle \Delta W \rangle}{h} \tag{2}$$

where $\Delta\nu^a$ is the frequency shift in absorption spectra. It is evident, therefore, that the calculation of solvent shift in electronic spectra effectively reduces to the calculation of stabilization energies of the ground and the excited states. Before proceeding to discuss the theoretical methods for calculating the stabilization energy, it is advisable to classify the solvent effects into following groups:

(1) the dielectric effects, or, from a molecular point of view, the dipolar interaction between the solute and the solvent molecules;

(2) the dispersive interaction due to van der Waals forces which exist in all solvent–solute systems;

(3) the short-range specific interaction between the solvent and the solute molecules, e.g., electron transfer, hydrogen bonding, etc.;

(4) the association effect between solute molecules; this effect changes with solute concentration and may be eliminated at low solute concentration;

(5) the electrochemical effects, i.e., the changes in the degree of dissociation of a solute in different solvents; this effect is studied by varying the pH of the medium;

(6) the long-range intermolecular resonance effects; this effect is more important in emission than in absorption spectra.

The calculation of stabilization energy of an electronic state due to solvent–solute interaction was first made by Ooshika (1954) using quantum mechanical perturbation theory. The same quantum mechanical formulation was used by Longuet-Higgins and Pople (1957) and by McRae (1957). In what follows we give a detailed quantum mechanical discussion of the problem in terms of second-order perturbation theory.

## II. Perturbation Theory for Solvent–Solute Interaction

We shall consider the effect of molecular interaction on the spectrum of a dilute solution of solute molecules in a solvent environment. The restriction to a dilute solution avoids the necessity of considering the solute–solute interaction which complicates the theory because of the energy delocalization by resonance interaction. The problem now is to find the appropriate stationary state energy levels of a system consisting of a single solute surrounded by a set of solvent molecules in a given configuration and then to average over-all possible configurations. Suppose the eigenfunction and the nondegenerate eigenvalue of an isolated solute molecule are $\varphi_m$ and $\mathscr{E}_m$ respectively, and those of solvent molecule are, respectively, $\psi_n$ and $E_n$. Then a set of basic functions $\Psi_{mn} = \varphi_m \psi_n$ can be used for the interacting pair. As long as the separation is large enough for there to be no overlap between the wave functions, the lack of antisymmetry of these total wave functions may be ignored. The next step is to introduce the perturbation Hamiltonian $H'$, and the interaction energy to second order in $H'$ may be written as

$$W_{mn} = (\varphi_m\psi_n|H'|\varphi_m\psi_n) + \sum_{n'\neq n} \frac{(\varphi_m\psi_n|H'|\varphi_m\psi_{n'})^2}{E_n - E_{n'}} + \sum_{m'\neq m} \frac{(\varphi_m\psi_n|H'|\varphi_{m'}\psi_n)^2}{\mathscr{E}_m - \mathscr{E}_{m'}} + \sum_{m'\neq m}\sum_{n'\neq n} \frac{(\varphi_m\psi_n|H'|\varphi_{m'}\psi_{n'})^2}{\mathscr{E}_m - \mathscr{E}_{m'} + E_n - E_{n'}}. \tag{3}$$

If we assume that the operator $H'$ represents the electrostatic interaction between the solute and the solvent molecules, then the perturbation operator may be written as

$$H' = -\sum_i \frac{\mu_0\mu_i}{r_i^3}\Theta_i \tag{4}$$

where $\mu_0$ and $\mu_i$ represent the dipole moments of solute and $i$th solvent molecule, respectively, and $r_i$ and $\Theta_i$ are the distance and the mutual orientation between the solute and the $i$th solvent molecule. Of course when the distance between molecules is very small, the intermolecular interaction cannot be represented by such a simple dipolar term. The treatment therefore does not apply to cases where specific short-range forces are operative, i.e., the hydrogen bonding, charge-transfer, etc., interactions are excluded from the present considerations.

Expression (3) may now be written as

$$\begin{aligned} W_{mn} = &- (\varphi_m|\mu_0|\varphi_m)\sum_i \frac{(\psi_n|\mu_i|\psi_n)}{r_i^3}\Theta_i \\ &+ (\varphi_m|\mu_0|\varphi_m)^2 \sum_{n'\neq n}\sum_{i,j} \frac{(\psi_n|\mu_i|\psi_{n'})(\psi_n|\mu_j|\psi_{n'})}{(E_n - E_{n'})r_i^3 r_j^3}\Theta_i\Theta_j \\ &+ \sum_{m'\neq m}\sum_{i,j} \frac{\mu_i\mu_j}{r_i^3 r_j^3}\Theta_i\Theta_j \frac{(\varphi_m|\mu_0|\varphi_{m'})^2}{\mathscr{E}_m - \mathscr{E}_{m'}} \\ &+ \sum_{m'\neq m}\sum_{n'\neq n}\sum_{i,j} \frac{(\varphi_m|\mu_0|\varphi_{m'})^2(\psi_n|\mu_i|\psi_{n'})(\psi_n|\mu_j|\psi_{n'})}{(\mathscr{E}_m - \mathscr{E}_{m'} + E_n - E_{n'})r_i^3 r_j^3}\Theta_i\Theta_j. \end{aligned} \tag{5}$$

The first term, arising from the first-order perturbation theory, represents the electrostatic interaction of the unperturbed charge distribution of the two molecules, i.e., the interaction between the permanent dipoles. The second term corresponds to the interaction of the permanent dipole of the solute with the dipole induced on the solvent. The third term represents the interaction of the permanent dipole of the solvent with the dipole induced on the solute. Finally, the last term, which represents the second-order interaction with states in which both molecules are excited, corresponds to dispersive force.

Although the formulation up to this point is more or less exact, evaluation of the various integrals appearing in Eq. (5) is not possible at the present state of our knowledge of molecular eigenfunctions. It is necessary, therefore, in order to be of any practical use, to make an explicit term-by-term reduction of expression (5) in terms of specific molecular constants of the solvent and the solute molecules. This can only be done if we assume a specific model for solvent–solute systems.

## III. Onsager Model for Solvent–Solute Systems

Most of the workers in the field have used the Onsager (1936) model for liquid dielectrics to simplify expression (5) and express it in terms of dielectric constant and refractive index of the solvent and the dipole moment and the polarizability of solute molecule. It is appropriate at this stage to briefly review the reasons for selecting the Onsager model as the basis for calculation even though a number of better theories exist. The most important reasons are the relative simplicity, descriptiveness, and broad physical meaning of this theory which contains a minimum number of parameters. This makes possible the derivation of relatively simple theoretical relationships which can be subjected to thorough experimental test. When we attempt to use more rigorous theories, which attempt to take account of the correlation between the solute molecule and its nearest neighbors (see Kirkwood, 1939), it becomes necessary to introduce undetermined parameters whose presence exclude the possibility of a quantitative comparison of the theory with experiment.

In Onsager's model the solute molecule is considered as a point dipole at the centre of a spherical cavity in a homogeneous solvent dielectric. There is thus an effective electric field acting on the solute molecule in solution. This effective field is called the reaction field $\mathscr{R}_i$, because the field arises from the orientation-induction polarization of the dielectric by the solute dipole. The expression for the reaction field is written as

$$\mathcal{R}_i = \frac{\mu_m + \alpha_m \mathcal{R}_i}{a^3} \frac{2(D-1)}{(2D+1)} \tag{6}$$

where $\mu_m$ is the dipole moment of the isolated solute molecule, $\alpha_m$ is the mean static isotropic polarizability of the solute, $D$ is the static dielectric constant of the solvent, and $a$ is Onsager's cavity radius. In this connection it is necessary to note that the static value of dielectric constant $D$ can be used only when the lifetime of the molecule in the appropriate electronic state is much larger than the rotational relaxation time of the solvent which is of the order of $10^{-11}$ sec at room temperature. This condition is rigorously fulfilled for the solute molecule in its ground state. This is also approximately satisfied by the excited solute molecule because the usual lifetime of the excited state is of the order of $10^{-8}$ sec, which is much greater than the rotational relaxation time of normal organic solvents at room temperature. In the range of temperature where vitrification of solvent takes place there is a rapid increase in the rotational relaxation time, and in that range it would be necessary to use values of $D$ corresponding to higher frequencies.

Formula (6) may be rewritten as

$$\mathcal{R}_i = \frac{2\mu_m}{a^3}\left[\frac{D-1}{2D\left(1-\frac{\alpha}{a^3}\right)+1+\frac{2\alpha}{a^3}}\right]. \tag{7}$$

For most molecules the isotropic polarizability is about one-half the cube of the most suitable cavity radius, so that we get from Eq. (7)

$$\mathcal{R}_i = \frac{2\mu_m}{a^3}\left[\frac{D-1}{D+2}\right]. \tag{8}$$

The reaction field due to orientation polarization of the solvent is obtained from Eq. (8) as

$$\mathcal{R}_i\,(\text{or}) = \frac{2\mu_m}{a^3}\left[\frac{D'-1}{D'+2}\right] \tag{9}$$

where $D'$ is the contribution of the orientation polarization of the solvent molecules to the magnitude of the dielectric constant. The reaction field due to inductive polarization is given as

$$\begin{aligned}\mathscr{R}_i\,(\text{ind}) &= \frac{2\mu_m}{a^3}\left[\frac{n_0^2 - 1}{2n_0^2(1 - \alpha/a^3) + 1 + 2\alpha/a^3}\right] \\ &= \frac{2\mu_m}{a^3}\left[\frac{n_0^2 - 1}{n_0^2 + 2}\right]\end{aligned} \tag{10}$$

where $n_0$ is the refractive index of the medium for extremely low frequency and $n_0^2$ is the component of the solvent dielectric constant as determined from the static electronic polarization of the solvent dielectrics. The reaction field due to orientation polarization may be expressed in terms of static dielectric constant, $D$, and $n_0$ of the solvent by replacing $(D' - 1)/(D' + 2)$ by $[(D - 1)/(D + 2) - (n_0^2 - 1)/(n_0^2 + 2)]$, i.e.,

$$\mathscr{R}_i\,(\text{or}) = \frac{2\mu_m}{a^3}\left[\frac{D - 1}{D + 2} - \frac{n_0^2 - 1}{n_0^2 + 2}\right]. \tag{11}$$

In Onsager's theory, the dipole moment of a solute in solution, $\mu_m'$, is related to the dipole moment of the isolated solute molecule, $\mu_m$, its static polarizability, $\alpha_m$, and a suitable reaction field, $\mathscr{R}_i$ as

$$\mu_m' = \mu_m + \alpha_m \mathscr{R}_i. \tag{12}$$

## IV. Reduction of the Perturbation Energy Expression

Let us now analyze how this model can help us in bringing about an effective reduction of the energy expression (5). It has already been mentioned that expression (5) has been deduced for one particular configuration and this must be averaged over all possible configurations using a suitable distribution function. One aspect of Onsager theory which is useful for the present work is that it is applicable to any arbitrary spatial distribution of electrical charges, and consequently an explicit expression for the distribution function is not necessary.

Imagine a solute molecule surrounded by $N$ solvent molecules. Fixing the solute molecule, let $N$ molecular distribution function be

$$f(1, 2, \ldots N) = f_0 + f_1 \tag{13}$$

where $f_0$ is the hypothetical distribution function when the dipole moment of the solute molecule is assumed to be zero and $f_1$ represents the orientation of the solvent molecules by the dipole of the solute in solution. The orientation relaxation time of the solvent molecule is much longer than the time required for the light absorption ($\sim 10^{-16}$ sec) by the solute molecule, hence the function does not change on electronic excitation of the solute molecule. While averaging the various interaction terms in Eq. (5) over the molecular distribution we shall write generally

$$\int g(1,2,\ldots N) f_l(1,2,\ldots N)\, d\tau_i \ldots d\tau_{N-k}$$

$$= (\langle g(N-k+1,\ldots N)\rangle_{\text{av}})^{l,k} f_l^k(N+k+1,\ldots N) \qquad (14)$$

$$(\text{where } l = 0, 1)$$

where $\tau_i$ represents the position and orientation of the $i$th solvent molecule and

$$f_l^k(1,2,\ldots k) = \int f_l(1,2,\ldots N)\, d\tau_{k+1} \cdots d\tau_N. \qquad (15)$$

Now we assume $f_0^{(1)}$ is a function of $r_i$ only and

$$\begin{aligned} \lim_{N\to\infty} \{N f_0^{(1)}(i)\} &= 1/v \qquad \text{if } r_i \geqslant a \\ &= 0 \qquad \text{if } r_i < a \end{aligned} \qquad (16)$$

($v$ being the molar volume and $a$ Onsager's cavity radius)

$$f_1^{(1)}(i) = f_1^{(1)}(\mathbf{r}_i, \omega_i) = -f_1^{(1)}(\mathbf{r}_i, -(\omega_i) \qquad (17)$$

where $\mathbf{r}_i$ and $\omega_i$ are the position vector of the $i$th molecule and the solid angle representing its orientation. These assumptions are allowed in the range where the concept of dielectric constant and refractive index is permissible.

*Reduction of first term in Eq.* (5) *i.e.*,

$$-(\varphi_m|\mu_0|\varphi_m) \sum_i \frac{(\psi_n|\mu_i|\psi_n)}{r_i^3}\, \Theta_i. \qquad (18)$$

Here $(\varphi_m|\mu_0|\varphi_m) = \mu_m$ the dipole moment of the solute and $(\psi_n|\mu_i|\psi_n) = \mu$, the dipole moment of the $i$th solvent molecule. Assuming $\mu$ to be independent of $r_i$, we have

$$\int \frac{(\psi_n|\mu_i|\psi_n)}{r_i^3}\, \Theta_i f_0\, d\tau_1 \cdots d\tau_N = 0 \qquad (19)$$

and

$$\sum_i \int \frac{(\psi_n|\mu_i|\psi_n)}{r_i^3}\, \Theta_i f_1\, d\tau_1 \cdots d\tau_N = N \int \frac{\mu\Theta_1}{r_1^3} f_1^{(1)}(1)\, d\tau_1$$

$$= \mathscr{R} \cos\theta_{mm} \qquad (20)$$

where $\mathscr{R}\cos\theta_{mm}$ is the component of the reaction field, due to orientation of the solvent molecules by the dipole $\mu_g'$ of the solute molecule in its ground state in solution, in the direction of $\mu_m$. $\mu_g'$ is not equal to $\mu_g = (\varphi_g|\mu_0|\varphi_g)$ due to polarization by the reaction field. Calculating the reaction field and dipole moment of the solute in solution by Onsager's model we get for expression (18)

$$-\left[\frac{D-1}{D+2} - \frac{n_0^2-1}{n_0^2+2}\right]\left\{\frac{2\mu_g\mu_m}{a^3} + \frac{2\mu_g\mu_m}{a}\left(\frac{D-1}{D+2}\right)\right\}. \tag{21}$$

*Reduction of second term in Eq.* (5) *i.e.,*

$$\mu_m^2 \sum_{n'\neq n} \sum_{i,j} \frac{(\psi_n|\mu_i|\psi_{n'})(\psi_n|\mu_j|\psi_{n'})}{(E_n - E_{n'})r_i^3 r_j^3}\,\Theta_i\Theta_j. \tag{22}$$

Averaging over $f_0$ we get

$$\int \sum_j \sum_{n'\neq n} \frac{(\psi_n|\mu_i|\psi_{n'})(\psi_n|\mu_j|\psi_{n'})}{(E_n - E_{n'})r_i^3 r_j^3}\,\Theta_i\Theta_j f_0 \mu_m^2\, d\tau_1 \ldots d\tau_N$$

$$= \sum_j \sum_{n'\neq n} \frac{\langle(\psi_n|\mu_i|\psi_{n'})(\psi_n|\mu_j|\psi_{n'})\Theta_i\Theta_j\rangle_{\text{av}}}{(E_n - E_{n'})r_i^3 r_j^3}\, f_0^{(1)}(i)\mu_m^2 \tag{23}$$

which is the mean energy of interaction between the dipole $\mu_m$ of the solute and the dipole induced on the $i$th solvent molecule fixed in position and orientation in solution by the field of $\mu_m$. Thus

$$-\sum_i \int \sum_j \sum_{n'\neq n} \frac{\langle(\psi_n|\mu_i|\psi_{n'})(\psi_n|\mu_j|\psi_{n'})\Theta_i\Theta_j\rangle_{\text{av}}}{(E_n - E_{n'})r_i^3 r_j^3}\, f_0^{(1)}(i)\mu_m\, d\tau_i \tag{24}$$

equals the Onsager's inductive reaction field

$$\frac{2\mu_m}{a^3}\left(\frac{n_0^2-1}{n_0^2+2}\right). \tag{25}$$

Assuming the mean polarizability of the solvent molecules is isotropic, it can be shown that averaging over $f_1$ will give zero contribution. Expression (22) thus takes the simple form

$$-\frac{2\mu_m^2}{a^3}\left(\frac{n_0^2-1}{n_0^2+2}\right). \tag{26}$$

*Reduction of the third term in Eq.* (5), *i.e.*,

$$\sum_{m'\neq m}\sum_{i,j}\frac{\mu^2\Theta_i\Theta_j}{r_i^3 r_j^3}\,\frac{(\phi_m|\mu_0|\varphi_{m'})^2}{\mathscr{E}_m-\mathscr{E}_{m'}}$$

$$(\mu_i=\mu_j=\mu). \tag{27}$$

While averaging over $f_0$, we write

$$\int\sum_j\frac{\mu^2\Theta_i\Theta_j}{r_i^3 r_j^3}f_0\,d\tau_1\cdots d\tau_N=\int\frac{\mu\mu_{\text{eff}}\Theta_i^2}{r_i^6}f_0^{(1)}(i)\,d\tau_i \tag{28}$$

where

$$\frac{\mu_{\text{eff}}\Theta_i}{r_i^3}=\sum_j\frac{\langle\mu\Theta_j\rangle_{\text{av}}}{r_j^3}. \tag{29}$$

$\mu_{\text{eff}}$ represents that, fixing the position and orientation of the *i*th solvent molecule, the other molecules are oriented and their dipole can polarize the solute molecule when averaging over the distribution other than the *i*th. It may of course be a function of the position and orientation of the *i*th molecule. But assuming that $\mu_{\text{eff}}$ is independent of the position of the *i*th molecule and that the solvent molecule is a point dipole at the center of a spherical cavity of radius *d*, the apparent charges appearing on the surface of the cavity are just those which show the orientation of the medium due to the correlation between the solvent molecules, and those apparent charges are equivalent to a dipole of moment (Onsager, 1936)

$$\left(\frac{2D-2}{2D+1}\right)\mu. \tag{30}$$

Therefore

$$\mu_{\text{eff}}=\mu-\left(\frac{2D-2}{2D+1}\right)\mu$$

$$=\frac{3}{2D+1}\mu. \tag{31}$$

Thus we have for distribution function over $f_0$

$$\sum_i\int\frac{\mu\mu_{\text{eff}}\Theta_i^2}{r_i^6}f_0^{(1)}(i)\,d\tau_i\sum_{m'\neq m}\frac{(\varphi_m|\mu_0|\varphi_{m'})^2}{\mathscr{E}_m-\mathscr{E}_{m'}}$$

$$=\left(\frac{3}{2D+1}\right)\frac{\mu^2}{a^3d^3}\sum_{m'\neq m}\frac{(\varphi_m|\mu_0|\varphi_{m'})^2}{\mathscr{E}_m-\mathscr{E}_{m'}}. \tag{32}$$

The solvent dipole moment $\mu$ appearing in Eq. (32) may be eliminated using the relation (Onsager, 1936)

$$\frac{\mu^2}{kT}=\frac{(2D+1)^2(D-n_0^2)}{3(2D+n_0^2)D}\cdot d^3. \tag{33}$$

Hence the average over $f_0$ is

$$\left(\frac{3}{2D+1}\right)\frac{(2D+1)^2(D-n_0^2)}{(2D+n_0^2)D}\,\frac{kT}{3a^3}\sum_{m'\neq m}\frac{(\varphi_m|\mu_0|\varphi_{m'})^2}{\mathscr{E}_m-\mathscr{E}_{m'}}. \tag{34}$$

Next we calculate the average over $f_1$,

$$\begin{aligned}\int\frac{\mu^2\Theta_i\Theta_j}{r_i^3r_j^3}f_1\,d\tau_1\cdots d\tau_N&=\int\frac{\mu^2\Theta_i\Theta_j}{r_i^3r_j^3}f_1^{(2)}(i,j)\,d\tau_i\,d\tau_j\\&=\int\frac{\mu\Theta_i}{r_i^3}f_1^{(1)}(i)\,d\tau_i\int\frac{\mu\Theta_j}{r_j^3}f_1^{(1)}(j)\,d\tau_j\end{aligned} \tag{35}$$

This approximation is equivalent to replacing the average of the square of the reaction field by the square of the average of the reaction field. Thus

$$\begin{aligned}\sum_{m'\neq m}\sum_{i,j}\int\frac{\mu\Theta_i}{r_i^3}f_1^{(1)}(i)\,d\tau_i\int\frac{\mu\Theta_j}{r_j^3}f_1^{(1)}(j)\,d\tau_j\,\frac{(\varphi_m|\mu_0|\varphi_{m'})^2}{\mathscr{E}_m-\mathscr{E}_{m'}}&\\=\sum_{m'\neq m}(\mathscr{R}\cos\theta_{mm})^2\,\frac{(\varphi_m|\mu_0|\varphi_{m'})^2}{\mathscr{E}_m-\mathscr{E}_{m'}}&\\=\left(\frac{2D-2}{2D+1}\right)^2\frac{\mu_m^2}{a^6}\sum_{m'\neq m}\frac{(\varphi_m|\mu_0|\varphi_{m'})^2}{\mathscr{E}_m-\mathscr{E}_{m'}}&\end{aligned} \tag{36}$$

This is an interaction energy between the reaction field due to the mutual orientation of solvent dipoles and the dipole induced on the solute molecule by it.

*Reduction of the fourth term in Eq.* (5) *i.e.*,

$$\sum_{m'\neq m}\sum_{n'\neq n}\sum_{i,j}\frac{(\varphi_m|\mu_0|\varphi_{m'})^2(\psi_n|\mu_i|\psi_{n'})(\psi_n|\mu_j|\psi_{n'})}{(\mathscr{E}_m-\mathscr{E}_{m'}+E_n-E_{n'})r_i^3r_j^3}\,\Theta_i\Theta_j \tag{37}$$

If we assume that the polarizability of the solvent molecule is isotropic, the average of Eq. (37) over $f_1$ vanishes. The average over $f_0$ is

$$\sum_{m'\neq m}\sum_{n'\neq n}\int\sum_{i,j}\frac{(\psi_n|\mu_i|\psi_{n'})(\psi_n|\mu_j|\psi_{n'})\Theta_i\Theta_j}{(\mathscr{E}_m-\mathscr{E}_{m'}+E_n-E_{n'})r_i^3r_j^3}f_0(\varphi_m|\mu_0|\varphi_{m'})^2\,d\tau_1\cdots d\tau_N$$

$$=\sum_{m'\neq m}\sum_{i}\int\sum_{n'\neq n}\sum_{j}\frac{(\psi_n|\mu_i|\psi_{n'})(\psi_n|\mu_j|\psi_{n'})\Theta_i\Theta_j}{(\mathscr{E}_m-\mathscr{E}_{m'}+E_n-E_{n'})r_i^3r_j^3}(\varphi_m|\mu_0|\varphi_{m'})^2f_0^{(1)}(i)\,d\tau_i. \tag{38}$$

We may write expression (38) as

$$\sum_{m'\neq m}\sum_{i}\int\sum_{n'\neq n}\sum_{j}\frac{(\psi_n|\mu_i|\psi_{n'})(\psi_n|\mu_j|\psi_{n'})\Theta_i\Theta_j}{(E_n-E_{n'})r_i^3r_j^3}f_0^{(1)}(i)\,d\tau_i\,\frac{(E_n-E_{n'})(\varphi_m|\mu_0|\varphi_{m'})^2}{\mathscr{E}_m-\mathscr{E}_{m'}+E_n-E_{n'}}$$

$$=-\left(\frac{n_0^2-1}{n_0^2+2}\right)\frac{2}{a^3}\sum_{m'\neq m}\frac{(\varphi_m|\mu_0|\varphi_{m'})^2}{E_n-E_{n'}+\mathscr{E}_m-\mathscr{E}_{m'}}(E_n-E_{n'}) \tag{39}$$

using relations (24) and (25). For solute molecules absorbing at a much longer wavelength than the solvent we have

$$|E_n-E_{n'}|\gg|\mathscr{E}_m-\mathscr{E}_{m'}|;$$

hence expression (39) reduces to

$$-\left(\frac{n_0^2-1}{n_0^2+2}\right)\frac{2}{a^3}\sum_{m'\neq m}(\varphi_m|\mu_0|\varphi_{m'})^2\left(1-\frac{\mathscr{E}_m-\mathscr{E}_{m'}}{E_n-E_{n'}}\right). \tag{40}$$

Considering all these reduction processes we finally get for the energy change of a solute molecule in the state $m$ due to solvent–solute interaction as

$$\begin{aligned}\langle W_{mn}\rangle = &-\left(\frac{D-1}{D+2}-\frac{n_0^2-1}{n_0^2+2}\right)\left\{\frac{2\mu_g\mu_m}{a^3}+\frac{2\mu_g\mu_m}{a^3}\left(\frac{D-1}{D+2}\right)\right\}\\ &-\frac{2\mu_m^2}{a^3}\left(\frac{n_0^2-1}{n_0^2+2}\right)+\left\{\left(\frac{3}{2D+1}\right)\frac{(2D+1)^2(D-n_0^2)}{(2D+n_0^2)D}\cdot\frac{kT}{3a^3}\right.\\ &\left.+\left(\frac{2D-2}{2D+1}\right)^2\frac{\mu_m^2}{a^6}\right\}\sum_{m'\neq m}\frac{(\varphi_m|\mu_0|\varphi_{m'})^2}{\mathscr{E}_m-\mathscr{E}_{m'}}\\ &+\left(\frac{n_0^2-1}{n_0^2+2}\right)\frac{2}{a^3}\sum_{m'\neq m}(\varphi_m|\mu_0|\varphi_{m'})^2\left(1-\frac{\mathscr{E}_m-\mathscr{E}_{m'}}{E_n-E_{n'}}\right).\end{aligned} \tag{41}$$

The frequency shift of the absorption maximum is the difference between $\langle W \rangle$ for the ground ($g$) and excited ($e$) states of the solute molecule, the solvent molecule being in the ground state; that is

$$
\begin{aligned}
h\Delta\nu^a &= \langle W_{eg}\rangle - \langle W_{gg}\rangle \\
&= \left[\frac{2}{a^3}\left(\frac{D-1}{D+2} - \frac{n_0^2-1}{n_0^2+2}\right)\left(\frac{2D+1}{D+2}\right)(\mu_g^2 - \mu_g\mu_e)\right. \\
&\quad \left. + \frac{2}{a^3}\left(\frac{n_0^2-1}{n_0^2+2}\right)(\mu_S^2 - \mu_e^2)\right] \\
&\quad + \left[\left(\frac{3}{2D+1}\right)\frac{(2D+1)^2(D-n_0^2)}{(2D+n_0^2)D}\frac{kT}{3a^3}\right. \\
&\quad \times \left\{\sum_{m\neq g}\frac{(\varphi_g|\mu_0|\varphi_m)^2}{\mathscr{E}_g - \mathscr{E}_m} - \sum_{m\neq e}\frac{(\varphi_e|\mu_0|\varphi_m)^2}{\mathscr{E}_e - \mathscr{E}_m}\right\} \\
&\quad \left. + \left(\frac{2D-2}{D+2}\right)^2\left\{\frac{\mu_e^2}{a^6}\sum_{m\neq e}\frac{(\varphi_e|\mu_0|\varphi_m)^2}{\mathscr{E}_e - \mathscr{E}_m} - \frac{\mu_g^2}{a^6}\sum_{m\neq g}\frac{(\varphi_g|\mu_0|\varphi_m)^2}{\mathscr{E}_g - \mathscr{E}_m}\right\}\right] \\
&\quad + \left[\left(\frac{n_0^2-1}{n_0^2+2}\right)\frac{2}{a^3}\left\{\sum_{m\neq g}(\varphi_g|\mu_0|\varphi_m)^2\left(1 - \frac{\mathscr{E}_m - \mathscr{E}_g}{E_n - E_{n'}}\right)\right.\right. \\
&\quad \left.\left. - \sum_{m\neq e}(\varphi_{e/}\mu_0|\varphi_m)^2\left(1 - \frac{\mathscr{E}_m - \mathscr{E}_e}{E_{n'} - E_n}\right)\right\}\right].
\end{aligned}
\tag{42}
$$

This expression represents the solvent effect on the frequency of 0–0 band of the solute molecule. As the 0–0 band cannot always be identified in solution spectra, the equation must be compared with the observed frequency shifts in the band maximum relative to the corresponding band maximum in the vapor spectrum. Unless the frequency shifts are comparable to or larger than the band width, the applicability of relation (42) is valid provided there is no significant solvent effect on band shape.

## V. General Discussion of Solvent Effect in Nonpolar Solvent

The terms in the first square bracket in expression (42) may be either positive or negative depending on the magnitude and direction of $\mu_g$ and $\mu_e$, and we call this the polarization term. The terms in the second square bracket are much more complicated, and its sign and/or magnitude cannot be guessed without making a complete calculation. The terms in the third square bracket represent the dispersion effect, and hence it exists in all systems irrespective of the polar character of the solvent and the solute molecules.

If we stick to weakly polar solvents, the expression in the second square bracket [in Eq. (42)] which represents the polarization effect of the solvent dipole on the solute molecule may be neglected, and we may draw certain general conclusions about the solvent effect on the absorption spectra of solute molecules.

(*a*) It is not only the dielectric constant $D$ but also the refractive index $n_0$ and the position of the solvent absorption band (because of the term $E_n - E_{n'}$) that determine the shift in the solute absorption band. This explains why in a series of solvents of increasing dielectric constant—chloroform, pyridine, acetone, and nitrobenzene—the absorption band of a dye shows lesser shift in nitrobenzene than in acetone (Brooker *et al.*, 1951). This is because of the much larger refractive index and much longer absorption wavelength of nitrobenzene compared with acetone.

(*b*) When the dielectric constant of the solvent is small, the first and the second terms in the first square bracket in Eq. (42) bring about a red shift, but, since the first term is predominate, the absorption maximum shifts towards red only if $\mu_g^2 < \mu_g\mu_e$, i.e., if the excited state has a larger dipole moment than the ground state. If the reverse is true, the shift will be towards blue.

(*c*) If the absolute value of $\mu_g$ is small the solvent effect is small, while for large $\mu_g$ the solvent effective is fairly large.

(*d*) The dispersive interaction always causes a red shift and is found even with nonpolar solutes in nonpolar solvents.

Let us now discuss the role of various types of solvent-solute interactions in greater detail.

### A. Dispersive Interaction

It was pointed out by Bayliss (1950; Bayliss and McRae, 1952) that while calculating the Onsager reaction field the contribution of the dipole moment induced on the solute by the light wave, i.e., the transition moment of the solute, must be taken into account in addition to the permanent moment of the solute. This may be termed a dynamical reaction field. The transition moment $P$ is related to the oscillator strength $f$ of the electronic transition by the relation

$$f_{ij} = \frac{8\pi^2 m_e}{e^2 h} \nu_{ij} |P_{ij}|^2 \tag{43}$$

where $\nu_{ij}$ refers to the frequency of electronic transition between the levels $i$ and $j$. The inductive polarization effect of this dipole may be expressed in the same way as the permanent dipole and may be written as

$$-\left(\frac{n_{ij}^2 - 1}{n_{ij}^2 + 2}\right)\frac{e^2 h}{8\pi^2 m_e a^3}\frac{f_{ij}}{\nu_{ij}}. \tag{44}$$

Like permanent dipole this will bring about a red shift. The $n_{ij}$ appearing in the expression refers to the refractive index of the solvent for the light of frequency $\nu_{ij}$. As pointed out by Bayliss this may make a very large contribution, even if the permanent dipole moment of the solute is small, for an allowed electronic transition with large $f$ value. McRae suggested an interpretation of the solvent effect on the spectra of various cyanine dyes in terms of this dynamical polarization effect. It is, however, doubtful how far transition moment can be considered a permanent dipole in calculating the reaction field.

It can be shown that the effect discussed by Bayliss is contained in the dispersion term of expression (39). This was first pointed out by Longuet-Higgins and Pople (1957), but, as they did not use the Onsager model for the solvent–solute system, their deduction is somewhat different from what is given below. The difference in stabilization energy due to dispersive interaction $\langle W\rangle_d$ in the excited and the ground state of a solute molecule is given as

$$\begin{aligned}\langle W_e\rangle_d - \langle W_g\rangle_d = {} & \frac{2}{a^3}\left(\frac{n_0^2 - 1}{n_0^2 + 2}\right)\frac{\langle E_n - E_{n'}\rangle_{\text{av}}}{\langle \mathscr{E}_g - \mathscr{E}_m\rangle_{\text{av}} + \langle E_n - E_{n'}\rangle_{\text{av}}}\sum_{m\neq g}(\varphi_g|\mu_0|\varphi_m)^2 \\ & - \frac{2}{a^3}\left(\frac{n_0^2 - 1}{n_0^2 + 2}\right)\frac{\langle E_n - E_{n'}\rangle_{\text{av}}}{\langle \mathscr{E}_e - \mathscr{E}_m\rangle_{\text{av}} + \langle E_n - E_{n'}\rangle_{\text{av}}} \\ & \times \sum_{m\neq e}(\varphi_e|\mu_0|\varphi_m)^2\end{aligned} \tag{45}$$

where $\langle E_n - E_{n1}\rangle_{\text{av}} = E$ and $\langle \mathscr{E}_g - \mathscr{E}_m\rangle_{\text{av}} \simeq \langle \mathscr{E}_e - \mathscr{E}_m\rangle_{\text{av}} = \mathscr{E}$, the average excitation energy of the solvent and the solute, respectively. Relation (45) may now be written as

$$\begin{aligned}\langle W_e\rangle_d - \langle W_g\rangle_d & \simeq \frac{2}{a^3}\left(\frac{n_0^2 - 1}{n_0^2 + 2}\right)\frac{E}{\mathscr{E} + E}\left\{(\varphi_g|\mu_0|\varphi_e)^2\right. \\ & \quad + \sum_{m\neq g,e}\frac{(\varphi\ |\mu_0|\varphi_m)^2}{\mathscr{E}^g - \mathscr{E}^m}(\mathscr{E}_g - \mathscr{E}_m\ ) \\ & \quad \left. - \sum_{m\neq e}\frac{(\varphi_e|\mu_0|\varphi_m)^2}{\mathscr{E}_e - \mathscr{E}_m}(\mathscr{E}_e - \mathscr{E}_m)\right\} \\ & \simeq \frac{2}{a^3}\left(\frac{n_0^2 - 1}{n_0^2 + 2}\right)\frac{E}{\mathscr{E} + E}\{|P_{eg}|^2 + \mathscr{E}(\alpha_g - \alpha_e)\}\end{aligned} \tag{46}$$

where $P_{eg} = (\varphi_g|\mu_0|\varphi_e)$, the transition moment for the electronic transition between the states $g$ and $e$. If $P_{eg}$ is expressed in terms of the oscillator strength of the absorption band, then the first term in Eq. (46) refers to the same effect discussed by Bayliss. The second term in Eq. (46) represents a universal shift in all systems. For weak transitions (such as singlet to triplet), this will be the only contribution. The first term predicts an increased shift for those transitions which are strongly allowed.

In the calculation of contribution of dispersive interaction to the solvent shift, it has been assumed implicitly that the dispersive force is a two-body force and is therefore additive. The works of Axilrod and Teller (1943) and of Rosen (1953) show that these forces are not purely two-body forces; consequently they are not additive. These nonadditive forces must be studied in greater detail before any further progress can be made in the calculation of the contribution of dispersive effect on electronic spectra. It has often been assumed that dispersive contribution is usually small compared to dipolar contribution. This is not the case with molecules containing an easily polarizable group or groups where dispersive contribution becomes very large (see Veljkovic, 1957).

### B. Dipolar Interaction

The representation of the dipolar interaction as a sum of terms is somewhat artificial, being a consequence of the second-order perturbation theory. The solvent shift due to electrostatic interaction alone can be deduced by the conventional method of electrostatics, with due cognizance of nonequilibrium polarization of the solvent immediately after the transition (Basu, 1964). According to the Frank–Condon principle, the configuration of the solvent molecules around a solute does not change during the light absorption by the solute molecule; hence the dipole moment and the interaction energies refer to equilibrium ground state and the Frank–Condon excite state of the solute. But the Frank–Condon state is not the most stable equilibrium state for excited solute molecules. The equilibrium excited configuration is realized by reorientation of the solvent molecules, which requires about $10^{-11}$ sec at room temperature. The lifetime of the excited state is about $10^{-8}$ sec, which is long enough for the equilibrium configuration to be realized prior to the emission of a light quantum.

The average interaction energy $\langle W_i \rangle$ of the solute molecule with the surrounding solvent is determined by the dipole moment, $\mu_i$, of the solute in the corresponding state and by the internal field, i.e., the Onsager reaction field, $\mathscr{R}_i$, acting on the solute molecule due to the surrounding solvent molecules. The reaction field $\mathscr{R}_i$ is made up of two parts: the field

$\mathscr{R}_i$ (or) associated with the orientation of the solvent molecules and the field $\mathscr{R}_i$ (ind) due to inductive polarization of solvent dielectrics. The difference in the stabilization energies $\langle \Delta W \rangle$ of the ground and the excited states is equal to work done in changing the dipole moment of the solute from its initial to its final value by the field $\mathscr{R}_i$. Thus for the absorption process we have

$$\langle \Delta W \rangle^a = -\int_{\mu_g{}^E}^{\mu_e{}^F} \mathscr{R}_i \, d\mu \tag{47}$$

where the superscripts $E$ and $F$ refer to equilibrium and Frank–Condon state, respectively. The magnitude of spectral shift may therefore be written as

$$h \, \Delta\nu^a = \langle \Delta W^a = -\int_{\mu_g{}^E}^{\mu_e{}^F} \{\mathscr{R}_g(\text{or}) + \mathscr{R}_g(\text{ind})\} \, d\mu. \tag{48}$$

The calculation of solvent shift thus reduces to the estimation of reaction field and the dipole moment, both of which can be obtained from Onsager theory as already mentioned [Eqs. (10) and (11)]. For the calculation of the dipole moment in the excited Frank–Condon state an expression similar to Eq. (12) holds, but $\mathscr{R}_i$ refers to the orientation field of the ground state (since the solvent configuration does not change during the electronic transition) and the induction field of the excited. That is

$$\mu_e^F = \mu_e + \alpha\mathscr{R}_i = \mu_e + \mu_g\left[\frac{D-1}{D+2} - \frac{n_0^2-1}{n_0^2+2}\right] + \mu_e\left[\frac{n_0^2-1}{n_0^2+2}\right]. \tag{49}$$

The solvent shift in the absorption spectra due to dipolar interaction alone is thus obtained as

$$\begin{aligned} h \, \Delta\nu^a = \frac{1}{a^3}\left(\frac{2n_0^2+1}{n_0^2+2}\right)^2 & \left\{2\mu_g(\mu_g - \mu_e)\left(\frac{D-1}{D+2} - \frac{n_0^2-1}{n_0^2+2}\right)\right. \\ & \left. + \left(\frac{n_0^2-1}{n_0^2+2}\right)(\mu_g^2 - \mu_e^2)\right\}. \end{aligned} \tag{50}$$

It may be observed that expression (50) is in many ways different from the terms in the first square bracket in expression (42). This difference, however, is only superficial and arises from the fact that in the derivation of Eq. (42) reaction field and dipole moment of the excited equilibrium state have been used for the absorption process. If the corresponding values for the Frank–Condon state are substituted, the two deductions give the identical result.

The general expression for the solvent shift in the absorption spectra of a solute in nonpolar solvent may therefore be written as

$$\begin{aligned} h\,\Delta\nu^{a} = {} & \frac{1}{a^3}\left(\frac{2n_0^2+1}{n_0^2+2}\right)\left\{2\mu_g(\mu_g-\mu_e)\left(\frac{D-1}{D+2}-\frac{n_0^2-1}{n_0^2+2}\right)\right. \\ & \left. + \left(\frac{n_0^2-1}{n_0^2+2}\right)(\mu_g^2-\mu_e^2)\right\} \\ & + \frac{2}{a^3}\left(\frac{n_0^2-1}{n_0^2+2}\right)\frac{E}{\mathscr{E}+E}\,\{|P_{eg}|^2+\mathscr{E}(\alpha_g-\alpha_e)\}. \end{aligned} \tag{51}$$

## VI. Experimental Verification

Although the general validity of expression (51) has been established in a number of cases (see Ooshika, 1954; McRae, 1957), the relation cannot be subjected to a quantitative test with the existing data available in chemical literature. Most of the recorded data are on the spectra of fairly complicated organic molecules like dyestuffs. These molecules are fairly elongated, so the assumption of isotropic polarizability of the solute molecule used in the deduction of expression (51) is not justified. Second, the electronic excitation in these molecules brings about a charge separation over a fairly large distance; hence the point dipole approximation of the Onsager theory is too crude a model for these systems. It is, however, possible to test the correctness of the assumptions made and the general validity of the model used with accurate spectral data on small molecules in nonpolar solvent, which unfortunately is not available at present. It is advisable at this stage to qualify the term "nonpolar solvents" as used in the present model. A solvent should not be considered nonpolar if its dipole moment is low because of the cancellation of the dipole moments of strongly polar groups present in the molecule, because the orientation–induction effect of the polar groups on the solute will not give a zero contribution on the average.

## VII. Solvent Shift in Mixed Solvents

Because of the assumption of identical solvent molecules in the derivation of all the previous relations, the formulas derived apply to frequency shift induced by pure solvents only. The generalization to mixed solvents can be achieved in cases where the solvent composition near the solute can be assumed equal to the bulk composition. In that case the weighted mean wave length of a mixed solvent is a linear combination of the weighted mean wave lengths of solvent components, the coefficient being the appropriate mole fractions. No experimental data are available to check this prediction.

## VIII. Solvent Shift in Polar Solvents

In addition to the two effects discussed in connection with the solvent shift in nonpolar solvents, there will be an interaction term due to the orientation–induction effect of solvent dipole on the solute molecule. The shift due to this interaction term is given by the terms in the second square bracket in Eq. (42), which may be written as

$$\begin{aligned}
&\left(\frac{3}{2D+1}\right)\frac{(2D+1)^2(D-n_0^2)}{(2D-n_0^2)D}\,\frac{kT}{3a^3}\left\{\sum_{m\neq e}\frac{(\varphi_e|\mu_0|\varphi_m)^2}{\mathscr{E}_e-\mathscr{E}_m}-\sum_{m\neq g}\frac{(\varphi_g|\mu_0|\varphi_m)^2}{\mathscr{E}_g-\mathscr{E}_m}\right\}\\
&\qquad+\left(\frac{2D-2}{D+2}\right)^2\left\{\frac{\mu_e^2}{a^6}\sum_{m\neq e}\frac{(\varphi_e|\mu_0|\varphi_m)^2}{\mathscr{E}_e-\mathscr{E}_m}-\frac{\mu_g^2}{a^6}\sum_{m\neq g}\frac{(\varphi_g|\mu_0|\varphi_m)^2}{\mathscr{E}_g-\mathscr{E}_m}\right\}\\
&\qquad=\left(\frac{3}{2D+1}\right)\frac{(2D+1)^2(D-n_0^2)}{(2D+n_0^2)D}\,\frac{kT}{3a^3}(\alpha_e-\alpha_g)\\
&\qquad+\frac{1}{a^3}\left(\frac{2D-2}{D+2}\right)^2(\mu_e^2\alpha_e-\mu_g^2\alpha_g).
\end{aligned}\tag{52}$$

Expression (52) is in no way more difficult to evaluate than the other terms in Eq. (42). As the expression depends on the square of the reaction field, this effect has been termed the quadratic Stark effect by McRae (1957). Further, it is this term which depends explicitly on temperature. Therefore, the study of the temperature effect on solvent shift can give us some information about the contribution of this effect in solvent shift. The available experimental data show that the effect of polar solvents is not simply on the position of the peak of the absorption band of a solute but also on the intensity and the band shape, which are considerably altered. Solvent effect on the intensity of the absorption band will be discussed in a subsequent section.

Most of the polar solvents are more or less associated, so when a solute molecule is dissolved in them the distribution of solvent around the solute does not take as simple a form as has been assumed in the present deduction. The calculation of reaction field using the Onsager model becomes too crude an approximation. Further short-range multipolar interactions assume considerable importance in highly polar solvents and the perturbing Hamiltonian cannot be described by simple dipolar terms.

## IX. Solvent Effect on Emission Spectra

When an excited molecule returns to ground state by radiative transition, the two electronic states of the solute involved in the process are the equilibrium excited state and the Frank–Condon ground state. If we assume that the solvent configuration around the solute has not changed during the electronic transition, we may express the reaction field of the Frank–Condon ground state as the sum of the orientation field of the excited state and the inductive field of the ground. Then, following the same procedure as discussed in the case of absorption spectra, we may express the solvent shift of emission spectra (fluorescence) in nonpolar solvents as follows:

$$\begin{aligned} h\,\Delta\nu^{f} = {} & \frac{2}{a^3}\left(\frac{2n_0^2+1}{n_0^2+2}\right)\left\{\mu_e(\mu_g-\mu_e)\left(\frac{D-1}{D+2}-\frac{n_0^2-1}{n_0^2+2}\right)\right. \\ & \left. + \frac{1}{2}\left(\frac{n_0^2-1}{n_0^2+2}\right)(\mu_S^2-\mu_e^2)\right\} \\ & + \frac{2}{a^3}\left(\frac{n_0^2-1}{n_0^2+2}\right)\frac{E}{\mathscr{E}+E}\,\{|P_f|^2+\mathscr{E}(\alpha_e-\alpha_g)\} \end{aligned} \tag{53}$$

where $|P_f|$ is the moment for the transition between states $e$ and $g$, and may be expressed in terms of fluorescence lifetime. Comparing Eqs. (51) and (53), it may be observed that solvent effect will be considerable if $\mu_g$ is large for absorption process and if $\mu_e$ is large for emission process. So if a molecule has considerably higher dipole moment in the excited as compared to the ground state, then the emission spectra will show larger shift than the absorption spectra by the solvent effect. This prediction appears to have been verified by Briegble and Czekalla (1960) from the measurement of absorption and emission spectra of a number of charge transfer complexes in nonpolar solvents. Apart from this conclusion, Eq. (53) has not been subjected to any experimental test at all.

## X. Solvent Shift and Excited State Dipole Movement

In the case of a polar solute in a nonpolar solvent, it has been suggested that solvent effect on emission and absorption spectra is determined primarily by the dipolar interaction. Since this interaction is determined by the static dielectric constant and the long wavelength refractive index of the solvent and the ground and excited state dipole moment of the solute, it has been suggested that the measurements of solvent shift provide us with a means for estimating excited state dipole moment of a solute molecule. For this purpose a new frequency term has been defined as

$$\Delta\nu^S = \frac{\Delta\nu^a + \Delta\nu^f}{2}, \tag{54}$$

and using Eqs. (51) and (53), it can be shown that

$$h\,\Delta\nu^S = \frac{1}{a^3}\left(\frac{2n_0^2 + 1}{n_0^2 + 2}\right)(\mu_e^2 - \mu_g^2)\left(\frac{D - 1}{D + 2}\right). \tag{55}$$

If we consider that the orientation effect alone is important, then we get

$$h\,\Delta\nu^S = \left(\frac{D - 1}{D + 2} - \frac{n_0^2 - 1}{n_0^2 + 2}\right)\frac{(\mu_e - \mu_g)^2}{a^3}. \tag{56}$$

Expression (56) has been used for calculating the excited state dipole moments of a number of hydrogen-bonded complexes by Mataga *et al.* (1956) and of a number of charge transfer complexes by Briegble and Czekalla (1960). Experimentalists may have great fascination for Eqs. (55) and (56), but they are not worth taking cognizance of for theoretical analysis.

## XI. Solvent Effect on the Intensity of the Absorption Band

So far we have discussed the effect of solvent on the wavelength of the absorption maximum of a solute. There are two other quantities which are characteristic for a continuous absorption band, namely its width and its strength. In this section we discuss the effect of solvent on the strength of the absorption band of a solute.

From considerations of the classical oscillator theory, Chako (1934) predicted the effect of a dielectric solvent on the electronic absorption intensities of molecules. He concluded that the apparent oscillator strength of a transition which is proportional to the integrated intensity under the molar absorption curve should increase by a factor $1/\gamma$ in going from the vapour state to dilute solution. This factor, called the Lorentz–Lorenz correction, is given by

$$1/\gamma = (n_0^2 + 2)^2/9n_0 \tag{57}$$

where $n_0$ is the refractive index of the solvent averaged over the absorption band. This result is derived only for allowed transitions and for nonpolar solvents. The first attempt to test this prediction on appropriate absorption bands was made by Pickett and co-workers (1941). Measurements on the

240-m$\mu$ bands of cyclopentadiene and cyclohexadiene, in vapour and in $n$-hexane solutions, gave values of 0.83 and 1.04, respectively, for the Lorentz–Lorenz correction. The theoretical value is 1.30 for this wave length and solvent. Very careful work of Jacobs and Platt (1948) showed that Chako's relation is not obeyed by most systems. In nonpolar solvents the absorption intensity of a solute increases very little over its gas phase value. In polar solvents the absorption intensity increases appreciably, but this increase is not expressed by Chako's relationship. Evidently the contribution of the Lorentz–Lorenz field has been overestimated in Chako's deduction.

From the quantum mechanical point of view the intensity of an absorption band, i.e., the so-called oscillator strength, is determined by the transition moment $Q$ for the particular electronic process

$$Q = \int \varphi_i r \varphi_j \, d\tau \tag{58}$$

where $\varphi_i$ and $\varphi_j$ refer to the wave functions of the two combining states, $i$ and $j$. Evidently $Q$ is very sensitive to the exact form of the wave functions of the combining states. Even if we assume that the wave function of a solvent–solute system may be represented as a simple product of the solute ($\varphi$) and the solvent ($\psi$) wave functions, the wave function of the solute in solution and in the gas phase may be somewhat different. How this may come about may be understood from a discussion of the near-ultraviolet absorption spectrum of benzene in gas and in solution.

In the near-ultraviolet region benzene shows an absorption band extending from 230 to 270 m$\mu$ with a well-developed vibrational structure in the gas phase. This represents an electronic transition ${}^1A_{1g} \rightarrow {}^1B_{2u}$, which is electronically forbidden by the hexagonal symmetry of benzene. If the sixfold symmetry of benzene is destroyed by a vibration of type $\mathscr{E}_g^-$, the system can appear with weak intensity (Sponer, 1940). Once the inhibition against transition is lifted by an interacting $\mathscr{E}_g^+$ vibration, we expect superimposed on such transition progression with totally symmetrical vibrations. But the 0-0 transition should be absent, and the first member in the progression should be 0-1 transition. All these predictions are well verified by the near-ultraviolet spectrum of benzene. In solution in nonpolar solvents benzene shows an absorption band with a well-developed vibrational structure in the same region and with the same vibrational progression as in the gas phase (Kronenberger, 1926, 1930). In polar solvents the situation is practically the same but the 0-0 transition which is absent in gas and in nonpolar solvents appears with very weak intensity. This evidently means that in polar solvents the $^1A_{1g} \rightarrow {}^1B_{2u}$ transition is weakly allowed electronically. We must assume that the hexagonal symmetry of benzene has been partially destroyed in polar solvents by the internal field produced by solvent dipoles. This deformation is not large enough to affect the energy values appreciably, but its effect is considerable enough on wave function to affect the intensity of the transition which is now weakly allowed electronically. The deformation effect of dipolar solvent on a solute molecule has also been stressed in the theory of solvent effect on optical rotatory power of a solute molecule (Beckmann and Cohen, 1936). This type of solvent effect will increase the intensity of a forbidden transition but will have very little effect on the intensity of an allowed transition.

It has been observed by Sheppard (1942) that the intensities of allowed transitions of various organic dyestuffs are greatly increased in polar solvents, although the increase cannot be related to the Lorentz-field effect of Chako. It is evident that in polar solvents effects other than those discussed above must be taken into consideration in analyzing the role of solvents on absorption spectra of a solute. While discussing the effect of polar solvents on the frequency shift of a solute, it has been mentioned that short-range multipolar interaction may be important in these systems. Existence of such short-range forces will impose restrictions on the type of wave functions that should be used for the system; i.e, the overlap between the solvent and solute wave functions cannot be neglected and the wave function for the solvent–solute pair must be suitably antisymmetrized. A theoretical study of the effect of short-range forces on the position and intensity of the absorption spectra of a solute in solution is badly needed.

## XII. Concluding Remarks

The proposed theory of solvent effect on the electronic spectra of a solute molecule is based on the following considerations. The distance between the two energy levels involved in a spectral transition $H_0 + H'$ is a function of the position of all perturbing molecules, since the perturbation $H' = \sum H_i'$, which is present in addition to the normal energy difference $H_0$, depends on the configuration of all the molecules surrounding the radiating one. This is in effect a statistical theory where we have neglected the translational motion of the molecules completely. The statistical theory has the shortcoming that it holds only for slow perturbation among the molecules. There is another type of theory which can be developed to account for the changes produced when a molecule is perturbed by its environment. This theory may be termed in impact theory in which explicit account may be taken of the time dependence of the Hamiltonian for the absorbing system. The difficulties associated with such a theory for solvent–solute interaction are obvious. For quite some time to come we shall have to devote our time to extending and modifying the statistical theory for solvent–solute interaction and its effect on the electronic spectra of solute molecules.

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# The Pi-Electron Approximation

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## I. Introduction

During the first few years following the discovery of quantum mechal nics, many interesting applications were made to problems of chemica- interest. However, it quickly became apparent that mathematical complexity and sheer mass of arithmetic would be an effective barrier to any extensive *ab initio* approaches to chemical problems. These simple applications, and the concepts which evolved from them, however, suggested many interesting empirical correlations, and the extensive use of these has influenced all of chemistry. The recent rapid evolution and proliferation of the electronic digital computer has stimulated a considerable increase in activity, both in the area of *ab initio* calculations on simpler systems and also in the area of semiempirical work on complex molecules.

In a way, pi-electron systems represent the most fruitful class of molecular systems to which quantum mechanics can be applied using a semiempirical approach. There are countless numbers of them, and they can be classified by forming homologous series where many variables can be suppressed; thus they lend themselves well to theoretical approximation methods. The quantum mechanical approach to them can be related very nicely to solid state physics as well as to atomic and molecular physics. On one hand crude approximations easily grasped by the neophyte undergraduate student can be used to advantage in showing the quantum mechanical framework for the systemization of their properties. On the other hand quantitative understanding of the empirical correlations which can be found for their physical properties challenges the most expert quantum mechanic. It has become relatively routine to study them experimentally from the point of view of ultraviolet, visible, infrared, and microwave spectroscopy. Pi-electron systems can be produced as diamagnetic or paramagnetic species and the whole range of magnetic phenomena used as additional probes into their structure. They can be coupled with or have incorporated in them many of the chemical elements. They are studied extensively within the framework of chemical kinetics. They are the basis for a substantial part of the chemical industry and of all living matter. Because they are so widespread they provide a means of communication between workers in many areas of science.

The study of pi-electron systems constitutes an important part of the history of quantum chemistry. It was only four years after the classical work by Heitler and London on the hydrogen molecule that Hückel advanced his method for handling pi-electron systems, and it has been widely used ever since. The paper by Goeppert–Mayer and Sklar (1938) represented a milestone in the evolution of pi-electron theory in that an attempt was made to consider explicitly the interaction between pi electrons as well as the effect of the other electrons on the pi electrons. More recently, the work of Pariser and Parr (1953) and Pople (1953) showed how the theoretical framework could be brought closer to experience by appropriate calibration of certain of the critical integrals. Shortly thereafter, Lykos and Parr (1956) extended an observation of McWeeny (1954a) and showed the essential quantum mechanical nature of the pi-electron approximation. Subsequently, Ruedenberg (1961) detailed the analysis using a minimal basis of Slater orbitals and showed that the integrals over atomic orbitals that arise can be resolved into two groups; one group where only nearest neighbor interactions were important and a second group where long range effects were operating.

Attention has recently been focused on the problem of electron correlation by the work on Löwdin's alternant orbital idea by de Heer and Pauncz (1963). Orloff and Fitts (1963) have studied a Hückel-like technique for handling heteroaromatics that should help relieve a long-standing problem peculiar to the Hückel method. The quantum chemistry of excited states is receiving considerable attention by Mataga and Torihasi (1963) and others while the rapidly growing use of electron paramagnetic resonance (ESR) and nuclear paramagnetic resonance (NMR) spectrometers has led to a flood of literature dealing with nuclear and electronic paramagnetic properties.

Finally, the molecular biologist has discovered pi-electron theory.

## II. Quantum Mechanical Foundation

The appropriate basis for a discussion of the pi-electron approximation is in terms of quantum mechanics. Any analysis which does not relate to that underlying structure cannot provide firm footing for any *a priori* predictions about chemical or physical behavior. Some attention has been given to the pi-electron approximation on that basis and its essential features seem to be fairly well understood.

What one normally does is to treat the pi electrons explicitly and to consider that the effect of the other electrons is to contribute to the potential which the pi electrons experience. Thus, for the methyl radical in its planar form, the single "pi electron" moves in the potential due to a planar $CH_3^+$ ion, i.e., the core. In this case the pi electron problem is simply a one electron problem and what is sought is the eigenvalue and eigenfunction of an operator, $\mathbf{H}_{\text{core}}(1)$, which includes not only the kinetic energy operator and nuclear attraction operators for the one pi electron but also the operators corresponding to Coulomb and exchange interaction between the pi electron and the other electrons which help comprise the core. If an adequate description of the core electrons were in hand so that $\mathbf{H}_{\text{core}}(1)$ could be precisely defined, then an accurate solution of the eigenvalue problem could be found. Accurate wave functions for the entire methyl radical are only just now becoming available, so that the adequacy of some of the approximations inherent in the pi-electron approximation can be examined in the context of this, the simplest pi-electron hydrocarbon.

It is instructive to develop the pi-electron approximation starting with the exact solution to the Schrödinger equation for the entire molecule in order that the approximations made can be systematically uncovered. Within the assumptions (1) that relativistic effects are unimportant here and (2) that the Born–Oppenheimer approximation relating to the separation of nuclear and electronic motion is adequate, the essential idea behind the pi-electron approximation is that some electrons in a many-electron problem can be treated separately from the rest. That is, if we designate as $\psi_\sigma(1, 2, \ldots n_\sigma)$ the many-electron antisymmetrized wave function characterizing the core or sigma electrons, and as $\psi_\pi(n_\sigma + 1, \ldots n_\sigma + n_\pi)$ the corresponding wave function for the peel or pi electrons, then the total wave function is approximated as the partially antisymmetrized product of $\psi_\sigma$ and $\psi_\pi$.

This is a generalization of the orbital concept in that, instead of considering that each electron is described by a single spin orbital, here groups of electrons are described by single wave functions. In this way, in a sense, the error that is introduced is the neglect of correlation between groups of electrons while, within a particular group, most of the correlation error can be considered to be relieved. For some cases, for example in a recent treatment of the intershell correlation between the 1*s* and 2*s* shells in the beryllium atom (McWeeny and Sutcliffe, 1963), the intergroup correlation is a small part of the total correlation error. Thus, although it is yet to be demonstrated quantitatively, it seems reasonable to suppose that intercore-peel correlation error will be small compared with intracore and intrapeel correlation.

The resolution of the total wave function into two parts is convenient here. However, a subsequent generalization of the Lykos and Parr (1956) treatment of the pi-electron approximation (Parr *et al.*, 1956) showed how the resolution may be effected into any number of parts up to the total number of electrons in which case the usual one-electron spin orbital antisymmetrized product results. The usual procedure has been to represent $\psi_\pi$, say, in terms of appropriate linear combinations of antisymmetrized products of one-electron spin orbitals. The problem that now remains is to determine the wave functions for the groups of electrons of interest.

The various ideas thus far presented can be summarized in the following form. If a properly antisymmetrized $\psi_\sigma$ is constructed from the one-electron spin orbitals $\sigma_i$ and a corresponding $\psi_\pi$ from the one-electron spin orbitals $\pi_j$, then the partially antisymmetrized product of $\psi_\sigma$ and $\psi_\pi$ can be represented as $\psi_{\text{total}} = P_{\sigma\pi}\psi_\sigma\psi_\pi =$

$$\frac{1}{\sqrt{(n_\sigma + n_\pi)!}} \left| \begin{array}{cccc|ccc} \sigma_1(1) & \cdots & \cdots & \cdots & \cdots & \cdots & \sigma_1(n_\sigma + n_\pi) \\ \vdots & \sigma_2(2) & & \vdots & & & \\ \vdots & & \ddots & \vdots & & & \\ \sigma_{n_\sigma}(1) & & & \sigma_{n_\sigma}(n_\sigma) & & & \\ \hline \vdots & & & \vdots & \pi_1(n_\sigma + 1) & & \\ \vdots & & & \vdots & & \ddots & \\ \pi_{n_\pi}(1) & & & \vdots & & & \pi_{n_\pi}(n_\sigma + n_\pi) \end{array} \right|$$

where the upper left partition is $\psi_\sigma$ up to a factor $(n_\sigma!)^{-1/2}$; the lower right partition is $\psi_\pi$ up to a factor $(n_\pi!)^{-1/2}$; and the upper right and lower left partitions are the additional elements which enter because of the requirement of antisymmetry on the total wave function with respect to exchange between sigma and pi electrons. If more than one determinant is used to represent either or both of $\psi_\sigma$ and $\psi_\pi$, then a linear combination of such forms results. Thus we see that an approximate wave function of the form $\psi_{\text{total}}$ does satisfy the Pauli exclusion principle and that $\sigma$–$\pi$ exchange is taken into account.

If the two sets of spin orbitals $\{\sigma_i\}$ and $\{\pi_i\}$ are the two mutually exclusive subsets which together comprise a complete orthonormal set of functions, then the strong orthogonality restriction that $\psi_\sigma$ be represented by elements of $\{\sigma_i\}$ only and $\psi_\pi$ by elements of $\{\pi_i\}$ only means that, in general, it will be impossible to represent the total wave function exactly. A job for the *ab initio*ists is to ascertain how serious this limitation is in selected test cases. A significant step forward in this direction is the recent paper by McWeeny and Sutcliffe (1963).

In order that such a resolution be operationally meaningful, the functions $\{\sigma_i\}$ and $\{\pi_i\}$ need to be further specified. Although in general electron spin is a function of position in space as given by a spin orbital, what is usually done is to assume that the spin orbital can be written as a product of a pure space-dependent part and a pure spin-dependent part. The problem then reduces to seeking appropriate forms for the space parts of the $\sigma_i$ and $\pi_i$.

A recent analysis of an orbital representation of $N_2$ is quite revealing (Nesbet, 1961). What was done there was to study the core and peel as a function of internuclear distance. Since flexible orbitals were used in a single determinantal representation, both the component multiplicities and the distortion of the orbitals were varied as function of internuclear distance. It is clear that near the limits of the united atom (internuclear distance small) and the separated atom (internuclear distance large) the molecular orbital (MO) representation and the valence bond (VB) representation, respectively, are the appropriate ones to use. Of interest in Nesbet's $N_2$ study were the ranges of appropriateness in the core and in the peel of the MO and VB approaches. In going from small internuclear distance to large internuclear distance he discovered that the peel orbitals approached the separated atom form before the core orbitals did. Put another way, it seems quite clear from Nesbet's study that a realistic description of the core will need to be a localized molecular orbital description—or something equivalent to it. Currently considerable attention is being given to the question of localized molecular orbitals. A definitive paper by Gilbert (1964) dealing with the closed shell case will appear shortly. For the peel, the molecular orbital description may be appropriate, the greater the excitation of the peel. Once again, these points await detailed *ab initio* work on appropriate test systems for a firm basis for analysis. A recent nonempirical series of calculations on the ethylene molecule by Moskowitz and Harrison (1963) using sets of Gaussian functions as a basis is a harbinger of things to come.

The conclusion one comes to is that the state of *ab initio* work, which is improving rapidly with the tremendous technological advances in the computers which do the work, will shortly enable *ab initio*ists to explore by accurate calculation a number of features of semiempirical pi-electron theory which present-day users guess at or accept as a matter of faith.

In order for the analysis presented in the foregoing to be operationally useful, it is necessary to specify further the form of the orbitals $\pi_i$. Although some attention has been given recently to the free-electron approximation in this context, most of the work has been with molecular orbitals $\pi_i$ represented in terms of a linear combination of atomic orbitals centered on each of the nuclei involved. Ordinarily it is assumed that the basis involves only one Slater-type orbital on each center, although there have been instances where free carbon atom Hartree–Fock orbitals have been used in a consistent fashion (Katz *et al.*, 1963). Also there have been attempts to deduce the shape and scale of best distorted atomic orbitals by working with simple model systems (Sovers and Kauzmann, 1963; Miller and Lykos, 1962). Extensive work on the methyl radical currently in progress in this laboratory and elsewhere should give considerable insight into the change in the pi atomic orbital on molecule formation. A less well understood situation is where second-row elements are involved and first-order $d$–$\pi$ orbital character needs to be considered (Breslow and Mohacsi, 1963). So long as the integrals over the atomic orbitals are treated in a consistent empirical fashion, however, it may not be necessary to know the precise nature of the atomic orbital comprising the basis set. This will be amplified in a following section.

The essential question which remains (the choice of best distorted atomic orbitals depends on this question as well) is: For the given electronic state, what are the appropriate linear combinations of distorted atomic orbitals to represent the molecular orbitals $\pi_i$? The variational theorem states that, if the exact Hamiltonian for the system is used, the expectation value of the energy is bounded below by the true ground state energy. Thus, if adjustable parameters such as linear coefficients (and the scale of the atomic orbitals) are present, these may be adjusted until the expectation value of the energy, as a function of those parameters, is at a minimum. Hopefully, then, an adequate representation of the state in question is achieved. However, application of the variational theorem to the pi electrons alone using some sort of pi-electron energy operator requires justification.

Considerable attention was given to this point by Lykos and Parr (1956), and their analysis can be outlined as follows. If we write the total Hamiltonian operator for the molecule in the form

$$\mathbf{H}_{\text{total}} = \sum_{i=1}^{n_\sigma}\left(-\tfrac{1}{2}\nabla_i^2 - \sum_\alpha z_\alpha/r_{\alpha i} + \sum_{j>i}^{n_\sigma} 1/r_{ij}\right) + \sum_{i=1}^{n_\sigma}\sum_{j=n_\sigma+1}^{n_\sigma+n_\pi} 1/r_{ij}$$
$$+ \sum_{i=n_\sigma+1}^{n_\sigma+n_\pi}\left(-\tfrac{1}{2}\nabla_i^2 - \sum_\alpha z_\alpha/r_{\alpha i} + \sum_{j>i}^{n_\sigma+n_\pi} 1/r_{ij}\right),$$

then it is clear that the first sum assesses the kinetic energy, nuclear attraction energy, and the mutual repulsion of the core or sigma electrons, while the last sum does the same for the peel or pi electrons. The second or middle group is the one concerned with the repulsion between each of the sigma electrons and each of the pi electrons, and it is this group which couples the core and the peel. It should be noted that nuclear repulsion has been omitted here as the nuclear coordinates enter parametrically. The expectation value for the total energy, resolved in the same way as the total Hamiltonian, then becomes

$$E_{\text{total}} = E_\sigma^0 + E_{\sigma\pi} + E_\pi^0$$

where we have assumed $\psi_{\text{total}}$, $\psi_\sigma$, and $\psi_\pi$ each to be normalized to unity and $\psi_\sigma$ and $\psi_\pi$ to be orthogonal in the strong sense. They showed that $E_{\text{total}}$ may be expressed as follows:

$$E_{\text{total}} = E_\sigma^0 + (E_{\sigma\pi} + E_\pi^0) = E_\sigma^0 + \int \psi_\pi^* \mathbf{H}_\pi \psi_\pi \, d\tau = E_\sigma^0 + E_\pi$$

where $\mathbf{H}_\pi$ is an energy operator which depends on the coordinates of the pi electrons while $E_\sigma^0$ depends on $\psi_\sigma$ only. In particular

$$\mathbf{H}_\pi = \sum_{i=n_\sigma+1}^{n_\sigma+n_\pi}\left(\mathbf{H}_{\text{core}}(i) + \sum_{j>i}^{n_\sigma+n_\pi} 1/r_{ij}\right)$$

where

$$\mathbf{H}_{\text{core}}(i) = -\tfrac{1}{2}\nabla_i^2 - \sum_\alpha Z_\alpha/r_{\alpha i} + G_\sigma(i).$$

It is the operator $G_\sigma(i)$ which takes into account the coupling between the sigma and pi electrons and may be further resolved as follows:

$G_\sigma(i) = \mathbf{J}_\sigma(i) - \mathbf{K}_\sigma(i)$ where the Coulomb operator $\mathbf{J}_\sigma(i)$ may be written

$$\mathbf{J}_\sigma(i)\psi_\pi = \int \psi_\sigma^* \left( \sum_{j=1}^{n_\sigma} 1/r_{ij} \right) \psi_\sigma \, dv \psi_\pi$$

and where the exchange operator $\mathbf{K}_\sigma(i)$ may be written

$$\mathbf{K}_\sigma(i)\psi_\pi = \int \psi_\sigma^* \left( \sum_{j=1}^{n_\sigma} 1/r_{ij} \psi_\sigma^i \psi_\pi^j \right) dv.$$

Thus we see that it is possible to define an energy operator $\mathbf{H}_\pi$ for the pi electrons alone such that the expectation value of that operator over a properly antisymmetrized product wave function for the pi electrons alone includes the pi electron contribution to the total energy including $\sigma$–$\pi$ Coulomb and exchange interactions.

Furthermore, the process whereby $\mathbf{H}_\pi$ was defined could have just as well been applied to the terms $E_{\sigma\pi}$ and $E_\sigma^0$ instead. In this case an energy operator $\mathbf{H}_\sigma$ would have resulted such that the expectation value of $\mathbf{H}_\sigma$ over a properly antisymmetrized product wave function for the sigma electrons alone would include the sigma electron contribution to the total energy including $\sigma$–$\pi$ Coulomb and exchange interactions. It follows quite naturally from this observation that one could take advantage of the formal symmetry between $\mathbf{H}_\pi$ and $\mathbf{H}_\sigma$ to proceed systematically to improve initial guesses to $\psi_\sigma$ and $\psi_\pi$. That is, guess a $\psi_\sigma$, use it to construct $\mathbf{H}_\pi$, and then proceed variationally to get the corresponding best $\psi_\pi$. Then use that improved $\psi_\pi$ to construct $\mathbf{H}_\sigma$ and proceed variationally to get an improved $\psi_\sigma$, and so on. This procedure would be useful, for example, in assessing the effect on $\psi_\sigma$ of a perturbation on $\psi_\pi$. The spirit of this idea is embodied in the variable electronegativity method used by Brown and Heffernan (1960). Here the effect of a nonuniform charge distribution in the peel on one hand is taken into account by adjusting the parameters relating to the potential due to the core on the other hand, and the two are adjusted back and forth until internal consistency obtains.

Roothaan (1960) has considered the problem of applying the variational theorem to determine the optimal form of an antisymmetrized-product-of-one-electron-orbitals wave function where the one-electron orbitals are represented as linear combinations of atomic orbitals. So long as the concern is with the linear coefficients only, a beautiful self-consistent matrix formalism results which lends itself particularly well to electronic digital computer manipulation. The matrix equation in the one-electron orbitals which results is of the form

$$\mathbf{F}\mathbf{C}_i = \varepsilon_i \mathbf{S}\mathbf{C}_i$$

where the vectors $\mathbf{C}_i$ are the sets of coefficients which define the one-electron or molecular orbitals $\pi_i$, $\mathbf{S}$ is the matrix of overlap integrals between the elements of the basis set (i.e., the atomic orbitals), $\mathbf{F}$ is the matrix representation of the Hartree–Fock operator, and the $\varepsilon_i$ are the Lagrangian multipliers which are introduced as part of the mathematical technique used in applying the calculus of variations to the problem of optimizing the approximate wave functions.

An important point to note here is that the operator $\mathbf{F}$ is itself a function of its eigenvectors, the $\mathbf{C}_i$. This implies that if $\mathbf{F}$ is generated by somehow guessing either a set of $\mathbf{C}_i$ or the elements of $\mathbf{F}$ directly, and then the eigenvectors, $\mathbf{C}_i$, of this approximate $\mathbf{F}$ are found, it does not necessarily follow that the eigenvectors of the approximate $\mathbf{F}$ will be the same as the guessed set. In fact, what is usually done in solving the Roothaan equations is to proceed iteratively by guessing a set of $\mathbf{C}_i$ to generate an approximate $\mathbf{F}$, getting the eigenvectors of the approximate $\mathbf{F}$ and using them to generate a hopefully improved approximate $\mathbf{F}$, and so on, until comparison of two successive sets of vectors, $\mathbf{C}_i$, generated by this iterative procedure agree to within some preset criterion, in which case self-consistency is said to obtain. For this reason the orbitals found by solving the Roothaan equations are called self-consistent orbitals.

The molecular orbitals which result from solving the Roothaan equations are, by construction, the best possible orbitals which can be found with the given atomic orbital building blocks. The term "best possible" refers to that set of one-electron orbitals which yields the lowest value for the energy of the system found by using an antisymmetrized product wave function, or a linear combination of antisymmetrized product wave functions, constructed from it. One additional point should be made here. An antisymmetrized product of one-electron orbitals is of course an approximation to the accurate group wave function, $\psi_\pi$. The use of one-electron orbitals in this way means that the detailed Coulomb and exchange interaction between the electron described by an orbital and each of the remaining electrons is being mathematically smoothed into an average Coulomb and exchange interaction. The error in the energy that is introduced by approximating the exact eigenfunction of the Hamiltonian for the molecule by a best possible antisymmetrized-product-of-one-electron-orbitals wave function is called the correlation energy.

Much attention has been given to the question of correlation energy (Slater, 1963a). Many calculations and analyses have been made dealing with simple atomic systems. However, the question is still an open one. An extensive analysis of the correlation energy in helium in its ground state suggested that configuration interaction is a slowly convergent process for correcting that error (Taylor and Parr, 1952). A more recent paper by Coulson and Neilson (1961) wherein they define a "Coulomb hole" shows in a graphical way why this is so, and, in an extension of their analysis, Gilbert (1963) cautions against an extrapolation of the $r_{12}$ expansion techniques found successful for the ground state of helium to other atoms. For example, Watson (1961) found for beryllium that the mixing of a single excited configuration $1s)^2$ $2p)^2$ with the usual ground state configuration $1s)^2$ $2s)^2$ in an extended Hartree–Fock framework was sufficient to pick up most of the $2s)^2$ intrashell correlation energy.

Finally, it should be noted that, although there may be a systematic way for estimating closed shell contributions to the correlation energy in atoms or ions where the only open shell possible is the outermost one (Allen *et al.*, 1963), a recent series of calculations by Bagus (1963) on some atoms and ions with open *inner shells* suggests that the notion of transferability of closed shell contributions to the correlation energy may have to be qualified somewhat.

Thus, even in the realm of atomic systems where accurate *ab initio* calculations are being made, the assessment of the correlation energy requires additional attention.

## III. Semiempirical Theory: The Over-all Structure

The question then naturally arises, having some information about the theoretical structure of the pi-electron approximation and a tremendous amount of empirical information about the chemical and physical properties of pi-electron systems, can some useful middle ground be found between completely empirical correlations on one hand and *ab initio* calculations based on the underlying theoretical structure on the other? The answer has been filling the literature in an ever-increasing amount and the answer is yes!

A number of monographs and review articles have appeared recently, the most relevant one being Parr's "Quantum Theory of Molecular Electronic Structure" (1963). Accordingly, except where deemed appropriate, most of the items dealt with here shall refer only to papers published since late 1962. As the concern of this chapter is with the pi-electron approximation itself, the list of references dealing with empirical results will not be exhaustive.

Many semiempirical approaches to pi-electron theory can be interpreted as attempts to approximate to the solutions of Roothaan's equations outlined in the preceding section.

For example, classical Hückel theory can be considered as an attempt to guess some set of matrix elements of **F**. The eigenvectors of that approximate **F** are the so-called Hückel orbitals. Unfortunately a common error still persists in the use of Hückel theory and that is to assume that the Lagrangian multipliers which enter the Roothaan equations are one-electron energies whose sum is the total energy. The general analysis of Hückel-like theory on the basis of Hartree–Fock theory has been presented by Löwdin (1962).

A more detailed examination of the quantum mechanical basis of Hückel theory for hydrocarbons was recently published by del Re and Parr (1963) in the Hylleraas Symposium proceedings where the observation is made that the adequacy of the usual Hückel methodology depends on how close the charge distribution in the molecule is to leaving the constituent "atom" electrically neutral. They point out that for asymmetrical systems, and in particular for heteronuclear pi-electron systems, that condition is not likely to obtain. However, some recent work of Orloff and Fitts (1963) proves interesting in this regard. Orloff and Fitts examined the matrix elements of **F** obtained by actually solving the Roothaan equations iteratively to self-consistency for a series of related heteronuclear pi-electron systems and they evolved a technique for using fragments of the **F**'s found for those related molecules to generate an **F** for a molecule not included in the original series. Their method is at least an improved way to generate a set of starting eigenvectors for the Roothaan equations. In addition, they may have uncovered a way of extending the usefulness of Hückel theory to heteronuclear pi-electron systems. The interpretation of their observation in terms of the underlying quantum mechanics should be an interesting problem.

The most important and widely used semiempirical pi-electron theory, however, is that due to Pariser and Parr and to Pople. Briefly stated, what they developed is an approach within the framework of the Roothaan equations with three essential features:

(a) One-electron two-center integrals over the atomic orbital building blocks and the operator $H_{\text{core}}(i)$ are handled as empirical quantities;

(b) Two-electron integrals over the atomic orbital building blocks and the operator $r_{12}^{-1}$ are assumed to be zero unless they are of the special Coulomb form

$$\iint |X_a(1)|^2 r_{12}^{-1} |X_b(2)|^2 \, dv_1 \, dv_2,$$

where $X_a(1)$ is the atomic orbital at center or nucleus "$a$" and $X_b(2)$ is the atomic orbital at center or nucleus "$b$" (called zero differential overlap);

(c) The one-center one-electron integrals and one-center two-electron integrals are related empirically to experimentally determined physical properties for the corresponding atom in its appropriate valence state.

The spirit of the Pariser–Parr–Pople approach, then, is to work within the best available theoretical framework and to "calibrate" the theory by appeal to a limited amount of experimental information characterizing the molecules under consideration and their constituent atoms as well. This approach has enjoyed a large measure of success in dealing with a variety of molecular species and a variety of phenomena.

Two nagging questions remain, however, namely:

(a) To what extent is the correlation energy taken into account by such a procedure?

(b) What justification is there for setting equal to zero the large number of electron repulsion integrals not of the Coulomb form?

With regard to the correlation error question, most of the comments in the literature have focused attention on the value of the one-center two-electron Coulomb repulsion integral,

$$\iint |X_a(1)|^2 r_{12}^{-1} |X_a(2)|^2 \, dv_1 \, dv_2 \equiv (aa|aa).$$

It has been pointed out many times that, when $X_a$ is a Slater $2p$ orbital for the carbon atom, $(aa/aa)$ takes on the value 16.9 eV while if its value is estimated by considering the change in state

$$2\mathrm{C}\cdot \rightarrow \mathrm{C}^- + \mathrm{C}^+,$$

$(aa|aa) = 11.1$ eV. The implication is clearly made that this 6 eV correction is related to the correlation error. An improved estimate of $(aa|aa)$ using a Hartree–Fock $2p$ orbital for neutral carbon together with a virial theorem analysis of the correlation error in the ground state of helium has shown that the error in $(aa|aa)$ due to an electron pair in a $2p$ orbital should be about twice the correlation error for the $2p$ electron pair (Arai and Lykos, 1963). Also recent *ab initio* Hartree–Fock calculations on the planar methyl radical and the corresponding positive ion (methyl radical core) suggest that the core-peel correlation is not negligible (Hermann *et al.*, 1964).

There has been an interesting attempt by Dewar (1963) and co-workers to assess the one-center correlation as being all vertical correlation. What Dewar did was to consider that when one pi electron was on one side of the molecular plane the other electron was on the other side, and in fact he developed a corresponding extension of Pariser–Parr–Pople theory using so-called split-*p* orbitals.

The split-*p* orbitals (SPO's) used by Dewar raised some interesting analytical as well as conceptual questions, and the conclusion seems to be that the orthogonality of the *p* orbitals to the core (or of $\psi_\pi$ to $\psi_\sigma$) is destroyed when SPO's are used, and the whole pi-electron approximation then breaks down. Dewar, however, seems to feel that it should be possible to include somehow the effect of using SPO's in estimating values of electron repulsion integrals while still working within the theoretical framework of the pi-electron approximation. An *ab initio* calculation by Chung (1963) on several states arising from the helium $2p)^2$ configuration reveals that the probability of finding the two *p* electrons on opposite sides of the nodal plane is about 0.7.

Having emphasized vertical correlation for the integral $(aa|aa)$, the question of molecular horizontal correlation arises. This will be considered following the discussion of the Pariser–Parr–Pople method. However, there is an aspect of the Pariser and Parr approach which serves to distinguish it from the Pople approach and which introduced a horizontal pi-electron correlation correction of as yet undetermined extent. What Pariser and Parr did was to use Hückel orbitals as a starting set and then invoke a limited amount of configuration interaction. This procedure corrects somewhat for the fact that self-consistent molecular orbitals are not used and, depending on the state being represented and the extent of configuration interaction invoked, may also introduce some horizontal correlation error correction. Pople, on the other hand, used the Roothaan theoretical framework but approximated the eigenvectors by using Hückel orbitals. Since then the best features of both have been taken and the two approaches, which were similar in philosophy, were merged into the technique widely used today.

The question of zero differential overlap and its implications has been examined by a number of workers. McWeeny (1954b) made the observation that, in the case of cyclobutadiene and benzene, if one used Slater orbitals $X_a$ as a basis but transformed them to Löwdin (1950) orthogonalized atomic orbitals, then indeed the non-Coulomb-type electron repulsion integrals over the Löwdin orbitals $X_a^\lambda$ became quite small, while the Coulomb-type electron repulsion integrals changed very little. This extremely interesting result made it quite clear that, if zero differential overlap were to be used consistently, then Roothaan's equation would need to be rewritten in the form

$$\mathbf{F}^\lambda \mathbf{C}_i^\lambda = \varepsilon_i \mathbf{C}_i^\lambda,$$

where the overlap matrix has been reduced to a unit matrix and the elements of $\mathbf{F}^\lambda$ need to be interpreted as being over Löwdin orbitals, or something close to them.

In general there are an infinite number of ways of orthogonalizing a set of functions. According to the Carlson–Keller (1957) theorem, Löwdin's technique corresponds to finding that set of orthogonal orbitals that best resembles the original set of nonorthogonal atomic orbitals by a "least squares" criterion, i.e.,

$$\sum_a \int |X_a^\lambda(1) - X_a(1)|^2 \, dv = \text{minimum},$$

where

$$\mathbf{X}^\lambda = \mathbf{S}^{-1/2}\mathbf{X}.$$

Thus Löwdin's orbitals, the $X_a^\lambda$, are really molecular orbitals in the sense that they are linear combinations of the original nonorthogonal basis atomic orbitals.

In addition, the various parameters which enter the semiempirical theory based on zero differential overlap need to be interpreted as integrals over Löwdin orbitals. As a consequence, even though those parameters are given indices implying they have only one-center or two-center dependence, the parameters evaluated empirically contain a dependence on molecular geometry due to the many-orbital composition of the Löwdin orbitals. This point was discussed at length by Lykos (1961) and incorporated in the open shell Roothaan equations by Berthier *et al.* (1963).

There are a number of variants of the Hückel-type and Pariser–Parr–Pople-type pi-electron theories, and these have been briefly described by Parr in his monograph. There has been further work done on Löwdin's alternant molecular orbital ideal but, as Parr pointed out, the implementation of the idea in dealing with the general molecule will be difficult, although the benzene calculation by de Heer and Paunez (1963) provides a firm estimate of horizontal correlation for that particular molecule.

An interesting method, which has not been fully exploited, is the so-called "Unrestricted Hartree–Fock" (UHF) method (Pople and Nesbet, 1954). The method is based on a single determinant representation of a system where the one-electron space-spin factored orbitals which make up the determinant are divided into two sets, those with alpha spin and those with beta spin. The space parts are determined by a self-consistent procedure without the constraint that the space parts in each of the two sets should be the same. This additional degree of freedom is important for cases when the number of electrons with alpha spin is different from the number with beta spin. The reason for this is that the usual Roothaan procedure with a minimal representation of a state will yield electron spin densities of one algebraic sign (or zero) only, whereas the Unrestricted Hartree–Fock method can yield spin densities of both signs, which seems to be in closer accord with experience. This method also introduces some allowance for electron correlation. A single determinantal wave function of this type will not, in general, be a pure spin multiplet but a mixture of all multiplets possible for the given number of the electrons. However, Amos (1962) has shown that the concentrations of the higher multiplets fall off rapidly with increasing multiplicity, and he has developed a modified Unrestricted Hartree–Fock method where the first higher multiplet is annihilated. Harriman (1963) has examined the first-order density matrix for a projected single UHF determinant.

## IV. Semiempirical Theory: The Parameters

With the advent of the now common large fast digital computers, and programs written for them for solving the Roothaan equations for open- and closed-shell systems, most interested researchers can, in a routine way, get solutions to the Roothaan equations for any particular case. All the researcher needs to do is to supply numbers for the parameters which enter the theory, including a specification of the geometry, and perhaps to make a nominal payment for the computer time required. The ease with which these solutions can be obtained has led to more and more utilization of the Pariser–Parr–Pople method by scientists working on many different kinds of problems, and this ever-increasing utilization makes it even more important to seek a deeper understanding of the structure and meaning of the basic parameters which are involved.

The analysis of parameter values needs to be done in such a way that an atom characterized empirically in one molecule can be characterized nonempirically in another molecule which is different but where, however, the local environment for the atom in question is similar. The overwhelming success of the Pariser–Parr–Pople theory suggests that this should be possible.

Within the restrictions noted in the foregoing, namely, that the many-electron group wave function, $\psi_\pi$, is approximated as an antisymmetrized product, or linear combination of antisymmetrized products, of one-electron space-spin factored spin orbitals, the parameter problem reduces to understanding the structure and values of integrals over the building blocks from which the space parts of the one-electron spin orbitals are constructed.

Strictly speaking, all that is needed is a single complete orthonormal set of functions as building blocks to represent, to whatever accuracy is desired, each of the one-electron or molecular orbitals. As a matter of fact, what is done is to take one or two elements of a set of atomic orbitals centered at each of the nuclei in the conjugated system. If enough such functions were to be centered at each of the nuclei involved, then the problem of over completeness of the representation arises.

Use of a single complete orthonormal set of basis functions to represent a molecular orbital has been examined by Howell and Shull (1959) and others using as a vehicle the hydrogen molecule ion. It was found that such a procedure was only slowly convergent to the accurate solution and would very likely be useful only under certain very restrictive conditions.

On the other hand, mathematical tests for the approach to near linear dependence of a potentially overcomplete set are available (Lykos and Schmeising, 1961), so it is possible to use as building blocks atomic functions centered on many nuclei. The fact that many different choices can be made that would lead to equivalent representations of molecular orbitals focuses attention on an essential and still open question; namely, What choice of distorted orbitals will permit maximum transferability of information about the localized system from one molecule to another?

At the moment there are three distinct procedures being used: (1) a Slater-type orbital representation which is optimized for an appropriate valence state of the corresponding free atom, possibly with the additional degree of freedom of adjustability of the over-all scale; (2) the parameters which are in fact integrals over the distorted atomic orbitals without ever specifying the explicit form of those orbitals, possibly with the additional degree of freedom of adjustability of the over-all scale; and (3) a combination of procedures (1) and (2).

The first procedure, where a particular choice of orbitals is made, perhaps adjusted in scale empirically, and used as a basis for an essentially *ab initio* calculation with some assumed core description, is not very widely used. An elaborate and detailed examination of unsaturated hydrocarbons by Ruedenberg (1961) falls into this category. The very limited basis set of atomic orbitals he was obliged to use meant that the numerical results were of semiquantitative significance. However, he was able to resolve the parameters into two classes according to whether they were sensitive to local environment in the molecule only or involved more long range interaction. The former depend essentially on nearest neighbor geometry only, while the latter depend on the over-all geometry of the molecule. A more extensive set of calculations was done by Gladney (1963) who concerned himself with the benzene, naphthalene, anthracene, and phenanthrene molecules. He included all overlap and the complete electron repulsion supermatrix, again with a minimal basis set of Slater orbitals. Although he took the nearest neighbor resonance integral as an empirical parameter, he notes that a theoretical estimate would have very likely done as well. Finally, the treatment of benzene by Moskowitz and Barnett (1963) should be mentioned here, where an extensive pi-electron configuration interaction calculation was done with an attempt to include all integrals allowing for a different scale for the Slater $2p\pi$ and Slater $2p\sigma$ orbitals. They expressed concern over the fact that there seemed to be no a priori way of determining which of the possible configurations should be included.

The second procedure, where the explicit form of the distorted atomic orbitals is never specified, is the procedure most widely used and is the basis of the Pariser–Parr–Pople method. All the parameters are handled as empirical quantities with the possible exception of the Coulomb repulsion integrals involving non-nearest, or non-next nearest neighbor centers. These are estimated using a charged sphere or closely related method. Such a procedure is justifiable on the grounds that the operator involved is simple in form and the asymptotic form of the interaction is well understood. The complication of correlation becomes more and more important with the increasing proximity of the two centers involved, and it is precisely for this reason that the empirical element becomes important in assessing electron repulsion.

An essential difficulty remains, however, in that the assumption of zero differential overlap in dealing with the two-electron integrals seems tantamount to the use of Löwdin orthogonalized orbitals. Accordingly, the one-electron integrals need to be examined on the same basis. In the particular case of benzene, it was shown that if the empirically evaluated one-electron integrals are consistently interpreted as being over Löwdin orthogonalized orbitals, $X_i^\lambda$, then the matrix whose elements are the one-electron integrals over the $X_i^\lambda$ needs to be transformed to a matrix whose elements are the one-electron integrals over the localized $X_i$. Then a systematic expansion of the many-center operator $\mathbf{H}_{\text{core}}(i)$ as a sum of many one-center operators plus the kinetic energy operator will permit a resolution of the empirically evaluated one-electron integrals into a sum of quantities, each of which can be identified with a particular center in the molecule. Thus, it is clear that the empirically evaluated one-electron integrals in the Pariser–Parr–Pople method depend on the geometry of the molecule in two distinct ways: (1) the Löwdin transformation matrix which depends on all the overlaps between the atomic orbitals used as a basis; and (2) the operator $H_{core}(i)$ which includes the potential due to the non-pi part of the molecule. While the resolution of $H_{core}(i)$ may be done without explicitly specifying the form of the atomic orbitals, the Löwdin transformation matrix requires that the overlap integrals be known. For an internuclear distance of 1.40 Å (the nearest neighbor distance in benzene in its ground state), the overlap integral takes on the values 0.25, 0.33, or 0.38 according to whether the distorted atomic orbitals are represented by one Slater orbital with scale optimized for the free carbon atom, the Hartree–Fock orbital for the free carbon atom, or an approximation to the Hartree–Fock pi orbital for the methyl radical, respectively. It seems clear that the situation here is far from being in a satisfactory condition. The clever idea presented by Berthier and co-workers (1963) of using atomic kinetic energy to scale the orbitals appropriate for one-electron integrals may provide a way out of the problem. This resembles the Slater–Zener calibration of the Slater–Zener orbitals. A similar approach was used by Flurry and Lykos (1963a) in assessing the effect of substituting a methyl group for a proton attached to a carbon atom.

The third procedure involves some combination of using empirical values for some integrals, without explicitly specifying atomic orbital forms, while using appropriately distorted atomic orbitals to aid in evaluating the remaining integrals. A refinement of the Pariser–Parr–Pople method, where overlap is explicitly included, would fall into this category. In the case of the Coulomb repulsion integrals, a technique used for some time in this laboratory and recently also proposed by Berthier and co-workers (1963) is to use a single Slater orbital scaled to give a reasonable one-center (or empirical atomic) repulsion integral as a basis for computing all the two-center repulsion integrals. Thus one is assured of reasonable values at the united atom and separated atom limit. Whether such an interpolation scheme is adequate for the intermediate integrals is open to question. In the case of hydrocarbons, for example, the calculated difference between the one-center and the nearest neighbor repulsion integral is too small when compared with the empirical value for that difference. Perhaps the use of more appropriate distorted atomic orbitals will decrease the apparent discrepancy. Otherwise a function of internuclear distance, which assesses the decrease in correlation energy with increasing internuclear distance, may have to be used, such as that proposed by Kolos (1957) or by Julg (1959). There is another problem which remains, however, and that is the question of the adequacy of zero differential overlap in systems which include heteroatoms and/or nontrivial variations in pi-electron charge density around the molecule. In this regard it might be more realistic to use the Mulliken approximation in a systematic fashion, especially since the Mulliken approximation can be interpreted as the first term in a converging series representation of the electron repulsion integrals (Ruedenberg, 1951).

In the case of the one-electron integrals the situation is much more complex because of the operator $\mathbf{H}_{\text{core}}(i)$. The idea of empirical evaluation of the one-center one-electron integrals (as well as the one-center two-electron integrals) by appeal to physical properties of the corresponding free atom is interesting and possibly useful as a guide. However, such a procedure leaves open the question of how one is to assess the changes in these parameters in molecule formation. Also such a procedure presupposes that the resolution of $\mathbf{H}_{\text{core}}(i)$ into a sum of one-center terms plus a kinetic energy operator can be effected in a reasonably accurate fashion. As pointed out by Berthier *et al.* (1963), although such a procedure is used with some apparent success in dealing with complex molecules, it seems to break down when applied to the simplest prototype which brings in two-center one-electron integrals. In fact, the case he considers, the formaldehyde molecule, also serves to illustrate the large difference that results according to whether penetration integrals which enter as a consequence of such an expansion of $\mathbf{H}_{\text{core}}(i)$ are ignored or are included in heteronuclear molecules. The role of penetration integrals has also been explored by Gladney (1963). Thus the least well-understood parameters are the two-center one-electron integrals, the so-called resonance integrals which Mulliken calls $\gamma_{pq}$; Pariser, Parr, and Pople call $\beta_{pq}$; and, more recently, Berthier designates as $\varepsilon_{pq}$. Hopefully some of the *ab initio* work now under way will be interpretable in a manner which will shed considerable light on the meaning and structure of these parameters.

Some of the physical properties used in the empirical evaluation of integrals over distorted atomic orbitals refer to the molecule in a condition resembling its ground state. Nuclear and electronic paramagnetic resonance properties fall into this class. Ultraviolet spectra, however, yield information about energy differences between different states. Now it may be that the same distorted atomic orbitals may be used as a basis for characterizing the molecule in each of several low-lying electronic states. However, calculations on simple model systems (Miller and Lykos, 1962) indicate that the atomic distortion undergoes considerable change on molecular excitation. Thus a recent redetermination of the benzene resonance integral is interesting in that horizontal correlation seems to have been taken into account in part; however, the number produced is really some sort of average over states and perhaps not the best one to use in assessing any given state (Anno and Sado, 1963).

Also, recent experimental work, which shows the change in nuclear configuration of benzene in going from the ground state to a low-lying triplet, focuses attention on the fact that the effect of changes in geometry will need to be examined in assessing empirically the values of the one- and two-electron parameters (de Groot and van der Waals, 1963).

Finally, there will need to be provision for allowing the core to relax in reaction to a calculated charge distribution, which is different from that for which the core description initially selected was appropriate. Prescriptions for estimating this effect have been provided by Brown and Heffernan (1960) and Hoyland and Goodman (1962), and more recently, in a different context, by Hinze *et al.* (1963) and Ferreira (1963).

## V. Areas of Application, Old and New

Use of the pi-electron approximation can be classified into several somewhat overlapping and broad categories. These may be ordered according to time of appearance, starting with the first use, roughly as follows: reactivity criteria, electronic spectra, geometry, dipole moments, magnetic effects, and excited states and internal conversion.

### A. Reactivity Criteria

A recent note by B. C. Webster, "Comparison of Some Theoretical Indices of Chemical Reactivity" (1963), summarizes very succinctly the current situation with regard to theoretical reactivity criteria. He points out that it has been necessary to define reactivity indices appropriate to a given class of reaction, and he classifies the rather large number of indices that have been introduced according to whether they should best apply to reaction at a stage prior to the transition state or to reaction at a stage beyond the transition state, or whether they imply a specific reaction mechanism to be operative. Webster suggests that, of the many indices at present defined, the following be retained: pi charge density, atom polarizability, pi-bond order, free valence, localization energy, *para* localization energy, and the reactivity number. He concludes that the growth of the reactivity index tree needs to be curtailed and a thorough examination made of the roots, perhaps indeed from a totally different viewpoint, if the extremely complex problem of the chemical reaction is ever to succumb to any realistic solution. Considering the fact that the primitive reaction in the gas phase between the hydrogen molecule and the hydrogen atom has not yet been adequately treated, it seems clear that there is much work to be done at both the *ab initio* and the semiempirical levels.

A refreshingly direct approach to reactivity, using as a vehicle the reaction between the ion $NO^+$ and the anilinium ion, has been presented by Bishop and Craig (1963). The relative orientation of the two species was explicitly taken into account. Also the interaction of two ethylene molecules has been assessed by Koutecky and Poldus (1963) who performed an extensive configuration interaction calculation.

Considerable attention is now being given to the reactivity in excited states of molecules (Land and Porter, 1963; Beckett and Porter, 1963; Fukui *et al.*, 1961; Mori, 1962). This serves to focus attention on the fact that the relative reactivities of unique positions in an excited state of a molecule may differ radically from the pattern characterizing the ground state. For example, the bonding pi molecular orbital describing the pi electrons in formaldehyde is likely to be skewed toward one end of the molecule (Peters, 1963a). The requirement that the corresponding antibonding pi molecular orbital be orthogonal to that bonding orbital usually constrains the antibonding orbital to be skewed in the opposite sense. Thus, excitation of an electron from the bonding to the antibonding molecular orbital will lead to an intra molecular charge transfer and possibly to a corresponding change in reactivity site. A common procedure for characterizing excited states is to use the occupied and by-product virtual orbitals found by a variational procedure for the ground state. The Roothaan open-shell self-consistent method, however, permits the optimization of the excited state description itself (Flurry and Lykos, 1963b; Goodman and Hoyland, 1963). The change in geometry of the molecule on excitation also may well play an important role in determining the values of reactivity indices in the excited state.

### B. Electronic Spectra

Many calculations on particular systems have been performed recently, and most of these have involved the straightforward application of existing methods. The work of Gouterman *et al.*, (1963) on the porphyrins is interesting from the point of view of the pi-electron approximation in that the pi-group wave function was resolved on the basis of a four-orbital model. Jaffe and Chalvet (1963) concerned themselves with the interaction of perpendicular pi-electron systems and were able to resolve an apparent spectroscopic anomaly by explicitly considering group MO's rather than focusing attention on nearest neighbor distorted atomic orbitals only.

Hush and Rowlands (1963) considered an interesting series which involves a neutral hydrocarbon and the corresponding negative and positive ions. Since the formation of positive and negative ions represents a strong perturbation of the parent neutral molecule, studies of this kind can shed light on the adequacy of a simple approach in assessing lesser perturbations such as electronic excitation.

Transitions involving a change in the number of pi electrons are of particular interest as a basis for studying the pi electron approximation. Excitation of core lone pair or of core bonding electrons into the peel leads to a significant change in the core potential. Anno (1958) has already extended the Pariser–Parr–Pople theory to the case where lone pair electrons are excited into the peel, and recent polarization studies of phosphorescence spectra of *N*-heterocyclics (El-Sayed and Brewer, 1963) have made possible estimates of the extent of mixing of excited configurations corresponding to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Theoretical assessment of these phenomena transcends the usual pi-electron approximation which involves the assumption that the core remain essentially unchanged on peel excitation.

Electron impact spectroscopy, an exciting new kind of spectroscopy, is being developed by Kuppermann and co-workers (see Kuppermann and Raff, 1963). The usual optical excitation selection rules do not operate for excitation by slow electron scattering, and many hitherto undiscovered excited electronic states are being uncovered.

### C. Geometry

The geometry of the molecule has an effect on the pi-electron structure in that the potential due to the core depends on the geometry. The nuclear arrangement in the core depends not only on the core electrons, however, but on the distribution of the pi electrons as well.

Thus far, the procedure has been to separate the effect of core and peel electrons on geometry and to assess nearest neighbor distances between bonded atoms by using a semiempirical Morse curve for the core or "sigma", bond and a bond order–bond length empirical relationship for the "pi" bond (Dewar and Schmeising, 1960).

Even if such a procedure were adequate, however, it is not sufficient to determine uniquely the over-all geometry of the molecule. Additional information is needed such as some non-nearest neighbor distances or bond angles.

Hameka and co-workers (see Kim and Hameka, 1963; de la Vega and Hameka, 1963) and, more recently, Coulson (1963) have concerned themselves with calculation of valence angles in aromatic molecules. A number of simplifying assumptions characterize both works. Nevertheless the advent of the large, fast, digital computer makes it possible to consider the vibrational motion of fairly complex molecules so that additional empirical information will be made available to help in checking estimates of bending force constants.

The bent excited state of acetylene (Burnelle, 1961) is a familiar example of a significant change in geometry on excitation. In addition, there now seems to be clear evidence that benzene changes its symmetry from $D_{6h}$ in the ground state to $D_{2h}$ in a low-lying triplet (de Groot and van der Waals, 1963).

The roles of atomic valency-state energies and of ionicity have been examined from the point of view of their effect on geometry (Wilmshurst, 1960; Hutchinson, 1962). Also some attention has been given to the application of the Jahn–Teller theorem to conjugated ions and radicals (Hobey and McLachlan, 1960; Coulson and Golebiewski, 1962; Ham, 1962).

A recent treatment of the entire molecule as a many-body problem, thus stepping outside the pi-electron approximation, was aimed at an *ab initio* determination of geometry (Hoffmann, 1963). Based on the observation that approximate *ab initio* calculations on diatomic molecules seem to be effective in predicting equilibrium internuclear distance while still in error in predicting total energy, Hoffmann devised an extended Hückel theory designed to determine the conformation, or geometry, of saturated hydrocarbons as well as unsaturated hydrocarbons. He concludes that the geometry of a molecule appears to be its most predictable quality. He also advances, as a justification of the Hückel method, Slater's observation (1963b) that the electron repulsion terms and nuclear repulsion terms almost cancel each other out by difference, leaving the energy essentially determined by the sum of the one-electron energies of the Hartree–Fock Hamiltonian. Pople and Santry (1963–1964) have recently developed a similar extended Hückel theory. Also Brown and Harcourt (1963) considered the electronic structure of $A_2Y_4$ molecules on a similar basis.

The subject of deviation from planarity of aromatic systems was summarized by Ferguson and Robertson (1963), while the stereochemistry of hydrocarbon ions was considered by Lorquet (1963).

### D. Dipole Moments

The usual approach to the assessment of the electric dipole moment of a complex molecule has been to consider as additive bond group and lone pair moments characterizing the core, plus an additional contribution due to the delocalized pi-electron system (Sparatore, 1960: Maeda, 1962; Lounsbury, 1963). These molecular fragment or bond moments are estimated empirically, although the resolution into core and peel contributions is fraught with uncertainty. For example, the resolution of the dipole moment in formaldehyde into core and peel parts requires knowledge about the pi-electron distribution, and recent treatments of carbonyl systems bring out the rudimentary state of knowledge in this regard. The observation is sometimes made that it is highly artificial to attempt to resolve the molecular dipole moment, an observable, into a sum of contributing parts, each not an observable. The apparent futility of such an attempt is underscored by reference to molecules like $CH_3F$ and $CHF_3$, where the total dipole moments are 1.81 and $1.61\,D$, respectively. Should the tetrahedral symmetry and CH and CF bond lengths be the same in both $CH_3F$ and $CHF_3$, then the observed moments should be the same in magnitude for both molecules if the resolution into bond moments is meaningful. The fact that the observed moments are not the same, however, is at least in part due to differences in geometry of the two systems.

Insofar as the sigma–pi separation is concerned, the resolution into sigma and pi contributions is well defined. The further resolution of the core on this basis also may be effected in a well-defined way. A recent analysis of SCF wave functions into localized molecular orbitals constitutes one possible approach (Peters, 1963b). A localized Hartree–Fock procedure suggested by Gilbert (1964) is yet another. Further experience and usage will determine the future development of such empiricism.

### E. Magnetic Effects

The rapid increase in the number of experiments being done involving the magnetic properties of molecules, radicals, and ions has produced an enormous amount of information to be analyzed on the basis of the underlying theory. There are essentially two kinds of effects observed: nuclear paramagnetic resonance (NMR) and electron paramagnetic resonance (EPR). Both the position of the resonance line and its structure contain information about the electron distribution in the molecule as well as about the nuclear configuration. The principal nuclear constituents of naturally occurring carbon and oxygen have nuclear spin of zero and hence contribute nothing to nuclear paramagnetic resonance as a direct effect nor to electron paramagnetic resonance via a perturbing effect. Fortunately, advances in technology have made it possible to introduce isotopes of carbon and oxygen with finite spin as magnetic probes in selected parts of molecules, and a variety of effects can be studied thereby in both NMR spectroscopy (Lauterbur, 1963; Hobgood *et al.*, 1963) and EPR spectroscopy (Bolton, 1963; de Boer and Mackor, 1963).

From a quantum mechanical point of view, what is usually done is to regard the magnetic effects as perturbations. The majority of the magnetic interactions assessed by NMR and EPR techniques are sufficiently mild that perturbation theory works extremely well (Karplus and Kolker, 1963). Also McWeeny and Mizuno (1961) have very neatly resolved the space and spin parts of the density matrix representation for any system.

Unfortunately, the theoretical assessment of magnetic phenomena has not been part of most chemists' training so that much of the information contained in the large amount of data being collected is not extracted. In the case of NMR high resolution nuclear spin–nuclear spin coupling constants, however, the analysis can be organized conveniently on readily available computers (Hobgood *et al.*, 1963), and programs such as that written by Whitman (1962) are widely used by nonquantum chemists as an aid in determining molecular structure. A large mass of empirical information about the coupling constants comes out as a by-product (Smith and Kriloff, 1963). Similar computer programs exist for EPR hyperfine structure.

A recent symposium on high resolution NMR spectroscopy brings out some of the complications involved in the theoretical analysis of NMR spectral characteristics (Pople, 1962; Hall *et al.*, 1962). Since then there has appeared an NMR analysis of aryl methyl carbanions which is interesting in that, even in this case of no heteroatoms, the Roothaan procedure is superior to the Hückel method (Sandel and Freedman, 1963). The whole question of NMR shifts and the electron density distribution in aromatic systems was reexamined by Schaefer and Schneider (1963), while the question of the relative signs of fluorine spin coupling constants in aromatic compounds seems to have been settled (Evans, 1963). The carbon–carbon spin-coupling constants in some characteristic C–C bond types have been examined by Frei and Bernstein (1963). Even a molecule as complex as purine has been characterized, with theory and experiment working hand in hand (Matsurra and Goto, 1963; Schweizer *et al.*, 1963).

The resolution into long range weak pi-electron coupling and short range strong core-electron coupling is a natural and fruitful consequence of the pi-electron approximation. Once again, accurate *ab initio* calculations on appropriate prototype systems would be very helpful in relieving some of the uncertainty in the empirical analyses.

In the case of electron paramagnetic resonance studies involving radicals with one odd electron, *ab initio* work is much further along since significant results can be found by considering relatively simple molecular fragments (Higuchi, 1961, 1963). Also the question of the effect of electron densities at nearest neighbors on hyperfine coupling constants has been explored further (Colpa and Bolton, 1963). In addition, the relative importance of hyperconjugation and spin polarization has been examined in a system where the former effect appears to dominate the latter (Colpa and de Boer, 1963).

Vincow and Johnson (1963) have exploited the use of the second moments of electron spin resonance hyperfine spectra in an analysis of the benzyl radical and conclude that this is indeed a sensitive method.

The now classical magnetic analysis of the zero-field splitting of the phosphorescent or triplet "state" of the naphthalene molecule has been presented again by Hutchison (1963) together with further application of the technique to a distinctly different kind of aromatic system. In addition, an experimental study of the temperature dependence of the naphthalene triplet between 1.65 and 4.2°K (Hornig and Hyde, 1963) has confirmed the theoretical prediction about the absolute signs of the zero-field splitting parameters.

The theoretical analysis of zero-field splitting leading to the conclusion that the effect is due mainly to the dipole–dipole interaction of the two unpaired electrons seems to be correct (Boorstein and Gouterman, 1963; Chiu, 1963), and the recent elegant treatment by Geller (1963) of some of the difficult integrals involved will permit more comprehensive *ab initio* work on prototype hydride molecular fragments and related systems (Higuchi, 1963).

The recent semiempirical study of some nitrenes (Smolinsky *et al.*, 1963) was of interest in that not only are the three lowest states resolved because of zero-field splitting but also because one of the unpaired electrons is highly localized in the core while the other is in the peel. Of course another example of coupling between a doublet peel and a doublet core is the situation that arises when a lone pair electron is excited into the peel, i.e., an $n \rightarrow \pi^*$ excitation. Unfortunately, unless the experiment is performed with oriented molecules, the magnetic resonance spectrum involving transitions between components of the triplet is not as rich in detail as the magnetic spectra of molecules with one odd electron.

### F. Excited States and Internal Conversion

Recent emphasis on reactivity in excited states together with improved spectroscopic techniques are fostering a rapidly growing emphasis on studies on the structure of and transitions between excited states. An example is the work of Hunt *et al.* (1962) on uncovering pathways of internal conversion between excited states of aromatic hydrocarbons. Krishna and Goodman (1962) emphasize the role of the ground state in assessing singlet–triplet transition probabilities. Coon *et al.* (1962) reconsider the Franck–Condon principle and the structure of excited electronic states of molecules.

Hadley *et al.* (1963) studied the temperature dependence of the spectrum of naphthalene, together with isotopic substitution effects, to resolve the radiationless transitions. They found the transition from the first excited singlet to be temperature independent but the decay of the triplet to require activation, probably through vibrational excitation.

The photo-induced conversion of allyl-type to alkyl-type radicals in irradiated polyethylene was considered by Ohnishi *et al.* (1963). The hydrogen atom shift reaction was monitored by observation of the EPR spectrum.

To illustrate a different kind of data becoming available, Braun *et al.* (1963) conducted a detailed examination of the dependence, on successive substitution in a homologous series, of fluorescence efficiencies.

Finally, there have been some experiments performed to shed light on the controversy over the mechanism of energy transfer in crystals of conjugated systems (Eisenthal and Murashige, 1963), and the results suggest that the formation of donor–acceptor complexes need not be postulated to support the idea of triplet–triplet transfer.

## VI. Conclusion

The structure of the pi-electron approximation is well understood on the basis of the underlying quantum mechanics. Semiempirical elements are being systematically introduced in the theory in a way which permits an understanding of the basic parameters in terms of the underlying quantum mechanics.

While "back of an envelope" estimates are still the most convenient kind to make, the advent of the electronic digital computer places at the disposal of any interested scientist, with only a little more effort, the full power of the most sophisticated form of pi-electron theory extant. It is no longer necessary for the more casual user of pi-electron theory to be restricted to using methods whose validity is open to serious question.

With the number of different kinds of phenomena involving conjugated systems steadily increasing, it becomes more and more necessary to interpret experimental results in terms of the underlying and unifying quantum mechanics.

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# Recent Developments in the Generalized Hückel Method

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## I. Introduction

The Hückel method has been used quite successfully for calculating the electronic structure and electronic spectra of certain types of molecules, specifically of complex unsaturated molecules. However its usefulness has been to correlate or estimate observed phenomena, not to predict quantitatively the unknown properties of complex molecules. During the last decade, there has been a great deal of work reported, in an effort to obtain better agreement with experiment.

In particular, the way that Pariser and Parr combined the Hückel method with the Goeppert-Meyer and Sklar method or ASMO (antisymmetric molecular orbitals) method, and also with the concept of atoms-in-molecules of Moffitt for the quantitative correlation and prediction of several properties of complex unsaturated molecules, has proved to reduce greatly the mathematical and computational complexities and at the same time to correct some inherent errors in usual nonempirical calculations. This we shall hereafter call the "generalized Hückel method" following Parr (Parr and Ellison, 1955; Parr, 1958), while the original one (Hückel, 1931, 1932) may be called the "formal Hückel method."[1]

In the following two sections, some of the approximations and assumptions incorporated into the generalized Hückel method will be reexamined first, and then several devices will be described to improve some weaknesses of this method. In Sections IV and V, applications of an improved method to ethylene will be illustrated in detail, where most of the work was taken from the author's recent publications (I'Haya, 1960a,b). Section VI contains a scheme for evaluating two-center repulsion integrals. Further applications to large molecules are made in Section VII, and basic prescriptions of an improved method are restated in the final section.

## II. Outline of the Generalized Hückel Method

In well-known 1953 papers, Pariser and Parr presented a way to synthesize some of the best elements of the more complex and more purely theoretical approaches than the formal Hückel method and some of the best elements of the empirical approaches in order to rationalize the electronic structures and spectra of complex unsaturated molecules (Pariser and Parr, 1953a,b). This approach may be called the generalized Hückel method as mentioned before. This method may be characterized as having the following assumptions and procedures.

(1) Only $\pi$ electrons are explicitly considered. That is, "the $\pi$-electron approximation is invoked."

(2) The $\pi$-electron wave functions are built from $2p\pi$ atomic orbitals (AO) $\chi_p$, being combined linearly to give molecular orbitals (MO) $\phi_i$

$$\phi_i = \sum_p \chi_p C_{ip}, \tag{1}$$

then $n$-electron wave functions for molecular state $\Lambda$ are formed as antisymmetrized products $\Phi_m$ of appropriate molecular orbitals $\phi_i$ and spin functions (ASMO) as follows:

$$\Phi_m(\Lambda) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \phi_2(1)\alpha(1) \cdots \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \phi_2(2)\alpha(2) \cdots \\ \cdots\cdots & \cdots\cdots & \cdots\cdots \end{vmatrix},$$
$$= (1\bar{1}2\cdots) \tag{2}$$

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[1] The author regrets that he has had no opportunity to refer to Professor Parr's recent book, which contains a detailed review of the generalized Hückel method (see Parr, 1963).

and finally actual wave functions for the molecular $\Lambda$ state are expressed as linear mixing of those $\Phi_m(\Lambda)$ (the configuration interaction or CI procedure):

$$\Psi(\Lambda) = \sum_m \Phi_m(\Lambda) A_m . \tag{3}$$

In the SCF (self-consistent field) treatment, one can determine the values of the coefficients $C_{ip}$ by minimization of the total molecular energy, employing a single $\Phi(\Lambda)$ as the representation of the molecular state. When one employs the linear variation method or CI procedure described above, one must use an orthonormal set of $\phi_i$ as a starting molecular orbital, the values of the coefficients $C_{ip}$ being immaterial. For this purpose the Hückel MO is most convenient.

(3) The Hamiltonian operator for the $\pi$-electron system is taken to have the form

$$\mathbf{H}(1, 2, \ldots n) = \sum_{\mu=1}^{n} \mathbf{H}_{\text{core}}(\mu) + \frac{1}{2} \sum_{\mu,\nu=1}^{n}{}' \frac{e^2}{r_{\mu\nu}} . \tag{4}$$

The last term represents electronic repulsions between $\pi$ electrons. $\mathbf{H}_{\text{core}}$, a one-electron Hamiltonian operator, may be defined through reasonable approximations invoked.

(4) The $\pi$-electron energy $\mathbf{E}$ is determined by solving a secular equation

$$|\mathbf{H}_{mn} - \delta_{mn}\mathbf{E}| = 0, \tag{5}$$

the coefficients $A_m$ being determined by solution of simultaneous equations

$$\sum_m (\mathbf{H}_{mn} - \delta_{mn}\mathbf{E}) A_m = 0. \tag{6}$$

Here $\mathbf{H}_{mn} = \int \Phi_m^* \mathbf{H} \Phi_n \, dv$ and $\delta_{mn}$ is the Kronecker symbol.

(5) The matrix elements $H_{mn}$ are expressed in terms of core and electron repulsion integrals over molecular orbitals, and then turn out to be expressible in terms of core integrals over atomic orbitals of the types

$$\alpha_p = \int \chi_p^*(\mu) \mathbf{H}_{\text{core}}(\mu) \chi_p(\mu) \, dv(\mu) \tag{7}$$

and

$$\beta_{pq} = \int \chi_p^*(\mu) \mathbf{H}_{\text{core}}(\mu) \chi_q(\mu) \, dv(\mu) \tag{8}$$

and electronic repulsion integrals over atomic orbitals

$$(pq|st) = \int \chi_p^*(\mu) \chi_s^*(\nu) (e^2/r_{\mu\nu}) \chi_q(\mu) \chi_t(\nu) \, dv(\mu) \, dv(\nu). \tag{9}$$

(6) Procedures for obtaining the integrals (7), (8), and (9) are as follows:

(a) If one deals with unsaturated hydrocarbons, $\mathbf{H}_{\text{core}}$ for electron $\mu$ may have the form (Goeppert-Meyer and Sklar approximation, 1938)

$$\mathbf{H}_{\text{core}}(\mu) = \mathbf{T}(\mu) + \mathbf{U}_p(\mu) + \sum_{q \neq p} \mathbf{U}_q(\mu) + \sum_r \mathbf{U}_r(\mu). \tag{10}$$

Here, $\mathbf{T}$ is the kinetic energy operator, $\mathbf{U}_p$ the potential energy operator due to the $p$th carbon center in the core, and $\mathbf{U}_r$ the potential energy operator due to the $r$th hydrogen atom in the core (more generally, $r$th neutral atom which does not contribute $\pi$ electrons to the system being considered). The AO's $\chi_p$ for which precise forms are not specified in Eq. (1) are now taken to be atomic eigenfunctions of the operator $\mathbf{T} + \mathbf{U}_p$ such that

$$[\mathbf{T}(\mu) + \mathbf{U}_p(\mu)]\chi_p(\mu) = W_{2p}\chi_p(\mu), \tag{11}$$

where $W_{2p}$ is the energy of the electron $\mu$ in the $2p_z$ AO of a carbon 1+ ion in its appropriate valence-state. Further, the potential energy operators $\mathbf{U}_p$ are expressed as

$$\mathbf{U}_p(\mu) = \overline{\mathbf{U}}_p(\mu) - \int \chi_p^*(\nu)\chi_p(\nu)(e^2/r_{\mu\nu})\, dv(\nu), \tag{12}$$

where the bar connotes a potential due to a *neutral* atom. Introduction of these Goeppert-Mayer and Sklar formulations makes $\alpha_p$ of Eq. (7) resolve into

$$\alpha_p = W_p - \sum_{q \neq p} [(pp|qq) + (q:pp)] - \sum_r (r:pp). \tag{13}$$

Here $(pp|qq)$ is the Coulomb repulsion integral between AO's $\chi_p$ and $\chi_q$ and $(q{:}pp)$ and $(r{:}pp)$ are Coulomb penetration integrals between $\chi_p$ and neutral atoms $q$ and $r$, viz.,

$$(q:pp) = -\int \overline{\mathbf{U}}_q(\mu)\chi_p^*(\mu)\chi_p(\mu)\, dv(\mu). \tag{14}$$

The sum over $q$ in Eq. (13) is taken over all atoms other than $p$th that contribute $\pi$ electrons in the molecule being considered, while the sum over $r$ is over all atoms which are uncharged in the core (hydrogen atoms in unsaturated hydrocarbons for example).

(*b*) Two-center integrals $\beta_{pq}$ of Eq. (8) are usually treated as empirical parameters to be fixed through the molecular spectral data and are set equal to zero for nonbonded atom pairs.

(*c*) Overlap integrals

$$S_{pq} = \int \chi_p^*(\mu)\chi_q(\mu)\, dv(\mu) \qquad (p \neq q) \tag{15}$$

are set equal to zero. This corresponds to the assumption of "formal neglect of differential overlap" or simply "zero differential overlap," and leads to a great reduction in the number of electronic repulsion integrals over atomic orbitals to be evaluated:

$$\chi_p^*(\mu)\chi_q(\mu) = 0 \qquad (p \neq q). \tag{16}$$

(*d*) Thus, the only electronic repulsion integrals which appear in the final expressions are of the Coulomb type, of which the one-center integrals $(pp|pp)$ are calculated from atomic valence-state ionization energies $I_p$ and atomic valence-state electron affinities $A_p$ by use of the formula.

$$(pp|pp) = I_p - A_p. \tag{17}$$

(*e*) The second type, the two-center Coulomb repulsion integrals $(pp|qq)$, $p \neq q$, are obtained from empirical fitting of both theoretical or pseudoclassical values for large internuclear distances and empirical one-center values $(pp|pp)$ given by Eq. (17). Pariser and Parr first employed an equation of the form

$$mr + nr^2 = \tfrac{1}{2}[(pp|pp) + (qq|qq)] - (pp|qq) \tag{18}$$

in which the constants $m$ and $n$ are determined by fitting $(pp|qq)$ calculated from the uniformly charged sphere model formula (Pariser and Parr, 1953b). Later Pariser treated both $(pp|pp)$ and $(pp|qq)$ as entirely empirical parameters in his polyacene calculation (Pariser, 1956).

(*f*) Penetration integrals are computed purely theoretically using appropriate atomic orbitals, or estimated through suitable approximations.

Up to this time quite a number of works have been published to improve the framework of the generalized Hückel method. The characteristics stated above are just the point that Pariser and Parr suggested and also the requirements that would be desirable to make calculations of large molecules manageable. The more detailed elucidation and critique and also some improvements that will have to be made are given in the following section.

## III. General Criticisms and Some Improvements on the Generalized Hückel Method

We shall now comment on the generalized Hückel method outlined before. Assumption (1) in the preceding section has been reexamined by several authors under the title of separability theorem of electron pairs (McWeeny, 1954, 1956; Lykos and Parr, 1956a,b; Parks and Parr, 1958;

Arai, 1960; Löwdin, 1961). The results obtained so far make it seem plausible that this assumption could be fitted into an exact theory when some conditions of separability of $\sigma$ and $\pi$ electrons are satisfied. Whether the assumption is rigorously justified in more general cases, however, remains to be more thoroughly investigated. In Section V we shall examine how to take account of $\sigma$ electrons through a scheme that takes into account the $\sigma$–$\pi$ configuration interaction.

We shall skip over procedures (2) to (4) of the preceding section, admitting that we will not be able to escape from explicit consideration of electron spins and electron repulsions, without which we cannot obtain singlet–triplet split. What starting molecular orbitals are to be used and how much configuration interaction should be included are far-reaching problems and have not been hitherto solved.

Before commenting on assumption (5), we should mention some problems that been have a bottleneck of the generalized Hückel method. The first question is: Can parameters obtained from the theory of electronic spectra be used to predict ionization energy? Parr and Pariser (1955), after they carefully investigated the problem on the electronic structure and spectrum of ethylene, showed that the vertical ionization energy, computed with the parameters which are considered to be optimum for the calculation of the electronic excitation energies, comes out much higher than the observed value. The generalized Hückel method in general results in higher ionization energies to the extent of about 2 to 4 eV. This failure has been quite disturbing (ionization energy catastrophe) in contrast with its remarkable success in accounting for the electronic spectra. There have been several papers that have treated, independently of electronic spectra, ionization energy increments of unsaturated molecules relative to a reference molecule quite successfully; we need not dwell on these calculations because our interest is an *absolute* prediction (Hall, 1952; Pople, 1953; Hush and Pople, 1955; Matsen, 1956; Hedges and Matsen, 1958).

The essential feature is that, in the absolute calculation of vertical ionization energies, the core integrals over atomic orbitals of the type

$$\int \chi_p^*(\mu)\mathbf{H}_{\text{core}}(\mu)\chi_p(\mu)\, dv(\mu)$$

no longer cancel out, while they cancel out in the formulation of the low-lying electronic energy levels. Since this core integral $\alpha_p$ depends to a significant extent upon the *core-states* of all the centers in the molecule, it will not be sufficient to consider $\alpha_p$ as a fixed basic parameter in our scheme. Then the question is: Is it correct to use the same core parameters for the calculation of the energies of both ground and ionized states? Put another way: Is it correct to use fixed values of the effective nuclear charge for both states? For example, in the positive molecular ion the charge clouds must presumably be less spread out than those of the neutral molecule due to the decrease in the electronic repulsion.

Recently the author presented a new approach for determining the molecular integrals, in which an allowance is made for the change in the effective nuclear charge of a nucleus accompanying the variation of the electron distribution around the nucleus (I'Haya, 1960a). The like idea was inaugurated by R. D. Brown and co-workers in their series of elaborate calculations on conjugated heterocyclic systems (Brown and Penfold, 1957; Brown and Heffernan, 1958; Heffernan, 1959). The detailed elucidation of the improved method will be given in the subsequent sections. It should be added here that like improvements on the Koopmans' theorem in SCF formulation have been made quite recently by Hoyland and Goodman (1960, 1962).

A step further, one may ask: Can the method correlate and predict many diverse properties of molecules simultaneously with common parameters? Few attempts have been made to challenge this very interesting problem (Pople, 1953, 1957); in particular, Lykos (1954, 1961) showed that a set of semiempirical parameters can be assigned to reproduce the electronic spectrum, ionization energy, electron affinity, resonance energy, and anisotropy of the diamagnetic susceptibility of benzene simultaneously. There still remains a question, however: Can the parameters found for one molecule be carried over to another molecule? As a first approximation the answer would be "yes," but always small and sometimes considerably drastic adjustments should be anticipated. This situation is caused, in the main, by the fact that it is not clear at this time what defining resolution of $\mathbf{H}_{\text{core}}$ would be most adequate for this kind of semiempirical theory. Once the more precise understanding of what expression $\mathbf{H}_{\text{core}}$ must have and then what dependence $\mathbf{H}_{\text{core}}$, and hence $\alpha_p$ and $\beta_{pq}$, will show on the nature and arrangement of the core would be obtained, one will be able to incorporate the more workable parameters into the theory, which can be carried over from molecule to molecule.

The author's present view on this matter is as follows: One should try to get meaningful expressions for $\alpha_p$ and $\beta_{pq}$ even within the framework of the Goeppert-Mayer and Sklar formulation. Certain simplifications are of course necessary to make theoretical calculations possible. We are ready to employ Eq. (13) for the theoretical estimate of $\alpha_p$. It was shown by Pariser and Parr (1953b) that the theoretical expression for another core integral $\beta_{pq}$, when atoms $p$ and $q$ are alike, takes the form

$$\beta_{pq} = \sum_{l \neq q} \{S_{pq}[(ll|qq) + (l:qq)] - (ll|pq) - (l:pq)\} + \sum_{r} [S_{pq}(r:qq) - (r:pq)] \tag{19}$$

with the definition (Mulliken, 1949)

$$\beta_{pq} + (S_{pq}/2)(\alpha_p + \alpha_q) = \int \chi_p^*(\mu)\mathbf{H}_{\text{core}}(\mu)\chi_q(\mu)\, dv(\mu). \tag{20}$$

Further, if one employs Mulliken-type approximations (Mulliken, 1949),

$$(pp|pq) = \tfrac{1}{2}S_{pq}[(pp|pp) + (pp|qq)], \tag{21}$$

$$(pq|pq) = \tfrac{1}{2}S_{pq}^2[(pp|pp) + (pp|qq)], \tag{22}$$

$$(s:pq) = \tfrac{1}{2}S_{pq}[(s:pp) + (s:qq)], \tag{23}$$

the complexity of computations is greatly reduced:

$$\beta_{pq} = -\tfrac{1}{4}S_{pq}[(pp|pp) + (qq|qq) - 2(pp|qq) + (p:pp) + (q:qq) - (p:qq) - (q:pp)], \tag{24}$$

and if the orbitals $\chi_p$ and $\chi_q$ are alike one gets, finally,

$$\beta_{pq} = -(S_{pq}/2)[(pp|pp) - (pp|qq) + (p:pp) - (p:qq)]. \tag{25}$$

Here it should be noted that the quantity $\beta_{pq}$ is entirely intrinsic for the bond $p$—$q$ and does not depend upon other centers. This certainly provides us with a theoretical justification for a priori determination of $\beta_{pq}$ and also for its applicability from molecule to molecule, but the problem of how to estimate empirically the one-center Coulomb penetration integral $(p:pp)$ that appeared in Eq. (25) remains unsettled. If one employs purely theoretical values for all integrals in Eq. (25) one will obtain too high negative values for $\beta_{pq}$ (for example, about $-4.6$ eV for ethylene; cf. Section IV). This we shall return to later.

Now returning to Eq. (20), the alternative expression for $\beta_{pq}$ may be obtained when the Goeppert-Mayar and Sklar assumption of Eq. (11) is used (this assumption has been reexamined recently by Stewart, 1959a):

$$\beta_{pq} = (S_{pq}/4)\left\{W_p + W_q - \int \chi_p^*(\mu)[\mathbf{T}(\mu) + \mathbf{U}_q(\mu)]\chi_p(\mu)\, dv(\mu) - \int \chi_q^*(\mu)[\mathbf{T}(\mu) + \mathbf{U}_p(\mu)]\chi_q(\mu)\, dv(\mu)\right\} \tag{26}$$

and when $p$ and $q$ are alike

$$\beta_{pq} = (S_{pq}/2)\left\{W_p - \int \chi_p^*(\mu)[\mathbf{T}(\mu) + \mathbf{U}_q(\mu)]\chi_p(\mu)\, dv(\mu)\right\}. \tag{27}$$

To avoid complicated computations, one may tentatively put the second term in the bracket of Eq. (27) equal to $-W_p$. Then we have

$$\beta_{pq} = S_{pq}W_p, \tag{28}$$

or Eq. (26) reduces to

$$\beta_{pq} = (S_{pq}/2)(W_p + W_q). \tag{29}$$

Strictly speaking, the values of both terms in Eq. (27) are, of course, not equal to each other, though the difference will not be too great.

The relation

$$\left| -\int \chi_p^*(\mu)[\mathbf{T}(\mu) + \mathbf{U}_q(\mu)]\chi_p(\mu)\, dv(\mu)\right| < |W_p| \tag{30}$$

holds for general cases, so that the approximate formulas in Eqs. (28) and (29) are considered to produce a somewhat large value for $-\beta_{pq}$. These considerations for reformulation of two-center core integrals are only tentative and will have to be scrutinized through numerical comparison. At the same time, the workability of these formulas depends upon the type of molecular calculations in which some sort of approximations more or less have to be done. Whether nonneighbor two-center core integrals can be neglected depends also on the size of the molecule being considered and the approximation adopted.

The consequence of the use of zero differential overlap has been examined by several authors (Mulliken, 1949; Fumi and Parr, 1953; Hall, 1954; McWeeny, 1955), though a reliable conclusion has not yet been obtained. Analysis by the use of semilocalized orthonormalized atomic orbitals shows that the Coulomb integrals over atomic orbitals of this kind have just about the same values as for the original nonorthogonalized orbitals, the integrals of other kinds being very small. In this connection, Parr gave a prescription for handling the general benzene-like molecules in terms of the orthogonal atomic orbitals of Löwdin without the zero differential overlap approximation (Parr, 1960). The author's comment on this matter is that there would be no alternative but to admit this assumption in order to make the formidable computation of matrix elements possible, and the evaluation of $\beta_{pq}$, as an exceptional case, should be made *without* that assumption, as stated above. One should, of course, have reservations about simple molecules and heteronuclear systems; several authors have pointed out that the approximation of zero differential overlap is unreliable when applied to such cases (Stewart, 1959b; Coulson and Schaad, 1961).

Concerning assumption (6*d*) in Section II, formula (17) can be derived through incorporations of atoms-in-molecules concepts and atomic valence-state considerations, as has been suggested and fully discussed by Pariser and Parr (1953b). The same authors have pointed out that considerations of this kind lead to Mulliken's original electronegativity definition (Parr and Pariser, 1955). Looking over repeated discussions and successful applications of this formula, one may conclude that the idea is quite sound. It is not clear at this time, however, whether each atom in a conjugated hydrocarbon can be assumed to have a core which does not change in going from one valence-state to another and even under ionization. Heuristic calculations therefore seem to transcend the formulation. In Section V, the method of evaluating one-center core integrals from complete computation of atomic valence-state energies will be given through a somewhat refined prescription that takes account of changes in effective nuclear charges of the corresponding valence-states.

As for procedure (6*e*) in Section II, Pariser and Parr, (1953a,b) introduced nonoverlapping uniformly charged sphere approximations for $\pi$ orbitals to give a formula of reciprocal square roots of distance for two-center Coulomb repulsion integrals. Pople (1953) first employed the $e^2/R$ formula ($R$ is the internuclear distance) for the same integral, but he later turned to the Pariser–Parr formula (Brickstock and Pople, 1954). Since there is no doubt that the two-center repulsion integrals for considerably large internuclear distances have values which are in the vicinity of values that can be obtained by a priori theoretical computations, one should employ purely theoretical procedures or their substitutes for the estimation of these integrals. Some discussions on this matter will be given later, in particular in Section VI.

## IV. Ethylene as a Two-Electron Problem

Several types of calculations will now be carried out to set forth to what extent the generalized Hückel method is quantitatively applicable and whether the proposed improvements described before make the situation better fundamentally or numerically. Here the electronic structure of the ethylene molecule is reexamined within the framework of the $\pi$-electron theory. The same problem has been examined in detail by Parr and Pariser (1955), but the theoretical calculation of the vertical ionization energy has remained a difficult question, as stated before. Therefore, particular attention will be placed on removing some of the uncertainties in the problem of the ionization energy in line with the arguments made in the opening paragraph of Section III.

### A. The Electronic Spectrum

Following assumptions (1) and (2) in Section II, the starting antisymmetrized wave functions of ethylene are for three singlet states

$$\Phi_1 = (1\bar{1}), \qquad \Phi_2 = (2\bar{2}), \qquad \Phi_V = 2^{-1/2}[(1\bar{2}) + (2\bar{1})], \tag{31}$$

and for a triplet

$$\Phi_T = 2^{-1/2}[(1\bar{2}) - (2\bar{1})]. \tag{32}$$

Here $(1\bar{2})$ etc. stand for the Slater determinants constructed from molecular orbitals

$$\phi_1 = (2 + 2S)^{-1/2}(\chi_a + \chi_b), \qquad \phi_2 = (2 - 2S)^{-1/2}(\chi_a - \chi_b) \tag{33}$$

with normalized $2p\pi$ atomic orbitals $\chi_a$ and $\chi_b$ and overlap integral $S$ (the assumption of zero differential overlap is relaxed for the time being). The singlet functions $\Phi_1$ and $\Phi_2$ will mix to give two functions, $\Psi_N$ and $\Psi_Z$, the mixing giving the $\pi$-bond appropriate covalent and ionic characters, and each has the form

$$\Psi_J = \Phi_1 A_{J1} + \Phi_2 A_{J2}, \tag{34}$$

whereas the singlet function $\Phi_V$ does not interact with $\Phi_1$ and $\Phi_2$ states.

Using the Hamiltonian operator

$$\mathbf{H} = \mathbf{H}_{\text{core}}(1) + \mathbf{H}_{\text{core}}(2) + \frac{e^2}{r_{12}}, \tag{35}$$

the nonzero matrix elements of $\mathbf{H}$ between the various $\Phi$ functions are easily obtained by the Slater–Condon rules (Condon and Shortley, 1951) in terms of integrals over molecular orbitals:

$$\begin{aligned} H_{11} &= 2I_{11} + (11|11), \\ H_{22} &= 2I_{22} + (22|22), \\ H_{VV} &= I_{11} + I_{22} + (11|22) + (12|12), \\ H_{TT} &= I_{11} + I_{22} + (11|22) + (12|12), \\ H_{12} &= (12|12), \end{aligned} \tag{36}$$

where

$$I_{ij} = \int \phi_i^*(\mu)\mathbf{H}_{\text{core}}(\mu)\phi_j(\mu)\, dv(\mu) \tag{37}$$

and

$$(ij|kl) = \int \phi_i^*(\mu)\phi_k^*(\nu)(e^2/r_{\mu\nu})\phi_j(\mu)\phi_l(\nu)\, dv(\mu)\, dv(\nu). \tag{38}$$

As Moser (1953a) and Parr and Pariser (1955) have already suggested, the following Mulliken-type approximation formulas (Mulliken, 1949) are convenient at the stage of expansion of the integrals over molecular orbitals into integrals over atomic orbitals:

$$(aa|ab) = \tfrac{1}{2}S[(aa|aa)_t + (aa|bb)], \tag{39}$$

$$(ab|ab) = \tfrac{1}{2}S^2[(aa|aa)_t + (aa|bb)]. \tag{40}$$

Here $(pq|st)$ are the electronic repulsion integrals over atomic orbitals $p$, $q$, $s$, and $t$:

$$(pq|st) = \iint \chi_p^*(\mu)\chi_s^*(\nu)(e^2/r_{\mu\nu})\chi_q(\mu)\chi_t(\nu)\, dv(\mu)\, dv(\nu), \tag{41}$$

and specifically $(aa|aa)_t$ stands for the one-center repulsion integral that should be evaluated *purely theoretically* [cf. Eqs. (21) and (22)]. This corresponds to the procedure in which the atoms-in-molecules correction (Moffitt, 1951) for $(aa|aa)$ should be applied *before* the Mulliken-type approximations are made (*vide post*).

The complete formulas for the electronic energy levels relative to $H_{11}$ are then obtained as follows:

$$\begin{aligned}
E_N &= H_{11} - (1 - S^2)^{-1}[2\beta + 2S\delta + \{4(\beta + S\delta)^2 + K^2\}^{1/2}]\\
E_V &= H_{11} - (1 - S^2)^{-1}[2\beta + 2S(1 - S)\delta - K],\\
E_T &= H_{11} - (1 - S^2)^{-1}[2\beta + 2S(1 - S)\delta + K],\\
E_Z &= H_{11} - (1 - S^2)^{-1}[2\beta + 2S\delta - \{4(\beta + S\delta)^2 + K^2\}^{1/2}].
\end{aligned} \tag{42}$$

Here

$$\begin{aligned}
H_{11} &= 2\alpha + 2\beta/(1 + S) + J + S(1 - S)(2 + S)\delta/(1 + S),\\
J &= \tfrac{1}{2}[(aa|aa) + (aa|bb)], \qquad K = \tfrac{1}{2}[(aa|aa) - (aa|bb)],\\
\delta &= \frac{1}{2(1 - S^2)}[(aa|aa)_t - (aa|aa)],
\end{aligned} \tag{43}$$

$\alpha$ is a core integral over atomic orbitals

$$\alpha = \int \chi_a^*(\mu)\mathbf{H}_{\text{core}}(\mu)\chi_b(\mu)\, dv(\mu), \tag{44}$$

and $\beta$ is defined by Eq. (20) instead of Eq. (8), namely,

$$\beta + S\alpha = \int \chi_a^*(\mu)\mathbf{H}_{\text{core}}(\mu)\chi_b(\mu)\, dv(\mu). \tag{45}$$

These core integrals are usually treated as empirical parameters to reproduce the experimental data. We shall examine here prescriptions of a priori calculations of $\alpha$ and $\beta$ in line with the arguments given in the preceding section.

The core Hamiltonian of Eq. (35) may be written as

$$\mathbf{H}_{\text{core}}(\mu) = \mathbf{T}(\mu) + \mathbf{U}_a(\mu) + \mathbf{U}_b(\mu) + \sum_{\text{H}} \mathbf{U}_{\text{H}}(\mu) \tag{46}$$

where $\mathbf{U}_a$ and $\mathbf{U}_b$ are the potentials due to the carbon atoms $a$ and $b$ which are charged in the core and $\mathbf{U}_{\text{H}}$ is a potential due to the attached hydrogen atom which is neutral in the core. The core integrals $\alpha$ and $\beta$ of Eqs. (44) and (45) then take on the following forms:

$$\alpha = -I_{2p} - (aa|bb) - (b:aa)_t - 2(\text{H}_1:aa)_t - 2(\text{H}_2:aa)_t, \tag{47}$$

$$\beta = -(a:ab)_t + S(a:bb)_t - (S/2)[(aa|aa)_t - (aa|bb)]. \tag{48}$$

Here $I_{2p}$ is an appropriate atomic valence-state ionization energy and $(b:aa)_t$ and $(\text{H}_i:aa)_t$ are Coulomb penetration integrals [of the type shown in Eq. (14)] between atomic orbital $\chi_a$ and neutral atoms $b$ and $\text{H}_i$ ($\text{H}_1$ and $\text{H}_2$ denote the hydrogen atoms attached to atom $a$ and atom $b$, respectively, and subscript $t$ means that the integral should be evaluated purely theoretically). In Eq. (48) the penetration integrals of the type $(\text{H}_i:pq)$ cancel out because the following Mulliken-type approximation is assumed [cf. Eq. (23)]:

$$(\text{H}_i:pq) = (S_{pq}/2)[(\text{H}_i:pp) + (\text{H}_i:qq)], \tag{49}$$

while the hybrid penetration integral $(a:ab)_t$ is saved without any approximation.

All penetration integrals are computed nonempirically using Slater orbitals with effective nuclear charge $Z = 3.25$ and are shown in the second column of Table I. The empirical value 10.842 eV for integral $(aa|aa)$ which was determined by Parks and Parr (1960; Parks, 1956) from the atomic valence-state consideration of carbon is used, while $(aa|bb)$ is determined in such a way that it fits a parabola to two theoretical values calculated for 2.8-Å and 3.5-Å internuclear separations using Slater orbitals with effective charge $Z = 3.25$ and the empirical value at $r = 0$ [see assumption (6*e*) of Section II]. The value 7.657 eV for *a*–*b* distance $r = 1.353$ Å is obtained by use of the empirical equation

$$(aa|bb) = 10.842 - 2.5924r + 0.1761r^2. \tag{50}$$

These values yield $J = 9.250$ eV and $K = 1.593$ eV. The theoretical $(aa|aa)_t$ for Slater $2p\pi$ atomic orbitals with $Z = 3.25$ is 17.302 eV. This gives $\delta = 3.498$ eV. Using these integrals and theoretical values for the penetration integrals, we get $\beta = -3.043$ eV.

The energy level scheme then obtained from Eq. (42) is as follows:

$$\begin{aligned} E_N &= H_{11} - 0.311 \text{ eV}, \\ E_V - E_N &= 7.104 \text{ eV}, \\ E_T - E_N &= 3.680 \text{ eV}, \\ E_Z - E_N &= 0.736 \text{ eV}. \end{aligned} \tag{51}$$

Since the experimental value of the *N*–*V* transition is probably 7.6 eV (Wilkinson and Johnston, 1950), the agreement is fairly good. The location of the lowest triplet state ($E_T$) has not been definitely established. Several authors have assigned its location in the range 3.1 to 6.4 eV. The problem of *V*–*T* separation will be discussed later. It is shown here at any rate that a theoretically calculated $\beta$ gives a reasonable picture of the electronic spectrum of ethylene.

### B. The Ionization Energy—The Concept of Differential Ionization

A method for calculating the ionization energy of ethylene will now be described. Part of this was discussed in Section III. The total $\pi$-electron energy of the ground state ethylene molecule is easily derived as

$$E(C_2H_4) = 2[\alpha + \beta/(1 + S)] + J + S(1 - S)(2 + S)\delta/(1 + S) + \Delta E_N \tag{52}$$

where $\Delta E_N$ stands for $E_N - H_{11}$ of Eq. (42). For the $C_2H_4^+$ ion, on the other side, the effective nuclear charge $Z$ of each carbon atom may be presumed to be different from that of the ground state ethylene molecule. As will be discussed below, both integrals $\alpha$ and $\beta$ (and also electron repulsion and penetration integrals) are functions of $Z$, so that use of the same $\alpha$ and $\beta$ for both neutral and ionized molecules is quite wrong. We should therefore write

$$E(C_2H_4{}^+) = \alpha^* + \beta^*/(1 + S^*), \tag{53}$$

where $\alpha^*$ and $\beta^*$ have exactly the same expressions as in Eqs. (47) and (48), respectively, but should be evaluated with different $Z$ values. The formula for the first vertical ionization energy then becomes

$$\begin{aligned} I = &-2\alpha + \alpha^* - 2\beta/(1 + S) \\ &+ \beta^*/(1 + S^*) - J - S(1 - S)(2 + S)\delta/(1 + S) - \Delta E_N. \end{aligned} \tag{54}$$

The effective nuclear charge $Z^*$ for a carbon atom in the ionized ethylene molecule is assumed to have the value 3.425, which is the mean of the Slater values for C ($Z = 3.25$) and $C^+$ ($Z = 3.60$). This may be called "differential ionization." Assuming that this increase in effective charge accompanies the actual ionization, we will get slightly different values of molecular integrals for the two states appearing in Eq. (54). To calculate the atomic valence-state ionization energy $I_{2p}^*$ in $C_2H_4{}^+$, the following empirical formula may be obtained from the values of the valence-state ionization energies of the isoelectronic series C ($Z = 3.25$ $I_{2p} = 11.424$ eV), $N^+$ ($Z = 4.25$, $I_{2p} = 28.885$ eV), and $O^{2+}$ ($Z = 5.25$, $I_{2p} = 53.494$ eV) (Moore, 1949):

$$I_{2p} = 3.604Z^2 - 9.599Z + 4.5535. \tag{55}$$

The ionization energy derived from this kind of formulation may be called "differential ionization energy" of the corresponding atomic valence-state. Formula (55) gives $I_{2p}^* = 13.954$ eV for $Z = 3.425$. All penetration integrals including hydrogen penetrations for both states are evaluated purely theoretically using Slater orbitals for $Z$ values of 3.250 and 3.425, respectively, the same $a$–$b$ distance, 1.353 Å, being assumed for both states. Results are listed in Table I together with the electronic repulsion integrals that are evaluated in the same way as before, but with corresponding values of $(aa|aa)$, which are assumed to be proportional to $Z$ values. These values yield $\alpha = -21.119$, $\alpha^* = -23.829$, and $\beta^* = -2.850$ eV. It should be noted that the value $-21.119$ eV is close to the value $-20.972$ eV obtained by Parks and Parr (1960) from a more complete consideration of the atomic valence-states of the carbon atom.

The first vertical ionization energy of ethylene can then be calculated from Eq. (54), which gives $I = 10.750$ eV. This is a very satisfactory result indeed, compared with the experimental value 10.62 eV (Honig, 1948) or

TABLE I

MOLECULAR INTEGRALS IN ETHYLENE (eV)

| Integral | $C_2H_4$ ($Z = 3.250$) | $C_2H_4^+$ ($Z = 3.425$) | $C_2H_4^-$ ($Z = 3.075$) |
|---|---|---|---|
| $(aa\|aa)_t$ | 17.302 | 18.234 | 16.371 |
| $(aa\|aa)$ | 10.842 | 11.426 | 10.258 |
| $(aa\|bb)$ | 7.657 | 7.949 | 7.386 |
| $(b:aa)_t$ | 0.744 | 0.600 | 0.936 |
| $(H_1:aa)_t$ | 0.627 | 0.646 | 0.610 |
| $(H_2:aa)_t$ | 0.020 | 0.022 | 0.020 |
| $S$ | 0.264 | 0.235 | 0.298 |
| $\alpha$ | −21.119 | −23.839 | −18.697 |
| $\beta$ | −3.043 | −2.850 | −3.283 |

10.52 eV (Watanabe, 1954). How will the situation be without the aforementioned allowances? If one assumes $\alpha = \alpha^*$ and $\beta = \beta^*$, as is customarily done (that is assumed to be $Z = Z^*$), Eq. (54) yields $I = 13.370$ eV. Further, if the Mulliken-type approximations

$$\chi_a(\mu)\chi_b(\mu) = (S_{ab}/2)[\chi_a(\mu)\chi_a(\mu) + \chi_b(\mu)\chi_b(\mu)] \tag{56}$$

are used systematically *before* the atoms-in-molecules corrections are applied [this means $\delta = 0$ in Eq. (54)], one obtains $I = 14.497$ eV with transition energies $E_V - E_N = 8.474$ eV and $E_T - E_N = 5.050$ eV.

### C. Applications to Other Properties

The variation in the total energy $E_N$ of the ground state when the two $CH_2$ groups are slightly twisted one another will yield the twisting frequency. The twisting force constant $k$ and the twisting frequency $\omega$ of the ground state ethylene molecule are defined by (Parr and Crawford, 1948):

$$\begin{aligned} k &= (\partial^2 E_N/\partial\theta^2)_{\theta=0} \qquad &&\text{(in eV)},\\ \omega &= 560k^{1/2} &&\text{(in cm}^{-1}\text{)}, \end{aligned} \tag{57}$$

where $\theta$ is an angle between the major axes of the atomic orbitals $\chi_a$ and $\chi_b$.

In the planar configuration, the approximation $E_N = H_{11}$ is not so serious in the neighborhood of the equilibrium position because of the small contribution of $\Phi_2$ to $\Psi_N$, as shown before. The total energy will then be the $\pi$-electron energy $H_{11}$ of Eq. (43) plus a core energy which is

$(aa|bb)$ plus angular independent terms. The dependence of the basic quantities $\beta$, $S$, and $(aa|bb)$ on the angle $\theta$ are given by

$$\begin{aligned} \beta = \beta_0 \cos\theta, \qquad S &= S_0 \cos\theta, \\ (aa|bb) = \cos^2\theta(aa|bb)_0 &+ \sin^2\theta(aa|bb)_{\pi/2}, \end{aligned} \tag{58}$$

where the subscripts 0 and $\pi/2$ denote angles between the axes of $\chi_a$ and $\chi_b$. The one-center core integral $\alpha$ depends on $\theta$ only through $(aa|bb)$, as can be seen from Eq. (47). The total energy then becomes

$$\begin{aligned} E_N = {} & 2\beta_0 \cos\theta/(1 + S_0 \cos\theta) - \tfrac{1}{2}\cos^2\theta(aa|bb)_0 - \tfrac{1}{2}\sin^2\theta(aa|bb)_{\pi/2} \\ & + S_0 \cos\theta(2 + S_0\cos\theta)[(aa|aa)_t - (aa|aa)]/(1 + S_0\cos\theta)^2 \\ & + \text{angular independent terms.} \end{aligned} \tag{59}$$

Thus Eq. (57), the subscripts 0 in $\beta_0$ and $S_0$ being omitted, yields

$$\begin{aligned} k = {} & -2\beta/(1 + S)^2 + [(aa|bb)_0 - (aa|bb)_{\pi/2}] \\ & - S[(aa|aa)_t - (aa|aa)]/(1 + S)^3. \end{aligned} \tag{60}$$

Using $(aa|aa)_{\pi/2} = 9.841$ eV (this is the value of $(aa|bb)_{\pi/2}$ for $r = 0$) obtained from the value of the Slater–Condon parameter, the value of $(aa|bb)_{\pi/2}$ for $r = 1.353$ Å is calculated to be 7.448 eV in the way described above.

With this and the numerical values of molecular integrals used before, one gets

$$\begin{aligned} k &= 3.17 \text{ eV}, \\ \omega &= 998 \text{ cm}^{-1}, \end{aligned} \tag{61}$$

which compare well with the corresponding observed values: $k = 3.36$ eV and $\omega = 1027$ cm$^{-1}$ (Arnett and Crawford, 1950). It should be added here that, in this calculation, the effect of hyperconjugation, which is supposed to favor twisted ethylene, is not taken into consideration.

Another important application is possible to the a priori calculation of the electron affinity of ethylene. The ideas to be used are just the same as those used for the calculation of the ionization energy. One can write the total $\pi$-electron energy of the $C_2H_4^-$ ion, in which two $\pi$ electrons are placed in orbital $\phi_1$ and one in $\phi_2$ of Eq. (33):

$$\begin{aligned} E(C_2H_4^-) = {} & 3\alpha' + \beta'(1 - 3S')/(1 - S'^2) + 3J' - K'/(1 - S'^2) \\ & + S'(2 - 3S' - 3S'^2)\delta'/(1 + S'). \end{aligned} \tag{62}$$

Here the various quantities are given by expressions like Eqs. (43), (47), and (48), but again should be calculated with different effective nuclear charge $Z'$. The formula for the electron affinity comes out simply as the difference of Eqs. (62) and (52):

$$\begin{aligned} A = {} & 2\alpha - 3\alpha' + 2\beta/(1 + S) - (1 - 3S')\beta'/(1 - S'^2) + J - 3J' \\ & + S(1 - S)(2 + S)\delta/(1 + S) - S'(1 - S')(2 + S')\delta'/(1 + S') \\ & + 2S'^2\delta' + K'/(1 - S'^2) + \Delta E_N . \end{aligned} \tag{63}$$

In line with the manner of treating the ionization energy, the effective charge $Z'$ for the carbon atom in $C_2H_4{}^-$ ion is assumed to be 3.075, which corresponds to the mean of the Slater values for $C^0$ and $C^{1-}$. The necessary integrals with $Z' = 3.075$ are evaluated by the same procedure as before, and are listed in the last column of Table I. With these values, Eq. (63) gives $A = -5.982$ eV.

Unfortunately the electron affinity of ethylene is experimentally unknown, while it may well be negative. The following facts support the method of the foregoing calculation. (*a*) Neglecting the change in $Z$ value from normal ethylene to ethylene negative ion, one obtains $A = +0.373$ eV. This value is highly improbable. (*b*) The high negative value obtained suggests that ethylene in general has little tendency to function as an electron acceptor in the stage of both molecular association and chemical reaction. This agrees with experimental indications.

### D. Remarks

It has been shown in the present section that the allowance made for the change in the effective nuclear charge accompanying the ionization can give a good account of both spectrum and ionization energy of ethylene, even with the framework of the $\pi$-electron approximation. Without such allowance, it is demonstrated that if one uses purely theoretical values for all molecular integrals throughout the calculation, that is, if one employs no atoms-in-molecules correction in the least, one obtains $I = 10.90$ eV at the sacrifice of the energy levels (Parr and Pariser, 1955). Although the author does not think that this attitude of calculation, using a theoretical one-center repulsion integral, is just right, this fact seems to suggest another fundamental aspect. To decide what approximations should be made and where they should most properly be placed, a good deal more experimental and theoretical information is required.

If one applies the atoms-in-molecules correction at the stage of expansion of integrals over molecular orbitals into integrals over atomic orbitals *after* the Mulliken-type approximations are made, not before, one obtains less satisfactory results: e.g., 8.47 eV for $N$–$V$ transition and 11.97 eV for ionization energy. Which method is preferable on fundamental grounds is, again, not clear.

Among several questions that still should be asked, the following two must be mentioned. What about the singlet–triplet split? Do the $\sigma$ electrons play significant roles? We need not dwell on the latter because the effect of $\sigma$ electrons will be discussed in the following section.

Now let us determine $\beta$, empirically this time, from molecular spectroscopic data, although its theoretical value was shown to give quite satisfactory results. Assuming the 7.6 eV band of ethylene to be the $N$–$V$ transition, $\beta_e$ must be given the value $-3.283$ eV from Eq. (42), which compares favorably with the theoretical $\beta_t = -3.043$ eV. Using this $\beta_e$ and also values of $\beta_e^*$ and $\beta'_e$ that can be obtained by reducing their theoretical values to "empirical size" by a factor of $\beta_t/\beta_e$, similar calculations give:

$$\begin{array}{rl} E_N = H_{11} - 0.28 \text{ eV}, & k = 3.47 \text{ eV}, \\ (E_V - E_N = 7.60 \text{ eV}), & \omega = 1044 \text{ cm}^{-1}, \\ E_T - E_N = 4.18 \text{ eV}, & I = 10.76 \text{ eV}, \\ E_Z - E_N = 10.76 \text{ eV}, & A = -6.00 \text{ eV}. \end{array} \tag{64}$$

These are again good enough, but no change in the singlet–triplet split can be obtained. The reason is that the theoretical expression for $E_V - E_T$ does not depend on $\beta$ in the least and is eaxctly equal to $2K/(1\text{–}S^2)$, as seen in Eq. (42). Assuming then Potts' (1953) assignment of $E_V - E_T = 1.2$ eV to be correct, $K$ can be determined to be 0.558 eV with $\beta = -3.918$ eV and $J = 10.284$ eV. In this case, one gets

$$\begin{array}{rl} E_N = H_{11} - 0.03 \text{ eV}, & k = 4.27 \text{ eV}, \\ (E_V - E_N = 7.60 \text{ eV}), & \omega = 1584 \text{ cm}^{-1}, \\ (E_T - E_N = 6.40 \text{ eV}), & I = 12.14 \text{ eV}, \\ E_Z - E_N = 12.93 \text{ eV}, & A = -8.04 \text{ eV}. \end{array} \tag{65}$$

This is much less satisfactory than before.

In view of the fact that, experimentally, no conclusive work has yet been done in this connection, we would say tentatively that the calculation in the preceding paragraph and the empirical calculation in Eq. (64) are both about right, so the location of the lowest triplet state would be around 4 eV. This value will be reexamined in a later section. It might be added here that slightly different $Z$ values would be expected for $V$ and $T$ states if the variational treatment could be performed, and these might give a different picture of the $V$–$T$ split.

## V. Ethylene as a Four-Electron Problem

In this section, it is intended to examine the problem of how to take account of $\sigma$ electrons through a scheme which has practically the same characteristics mentioned before and takes into account the $\sigma$–$\pi$ configuration interaction also. Much improvement over the two-electron calculation will be expected from mixing more excited configurations with those considered before. In particular, further preferential stabilization of the ethylene negative ion might be obtained from $\sigma$–$\pi$ interaction to reduce the value of ionization energy. As was emphasized in the previous section, on the contrary, an allowance for the change in the effective nuclear charge of a nucleus accompanying the variation of the electron density around the nucleus may again play an important part in determining the ionization energy.

Among several papers which treat $\sigma$–$\pi$ interaction in ethylene, Moser's (1953b) purely theoretical calculation should be cited. The results obtained were not very satisfactory; specifically, the electronic energy levels do not come out well, as is usual with the nonempirical ASMO method. This again suggests the desirability of a semiempirical calculation.

Whether the $\pi$- and $\sigma$-electron pairs can be separately treated remains unsettled (cf. Section III). If they could be separated, one could use the method of separated electron pairs proposed by Parks and Parr (1958). This method gave successful results for the electronic structure of formaldehyde (Parks and Parr, 1960), but $\sigma$–$\pi$ interchange was neglected. Furthermore, the method of estimating necessary molecular integrals through electron reorganization effects cannot be applied to a homonuclear case like ethylene.

The essential feature of the present method lies in a way that the most optimum values can be determined for a good deal of molecular integrals. Also, many of the parameters obtained in such a manner may be used as basis for similar calculations on other molecules.

### A. Formulation of the Four-Electron Treatment of Ethylene

As mentioned above, the procedure which will be described is of ASMO–CI type, and in it we explicitly consider carbon–carbon $\sigma$- and $\pi$-bonding electrons, the rest being relegated to a core of charge 4+ which is assumed to remain unchanged during processes of excitations and even of ionizations.

The appropriate molecular orbitals to be used, in order of increasing energy and with their corresponding symmetry, are

$$\begin{aligned} \chi_0 &= (2 + 2S_\sigma)^{-1/2}(a_\sigma + b_\sigma), & a_{1g} \\ \chi_1 &= (2 + 2S_\pi)^{-1/2}(a_\pi + b_\pi), & b_{3u} \\ \chi_2 &= (2 - 2S_\pi)^{-1/2}(a_\pi - b_\pi), & b_{2g} \\ \chi_3 &= (2 - 2S_\sigma)^{-1/2}(a_\sigma - b_\sigma), & b_{1u} \end{aligned} \tag{66}$$

with $a_\sigma = (1/\sqrt{3})(a_s + \sqrt{2}\, a_z)$ and a like expression for $b_\sigma$—the molecular axis $a$–$b$ is taken to be the $z$ axis and $sp^2$ hybridization is assumed. Here $a_s$, $a_z$, and $a_\pi$ denote the $2s$, $2p_z$, and $2p\pi$ atomic orbitals on atom $a$, respectively, and $S_i$ overlap integrals:

$$\begin{aligned} S_\sigma &= \int a_\sigma^*(\mu) b_\sigma(\mu)\, dv(\mu), \\ S_\pi &= \int a_\pi^*(\mu) b_\pi(\mu)\, dv(\mu). \end{aligned} \tag{67}$$

The precise form of the atomic orbitals is not specified here—this provides a degree of freedom, without which we cannot employ appropriate approximations at proper stages.

The ground state $A_{1g}$ configurations are obtained by taking closed shell functions and also by placing one electron in each orbital. The following eight antisymmetrized wave functions therefore belong to the $A_{1g}$ singlet:

$$\begin{aligned} &\Phi_1^N = (0\bar{0}1\bar{1}), \qquad \Phi_2^N = (0\bar{0}2\bar{2}), \qquad \Phi_3^N = (1\bar{1}2\bar{2}), \\ &\Phi_4^N = \tfrac{1}{2}[(0\bar{1}2\bar{3}) + (1\bar{0}3\bar{2}) + (0\bar{2}1\bar{3}) + (2\bar{0}3\bar{1})], \\ &\Phi_5^N = \tfrac{1}{2}[(0\bar{1}2\bar{3}) + (1\bar{0}2\bar{3}) + (0\bar{1}3\bar{2}) + (1\bar{0}3\bar{2})], \\ &\Phi_6^N = (0\bar{0}3\bar{3}), \qquad \Phi_7^N = (1\bar{1}3\bar{3}), \qquad \Phi_8^N = (2\bar{2}3\bar{3}). \end{aligned} \tag{68}$$

Here $(0\bar{0}1\bar{1})$, etc., again stand for Slater determinants constructed from the molecular orbitals of Eq. (66) [0 denotes $\chi_0$, and so on; cf. Eq. (2)]. Out of these eight functions, the last one, $\Phi_8^N$, comes from the four-electron jump in the original molecular orbitals and is supposed to make only a small contribution to the actual ground state. On the other side, there are four wave functions each for the singlet and triplet states belonging to $B_{1u}$ symmetry:

$$
\begin{aligned}
\Phi_1^{V,T} &= \frac{1}{\sqrt{2}}[(0\bar{0}1\bar{2}) \pm (0\bar{0}2\bar{1})],\\
\Phi_2^{V,T} &= \frac{1}{\sqrt{2}}[(2\bar{2}0\bar{3}) \pm (2\bar{2}3\bar{0})],\\
\Phi_3^{V,T} &= \frac{1}{\sqrt{2}}[(1\bar{1}0\bar{3}) \pm (1\bar{1}3\bar{0})],\\
\Phi_4^{V,T} &= \frac{1}{\sqrt{2}}[(3\bar{3}1\bar{2}) \pm (3\bar{3}2\bar{1})],
\end{aligned}
\tag{69}
$$

where $V$(singlet) takes an upper sign and $T$(triplet) a lower sign. We will not consider the remaining forty-four configurations here.

To calculate the ionization energy and also the electron affinity in the aforementioned manner, wave functions for the ground states of $C_2H_4{}^+$ and $C_2H_4{}^-$ ions are needed. For the former ($^2B_{3u}$), there are five configurations. They are

$$
\begin{aligned}
&\Phi_1^I = (0\bar{0}1), \qquad \Phi_2^I = (2\bar{2}1), \qquad \Phi_3^I = (3\bar{3}1),\\
&\Phi_4^I = \frac{1}{\sqrt{2}}[(0\bar{3}2) + (3\bar{0}2)],\\
&\Phi_5^I = \frac{1}{\sqrt{6}}[2(0\bar{2}3) + (0\bar{3}2) - (3\bar{0}2)].
\end{aligned}
\tag{70}
$$

To the latter ($^2B_{2g}$) also there are five configurations:

$$
\begin{aligned}
&\Phi_1^A = (0\bar{0}1\bar{1}2), \qquad \Phi_2^A = (0\bar{0}3\bar{3}2), \qquad \Phi_3^A = (1\bar{1}3\bar{3}2),\\
&\Phi_4^A = \frac{1}{\sqrt{2}}[(2\bar{2}0\bar{3}1) + (2\bar{2}3\bar{0}1)],\\
&\Phi_5^A = \frac{1}{\sqrt{6}}[2(2\bar{2}0\bar{1}3) + (2\bar{2}0\bar{3}1) - (2\bar{2}3\bar{0}1)].
\end{aligned}
\tag{71}
$$

Wave functions are then finally expressed as

$$
\Psi_i = \sum_j \Phi_j A_{ij} \tag{72}
$$

for each corresponding state.

The Hamiltonian operator for the whole system may be written in the form

$$\mathbf{H} = \sum_{\mu} \mathbf{H}^{4+}_{\mathrm{core}}(\mu) + \frac{1}{2}\sum_{\mu\nu}{}' (e^2/r_{\mu\nu}) \tag{73}$$

because the core of charge 4+ was assumed in the beginning. The matrix elements of $\mathbf{H}$ between the various $\Phi$ functions are easily obtained in terms of integrals over molecular orbitals. The Mulliken approximations of the forms shown in Eqs. (21) and (22) for both $\sigma$ and $\pi$ atomic orbitals are applied at the stage of expansion of the integrals over molecular orbitals into integrals over atomic orbitals; that is

$$\begin{aligned} a_\sigma(\mu)b_\sigma(\mu) &= \tfrac{1}{2}S_\sigma[a_\sigma(\mu)a_\sigma(\mu) + b_\sigma(\mu)b_\sigma(\mu)], \\ a_\pi(\mu)b_\pi(\mu) &= \tfrac{1}{2}S_\pi[a_\pi(\mu)a_\pi(\mu) + b_\pi(\mu)b_\pi(\mu)]. \end{aligned} \tag{74}$$

To evaluate core integrals of $\mathbf{H}^{4+}_{\mathrm{core}}$, one may write for the $\pi$ electrons

$$\mathbf{H}^{4+}_{\mathrm{core}}(\mu) = \mathbf{H}^{2+}_{\pi\text{-core}}(\mu) - \mathfrak{g}_\sigma(\mu) \tag{75}$$

and for the $\sigma$ electrons

$$\mathbf{H}^{4+}_{\mathrm{core}}(\mu) = \mathbf{H}^{2+}_{\sigma\text{-core}}(\mu) - \mathfrak{g}_\pi(\mu). \tag{76}$$

Here $\mathfrak{g}$ are Coulomb exchange operators which take care of mutual interaction of the $\sigma$ and $\pi$ electrons; namely,

$$\mathfrak{g}_\sigma(\mu) = \sum_{i=a,b} [\mathfrak{j}_{i\sigma}(\mu) - \tfrac{1}{2}\mathfrak{k}_{i\sigma}(\mu)], \tag{77}$$

$$\mathfrak{g}_\pi(\mu) = \sum_{i=a,b} [\mathfrak{j}_{i\pi}(\mu) - \tfrac{1}{2}\mathfrak{k}_{i\pi}(\mu)] \tag{78}$$

are, for example, defined by

$$\mathfrak{j}_{i\sigma}(\mu)[a_\pi(\mu)] = \int i^*_\sigma(\nu)i_\sigma(\nu)(e^2/r_{\mu\nu})a_\pi(\mu)\, dv(\nu), \tag{79}$$

$$\mathfrak{k}_{i\sigma}(\mu)[a_\pi(\mu)] = \int i^*_\sigma(\nu)a_\pi(\nu)(e^2/r_{\mu\nu})i_\sigma(\mu)\, dv(\nu). \tag{80}$$

Equations (75) and (76) may therefore be regarded as defining $\mathbf{H}^{2+}_{\pi\text{-core}}$ and $\mathbf{H}^{2+}_{\sigma\text{-core}}$.

The final expressions for the electronic energy levels are then obtained in terms of the following one- and two-center core integrals and one- and two-center repulsion integrals:

$$\alpha_\sigma = \int a_\sigma^*(\mu)\mathbf{H}_{\sigma\text{-core}}^{2+}(\mu)a_\sigma(\mu)\,dv(\mu), \tag{81}$$

$$\beta_\sigma + S_\sigma\alpha_\sigma = \int a_\sigma^*(\mu)\mathbf{H}_{\sigma\text{-core}}^{2+}(\mu)b_\sigma(\mu)\,dv(\mu), \tag{82}$$

$$\left.\begin{matrix} J_\sigma \\ K_\sigma \end{matrix}\right\} = \tfrac{1}{2}[(a_\sigma a_\sigma|a_\sigma a_\sigma) \pm (a_\sigma a_\sigma|b_\sigma b_\sigma)], \tag{83}$$

and like expressions for $\alpha_\pi$, $\beta_\pi$, $J_\pi$, and $K_\pi$, and

$$\left.\begin{matrix} J_{\sigma\pi} \\ K_{\sigma\pi} \end{matrix}\right\} = \tfrac{1}{2}[(a_\sigma a_\sigma|a_\sigma a_\sigma) \pm (a_\sigma a_\sigma|b_\pi b_\pi)], \tag{84}$$

$$\left.\begin{matrix} \omega \\ \zeta \end{matrix}\right\} = \tfrac{1}{2}[(a_\pi a_\sigma|a_\pi a_\sigma) \pm (a_\pi a_\sigma|b_\pi b_\sigma)]. \tag{85}$$

### B. One-Center Integrals—Consideration of Valence-States

In order to evaluate the one-center quantities appearing in Eqs. (81) to (85), we must (1) pick up numerical values for corresponding nonhybridized valence-state energies from atomic spectroscopic data, (2) evaluate the energies of corresponding hybridized valence-states using the values of nonhybridized valence-state energy obtained in step (1), (3) set simultaneous equations by expressing these energies in terms of Slater–Condon parameters, and (4) solve the equation obtained for a set of one-center quantities so as to give a best fit to the energies of all the valence-states that enter.

In step (3), it is customarily assumed that (a) the same atomic orbitals (the same $Z$ values) are used for both neutral atoms and positive and negative ions and (b) each atom possesses a core which remains unchanged in going from one valence-state to another or even under ionization. The present point of view, already supported in the former section, is that assumption (a) might be relaxed and allowance should be made for the change in the effective charge in case of ionization. This sort of treatment will presumably produce much more reliable numerical values for the one-center quantities. Parks' work (1956; Parks and Parr, 1960) seems to support this view; a set of one-center parameters determined under assumptions (a) and (b) cannot reproduce *exactly* the valence-state energies computed from atomic data. This is of course due partly to uncertainties in the atomic data, but it seems to be evident that assumption (a) should be relaxed at this stage.

TABLE II

NONHYBRIDIZED CARBON VALENCE-STATE ENERGIES AND THEIR FORMULATION IN TERMS OF ATOMIC SPECTROSCOPIC ENERGIES

| Valence-state | | Formulation[a] | Energy (eV)[b] |
|---|---|---|---|
| $C^0$ | $s^2xz;\ V_2$ | $(3/4)E(^3P) + (1/4)E(^1D)$ | 0.316 |
| $C^0$ | $sxz^2;\ V_2$ | $(3/8)E(^3D) + (1/8)E(^1D) + (3/8)E(^3P)$<br>$+ (1/8)E(^1P)$ | 9.851 |
| $C^{1-}$ | $s^2xyz;\ V_3$ | $(1/2)E(^4S) + (1/2)E(^2D)$ | (−1.00) |
| $C^{1-}$ | $sx^2yz;\ V_3$ | $(1/2)E(^4P) + (1/4)E(^2P) + (1/4)E(^2D)$ | (7.68) |
| $C^{2-}$ | $s^2xy^2z;\ V_2$ | $(3/4)E(^3P) + (1/4)E(^1D)$ | ((4.25)) |
| $C^{2-}$ | $sxy^2z^2;\ V_2$ | $(3/4)E(^3P) + (1/4)E(^1P)$ | ((11.85)) |
| $C^{1+}$ | $sxz;\ V_3$ | $(1/2)E(^4P) + (1/4)E(^2P) + (1/4)E(^2D)$ | 19.679 |
| $C^0$ | $sxyz;\ V_4$ | $(5/16)E(^5S) + (3/16)E(^3S) + (3/8)E(^3D)$<br>$+ (1/8)E(^1D)$ | 8.261 |
| $C^{2+}$ | $^1(sz);\ V_0$ | $E(^1P)$ | 48.326 |
| $C^{2+}$ | $^3(sx);\ V_0$ | $E(^3P)$ | 42.124 |
| $C^{2+}$ | $^3(zx);\ V_0$ | $E(^3P)$ | 52.667 |
| | $E_s^0(s^2)$ | $E(^1S)$ | 35.640 |
| | $E_{zx}^0(p^2)$ | $(7/15)E(^1D) + (8/15)E(^1S)$ | 56.640 |
| $C^{1+}$ | $^1(sz)y;\ V_1$ | $(3/4)E(^2P) + (1/4)E(^2D)$ | 23.870 |
| $C^{1+}$ | $^3(sx)y;\ V_1$ | $(1/12)E(^2P) + (1/4)E(^2D) + (2/3)E(^4P)$ | 18.282 |
| $C^{1+}$ | $^3(zx)y;\ V_1$ | $(1/3)E(^2D) + (2/3)E(^4S)$ | 29.216 |
| | $E_s^0(s^2p)$ | $E(^2P)$ | 11.264 |
| | $E_{zx}^0(p^3)$ | $(4/5)E(^2P) + (1/5)E(^4S)$ | 31.725 |
| $C^0$ | $^1(sz)y^2;\ V_0$ | $(1/2)E(^1D) + (1/2)E(^1P)$ | 13.490 |
| $C^0$ | $^3(sx)y^2;\ V_0$ | $(1/2)E(^3P) + (1/2)E(^3D)$ | 8.636 |
| $C^0$ | $^3(zx)y^2;\ V_0$ | $E(^3P)$ | (18.553) |
| | $E_s^0(s^2p^2)$ | $(2/3)E(^1D) + (1/3)E(^1S)$ | 1.737 |
| | $E_{zx}^0(p^4)$ | $(7/15)E(^1D) + (8/15)E(^1S)$ | (20.735) |

---

[a] In the notation of term values, corresponding configurations are omitted. For instance, it should be read as $C^0\ s^2xz;\ V_2$, $E(^3P;\ s^2p^2) + E(^1D;\ s^2p^2)$ and so on.

[b] While parentheses show that some error is involved due to the estimation of unknown term values, double parentheses indicate more serious uncertainties involved.

The process of step (1) is listed in Table II. The states of ($C^0$, $p^4$) are experimentally unknown, so that these have to be estimated somehow.

First, the Slater–Condon parameters must be obtained empirically from the following experimental data for ($C^0$, $sp^3$) states (Moore, 1949):

$$\begin{aligned}
{}^5S&: \quad W_0 - K_{sp} - 10F_2 = 4.181 \text{ eV},\\
{}^3D&: \quad W_0 - F_2 = 7.944 \text{ eV},\\
{}^3P&: \quad W_0 + 5F_2 = 9.328 \text{ eV},\\
{}^3S&: \quad W_0 + 3K_{sp} - 10F_2 = 13.114 \text{ eV}.
\end{aligned} \tag{86}$$

Interpolated data for ${}^1D$ and ${}^1P$ states are intentionally omitted because of their possible errors. To solve the simultaneous equations (86) the method of least squares is used; the values obtained are $W_0 = 8.323$ eV, $K_{sp} = 2.256$ eV, and $F_2 = 0.202$ eV. The ratio of the empirical $W_0$ determined above to the theoretical $W_0$ $(= I_p - I_s - J_{ss} - J_{sp} + 2F_0)$, computed to be 9.822 eV from the theoretical Slater–Condon parameters given by Moffitt (1950), is used as a factor, by which the individual theoretical values of parameters in the expression of $W_0$ above are reduced to corresponding empirical values. Using these parameters, one can obtain $E(C^0, p^4; {}^1S) = 21.583$ eV, $E(C^0, p^4; {}^3P) = 18.553$ eV, and $E(C^0, p^4; {}^1D) = 19.765$ eV. With these values, energies of the five valence-states in the bottom of Table II are estimated.

### TABLE III

### HYBRIDIZED CARBON VALENCE-STATE ENERGIES IN TERMS OF ONE-CENTER QUANTITIES

| Valence-State[a] | | | Energy (eV) | Formulation[b] |
|---|---|---|---|---|
| (1) | $C^0$ | $t_1t_2\sigma^2$; $V_2$ | 6.673 | $E + 2I_\sigma + j_{\sigma\sigma}$ |
| (2) | $C^{1-}$ | $t_1t_2\sigma^2\pi$, $V_3$ | 4.787 | $E + 2(I_\sigma + \Delta_\sigma) + (I_\pi + \Delta_\pi)$ $+ (Z^{-1}/Z^0)(j_{\sigma\sigma} + 2g_{\sigma\pi})$ |
| (3) | $C^{2-}$ | $t_1t_2\sigma^2\pi^2$; $V_2$ | (10.3) | $E + 2(I_\sigma + 2\Delta_\sigma) + 2(I_\pi + 2\Delta_\pi)$ $+ (Z^{-2}/Z^0)(j_{\sigma\sigma} + j_{\pi\pi} + 4g_{\sigma\pi})$ |
| (4) | $C^{+1}$ | $t_1t_2\sigma$; $V_3$ | 19.679 | $E + (I_\sigma - \Delta_\sigma)$ |
| (5) | $C^0$ | $t_1t_2\sigma\pi$; $V_4$ | 8.261 | $E + I_\sigma + I_\pi + g_{\sigma\pi}$ |
| (6) | $C^{1-}$ | $t_1t_2\sigma\pi^2$; $V_3$ | 7.68 | $E + (I_\sigma + \Delta_\sigma) + 2(I_\pi + \Delta_\pi)$ $+ (Z^{-1}/Z^0)(j_{\pi\pi} + 2g_{\sigma\pi})$ |
| (7) | $C^{2+}$ | $t_1t_2$; $V_2$ | 46.817 | $E$ |
| (8) | $C^{1+}$ | $t_1t_2\pi$; $V_3$ | 22.929 | $E + (I_\pi - \Delta_\pi)$ |
| (9) | $C^0$ | $t_1t_2\pi^2$; $V_2$ | 12.807 | $E + 2I_\pi + j_{\pi\pi}$ |

[a] $t_1$ and $t_2$ are $sp^2$ hybrid carbon atomic orbitals directed to hydrogen atoms $H_1$ and $H_2$.

[b] For notation, see text.

After nonhybridized valence-state energies are thus determined, step (2) is easily performed and gives theoretical hybridized valence-state energies as shown in Table III. The energies of valence-states (7) and (8) may contain small errors due to the use of empirical $K_{sp}$ value, and (9) contains another error due to the use of the ($C^0$, $p^4$) energy levels estimated above. Also, (2) contains an error due to the extrapolated data of the $C^{1-}$ states (Skinner and Pritchard, 1953). None of these errors, however, is considered to be more serious than the one involved in (3), where the estimation of the $C^{2-}$ states may cause considerable uncertainties.

Formulations of these valence-state energies are given in terms of one-center quantities and are listed in the last column of Table III. A characteristic feature here is that, while retaining the assumption of the unchanged core, assumption (*b*) above, we do *not* use the same atomic orbitals for ions as for neutral atoms, so that the effective nuclear charge $Z$ for $C^{1-}$, $C^0$, and $C^{1+}$ is assumed to be 2.90, 3.25, and 3.60, and so on (Slater, 1932). One-center electronic repulsion integrals of the same kind but associated with different valence-states—$j_{\sigma\sigma}$ for example, or $j_{\pi\pi}$, or $g_{\sigma\pi}$ (note $g_{\sigma\pi} = j_{\sigma\pi} - \frac{1}{2}k_{\sigma\pi}$)—then come out to be proportional to their corresponding $Z$ values. The one-center core integral $I_\pi$ or $\alpha_\pi$ has been found in the previous section to change its value almost linearly in going from $Z = 2.90$ to 3.60 (cf. Table I). Assuming the same dependence on $Z$ for $I_\sigma$ also, empirical parameters $\Delta_\pi$ and $\Delta_\sigma$ are used to adjust the core integrals $I_\pi$ and $I_\sigma$.

From the eight simultaneous equations with eight unknown parameters, shown in Table III [valence-state (3) is omitted for the reason indicated before], one finds

$$\begin{aligned} &I_\sigma = -25.126, \quad &\Delta_\sigma = 2.012, \quad &j_{\sigma\sigma} = 10.108, \quad &g_{\sigma\pi} = 8.587, \\ &I_\pi = -22.017, \quad &\Delta_\pi = 1.871, \quad &j_{\pi\pi} = 10.024, \quad &(E = 46.817), \end{aligned} \tag{87}$$

(all in eV). With $K_{sp} = 2.256$ eV and $F_2 = 0.202$ eV obtained before, one can separate $g_{\sigma\pi}$ into $j_{\sigma\pi}$ and $k_{\sigma\pi}$; namely $k_{\sigma\pi} = \frac{1}{3}(K_{sp} + 6F_2) = 1.156$ eV, and then $j_{\sigma\pi} = g_{\sigma\pi} + \frac{1}{2}k_{\sigma\pi} = 9.165$ eV. These parameters reproduce the energy of the valence-state (3) to be 10.809 eV, which compares well with the value 10.3 eV derived from the extrapolation of the atomic data. Ambiguities in the process of determining values of one-center quantities from atomic spectroscopic data are thus reduced by allowing a change in the effective nuclear charge upon ionization.

Calculation of the one-center repulsion integrals for $C_2H_4^+$ and $C_2H_4^-$ ions is straightforward. We only have to multiply the value obtained in Eq. (87) by the appropriate ratio of the effective nuclear charges $Z$. According to the concept of differential ionization, the $Z$ value for a carbon atom may be presumed to be 3.425 for $C_2H_4^+$ ion and 3.075 for $C_2H_4^-$ ion in the same way as before, the same effective charges for the 2*s* and 2*p* atomic orbitals being assumed. The results are listed in Table IV in terms of quantities defined in Eqs. (81)–(85).

**TABLE IV**

INTEGRALS OVER ATOMIC ORBITALS (eV)

| Integral | $C_2H_4^-$ ($Z = 3.075$) | $C_2H_4$ ($Z = 3.250$) | $C_2H_4^+$ ($Z = 3.425$) |
|---|---|---|---|
| $J_\sigma$ | 8.920 | 9.271 | 9.625 |
| $J_\pi$ | 8.488 | 8.796 | 9.108 |
| $J_{\sigma\pi}$ | 8.065 | 8.388 | 8.715 |
| $K_\sigma$ | 0.645 | 0.837 | 1.027 |
| $K_\pi$ | 0.996 | 1.229 | 1.457 |
| $K_{\sigma\pi}$ | 0.608 | 0.777 | 0.944 |
| $\omega$ | 0.768 | 0.800 | 0.832 |
| $\zeta$ | 0.326 | 0.356 | 0.386 |
| $\alpha_\sigma$ | −24.120 | −25.126 | −26.132 |
| $\alpha_\pi$ | −21.081 | −22.017 | −22.953 |
| $\beta_\sigma$ | −7.634 | −8.445 | −9.075 |
| $\beta_\pi$ | −3.040 | −2.777 | −2.532 |
| $S_\sigma$ | 0.796 | 0.773 | 0.744 |
| $S_\pi$ | 0.307 | 0.273 | 0.242 |

## C. Two-Center Integrals

As usual, Eq. (18) is again employed to obtain two-center repulsion integrals which will be appropriately used with the one-center integrals derived empirically. The constants *m* and *n* in Eq. (18) are found from the theoretical values of $r = 3.2$ Å and $r = 4.0$ Å for $(a_\sigma a_\sigma|b_\sigma b_\sigma)$ and $(a_\sigma a_\sigma|b_\pi b_\pi)$ and of $r = 2.8$ Å and $r = 3.5$ Å for $(a_\pi a_\pi|b_\pi b_\pi)$ and $(a_\pi a_\sigma|b_\pi b_\sigma)$, calculated by Slater orbitals with corresponding effective nuclear charges. The results are shown in Table IV.

The theoretical expressions for two-center core integrals $\beta_\pi$ and $\beta_\sigma$ are easily obtained using the Goeppert–Mayer and Sklar resolutions:

$$\mathrm{H}^{2+}_{\pi\text{-core}}(\mu) = \mathrm{T}(\mu) + \mathrm{U}_{\pi a}(\mu) + \mathrm{U}_{\pi b}(\mu) + \sum_i \mathrm{U}_{\mathrm{H}_i}(\mu), \tag{88}$$

$$\mathrm{H}^{2+}_{\sigma\text{-core}}(\mu) = \mathrm{T}(\mu) + \mathrm{U}_{\sigma a}(\mu) + \mathrm{U}_{\sigma b}(\mu) + \sum_i \mathrm{U}_{\mathrm{H}_i}(\mu), \tag{89}$$

where T is the kinetic energy operator, $\mathrm{U}(\mu)$ gives a potential energy of attraction between electron $\mu$ and the charged atom $a$ or $b$, and $\mathbf{U}_{\mathrm{H}i}(\mu)$ denotes a potential due to $i$th hydrogen atom. For instance, one gets

$$\beta_\pi = -(A : a_\pi b_\pi) - (a_\pi a_\pi | a_\pi b_\pi) + S_\pi[(A : b_\pi b_\pi) + (a_\pi a_\pi | b_\pi b_\pi)], \qquad (90)$$

where $(A:pq)$ is the usual penetration integral between atomic orbitals $p$ and $q$ and a neutral atom $A$ [symbol $A$ is used instead of $a$ to avoid confusion; cf. Eq. (14)]. The hybrid penetration integrals of the type $(H_i:pq)$ cancel out by the use of the Mulliken-type approximation. On the other hand, the use of the corresponding approximation for $(A:a_\pi b_\pi)$ and $(a_\pi a_\pi | a_\pi b_\pi)$ probably would produce serious errors, as was suggested in Section IV. We therefore adopted the a priori prescription that the hybrid integrals appearing in the expression of $\beta_\pi$ should be calculated purely theoretically using the Slater-type atomic orbitals. Assuming that the same line of discussion holds for $\beta_\sigma$, one obtains the numerical values for both $\beta_\pi$ and $\beta_\sigma$ (Table IV).

### D. Results and Remarks

With the numerical values of integrals over atomic orbitals given in Table IV, the secular equations, 8 × 8 for $N$ ($^1A_{1g}$), 4 × 4 for $V$ ($^1B_{1u}$) and $T$ ($^3B_{1u}$), and 5 × 5 for $I$ ($^2B_{3u}$) and $A$ ($^2B_{2g}$), are solved. The results for the electronic spectrum of ethylene are shown in Table V, together with several others reported previously. The calculations of the first vertical ionization energy (I.E.) and electron affinity (E.A.) are easily performed since

$$\begin{aligned} \text{I.E.} &= E(\Psi_I) - E(\Psi_N), \\ \text{E.A.} &= E(\Psi_N) - E(\Psi_A), \end{aligned} \qquad (91)$$

and their values obtained are listed in the last column of Table V.

It is clear that the present treatment including $\sigma$ electrons gives better result for the lower electronic transitions than the previous calculation in which the $\pi$-electron approximation was employed. In particular the energy of the $^3B_{1u}$ state (or singlet–triplet split) comes out much better than before. Moser's calculation (1953b) shows that the nonempirical ASMO-CI method produces too high an $N$–$V$ transition (and also too large a singlet–triplet split) as usual. Further improvement for the $V$–$T$ split might be expected if different atomic orbitals (different $Z$ values) were used for $V$ and $T$ states, as shown by Ohno and Ito (1955). Since Moffitt's (1953) and Craig's (1950) calculations treat only $\pi$ electrons (the latter also considers a change in $a$–$b$ internuclear distance and $Z$ values for ground and excited states), their predictions are not strictily comparable to those mentioned above.

The value obtained for the ionization energy is again in good agreement with experiment. From the fact that using the same $Z$ value for both neutral and ionized ethylene one gets too high an ionization energy (around 14 eV), it would seem clear that the present modification of differential ionization achieves a considerable improvement over the generalized Hückel method and also over the conventional ASMO method. As for the electron affinity of ethylene, we have discussed this in the previous section.

The $\sigma$–$\pi$ interchange interaction, in general, causes large energy intervals between the ground state and the excited states, as pointed out by several authors (Ohno and Ito, 1955; Niira, 1953). The bottom lines of Table V show that somewhat better agreement with observed spectrum and also ionization energy is obtained if $\sigma$–$\pi$ interchange is ignored. Nothing can be said at this time about which treatment is just right however. The new configurations introduced by the inclusion of $\sigma$ electrons do not fall among the pure $\pi$ configurations but fall at much higher levels. That is, it may be stated that the $\sigma$–$\pi$ interaction is so small as to be negligible—the same conclusion as from the nonempirical calculation.

TABLE V

ELECTRONIC STATES OF ETHYLENE (eV)

| State | $N(^1A_{1g})$ | $V(^1B_{1u})$ | $T(^3B_{1u})$ | $Z(^1A_{1g})$ | I.E. | E.A. |
|---|---|---|---|---|---|---|
| Observed | 0.0 | 7.6 | 6.4? | — | 10.62<br>10.52 | — |
| AO (Ohno and Ito) | 0.0 | 8.6 | 5.8 | 14.9 | — | — |
| Nonempirical ASMO (Moser) | 0.0 | 11.42 | — | 14.74 | — | — |
| Moffitt | 0.0 | 7.3 | 5.5 | — | — | — |
| Generalized Hückel | | | | | | |
| Two-electron (Section IV) | 0.0 | 7.10 | 3.68 | 9.74 | 10.75 | −5.98 |
| Four-electron, I[a] (Section V) | 0.0 | 7.94 | 5.35 | 12.80 | 10.94 | −5.16 |
| Four-electron, II[b] (Section V) | 0.0 | 7.83 | 5.23 | 12.60 | 10.83 | −5.06 |

[a] $\sigma$–$\pi$ interchange is included.

[b] $\sigma$–$\pi$ interchange is neglected.

In this section the adjustment of the effective nuclear charges is again shown to be significant. Further preferential stabilization of the molecule ion might be expected from $\sigma$–$\pi$ interaction, as suggested in the beginning, but this does not appear to be the case. This and negligibility of $\sigma$–$\pi$ interactions lead to the conclusion that, allowing for the change for the effective nuclear charge in the molecule ion, theoretical calculation of the electronic spectra and also of the ionization energies for unsaturated hydrocarbons should be made to give good results even within the framework of the $\pi$-electron theory.

## VI. Two-Center Electronic Repulsion Integrals

An improved method for obtaining one-center repulsion integrals from the complete consideration of the atomic valence-states has been mentioned in Section V. We now turn to the problem of two-center Coulomb repulsion integrals in the generalized Hückel method. Attention should be called to Parr's recent paper (1960), in which he emphasized the usefulness of multipole expansion methods for the evaluation of these integrals. Among several advantages that he pointed out, the following one is of interest: All two-center repulsion integrals involving $\pi$ orbitals could be computed from *simple classical* formulas of the scalar quadrupole moment, and the asymptotic formulas obtained are shown to be very good approximations for large values of internuclear distance (Mulligan, 1951; Parr and Taylor, 1951). We will not dwell on the whole feature of this matter but only reproduce the derivation of the formulas briefly.

In terms of charge distributions $\Omega_a$ and $\Omega_b$ of $p$ orbitals $\chi_a$ and $\chi_b$ (centered at nuclei $a$ and $b$, a distance $R$ apart), the Coulomb repulsion integral can be written as

$$(aa|bb) = \int \Omega_a(\mu)(e^2/r_{\mu\nu})\Omega_b(\nu)\, dv(\mu)\, dv(\nu). \tag{92}$$

If polar coordinates $\theta_a$, $\phi_a$ and $\theta_b$, $\phi_b$ which indicate the orientation of two $p$ orbitals are used, the above integral can be expanded in powers of $(1/R)$ when $R$ is not zero:

$$\begin{aligned}(aa|bb) \cong e^2\{&(1/R) + (1/(4R^3))[q_a(3\cos^2\theta_b - 1) + q_b(3\cos^2\theta_a - 1)] \\ &+ (3q_aq_b/(16R^5))[1 - 5\cos^2\theta_a - 5\cos^2\theta_b - 15\cos^2\theta_a\cos^2\theta_b \\ &+ 2(\sin\theta_a\sin\theta_b\cos(\phi_a - \phi_b) - 4\cos\theta_a\cos\theta_b)^2]\}.\end{aligned} \tag{93}$$

Here quantity $q$ is the scalar quadrupole moment of the distribution $\Omega$:

$$q_i = \int \Omega_i(\mu)(3\cos^2\theta_i - 1)r_i^2\,dv(\mu). \tag{94}$$

If $\chi_a$ and $\chi_b$ are $\pi$ orbitals of parallel type, as in the special case of Eq. (93), one obtains ($\theta_a = \theta_b = \pi/2$, $\phi_a - \phi_b = 0$):

$$(aa|bb) \cong e^2[(1/R) - (q_a + q_b)/(4R^3) + (9q_aq_b)/(16R^5)], \tag{95}$$

or for the homonuclear case ($q_a = q_b = q$) this reduces to

$$(aa|bb) \cong e^2[(1/R) - q/(2R^3) + (9q^2)/(16R^5)]. \tag{96}$$

Further, if Slater $2p\pi$ orbitals with effective nuclear charge $Z$ are used for $\chi_a$ and $\chi_b$, Eq. (94) yields $q = 24_a^2/Z^2$ ($a_0$, the 1-quantum Bohr radius), and Eq. (96) then becomes

$$(aa|bb) \cong Z(e^2/a_0)[(1/\rho) - (12/\rho^3) + (324/\rho^5)] \tag{97}$$

with $\rho = ZR/a_0$.

In Fig. 1 are shown the Coulomb repulsion integrals computed from Eq. (97) together with those obtained from usual theoretical calculation (Roothaan, 1951). For large values of $\rho$ the approximate values are very good. Equation (97) is thus found to be convenient for evaluation of two-center repulsion integrals for large values of internuclear distance $R$. For

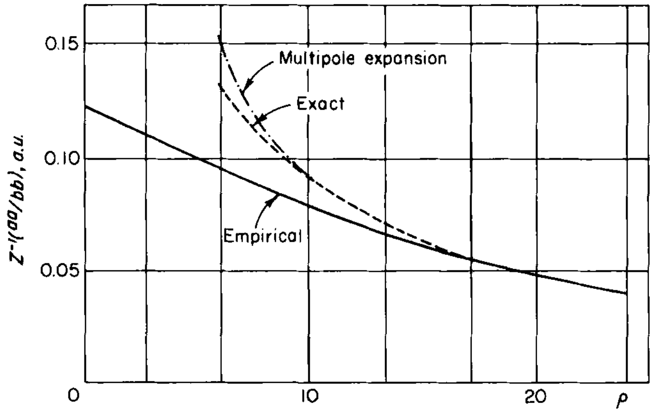

Fig. 1. Coulomb repulsion integrals involving $2p\pi$ orbitals.

small values of $R$, the asymptotic formula (97) and purely theoretical calculations are both irrational, so that we should follow the same procedure as mentioned in Section II. That is, one may use the relation

$$m\rho^2 + n\rho = Z^{-1}[(aa|aa) - (aa|bb)] \tag{98}$$

(in a.u.) where $m$ and $n$ are again constants to be determined by two-point interpolation. With the value of the one-center repulsion integral for carbon $2p\pi$ orbitals $(aa|aa) = 0.1227Z$ a.u. obtained before, one would have

$$Z^{-1}(aa|bb) = 0.1227 - 0.005093\rho + 0.000070\rho^2 \tag{99}$$

(in a.u.). Two-center integrals calculated in this way are shown as solid line in Fig. 1. Admitting some uncertainties of interpolation, the above formula may be used for the estimation of two-center repulsion integrals with various $R$ and $Z$ values.

One more remark must be made concerning Eqs. (95) and (96). Since the feature of these multipole expansions is purely classical in nature, one can treat $q$ (or $q_a$ and $q_b$) as an empirical parameter to be determined from some of the observed data. If this could be done, one would have a workable formula which is applicable to the Coulomb repulsion integrals for a wide range of internuclear distances.

## VIII. Further Applications to Larger Molecules

The improved prescriptions that have been set forth and shown to be workable in the case of ethylene are now applied to more complex molecules, butadiene and benzene. As the number of the carbon centers increases, the correction of differential ionization should be less significant. In order to simplify future calculations, one may make the following assumptions: (a) Only $\pi$ electrons are explicitly considered. (b) Only one-electron jump configurations are considered in the CI procedure, configurations in which more than two-electrons are raised being ignored. (c) Hydrogen penetration is neglected, while penetration integrals involving carbon atoms are computed theoretically. (d) The zero differential overlap is assumed. (e) Two-center core integrals $\beta$ *should* be calculated by the use of the formula

$$\beta_{pq} = -S_{pq}I_{2p} \tag{100}$$

instead of Eq. (19) or Eq. (25). The overlap integral here, of course, should not be zero; this is the only exception. (*f*) Two-center repulsion integrals should be computed by Eq. (99).

Now examples of calculation are shown for ethylene, butadiene, and benzene The results are summarized in Table VI (I'Haya and Parr, 1961; I'Haya, 1961, 1962). First, it is shown that the assumption of zero differential overlap brings no special errors in ethylene. For butadiene, the following simple starting molecular orbitals are used:

**TABLE VI**

ELECTRONIC STATES OF ETHYLENE, BUTADIENE, AND BENZENE (eV)

| Ethylene | | | Butadiene | | | | Benzene | | |
|---|---|---|---|---|---|---|---|---|---|
| | Calculated | Observed | | Calculated | | Observed | | Calculated | Observed |
| | | | | *Cis* | *Trans* | | | | |
| $^1B_{1u}$ | 7.87 | 7.6 | $^1B$ | 5.68 | 6.09 | 6.0 | $^1B_{2u}$ | 5.31 | 4.9 |
| $^3B_{1u}$ | 4.60 | 5.6? | $^1A$ | 7.71 | 7.80 | 7.2? | $^1B_{1u}$ | 6.24 | 6.2 |
| $^1A_{1g}$ | 12.41 | — | $^1A$ | 9.12 | 8.58 | — | $^1E_{1u}$ | 7.94 | 7.0 |
| | | | $^1B$ | 10.68 | 11.06 | — | | | |
| | | | $^3B$ | 3.83 | 3.87 | — | $^3B_{2u}$ | 5.31 | — |
| | | | $^3A$ | 5.14 | 5.12 | — | $^3B_{1u}$ | 4.10 | 3.8 |
| | | | $^3A$ | 8.53 | 8.78 | — | $^3E_{1u}$ | 5.35 | — |
| | | | $^3B$ | 9.83 | 10.03 | — | | | |
| I.E. | 10.84 | 10.62 | I.E. | 8.52 | 8.64 | 9.07 | I.E. | 9.17 | 9.24 |

$$\begin{aligned} 1 &= \phi_1 = \tfrac{1}{2}(\chi_a + \chi_b + \chi_c + \chi_d), \\ 2 &= \phi_2 = \tfrac{1}{2}(\chi_a + \chi_b - \chi_c - \chi_d), \\ 3 &= \phi_3 = \tfrac{1}{2}(\chi_a - \chi_b - \chi_c + \chi_d), \\ 4 &= \phi_4 = \tfrac{1}{2}(\chi_a - \chi_b + \chi_c - \chi_d). \end{aligned} \tag{101}$$

Following assumption (b) above, determinantal wave functions to be considered are

$$\begin{aligned} &N(^1A_{1g}) : (1\bar{1}2\bar{2}) \\ &V_{23}(^1B_{1u}),\ T_{23}(^3B_{1u}) : \frac{1}{\sqrt{2}}[(1\bar{1}2\bar{3}) \pm (1\bar{1}3\bar{2})] \\ &V_{13}(^1A_{1g}),\ T_{13}(^3A_{1g}) : \frac{1}{\sqrt{2}}[(1\bar{3}2\bar{2}) \pm (3\bar{1}2\bar{2})] \\ &V_{24}(^1A_{1g}),\ T_{24}(^3A_{1g}) : \frac{1}{\sqrt{2}}[(1\bar{1}24) \pm (1\bar{1}4\bar{2})] \\ &V_{14}(^1B_{1u}),\ T_{14}(^3B_{1u}) : \frac{1}{\sqrt{2}}[(142\bar{2}) \pm (4\bar{1}2\bar{2})], \end{aligned} \tag{102}$$

and for the molecule 1+ ion

$$I(^2B_{1g}) : (1\bar{1}2). \tag{103}$$

Using the concept of differential ionization, the $Z$ value for a carbon atom in the butadiene positive ion may be assumed to be 3.337. This corresponds to the postulate that one-fourth of an electron is removed from each atom under ionization. Again the results shown in Table VI are most encouraging. The predicted values of ionization energies for both *cis*- and *trans*-butadiene are somewhat lower than the observed ones. The reason for this discrepancy is twofold: (1) The starting molecular orbitals in Eq. (101) may not be appropriate for this sort of simple CI procedure, since there is a terminal effect in butadiene, (2) The assumption that one-fourth of an electron on each atom is ionized may lead to an error, for the same reason as (1). Ih view of the fact that if one starts from the Hückel MO's and even from SCF MO's instead of Eq. (101) one obtains not very much improved results for ionization energy, reason (2) above is considered to be more important. Reserving this matter for the present, emphasis should be placed again on the validity of the differential ionization correction, without which computed ionization energies come out to be 12.29 eV for *cis*- and 12.41 eV for *trans*-butadiene.

For benzene the starting molecular orbitals are

$$\phi_l = \frac{1}{\sqrt{6}} \sum_{p=1}^{6} \chi_p w^{lp} \qquad [l = 0, \pm 1, \pm 2, 3; \quad w = \exp(2\pi i/6)], \tag{104}$$

with $Z = 3.25$ for neutral benzene and $Z = 3.308$ for benzene positive ion [$+\frac{1}{6}$ charge on each atom after ionization]. The results (Table VI) are again encouraging.

Further applications have been made for the calculation of the electronic structures and spectra of benzene and naphthalene, in that all two-electron jump configurations are taken into account. The effects of these higher-order configuration interactions, however, are shown to be not very great (Ito and I'Haya, 1963).

## VIII. Concluding Remarks

As has been mentioned heretofore, we might hope that we could proceed confidently to the treatment of more complex molecules with the improved generalized Hückel method. In particular, various assumptions have been shown to have sound bases (in rather heuristic ways) and to be convenient method for making complicated problems manageable. These are:

(1) $\pi$ electrons are treated apart from the rest.

(2) Configuration interactions should be included, taking only one-electron excitations.

(3) Each $Z$ value for the corresponding molecular state should be determined by the concept of differential ionization. This is significant in the case of ionization energy prediction.

(4) One-center core integral $\alpha$ should be evaluated by use of Eq. (13), in which $W_{2p}$ (or $I_{2p}$) should be estimated from a relation of the differential ionization energy, Eq. (55), for example. Penetration integrals involving hydrogen might be ignored.

(5) Two-center core integral $\beta$ should be computed a priori [Eqs. (19) and (26)] .The simple relation

$$\beta_{pq} = -(S_{pq}/2)(I_p + I_q) \qquad (S_{pq} \neq 0) \tag{105}$$

holds with some degrees of accuracy. Here $I_p$ and $I_q$ should be obtained from like formulas of Eq. (55).

(6) Zero differential overlap may be assumed.

(7) One-center repulsion integrals $(pp|pp)$ should be determined from complete consideration of atomic valence-states, taking into account differential ionization.

(8) Two-center repulsion integrals $(pp|qq)$ should be estimated in line with the arguments of Section VI. Equation (99) or a like formula is useful.

The material stated above is, of course, far from perfect. Specifically, applications of the present method to heteronuclear systems and to other molecular properties have not been reviewed here. The importance of doubly excited configurations for some heteronuclear systems, for example, will be a good challenge to assumption (2) above (Murrell and McEwen, 1956; I'Haya, 1959). With further improvement of the generalized Hückel method we will be able to do better.

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# Accuracy of Calculated Atomic and Molecular Properties

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## I. Introduction

The intractability of the problem of calculating good wave functions and energies has tended to obscure the importance of the problem of using existing wave functions more efficiently in the calculation of various molecular and atomic properties. This problem arises because, for an approximate wave function with an error of order $\eta$, the error in the total energy is of order $\eta^2$ and so is relatively insensitive to improvements in the wave function, whereas, for most other properties, the error is of order $\eta$ and so is much larger and more sensitive. Since $\eta$ may be large, even for a function which gives a good total energy, the calculations of other properties fluctuate considerably and do not even seem to converge as $\eta$ is decreased. The usual method recommended for improving the calculations is to improve the wave function by further minimization of the energy. This is unsatisfactory as a general solution because it will never be available for elaborate systems and because it evades the real problem. The method to be discussed in this review is based on a more fundamental approach to the problem and leads to calculations of properties in which the errors are of order $\eta^2$. The essence of the method is that molecular properties can be defined in a number of ways which are entirely equivalent when an exact eigenfunction is used but have different dependence on the error when an approximate wave function is used. The problem becomes one of finding the appropriate formula for a property which minimizes its dependence on the error.

The basis of this new method of calculating molecular properties is primarily due to Dalgarno, Lewis, and Stewart (Dalgarno and Lewis, 1955; Dalgarno and Stewart, 1956, 1960). Their work was reformulated and extended by Schwartz (Schwartz, 1959a,b). Some of the ideas involved have a long history, however, and this will be shown in this review by considering the relation between this method and some other general methods of analyzing perturbation calculations.

## II. The Double Perturbation Expansion

For purposes of calculation, molecular properties fall into three classes. The largest class consists of those properties which are defined as the mean value of some operator taken over the exact eigenfunction for some state. Such properties usually arise physically through a small perturbation of the system represented by the perturbing operator, and the resulting first-order change in energy is just the mean value of the operator. The next class consists of properties defined in terms of higher-order perturbation theory. These include second-order energy changes such as are involved in polarizabilities and effects due to the combined application of several perturbations. For a recent review of these see Dalgarno (1962). The third class consists of those properties, such as transition probabilities, which depend on several states. This review deals exclusively with the first class.

The easiest way of understanding the nature of the basic problem is by formulating it in terms of a double perturbation theory. The Hamiltonian of the system is denoted by $H$ and the perturbing operator is $P$ with the small parameter $\varepsilon$ so that the perturbed Hamiltonian is

$$H + \varepsilon P. \tag{1}$$

The available wave function $\phi$ is not an eigenfunction of $H$, but it will be assumed that there is a Hamiltonian $h$ for which it is an exact eigenfunction, so that

$$h\phi = e_0\phi \tag{2}$$

and, for convenience, $\phi$ is normalized to unity. The error can be defined as

$$\eta v = H - h \tag{3}$$

where $v$ is the operator of the error and $\eta$ its magnitude. The perturbed Hamiltonian can then be written as

$$h + \eta v + \varepsilon P \tag{4}$$

and the perturbed eigenfunction and eigenvalue expanded as a double power series in both $\eta$ and $\varepsilon$. The eigenfunction is, therefore,

$$\psi = \phi + \eta\phi_{01} + \varepsilon\phi_{10} + \eta\varepsilon\phi_{11} + \cdots \tag{5}$$

and the eigenvalue

$$W = e_0 + \eta e_{01} + \varepsilon e_{10} + \eta\varepsilon e_{11} + \cdots . \tag{6}$$

From the eigenvalue equation

$$(h + \eta v + \varepsilon P)\psi = W\psi, \tag{7}$$

equations are deduced for the terms of the various orders. In particular, the first energy coefficients are

$$e_0 = \int \phi^* h\phi \, d\tau \tag{8}$$

$$e_{01} = \int \phi^* v\phi \, d\tau \equiv \langle v \rangle \tag{9}$$

$$e_{10} = \int \phi^* P\phi \, d\tau \equiv \langle P \rangle \tag{10}$$

and the bilinear coefficient is

$$e_{11} = \int \{\phi_{01}^*(P - \langle P \rangle)\phi + \phi^*(P - \langle P \rangle)\phi_{01}\} \, d\tau \tag{11}$$

or, alternatively,

$$e_{11} = \int \{\phi_{10}^*(v - \langle v \rangle)\phi + \phi^*(v - \langle v \rangle)\phi_{10}\} \, d\tau. \tag{12}$$

The perturbed wave functions involved in $e_{11}$ are determined by

$$(h - e_0)\phi_{01} = (e_{01} - v)\phi, \tag{13}$$

$$(h - e_0)\phi_{10} = (e_{10} - P)\phi. \tag{14}$$

It is of considerable importance to note that $e_{11}$ can be calculated in two quite different ways depending on whether $\phi_{01}$ is known and Eq. (11) used or $\phi_{10}$ with Eq. (12).

In relation to the original form of the Hamiltonian, the terms in $\eta$ give the effect of the error in $\phi$. The first-order change in the energy caused by $P$ becomes

$$w_1 = \left(\frac{\partial W}{\partial \varepsilon}\right)_{\varepsilon=0} = e_{10} + \eta e_{11} + O(\eta^2). \tag{15}$$

Thus to obtain an estimate of $w_1$ whose error is quadratic in $\eta$ it is necessary to calculate, instead of the customary mean value $e_{10}$, the more elaborate expression

$$w_1 = e_{10} + \eta e_{11}. \tag{16}$$

The bilinear term $e_{11}$ measures the extent to which the two perturbations interfere with one another. The first-order error is, similarly,

$$e_{01} + \varepsilon e_{11}, \tag{17}$$

and this will vanish for arbitrary $\varepsilon$ only if both $e_{01}$ and $e_{11}$ vanish.

Although the Hamiltonian $h$ can always be constructed formally by using the projection operator on to $\phi$, the subsequent calculations are much simpler if $\phi$ is such that $h$ can be written down explicitly in operator form. The ground state of the helium atom isoelectronic sequence is an example of this which has been discussed by Dalgarno and Stewart (1956). Corresponding to the wave function

$$\phi = \zeta^3\pi^{-1}\exp\{-\zeta(r_1 + r_2)\} \tag{18}$$

the Hamiltonian can be taken as

$$h = (-\tfrac{1}{2}\nabla_1^2 - \zeta/r_1) + (-\tfrac{1}{2}\nabla_2^2 - \zeta/r_2) \tag{19}$$

and the error is

$$\eta v = 1/r_{12} - (Z - \zeta)/r_1 - (Z - \zeta)/r_2. \tag{20}$$

Because of the presence of the interelectronic repulsion term, the equation for $\phi_{01}$ cannot be solved in terms of known functions, but there is a variational method of solution (Hylleraas, 1930), and series solutions can be calculated to high accuracy (Knight and Scherr, 1962). For most perturbations it is easier to solve Eq. (14) for $\phi_{10}$ and use Eq. (12) to calculate $w_1$. Dalgarno and Stewart (1956) compare the results of the two methods of calculation and show how the rate of convergence of the series for $e_{11}$ may vary depending on the trial functions used for $\phi_{01}$.

This method can be extended to include other atoms and even some simple molecules. The Hamiltonian $h$ is taken as the sum of one-electron operators

$$h = \sum_i g(i) \tag{21}$$

for which spin orbitals $\omega_r$, defined by the eigenfunction equation

$$g\omega_r = \lambda_r \omega_r, \tag{22}$$

can be found exactly. The hydrogen-like form of $g$, as in Eq. (19), will serve for atoms and even for diatomic hydrides (see Hall and Rees, 1963). If the total energy is nondegenerate, the ground state eigenfunction of $h$ has the form of a determinant of the orbitals $\omega_r$. When there is degeneracy, the eigenfunction contains several determinants, and the theory becomes much more elaborate. The error operator can still be written down and, if $g$ consists of the usual one-electron kinetic energy operator and some potential terms, $\eta v$ will consist of potential terms alone. When the perturbation $P$ has the particular form of a sum of one-electron operators

$$P = \sum_i p(i) \tag{23}$$

then the $\mu_r$, the first-order changes in the orbitals, are determined by

$$(g - \lambda_r)\mu_r = (\lambda_r' - p)\omega_r \tag{24}$$

where

$$\lambda_r' = \int \omega_r^* p \omega_r \, d\tau. \tag{25}$$

The perturbed wave function $\phi_{10}$ has the form of a sum of determinants each having one $\mu_r$ replacing a $\omega_r$ in the original determinant. If Eq. (24) can be solved for the $\mu_r$, the value of $w_1$ is readily obtained in terms of one- and two- electron integrals.

## III. The *F*-Function Technique

A major disadvantage of the double perturbation treatment described in Section II is that it requires the approximate wave function to be an eigenfunction of some Hamiltonian $h$ and, in practical calculations, needs to know $h$ explicitly in order to calculate the effect of the error. This disadvantage is removed in a modification of the method due to Schwartz (1959a,b). The essential step in his method is the writing of the perturbed function $\phi_{10}$ as

$$\phi_{10} = F\phi \tag{26}$$

where $F$ is a function of the same variables as $\phi$. The perturbation equation is

$$(h - e_0)F\phi = (e_{10} - P)\phi \tag{27}$$

and, since $\phi$ is an eigenfunction of $h$, this becomes

$$(hF - Fh)\phi = (e_{10} - P)\phi. \tag{28}$$

Now, if $h$ has the same kinetic energy operator as $H$ and $F$ is a function of the coordinates alone, then their commutators with $F$ are identical,

$$[h, F] \equiv hF - Fh = HF - FH \equiv [H, F], \tag{29}$$

and the equation determining $F$ becomes

$$[F, H]\phi = (P - \langle P \rangle)\phi. \tag{30}$$

The expression for $w_1$ in terms of $F$ is

$$w_1 = \int \phi^* P \phi \, d\tau + \int \phi^* \{F^*(\eta v - \eta e_{01}) + (\eta v - \eta e_{01})F\} \phi \, d\tau \tag{31}$$

and the error operator can be eliminated from this by putting

$$\begin{aligned} \int \phi^* F^* (\eta v - \eta e_{01}) \phi \, d\tau &= \int \phi^* F^* (H - h - \eta e_{01}) \phi \, d\tau \\ &= \int \phi^* F^* (H - e_0 - \eta e_{01}) \phi \, d\tau \\ &= \int \phi^* F (H - \langle H \rangle) \phi \, d\tau \end{aligned} \tag{32}$$

where

$$\langle H \rangle = \int \phi^* H \phi \, d\tau \tag{33}$$

so that

$$w_1 = \int \phi^* P \phi \, d\tau + \int \phi^* \{F^*(H - \langle H \rangle) + (H - \langle H \rangle)F\} \phi \, d\tau. \tag{34}$$

In this method, therefore, no splitting of the original Hamiltonian $H$ is needed to calculate either the perturbed wave function from Eq. (30) or the accurate mean value from Eq. (34). Equations (30) and (34) can be derived directly without invoking the double perturbation theory, but it is more difficult to show the order of magnitude of the error.

Schwartz (1959b) discusses three different methods of solving Eq. (30). In some especially simple instances a particular integral of the equation can be discovered by inspection. Alternatively, if Eq. (30) can be reduced to a number of separate equations, each involving one function of one variable, then the solution can be written down as an indefinite integral (Young and March, 1958). The difficulties involved in this solution due to the presence of singularities are discussed by Brown and Hirschfelder (1963). The solution often involves integrals which are only conditionally convergent and have to be handled with great care. Since the functional

$$J = \int \phi^*\{F^*(P - \langle P\rangle) + (P - \langle P\rangle)F - \tfrac{1}{2}F^*[F, H] + \tfrac{1}{2}[F^*, H]F\}\phi \, d\tau \tag{35}$$

is stationary for fixed $\phi$ when $F$ satisfies Eq. (30) and $F^*$ the conjugate equation, the third method of determining $F$ is to assume some parametric form for it and make $J$ stationary with respect to those parameters. This variation principle is closely related to that used in ordinary perturbation theory (Hylleraas, 1930).

One particular example of the $F$-function technique has been known for some time. In this

$$F = e^{if} - 1 \tag{36}$$

where $f$ is a real function. This is a unitary transformation when applied to the function $\phi$ since the perturbed wave function is

$$\psi = \phi + F\phi = e^{if}\phi. \tag{37}$$

When there is a perturbing magnetic field present the first-order change in the wave function can be determined by finding an $f$ which depends linearly on the field. In a uniform magnetic field, for example, $f$ is the scalar product of the vector potential and the position vector and, hence, is the gauge. The theory of the gauge, therefore, is a special application of the theory of the $F$ function (Parr and Snyder, 1961).

## IV. The First-Order Density Matrix

One disadvantage of the $F$-function technique is that, for each new perturbation, a new $F$ function has to be calculated by solving Eq. (30). This arises because, in effect, $e_{11}$ is being calculated using Eq. (11) instead of Eq (12). The exact solution of Eq. (12) is too difficult for the reasons already discussed, but it was first appreciated by Schwartz (1959a) that a partial solution could be obtained. He showed that the first-order correction to the electron density for the helium atom ground state could be calculated exactly without knowing the first-order correction to the wave function.

This method of calculating the first-order density matrix has been generalized by Hall *et al.* (1964). The argument is developed from that in Section II where the zero-order wave function is taken in the form

$$\Phi = (N!)^{-1/2} \det\{\omega_1(1), \omega_2(2), \ldots \omega_N(N)\} \tag{38}$$

with a nondegenerate total energy and spin orbitals which satisfy a one-electron equation of the type

$$g\omega_r = \lambda_r \omega_r . \tag{39}$$

The zero-order density matrix is

$$\rho_0(1|2) = \sum_r^N \omega_r(1)\omega_r^*(2). \tag{40}$$

The first-order correction to the wave function can be expressed in terms of the determinants formed from $\Phi$ by replacing one or more of its orbitals by unused orbitals also determined by Eq. (39). Because of the form of the density matrix, only those determinants which differ from $\Phi$ by one orbital will contribute to the density matrix. These determinants can be denoted by $\Phi_{rs}$ where $\omega_r$ is the orbital omitted and $\omega_s$ the orbital replacing it. The coefficient of this determinant in the expansion of the first-order correction to the wave function is $c_{rs}$ and can be calculated using ordinary perturbation theory. Since the error operator is purely potential, it can be expressed as

$$H - h = \sum_{i<j} \theta_{ij} \tag{41}$$

where $\theta_{ij}$ includes the interelectronic repulsions and expresses the other potentials as two-electron potentials symmetric in the coordinates of electrons *i* and *j*. With this perturbation the coefficient $c_{rs}$ reduces to

$$c_{rs} = (\lambda_r - \lambda_s)^{-1} \sum_{t \neq r}^{N} \int \{\omega_s^*(1)\omega_t^*(2) - \omega_t^*(1)\omega_s^*(2)\}\theta_{12}\omega_r(1)\omega_t(2)\, d\tau_{12} . \tag{42}$$

If a set of functions $F_r$ is defined by the equation

$$[g, F_r]\omega_r = \sum_{t \neq r}^{N} \omega_t \int \omega_t^*(2)\theta_{12}\omega_r(2)\, d\tau_2 - \omega_r \sum_{t \neq r}^{N} \int \omega_t^*(2)\theta_{12}\omega_t(2)\, d\tau_2 + K_r\omega_r \tag{43}$$

where the constant $K_r$ is

$$K_r = \sum_{t \neq r}^{N} \int \omega_r^*(1)\omega_t^*(2)\theta_{12}\{\omega_r(1)\omega_t(2) - \omega_t(1)\omega_r(2)\}\, d\tau_{12} \tag{43a}$$

then these coefficients can be expressed in the simpler form

$$c_{rs} = \int \omega_s^* F_r \omega_r \, d\tau. \tag{44}$$

From this result the first-order correction to the density matrix can be calculated and is found to be

$$\rho_1(1|2) = \sum_r \{F_r(1) + F_r^*(2) - \langle F_r \rangle - \langle F_r^* \rangle\} \omega_r(1)\omega_r^*(2) \tag{45}$$

where

$$\langle F_r \rangle = \int \omega_r^* F_r \omega_r \, d\tau. \tag{46}$$

Thus the calculation of $\rho_1$ is reduced effectively to the solution of Eq. (43). The practical application of this method has been delayed by the difficulties of solving this equation, but the method has been applied to the ground state of helium, the lowest triplet state of helium, and the ground state of lithium.

Schwartz used the density to compare with the density obtained from approximate wave functions. It can also be used to derive the natural orbitals of the system. The principal importance of the method, however, is that it enables the value of $w_1$ for any one-electron perturbation $P$ to be calculated by a single integration

$$w_1 = \int p(1)\{\rho_0(1|1) + \rho_1(1|1)\} \, d\tau_1 \tag{47}$$

without solving any further equation. The extra labor of calculating the density matrix is repaid, therefore, when several different perturbations are to be considered.

## V. Stable Wave Functions

The problem of calculating accurate values of properties can also be approached using the minimum energy principle. If $\chi$ is the first-order change in the wave function due to a perturbation $P$, then the perturbed energy defined as

$$\int (\phi^* + \varepsilon\chi^*)(H + \varepsilon P)(\phi + \varepsilon\chi) \, d\tau \Big/ \int |\phi + \varepsilon\chi|^2 \, d\tau \tag{48}$$

is stationary in the sense that it depends quadratically on the errors in $\phi$ and $\chi$. In particular, the term linear in $\varepsilon$ is

$$\int \phi^* P\phi \, d\tau + \int \phi^*(H - \langle H\rangle)\chi \, d\tau + \int \chi^*(H - \langle H\rangle)\phi \, d\tau \qquad (49)$$

and, provided that

$$\chi = F\phi, \qquad (50)$$

this gives an alternative proof that $w_1$ depends quadratically on the error.

When $\phi$ is an exact eigenfunction of $H$ the two extra integrals in Eq. (49) vanish irrespective of how $\chi$ is defined. It has been proposed (Hall, 1961) that wave functions for which these extra terms vanish for the $\chi$ corresponding to a particular perturbation should be called stable under that perturbation. Thus, for a stable wave function the first-order energy reduces to

$$w_1 = \langle P\rangle \qquad (51)$$

but is still quadratic in the error. (This stability should be distinguished from the mathematical stability of certain iterative methods of calculating wave functions and the physical stability of the state in relation to other states.)

There are a number of general theorems about the stability of certain forms of wave function under certain forms of perturbation. The simplest of these states that a wave function will be stable under an arbitrary perturbation if and only if it is an exact eigenfunction of $H$. A less general but more useful theorem states that the single determinantal wave function with optimized orbitals and nondegenerate total energy is stable under any one-electron form of perturbation (Hall, 1961; Cohen and Dalgarno, 1961; Stanton, 1962). When there is degeneracy due entirely to spin the single determinant again becomes stable, but the orbitals which have different spins will have different spatial functions also. This is the unrestricted (or spin-polarized) molecular orbital wave function (Amos and Hall, 1961). It is this stability of the molecular orbital wave function which is so significant for the accurate calculation of one-electron properties of molecules and larger atoms. For these systems the analytical techniques discussed in previous sections are quite impractical, and the calculation of an accurate molecular orbital wave function may be the only way of obtaining estimates having quadratic errors.

In most practical calculations the wave function is determined by writing a trial function containing a finite number of parameters and varying these to obtain the minimum energy. Such a set of parameters defines a manifold in function space. If $\alpha$ is one of these parameters then, for least energy,

$$\int \phi^*(H - \langle H\rangle)\frac{\partial\phi}{\partial\alpha}\,d\tau + \int \left(\frac{\partial\phi}{\partial\alpha}\right)^*(H - \langle H\rangle)\phi\,d\tau = 0 \tag{52}$$

so that $\phi$ becomes stable for any perturbation whose $\chi$ can be expressed in terms of a linear combination of the derivatives such as $\partial\phi/\partial\alpha$ (Hall, 1961). This means, in practice, that a wave function can be made approximately stable under a given perturbation by introducing into the trial function parameters which enable these derivatives to approximate to the corresponding $\chi$. Since $\chi$ is not known exactly and since the number of parameters has to be limited, there will always be a truncation problem. The linear errors due to the part of function space outside the manifold of trial functions are probably always the largest source of error. Nevertheless this does give a practical method of approaching the ideal of a stable wave function.

There is one other more specialized application of the idea of stability. This concerns the determination of parameters such as the $\zeta$ in Section II. For a particular perturbation, the value of $w_1$ can be calculated as a function of $\zeta$ and the error is quadratic in $\eta$ for all $\zeta$. It has been argued that $\zeta$ should be chosen so as to minimize the unperturbed energy, but in practice it is found that better results are obtained if $\zeta$ is chosen to make the wave function stable under the particular perturbation involved. This value of $\zeta$ varies from perturbation to perturbation. It happens also that the stable value of $\zeta$ is the one for which $w_1$ is stationary with respect to $\zeta$. This means that $w_1$ is then least dependent on $\zeta$ and, hence, on the errors in $\phi$. It also means, according to Section II, that the error in the perturbed energy becomes independent of $\varepsilon$ to first order. Because of the fact that the perturbed wave function $\chi$ has to be calculated as a function of the parameter, this application is much more limited.

## VI. Some Illustrative Results

The effects of some of the different choices of methods of estimating the first-order value of a perturbation are illustrated in Table I. The perturbation is

$$P_\delta = 4\pi\{\delta(\mathbf{r}_1) + \delta(\mathbf{r}_2)\} \tag{53}$$

and the wave function is a determinant of $(1s)$ and $(2s)$ orbitals for the $^3S$ state of helium. The accurate value is quoted from Pekeris (1959).

### TABLE I

Estimates of the Value of $P_\delta$

| | |
|---|---|
| $<P_\delta>$ when $\zeta$ minimizes $e_0$ | 22.082 |
| $w_1$ when $\zeta$ minimizes $e_0$ | 31.361 |
| $w_1 = <P_\delta>$ when $\zeta$ makes $\phi$ stable | 32.721 |
| Accurate value (Pekeris, 1959) | 33.185 |

Table II compares the results obtained for the ground state of helium calculated using the double perturbation method (or by the $F$ technique or by the density matrix), evaluated at the stable value of $\zeta$, with the self-consistent field results and with the most accurate available results. For convenience only the first part of the perturbation is listed. Some earlier versions of this table contained errors or did not use stable values. A more extensive table of the positive powers has been calculated by Gordon (1964). The X-ray scattering factor has been considered by Weiss (1963). Table III shows some similar results for the $^3S$ state of helium.

### TABLE II

Ground State Properties for Helium Atom

| $p(1)$ | $<P>$ with stable $\zeta$ | Self-consistent field | Accurate |
|---|---|---|---|
| $4\pi\delta(\mathbf{r})$ | 44.925[a] | 45.194[b] | 45.501[c] |
| $r_1$ | 1.846[d] | 1.854[b] | 1.859[c] |
| $r_1^2$ | 2.339[a] | 2.369[b] | 2.387[c] |
| $r_1^{-1}$ | 3.375[a] | — | 3.377[c] |

[a] Dalgarno and Stewart (1960).
[b] Roothaan *et al.* (1960).
[c] Pekeris (1959, 1962).
[d] Hall *et al.* (1965).

### TABLE III

Lowest Triplet State Properties for Helium Atom

| $p(1)$ | $<P>$ with stable $\zeta$ | Accurate |
|---|---|---|
| $4\pi\delta(\mathbf{r}_1)$ | 32.721[a] | 33.185[b] |
| $r_1$ | 4.808[a] | 5.101[b] |
| $r_1^2$ | 20.131[a] | 22.929[b] |
| $r_1^{-1}$ | 2.312[a] | 2.309[b] |

[a] Hall *et al.* (1965).
[b] Pekeris (1959).

Results for more elaborate systems are more difficult to obtain, but there are some available for the lithium ground state (Hall *et al.*, 1965) and some approximate ones for the beryllium ground state (Hall and Hardisson, 1964).

## VII. Conclusions

The technique of transforming a function by multiplying it by an $F$ function has some importance in a wider context. There are two other types of functional transformation which are also of importance. The hypervirial operators investigated by Hirschfelder and his associates (Hirschfelder, 1960; Epstein and Hirschfelder, 1961; Hirschfelder and Coulson, 1962) involve the transformation of the function by differentiation. The more general transformation is by integrating the function over a kernel. The kernel, in the context of Eqs. (13) and (14), is the Green's function for the Hamiltonian $h$, and the solution of these equations is the integral over this Green's function multiplied by the terms on the right of the equation (see for example Kumar, 1962). It is interesting to note that the existence of all the analytical solutions obtained so far can be traced to the fact that a Green's function can be found in convenient form for the spherically symmetric states of the hydrogen atom. The possibility of calculating the first-order density matrix from Eq. (43) also becomes more significant in terms of Green's functions because of its relation to the one-electron Green's function (one-electron propagator) familiar in field theory (see for example Thouless, 1961).

Apart from the small number of atoms and the small number of approximate wave functions for which an analytical treatment is possible, the problem of calculating accurate values of atomic and molecular properties has no easy solution. This review has concentrated on these examples in order to demonstrate, as in Table I, the seriousness of the problem and the difficulty of solving it. In the more general circumstances of larger atoms and molecules the search for stable wave functions seems the only hopeful method and the results in Table II show that, when the orbitals are sufficiently optimized, the errors in the properties calculated using an orbital wave function are fairly small.

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# Recent Developments in Perturbation Theory

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# I. Introduction

In recent years there has been a great increase of interest in the application of perturbation theory to the fundamental problems of quantum chemistry. Perturbation theory is designed to deal systematically with the effects of small perturbations on physical systems when the effects of the perturbations are mathematically too difficult to calculate exactly, and the properties of the unperturbed system are known. It is therefore usually the appropriate tool for dealing with the effects of external fields, with the long-range interactions between atoms and molecules, and with small internal perturbations such as those that give rise to the fine and hyperfine structure of spectral lines. Perturbation theory has been used for these purposes since the inception of quantum mechanics, but it is only recently that it has been applied seriously to what may be called the fundamental "few-body" problems of quantum chemistry, where the perturbation is not small; namely, electron repulsion and the many-center Coulomb field in molecules.

The new applications have been mainly to atoms where the reciprocal of the atomic number, $1/Z$, provides a natural perturbation parameter.[1]

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[1] If the coordinates $\mathbf{r}_i$ are transformed to the new coordinates $\mathbf{r}_i' = Z\mathbf{r}_i$, the new Hamiltonian is $H' = Z^{-2}H$ with the new energy $E' = Z^{-2}E$. Then the electron repulsion terms in $H'$ have the form $(1/Z)\,(1/r_{ij}')$ and the rest of $H'$ is independent of $Z$ (see Section XI).

They may be divided into two groups. The first consists of calculations of energy levels, and is a natural outgrowth of Hylleraas's classic work on the $1/Z$ expansion for two-electron atoms. It includes the continuation of Hylleraas's calculation to higher orders by Scherr and collaborators, the work of Dalgarno and Linderberg on the $1/Z$ expansions within the Hartree–Fock approximation for atoms, and explorations by Parr and others on the united atom (single-center) approach to molecules. The applications in the second group are to the calculation of expectation values and other properties of atoms and molecules, and are of much more recent origin. They include calculations begun by Sternheimer and developed by Dalgarno and by Schwartz on the polarizabilities and nuclear shielding constants of atoms, and recent attempts to extend these ideas to molecules.

There are two principal reasons for the success of these new applications. First, sufficient accuracy is frequently obtained from knowledge of a first-order perturbed wave function. From such a function, the energy can be computed accurate through the third order, and good values can be obtained for the expectation values of properties other than the energy. Second, a great advantage of perturbation theory is that the functional form of the perturbed wave function is shaped by the perturbation itself. This is in contrast with the usual methods where the choice of trial function is arbitrary. For example, Schwartz (1959a), starting with the simplest hydrogenic wave function, obtained a simple closed-form perturbation expression for the charge density of the helium atom, which agrees almost precisely with the charge density calculated with the use of Hylleraas's eight-parameter wave function.

The recent renewal of interest in the potentialities of perturbation theory has been sparked by three developments:

(a) It had long been recognized in the literature, both implicitly and explicitly, that the standard summation formulas of perturbation theory are formal solutions of certain inhomogeneous equations, whose solution might be better accomplished in some other fashion. Moreover, in many cases an examination of the equations revealed the possibility of solution in closed form. However, in spite of successes, such techniques were not pursued systematically and, curiously enough, are rarely mentioned in the usual textbooks. Today, impressed by the many fruitful applications made by Dalgarno, by Schwartz, and by others, one is looking more and more to the equations themselves rather than to their formal solutions. The methods used to obtain explicit solutions of the perturbation equations are reviewed in Section III,A.

(b) Although closed solutions are possible in some problems, in particular for many one-electron atomic problems, this is not the case when the perturbation involves the two-particle electron repulsion potential $1/r_{12}$, or indeed for most problems. Faced with this situation, there has been increasing recognition of the fact, pointed out long ago by Hylleraas, that one can often get satisfactory variational approximations to the *individual terms* in the perturbation series. The methods used to obtain variational solutions of the perturbation equations are reviewed in Section III, B.

(c) Whereas the total energy calculated by means of approximate zero order wave functions is accurate up to the second order, most physical properties calculated with such functions are only accurate up to the first order. The first correction to approximate properties for badness of the wave function can be written in terms of accessible functions by means of what may be called Dalgarno's interchange theorem. This is discussed and proved in Section IV.

These developments, which have been mainly applied to atoms, are far from having exhausted their usefulness, or their power to stimulate further work. Perturbation theory appears destined to play an increasingly important role in quantum chemistry, and it therefore seems timely to review the basic theory underlying the new developments in a thorough manner. The present article is not intended to provide a comprehensive account of all aspects of perturbation theory, such as those given in the excellent review articles of Dalgarno (1962) and Preuss (1962). Nor are all the important new developments discussed, such as the infinite-order perturbation treatments associated with the names of Brueckner (1955), Löwdin (1962), and Primas (1961), or the selective summation technique of Kelley (1963). Instead, most of our discussion is restricted to the first few orders of perturbation theory and devoted to the recent developments which have been most successful, or to those that seem most promising.

The only form of perturbation theory we discuss in this article is the Rayleigh–Schrödinger (reviewed in Section II) which was developed by Lord Rayleigh for vibrating systems and introduced into quantum mechanics by Schrödinger.[2] In this treatment, a Hamiltonian $H$ for a system is regarded as consisting of an unperturbed Hamiltonian $H_0$ and a perturbation operator

$$\lambda V = H - H_0 .$$

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[2] The Brillouin–Wigner or Feenberg perturbation series converge faster than the Rayleigh–Schrödinger, but they require that the energy be determined in an iterative manner.

The eigenvalues $E(\lambda)$ and eigenfunctions $\Psi(\lambda)$ of $H$ are expanded in power series in $\lambda$. The essential role of $\lambda$ is thus to define the different orders of perturbation, and this is a unique feature of the Rayleigh–Schrödinger theory. In certain problems, $\lambda$ has an obvious physical significance. Otherwise, $\lambda$ is usually assigned the value of unity. Thus the perturbation equations arise from the Schrödinger equation

$$(H - E)\Psi = 0$$

by equating the coefficient of every individual power of $\lambda$ to zero. There is a very important consequence of this procedure which it is appropriate to mention here, namely, that any theorem which is true for the exact solutions of the Schrödinger equation for any value of $\lambda$ must have an analog for the solutions of each perturbation equation separately. The most interesting examples are the variational principle (discussed in section V), the virial and hypervirial theorems, and the Hellmann–Feynman theorem.

The variational principle and perturbation theory are deeply intertwined. On the one hand, given a quantity accurate through a particular order of perturbation, a corresponding variational principle can be constructed. On the other hand, given a variational principle, individual variation principles for the different orders of perturbation can be derived. These provide a fruitful and practical source of approximate perturbation energies and approximate perturbed wave functions. A striking instance of the interconnection is the fact that one of the most important theorems in perturbation theory, namely, that knowledge of the $n$th order wave function suffices to determine the energy to order $(2n + 1)$, is an immediate consequence of the variation principle, as shown in Section II. These and other aspects of the variation principle and variational approximations are discussed at length in Section V.

A familiar complaint about perturbation theory is that when the perturbation becomes large the treatment ceases to give meaningful results. The usual rule of thumb is that the energy shifts should be small compared with the spacings of the unperturbed levels. If the energy levels tend to cross, one expects difficulties and special methods must be used (see Section VII). However, near degeneracy is not the only source of difficulties. The energy levels and eigenfunctions may not be analytic functions of the perturbation parameter, and there may be *no* solutions to the equations. In other cases, the series may only be asymptotic.

The questions of the existence, nature, and convergence of the perturbation series pose difficult mathematical problems. Nevertheless some very powerful theorems, apparently little known to chemists, have been proved by Rellich (1939, 1940), Kato (1951a), Titchmarsh (1958), and others, which cover most of the applications of interest in quantum chemistry. A basic theorem, due originally to Rellich (1939), is that the Rayleigh–Schrödinger perturbation series for $E(\lambda)$ and $\Psi(\lambda)$ converge for sufficiently small $\lambda$ if the unperturbed Hamiltonian is self-adjoint (Section XII) and if two constants $a$ and $b$ can be found such that $V\phi$ and $H_0\phi$ satisfy the inequality

$$\langle V\phi, V\phi\rangle \leqslant a\langle H_0\phi, H_0\phi\rangle + b\langle \phi, \phi\rangle \tag{I.1}$$

for all functions $\phi$ in the domain of $H_0$. The most important application of this theorem has been made by Kato (1951a), who succeeded in proving that it is satisfied for any decomposition of the potential $U$ of the nonrelativistic Schrödinger Hamiltonian operator $H$ for any atom, molecule, or finite crystal, provided no new singularities stronger than Coulomb poles are introduced. In particular the theorem is true in the following important cases:

(a) The perturbation $V$ is the electron repulsion term in the potential $U$. This result justifies the $1/Z$ expansion and proves that it is absolutely convergent for large enough $Z$. Although Kato could only obtain the crude estimate $Z \cong 7.6$ for the radius of convergence of the two-electron atom, the calculations of Scherr and Knight (1963) indicated that the true value is as low as $Z \cong 0.8$.

(b) The perturbation $V$ is the difference between the many-center Coulomb potential terms in a molecule and single-center terms for the united atom nucleus. This application justifies the united atom (single-center) expansions.[3]

For some unbounded operators the theorem of Eq. (I.1) is not satisfied and the series does not converge, but is nevertheless valid in the asymptotic sense that it is useful only up to a certain finite order. Kato (1951a) has derived very general conditions under which the perturbation series will at least be asymptotic, although unfortunately these are harder to verify than Eq. (I.1). An even less well-behaved class of perturbations, namely, those which are unbounded from below, causes the discrete spectrum of $H_0$ to vanish and be replaced by a continuous spectrum. A typical example is the Stark effect for an atom, where the discrete energy levels are converted to metastable levels. The physical situation is quite clear in such cases of "weak quantization," and the series gives sensible results for small

[3] Note that it does not justify expansions in powers of internuclear distances. These are, indeed, nonanalytic in the simplest case of a one-electron diatomic molecule, where a term in $R^5 \log R$ occurs (see Section XI).

$\lambda$, but the mathematical justification is quite difficult. All these aspects of the theory of convergence are described in more detailed in Section XII.

The starting point in perturbation theory is the division of the intractable Hamiltonian $H$ into a simple unperturbed part $H_0$, whose eigenfunctions are known, and a remainder $V$ containing the awkward terms. In the actual treatment of atoms and molecules, however, we are given $H$ and some function $\psi$ which is an approximation to the true wave function $\Psi$. The choice of $\psi$ is generally made on the basis of physical intuition, mathematical expediency, etc. It is desired to treat $\psi$ as a zero-order wave function and use perturbation theory to improve it. In order to apply the usual formalism of perturbation theory it is necessary to construct an unperturbed Hamiltonian $H_0$ corresponding to $\psi$. It is important to realize that this problem can always be solved formally, as pointed out by Makinson and Turner (1953) and by Sternheimer (1954). We write the perturbed Hamiltonian $H$ in the form

$$H = T + U, \tag{I.2}$$

where $T$ is the kinetic energy operator and $U$ is the potential energy, assumed to be a function of coordinates. We then define the operator $H_0$ by

$$H_0 = T + U_0, \tag{I.3}$$

where

$$U_0 = \varepsilon - \frac{T\psi}{\psi} \tag{I.4}$$

and the value of $\varepsilon$ can be chosen arbitrarily. Then it follows from Eqs. (I.3) and (I.4) that $\psi$ is an eigenfunction of $H_0$ with eigenvalue $\varepsilon$ so that

$$H_0\psi = \varepsilon\psi. \tag{I.5}$$

The perturbation potential $V$ is then defined by ($\lambda = 1$)

$$V = U - U_0. \tag{I.6}$$

The next step in obtaining an improved wave function is to solve the first-order equation. Dalgarno and Lewis (1955) defined a function $F$ such that the first-order wave function is equal to $F\psi$. The first-order equation then becomes (for one electron, in atomic units)

$$\nabla\cdot(\psi^2\nabla F) = 2\psi(V - \langle V\rangle)\psi. \tag{I.7}$$

By analogy with electrostatics, this is a Poisson-type equation for the "potential" $F$ produced by a charge distribution $-(2\pi)^{-1}\psi(V - \langle V\rangle)\psi$ in a region of variable dielectric constant $\psi^2$ (Prager and Hirschfelder, 1963). When separable, it can be integrated by quadrature; in which case the $F\psi$ procedure has determined the integrating factor. When Eq. (I.6) is not separable, approximate solutions for $F$ can be obtained by using the excellent variational procedures discussed in Section III, B.

The calculation of physical properties of a system, other than the energy, is a problem of great importance and interest. Typical properties are of two kinds, both associated with an operator $W$, and frequently also with an external field $\mu$; they are considered in detail in Section IV. The simplest properties are straight expectation values $\langle W\rangle$ such as a dipole moment and can be regarded as first-order perturbation energies for a perturbation $\mu W$. The other kind can be regarded as the second-order perturbation energies for the perturbation $\mu W$, and have the form

$$\langle Q\rangle = \langle \chi, (W - \langle W\rangle)\Psi\rangle,$$

where $\chi$ is the first-order wave function corresponding to the Hamiltonian $H + \mu W$; a typical example is the electric polarizability. If the only wave function $\psi$ available is approximate, with an error $\Psi - \psi$ of order $\lambda$, the calculated values of $\langle W\rangle$ and $\langle Q\rangle$ will also be in error by terms of order $\lambda$; only the energy $\langle H\rangle$ has an error of order $\lambda^2$. The problem of devising a practical way of calculating the leading corrections has been solved by Dalgarno and Stewart (1956a) and by Schwartz (1959a) for the nondegenerate case, and is discussed in section IV. The simplest approach is to use a double perturbation procedure (Dalgarno and Stewart, 1958) based on the Hamiltonian

$$\mathscr{H} = H_0 + \lambda V + \mu W.$$

Since the calculation of the first-order energy for a perturbation only requires the corresponding zeroth-order wave function, the first-order $\lambda$ correction to the $W$ perturbed energies (properties associated with $W$) only requires perturbation solutions of the singly perturbed Hamiltonian

$$H_* = H_0 + \mu W.$$

This is the point of Dalgarno's interchange theorem (Dalgarno and Stewart, 1956a, 1958). Its importance lies in the fact that the "badness" of the initial wave function is due to neglect of two-particle electron repulsion terms which therefore appear in $V$ and make the first-order $\lambda$ equation impossible to solve explicitly. The operator $W$, on the other hand, is usually the sum of one-particle terms, and the corresponding $\mu$ equations are often easy to solve explicitly. The $\lambda$ corrections to $\langle W\rangle$ and $\langle Q\rangle$ then involve simply an integration over $V$, which is usually straightforward. Difficulties can arise in the degenerate case, which are discussed in Section IV, E.

Perturbation methods are particularly valuable for the calculation of intermolecular potentials. Their great advantage is that the interaction energy is calculated directly rather than obtained as the difference between two large numbers. In this manner, Dalgarno and Lynn (1956 determined the long-range forces between two hydrogen atoms in excellent agreement at $R = 4a_0$ with the precise variational calculations of Kolos and Roothaan (1960). Other perturbation calculations have been made by Dalgarno and Lewis (1955, 1956), Dalgarno and Stewart (1956b), and Salem (1960, 1962). Since the wave functions are not known accurately for the separated molecules, the calculations of intermolecular potentials require not only double, but triple perturbation techniques.

The following more recent developments are described in the later sections of the review:

(1) *Iterative Perturbation Methods* (Sections VI and VII). Frequently it is sufficient to obtain the first-order perturbed wave function since this permits the calculation of the energy accurate through the third order. Indeed, from the Rayleigh–Schrödinger wave function through the $n$th order, the energy can be determined through the $(2n + 1)$th order. However even faster convergence can be obtained by an iterative procedure (FOPIM) such that, from the $n$th iterated wave function, the energy can be calculated up to terms involving the $2^{n+1}$ power of the perturbation parameter.

A combination of perturbation and variational techniques can be used (DE-FOP-VIM) to solve problems involving degenerate or almost-degenerate states without special consideration of the order in which the degeneracy is broken up or worry about the crossing of the energies as the perturbation parameter increases.

(2) *Time-Dependent Problems* (Sections VIII and IX). These are of two kinds: those in which the perturbation causes transitions, and those in which the stationary properties are modified by an oscillating field. The techniques developed for time-independent problems can be applied to both types. Interchange theorems have been proved in both cases under fairly general conditions by one of us (STE) and are presented here for the first time.[4] Section VIII is devoted to second-order steady state properties and Section IX to the calculation of off-diagonal elements.

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[4] An interchange theorem for transitions has been proved independently using a variational method by Borowitz (1964).

(3) *Sum Rules* (Section X). Useful sum rules can frequently be obtained by comparing the explicit solutions to the perturbation equations with their equivalent spectral representations expressed in infinite series. The family of sums involving oscillator strengths is of particular interest since it has a wide variety of physical applications. Sum rules can now be applied to dispersive intermolecular forces, thanks to an ingenious mathematical trick which has been pointed out by Mavroyannis and Stephen (1962). Because of its importance, this application is reviewed in considerable detail.

(4) *Applications* (Section XI). This section contains a list of references to the recent literature on applications of perturbation theory to quantum chemistry. An effort has been made to make the bibliography complete apart from references to polarizability, nuclear shielding constants, etc., which have recently been reviewed by Dalgarno (1963).

In proceeding from the formal theory to the practical applications many questions arise. At the present time considerable effort is being expended to obtain Hartree-Fock wave functions. Is it necessary or desirable to use these as the starting point for perturbation calculations (Szasz, 1963)? The success of the work of Dalgarno and Stewart (1960b), using Slater-type orbitals with screening constants adjusted to make the first-order perturbation vanish, suggests that simpler orbitals may provide a more convenient starting point. The perturbation equations themselves mold the wave function into the proper form.

The idea of applying perturbation theory to improve the familiar orbital model of atoms and molecules has been greatly stimulated by Sinanoglu's (1961a–d, 1962) discussions of the electron correlation problem. Sinanoglu points out that the Hartree-Fock potential correctly represents the behavior when the electrons are far apart. It follows that the perturbation potential contains only short-ranged electron-electron interaction terms when the unperturbed wave function is of the self-consistent field type. Furthermore, because of the Pauli principle, it is improbable that more than two electrons will come sufficiently close together to simultaneously feel the effects of these short-ranged forces. This supports the idea that electrons are mainly correlated in pairs belonging to the same spatial orbitals. And thus, in agreement with the G. N. Lewis notions which underlie present-day chemistry, the wave functions for even complex molecules can be broken up into sets of two-electron functions (geminals). Our hope is that, to a chemically useful approximation, perturbation theory need only cope with problems involving two electrons at a time.

## II. Rayleigh–Schrödinger Perturbation Theory for a Nondegenerate State

In order to lay the foundation for the new developments, let us review the Rayleigh–Schrödinger perturbation theory for a nondegenerate state. The unperturbed Hamiltonian $H_0$ has the complete set of normalized eigenfunctions $\psi_j$ with the corresponding energies $\varepsilon_j$. The perturbed Hamiltonian $H = H_0 + \lambda V$ has the eigenfunctions $\Psi_j$ with the corresponding energies $E_j$. We fix our attention on that perturbed state which in the limit as $\lambda$ approaches zero has $\Psi_q = \psi_q$ and $E_q = \varepsilon_q$ where $\varepsilon_q$ is not degenerate.

The basic assumption of the Rayleigh–Schrödinger theory is that $\Psi$ and $E$ may be expanded in power series in the perturbation parameter:

$$\Psi = \sum_{n=0}^{\infty} \lambda^n \psi^{(n)} \qquad \text{and} \qquad E = \sum_{n=0}^{\infty} \lambda^n \varepsilon^{(n)}. \tag{II.1}$$

In order to keep the notation from becoming too clumsy, the subscript $q$ is omitted except where it is necessary to avoid confusion between different states of the system. The power series Eq. (II.1) are substituted into the perturbed Schrödinger equation. Since the resulting equation must be true for all sufficiently small values of $\lambda$, the coefficient of *each* power of $\lambda$ in the equation must be equal to zero. This leads to the family of perturbation equations. Clearly, since the state $q$ is nondegenerate, $\psi^{(0)} = \psi$ and $\varepsilon^{(0)} = \varepsilon$, so that the zeroth-order equation is

$$H_0' \psi = 0, \tag{II.2}$$

where $H_0' = H_0 - \varepsilon$. The first-order equation is

$$H_0' \psi^{(1)} + V' \psi = 0, \tag{II.3}$$

where $V' = V - \varepsilon^{(1)}$. And the $n$th order relation is

$$H_0' \psi^{(n)} + V' \psi^{(n-1)} = \sum_{k=2}^{n} \varepsilon^{(k)} \psi^{(n-k)}, \qquad n = 2, 3, \ldots . \tag{II.4}$$

Normalization conditions are required to complete the specification of the perturbed functions. We require that the exact wave function $\Psi$ be normalized to unity. Substituting the power series Eq. (II.2) into $\langle \Psi, \Psi \rangle = 1$ and requiring that the coefficient of each power of $\lambda$ in this equation be individually zero, we obtain the normalization conditions for the various orders of perturbed wave functions,

$$\sum_{k=0}^{n} (k, n-k) = 0, \qquad n = 1, 2, \ldots, \tag{II.5}$$

where $(j,k) = \langle \psi^{(j)}, \psi^{(k)} \rangle$. For $n = 1$, this gives $(0,1) + (1,0) = 0$, which for real functions is the familiar orthogonality condition $(0,1) = 0$.

Expressions for the perturbation energies can be obtained by taking the scalar product of Eqs. (II.3) and (II.4) with $\psi$. Thus

$$\varepsilon^{(1)} = \langle \psi, V\psi \rangle, \tag{II.6}$$

$$\varepsilon^{(2)} = \langle \psi, V\psi^{(1)} \rangle = \langle \psi, V'\psi^{(1)} \rangle, \tag{II.7}$$

$$\varepsilon^{(n)} = \langle \psi, V'\psi^{(n-1)} \rangle - \sum_{k=1}^{n-2} (0, k)\varepsilon^{(n-k)}, \qquad n = 3, 4, \ldots. \tag{II.8}$$

In deriving Eqs. (II.7) and (II.8), we have assumed that $H_0$ is Hermitian. If $V$ is also Hermitian, additional relations can be obtained for the higher order perturbation energies by carrying out a sequence of algebraic manipulations of the perturbation equations, as explained in Appendix A. The most important of these relations are [5]

$$\varepsilon^{(3)} = \langle \psi^{(1)}, V'\psi^{(1)} \rangle, \tag{II.9}$$

$$\varepsilon^{(4)} = \langle \psi^{(1)}, V'\psi^{(2)} \rangle - \varepsilon^{(2)}(2, 0), \tag{II.10}$$

$$\varepsilon^{(5)} = \langle \psi^{(2)}, V'\psi^{(2)} \rangle - \varepsilon^{(2)}\{(1, 2) + (2, 1)\}, \tag{II.11}$$

$$\varepsilon^{(2n)} = \langle \psi^{(n-1)}, V'\psi^{(n)} \rangle - \sum_{k=2}^{n} \varepsilon^{(k)} \sum_{j=0}^{k-1} (n + j - k, n - j), \qquad n = 2, 3, \ldots, \tag{II.12a}$$

$$\varepsilon^{(2n+1)} = \langle \psi^{(n)}, V'\psi^{(n)} \rangle - \sum_{k=2}^{n} \varepsilon^{(k)} \sum_{j=0}^{k-1} (n + 1 + j - k, n - j), \qquad n = 2, 3, \ldots. \tag{II.12b}$$

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[5] There is another type of normalization which is commonly used. Instead of requiring that $\langle \Psi, \Psi \rangle = 1$, the perturbed components of the wave function are taken to be orthogonal to the original function, $(0, n) = 0$ for $n = 1, 2, \ldots$. This makes $\varepsilon^{(n)} = \langle \psi, V\psi^{(n-1)} \rangle$. Or, according to Dupont-Bourdelet *et al.* (1960):

$$\varepsilon^{(2n)} = \langle \psi^{(n-1)}, V\psi^{(n)} \rangle - \sum_{k=1}^{n-1} \sum_{j=n-k}^{2n-k-1} \varepsilon^{(j)} (k, 2n - k - j),$$

$$\varepsilon^{(2n+1)} = \langle \psi^{(n)}, V\psi^{(n)} \rangle - \sum_{k=1}^{n} \sum_{j=n+1-k}^{2n-k} \varepsilon^{(j)} (k, 2n + 1 - k - j).$$

Equations (II.12a) and (II.12b) demonstrate the well-known theorem that the perturbation energy to the $(2n+1)$th order can be obtained from knowledge of the wave function perturbed through the $n$th order. Hylleraas (1930) first showed that the energy through $\varepsilon^{(3)}$ is determined by the wave function through $\psi^{(1)}$. Later, Dalgarno and Stewart (1956a), Dupont-Bourdelet *et al.* (1960), and Sinanoglu (1961a) made explicit demonstrations of the general theorem. Actually, this theorem is an immediate consequence of the variational principle given in Section V (Wigner, 1935; Silverman, 1952; Sinanoglu, 1961a). From the variational principle we know that if the trial wave function is in error by order $\eta$ the energy is in error by order $\eta^2$. Putting $\eta = \lambda^{n+1}$ proves the theorem.

We shall have need for the explicit energy expectation $\mathscr{E}(n) = \langle \Psi(n), H\Psi(n)\rangle$ corresponding to $\Psi(n)$, the perturbed wave function truncated after the $n$th-order term and normalized to unity,

$$\Psi(n) = \sum_{k=0}^{n} \lambda^k \psi^{(k)}/D(n). \tag{II.13}$$

Here the $D(n)$ is the normalization constant,

$$D(n) = \left[1 + \lambda^{n+1} \sum_{k=1}^{n} \lambda^{k-1} \sum_{j=0}^{n-k} (n-j,\, j+k)\right]^{1/2} \tag{II.14}$$

Thus, we find

$$\mathscr{E}(0) = \varepsilon + \lambda\varepsilon^{(1)} \tag{II.15}$$

and

$$\mathscr{E}(1) = \varepsilon + \lambda\varepsilon^{(1)} + \frac{\lambda^2\varepsilon^{(2)} + \lambda^3\varepsilon^{(3)}}{1 + \lambda^2(1, 1)}. \tag{II.16}$$

The results for larger values of $n$ are given in Appendix A. In general, the $\mathscr{E}(n)$ are accurate through the order of $\lambda^{2n+1}$ and provide a sequence of upper bounds to the exact energy, to which they converge.

## Expansions in Unperturbed Wave Functions

In the usual presentation of Rayleigh–Schrödinger perturbation theory, the perturbed wave functions are expressed in terms of a spectral distribution of a complete function set. The formulas are given in Appendix B for a general function set which has no relation to the unperturbed problem (with the possible exception of one member of the set). Considerable simplifications are obtained if the function set is the complete set of unperturbed wave functions. Then (Dalgarno, 1961, has the indices for $\psi^{(2)}$ and $\psi^{(3)}$ in the reverse sequence), using the notation $V_{jk} = \langle \psi_j, V\psi_k \rangle$ and $V'_{jk} = \langle \psi_j, V'\psi_k \rangle$, where $V' = V - V_{qq}$, we have

$$\psi^{(1)} = \sum_j{}' \frac{V_{jq}\psi_j}{\varepsilon_q - \varepsilon_j}, \tag{II.17}$$

$$\psi^{(2)} = \sum_j{}' \sum_k{}' \frac{V'_{kj}V_{jq}\psi_k}{(\varepsilon_q - \varepsilon_j)(\varepsilon_q - \varepsilon_k)} - \frac{1}{2}\sum_j{}' \frac{V_{qj}V_{jq}}{(\varepsilon_q - \varepsilon_j)^2}\psi_q . \tag{II.18}$$

$$\begin{aligned}\psi^{(3)} = {} & \sum_j{}' \sum_k{}' \sum_l{}' \frac{V'_{lk}V'_{kj}V_{jq}\psi_l}{(\varepsilon_q - \varepsilon_j)(\varepsilon_q - \varepsilon_k)(\varepsilon_q - \varepsilon_l)} \\ & - \frac{1}{2}\sum_j{}' \sum_k{}' \frac{V_{qj}V_{jq}V_{kq}\psi_k}{(\varepsilon_q - \varepsilon_j)^2(\varepsilon_q - \varepsilon_k)} - \varepsilon_q^{(2)} \sum_j{}' \frac{V_{jq}\psi_j}{(\varepsilon_q - \varepsilon_j)^2} \\ & - \sum_j{}' \sum_k{}' \frac{V_{qj}V'_{jk}V_{kq}\psi_q}{(\varepsilon_q - \varepsilon_j)^2(\varepsilon_q - \varepsilon_k)} .\end{aligned} \tag{II.19}$$

Here the primed sigmas indicate the sum over all of the discrete states plus the integral over the continuum but omitting the state (or states) with energy $\varepsilon_q$.

The corresponding expressions for the second- and third-order perturbation energies are

$$\varepsilon^{(2)} = \sum_k{}' \frac{V_{qk}V_{kq}}{\varepsilon_q - \varepsilon_k} \tag{II.20}$$

and

$$\varepsilon^{(3)} = \sum_j{}' \sum_k{}' \frac{V_{qj}V'_{jk}V_{kq}}{(\varepsilon_q - \varepsilon_j)(\varepsilon_q - \varepsilon_k)} . \tag{II.21}$$

As Brueckner (1955), Huby (1961), Primas (1961), and Löwdin (1962) have shown, compact explicit formulas for the higher-order perturbation energies and wave functions may be written in terms of the operator

$$Q = \sum_j{}' \frac{|\psi_j\rangle\langle\psi_j|}{(\varepsilon_q - \varepsilon_j)} . \tag{II.22}$$

Thus, for example, the higher order energies are

$$\varepsilon^{(4)} = \langle \psi, VQ[V'QV' - \varepsilon^{(2)}]QV\psi \rangle, \tag{II.23}$$

$$\varepsilon^{(5)} = \langle \psi, VQ[V'QV'QV' - \varepsilon^{(3)} - \varepsilon^{(2)}\{V'Q + QV'\}]VQ\psi \rangle, \tag{II.24}$$

# III. Solution of Perturbation Equations

In this chapter methods for solving the perturbation equations of Rayleigh–Schrödinger perturbation theory are discussed. The $n$th-order Eq. (II.4) for $\psi^{(n)}$ involves all the wave functions of lower order, so that the equations must be solved stepwise starting with the first-order Eq. (II.3), substituting its solution into the second, solving the second-order equation, and so on. The same is true for the equations of double perturbation theory discussed in Section IV. The methods of solution of the first-order equation are also applicable to the higher order equations. The basic problem is therefore to solve a first-order perturbation equation of the type

$$(H_0 - \varepsilon)\psi^{(1)} + (V - \varepsilon^{(1)})\psi = 0, \qquad \text{(III.1)}$$

where $H_0$ is the unperturbed Hamiltonian, $\psi$ and $\varepsilon$ are the unperturbed eigenfunction and energy (assumed nondegenerate) of the state under consideration, $\psi^{(1)}$ and $\varepsilon^{(1)}$ are the first-order eigenfunction and energy and $V$ is the perturbation operator. The solution of this equation makes it possible to evaluate the second- and third-order energies by means of Eqs. (II.7) and (II.9). However the recent developments mentioned in the Introduction have been more concerned with using the solution of this type of equation to obtain the first-order corrections to expectation values. In this case the perturbation is the operator $W$ whose expectation value is sought.

The solution of perturbation equations is usually much easier than that of the original perturbed equation because they are inhomogeneous differential equations for which general techniques are available, whereas the original equation is an eigenvalue equation. This is especially true in the most usual situation when $H_0$ is a one-electron Hamiltonian or the sum of one-electron Hamiltonians. Unfortunately, however, in the case of the perturbation of greatest importance, namely, the electron repulsion terms $1/r_{12}$, analytic solutions have not been found and their discovery is no longer a matter for hope. The same is true of other two-electron perturbations such as the dipole–dipole and higher multipole interaction terms occurring in the treatment of long-range forces. The first-order equations involving two-electron terms in $V$ must therefore be treated by alternative approximate methods, such as the variation method discussed in Part B of this section or the familiar method of expansion in a complete set as discussed in Section II and Appendix B. The explicit solution of perturbation equations in closed form is therefore effectively limited to perturbations which only involve one-electron operators or the sum of one-electron operators. Fortunately most properties of interest other than the energy are associated with operators $W$ of this kind.

## A. Explicit Solution

There is a well-known device in the treatment of inhomogeneous differential equations (see Morse and Feshbach, 1953) which is used to simplify Eq. (III.1), and which has been employed very effectively by Dalgarno and his colleagues (Dalgarno and Lewis, 1955). This is to put

$$\psi^{(1)} = F\psi, \tag{III.2}$$

where $F$ is a scalar function (of the coordiates) to be determined, and to note that

$$(H_0 - \varepsilon)F\psi = (H_0F - FH_0)\psi,$$

so that Eq. (III.1) may be written

$$[H_0, F]\psi + V'\psi = 0, \tag{III.3}$$

where the square brackets denote a commutator and $V' = V - \varepsilon^{(1)}$. This form already has the advantage that it is usually unnecessary to know the explicit form of the unperturbed Hamiltonian $H_0$, since

$$[H_0, F] = [H, F]$$

as long as the perturbation $H - H_0$ is a scalar, and $V'\psi$ can be replaced by $(H - \langle H \rangle)\psi$, where $\langle H \rangle = \varepsilon + \varepsilon^{(1)}$. Equation (III.3) can be then written in the form

$$[H, F]\psi + (H - \langle H \rangle)\psi = 0 \tag{III.4}$$

To proceed further it is necessary to specify the form of the Hamiltonian. For the many-electron Hamiltonian (atomic units: energy $\sim e^2/a_0$ and length $\sim a_0$),

$$H_0 = -\tfrac{1}{2}\sum_i \nabla_i^2 + U_0, \tag{III.5}$$

where the unperturbed potential energy $U_0$ is a scalar, so that Eq. (III.3) becomes

$$\sum_i [\nabla_i^2, F]\psi = 2V'\psi. \tag{III.6}$$

If this equation is multiplied by $\psi^*$ and its complex conjugate by $\psi$, the sum of the two equations can be rearranged to give

$$\sum_i \nabla_i \cdot (\psi^*\psi\nabla_i F) = \psi^* V'\psi + \psi V'^*\psi^*, \tag{III.7}$$

where we have assumed we can choose $F$ to be real.[6] For simplicity of presentation we shall only consider the case when $\psi$ is real so that Eq. (III.7) becomes

$$\sum_i \nabla_i \cdot (\psi^2 \nabla_i F) = 2\psi V' \psi. \tag{III.8}$$

The boundary conditions on the perturbed wave function, and therefore on all $\psi^{(n)}$, are the same as those on the unperturbed eigenfunction $\psi$. Thus on the boundaries at infinity the conditions on $F$ are

$$F\psi = 0, \qquad \psi^2 \nabla_i F = 0. \tag{III.9}$$

This guarantees that the integral of the right-hand side of Eq. (III.8) vanishes. The solution $F$ of Eq. (III.8) is of course arbitrary to the extent of an additive constant, which may be chosen so that the orthogonality condition (II.5) is satisfied; that is

$$\langle \psi, F\psi \rangle = 0. \tag{III.10}$$

In terms of $F$, the second-order energy $\varepsilon^{(2)}$ given by Eq. (II.7) is

$$\varepsilon^{(2)} = \langle \psi, V' F \psi \rangle. \tag{III.11}$$

By substituting from Eq. (III.8) and using Green's theorem we get

$$\begin{aligned} \varepsilon^{(2)} &= \tfrac{1}{2} \sum_i \langle F \nabla_i \cdot (\psi^2 \nabla_i F) \rangle \\ &= -\tfrac{1}{2} \left\langle \psi, \sum_i (\nabla_i F)^2 \psi \right\rangle, \end{aligned} \tag{III.12}$$

since the surface integral vanishes because of the boundary condition (III.9). Thus the second-order energy need only involve $\nabla_i F$ in the integrand rather than $F$ itself, and in principle only a single integration of Eq. (III.8) is needed. In terms of $F$ the third-order energy given by Eq. (II.9) becomes

$$\varepsilon^{(3)} = \langle \psi, F V' F \psi \rangle \tag{III.13}$$

$$\begin{aligned} &= \tfrac{1}{2} \sum_i \langle F^2, \nabla_i \cdot (\psi^2 \nabla_i F) \rangle \\ &= -\sum_i \langle \psi, F (\nabla_i F)^2 \psi \rangle. \end{aligned} \tag{III.14}$$

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[6] This is possible if the perturbation $V$ is a real Hermitian operator, which is usually the case. The only important exceptions are magnetic perturbations.

The integral for the third-order energy thus involves $F$ explicitly and the forms (III.13) and (III.14) are only valid if $F$ satisfies the orthogonality condition (III.10).

### *1. Reduction of the Many-Electron Equation*

For completeness let us indicate how the many-electron problem may be reduced to one-electron equations in the simplest case. This is when the total Hamiltonian $H$ is the sum of one-electron Hamiltonians,

$$H = \sum_i \{h(i) + \lambda v(i)\}. \tag{III.15}$$

The only significant remark to be made is that it is best to separate the many-electron equation into the one-electron equations

$$(h + \lambda v)\phi_i = e_i \phi_i \tag{III.16}$$

*before* considering the perturbation problem. The one-electron first-order perturbation equations derived from Eq. (III.16) are

$$(h - \varepsilon_i)\phi_i^{(1)} + (v - \varepsilon_i^{(1)})\phi_i^{(0)} = 0, \tag{III.17}$$

and the total wave function correct to the first order in $\lambda$ for each electron is now

$$\Psi = \mathscr{A} \prod_i \{\phi_i^{(0)} + \lambda\phi_i^{(1)}\}, \tag{III.18}$$

where $\mathscr{A}$ is the antisymmetrizer and the $\phi$'s include spin factors. This procedure leads to simple sums over the electrons for all the perturbation energies: for example,

$$\begin{aligned} \varepsilon^{(1)} &= \sum_i \varepsilon_i^{(1)} = \sum_i \langle \phi_i^{(0)}, v\phi_i^{(0)} \rangle, \\ \varepsilon^{(2)} &= \sum_i \varepsilon_i^{(2)} = \sum_i \langle \phi_i^{(1)}, (v - \varepsilon_i^{(1)})\phi_i^{(0)} \rangle. \end{aligned} \tag{III.19}$$

### *2. One-Dimensional Equations*

As an introduction to the solution of Eq. (III.8) let us consider the simplest case of a one-dimensional system described by a variable $x$ confined to the interval $(a, b)$. Equation (III.8) may then be integrated directly to give

$$\psi^2 \frac{dF}{dx} = M(x), \tag{III.20}$$

where

$$M(x) = 2\int_a^x \psi(\xi)V'(\xi)\psi(\xi)\,d\xi \tag{III.21}$$

and the constant of integration vanishes because of the boundary condition (III.9).

*a. Ground State.* For the ground state in which the unperturbed wave function $\psi$ does not possess any nodes inside the interval $(a, b)$, Eq. (III.20) may be integrated immediately to give

$$F(x) = F(a) + \int_a^x M(\xi)\psi^{-2}(\xi)\,d\xi \tag{III.22}$$

as pointed out by W. H. Young and March (1958). The one-dimensional equations for $\varepsilon^{(2)}$ and $\varepsilon^{(3)}$ corresponding to Eqs. (III.11) and (III.13) can be written in terms of $M$ as

$$\varepsilon^{(2)} = -\frac{1}{2}\int_a^b \left[\frac{M(x)}{\psi(x)}\right]^2 dx, \tag{III.23}$$

$$\varepsilon^{(3)} = -\int_a^b dx \left\{\left[\frac{M(x)}{\psi(x)}\right]^2 + 2\varepsilon^{(2)}\psi^2(x)\right\}\int_a^x d\xi\,\frac{M(\xi)}{\psi^2(\xi)}. \tag{III.24}$$

*b. Excited States.* Consider now the case in which $\psi(x)$ is the $n$th unperturbed eigenfunction with $n$ simple zeros at $a_1, a_2, \ldots a_n$ in the interval $(a,b)$. This case has been treated by Byers Brown and Hirschfelder (1963). If the first-order wave function $\psi^{(1)}$ is well-behaved the function $F$ will have simple poles at $a_1, a_2, \ldots a_n$. The direct integration of Eq. (III.20) to yield $F$ presents difficulties because $M(x)$ does not in general vanish at the nodes of $\psi$, and for the same reason Eqs. (III.23) and (III.24) are not valid for excited states. To avoid the singularities in these equations let us assume that $\psi$, $F$, and $M$ are analytic functions in the vicinity of the real interval $(a,b)$. It may be shown that Eq. (III.22) and (III.23) can then be replaced by

$$F(x) = F(a) + \oint_a^x M(z)\psi^{-2}(z)\,dz \tag{III.25}$$

and

$$\varepsilon^{(2)} = -\frac{1}{2}\oint_a^b \left[\frac{M(z)}{\psi(z)}\right]^2 dz, \tag{III.26}$$

where the contours C in the $z$ plane do not pass through $a_1, a_2, \ldots a_n$. A similar equation can be written for $\varepsilon^{(3)}$ in place of Eq. (III.24).

An alternative method for dealing with excited states, more suited to numerical work, is to remove the singularities by subtracting out the poles of $F$. This may be accomplished by defining a new function $\Phi(x)$ by

$$F = \Phi - \sum_{j=1}^{n} \frac{C_j}{x - a_j} \tag{III.27}$$

and choosing the coefficients $C_j$ so that $\Phi$ is analytic at the points $a_j$. By substituting Eq. (III.27) into the differential equation (III.20) we get

$$\frac{d\Phi}{dx} = \frac{M(x)}{\psi^2(x)} - \sum_{j=1}^{n} \frac{C_j}{(x - a_j)^2}. \tag{III.28}$$

The coefficients $C_j$ are therefore given by

$$C_j = M(a_j)/[\psi'(a_j)]^2, \qquad j = 1, 2, \dots n. \tag{III.29}$$

Equation (III.28) may now be integrated along the real axis to give

$$\Phi(x) = \Phi(a) + \int_a^x \left[\frac{M(\xi) - \Lambda(\xi)}{\psi^2(\xi)}\right] d\xi \tag{III.30}$$

where

$$\Lambda(x) = \psi^2(x) \sum_{j=1}^{n} \frac{C_j}{(x - a_j)^2}, \tag{III.31}$$

and the second-order energy is given by

$$\varepsilon^{(2)} = -\tfrac{1}{2} \int_a^b M\left[\frac{M - \Lambda}{\psi^2}\right] dx - \tfrac{1}{2} \sum_{j=1}^{n} C_j \int_a^b \frac{\psi V' \psi}{x - a_j} dx. \tag{III.32}$$

*c. Separable Equations.* Direct quadrature, as in the one-dimensional Cartesian case above, is also possible when the original Schrödinger equation is separable in curvilinear coordinates. In this case, as in the reduction of the many-electron equation, it is advantageous to separate the exact Schrödinger equation into ordinary differential equations first and then to expand into the different orders of perturbation. Details of the separation and equations are given in Appendix D. The most important chemical application is to the two-center problem in molecules which is separable in confocal elliptic coordinates (see Section XI).

### 3. *Separation by Partial Expansion*

The perturbation equations can be solved explicitly in a much wider class of cases than the strictly separable one of the previous sub-section.

When a one-electron equation of the form (III.1) is not separable as it stands, the first step towards finding a solution is usually to expand the perturbation $V$ and the wave function $\psi^{(1)}$ in terms of a complete orthogonal set in one or two of the coordinates. To illustrate the method, consider first the important case of a spherically symmetric unperturbed wave function $\psi(r)$ perturbed by a potential $V(r,\theta,\phi)$ which may be expanded in spherical harmonics $Y_{lm}$:

$$V' = \sum_{l,m} V'_{lm}(r) Y_{lm}(\theta, \phi). \tag{III.33}$$

$F$ may be similarly expanded to give

$$F = \sum_{l,m} F_{lm}(r) Y_{lm}(\theta, \phi). \tag{III.34}$$

By substituting these expansions into Eq. (III.8) and separating the harmonic components we get

$$\frac{d}{dr}\left(r^2\psi^2 \frac{dF_{lm}}{dr}\right) - l(l+1)\psi^2 F_{lm} = 2r^2\psi V'_{lm}\psi$$

$$(m = -l, \ldots l; \quad l = 0, 1, 2, \ldots). \tag{III.35}$$

This is a set of ordinary linear inhomogeneous second-order differential equations which, although they are not directly integrable by quadrature for $l \neq 0$, may be solved either by inspection or by standard procedures.

From the formal standpoint the key to solving an equation of the type (III.35) is a solution of the corresponding homogeneous equation, which may be written

$$\frac{d^2K}{dr^2} + 2\frac{d \ln(r\psi)}{dr}\frac{dK}{dr} - \frac{l(l+1)}{r^2}K = 0. \tag{III.36}$$

If such a solution $K$ is known, we repeat the device (III.2) used in simplifying the original perturbation equation and put

$$F_{lm} = Kf. \tag{III.37}$$

By substituting into Eq. (III.35), multiplying by $K$, and rearranging, we get

$$\frac{d}{dr}\left(r^2\psi^2K^2 \frac{df}{dr}\right) = 2r^2K\psi V'_{lm}\psi. \tag{III.38}$$

The equation is now in the one-dimensional form discussed in Section III, 2,*a* [see Eq. (III.20)] and may be integrated immediately to give[7]

$$r^2\psi^2K^2\,\frac{df}{dr} = M_{lm}(r), \tag{III.39}$$

where

$$M_{lm}(r) = 2\int_0^r s^2K\psi V'_{lm}\psi\,ds. \tag{III.40}$$

For the ground state Eq. (III.39) may be integrated again directly. For excited states the unperturbed wave function $\psi$ will possess nodes, and so also may the solution $K$ of the homogeneous Eq. (III.36). This situation has been discussed in Section III, 2, *b*. The singularities of $f$ may be avoided by integrating along a contour C in the complex plane which avoids the zeros of $\psi$ and $K$, or the poles may be subtracted out. For reasons of space we shall give only the complex integral form of $F$ which is

$$F_{lm}(r) = K(r)\left\{f(0) + \oint_0^r \frac{M_{lm}}{s^2\psi^2K^2}\,ds\right\}. \tag{III.41}$$

The second-order energy can be written in a form analogous to Eq. (III.26),

$$\varepsilon^{(2)} = -\frac{1}{2}\sum_{l,m}\oint_0^\infty \left[\frac{M_{lm}}{s\psi K}\right]^2 ds, \tag{III.42}$$

and likewise the third-order energy. In many cases, however, it may be easier and quicker to obtain a particular integral of the inhomogeneous equation than to solve the homogeneous one and integrate.

The case in which $\psi$ is an orbital eigenfunction with nonzero angular momentum $L$,

$$\psi = R_L(r)Y_{LM}(\theta, \phi), \tag{III.43}$$

is similar in principle but somewhat more complicated in general, and is therefore treated in Appendix E. However when the perturbation $V$ is radial, that is for the component $V'_{00}$, the first-order equation may be integrated directly to give

$$F(r) = F(0) + \oint_0^r [M/s^2R_L^2]\,ds, \tag{III.44}$$

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[7] Attention must be paid to the behavior of the right-hand side of Eq. (III.38) at the lower limit when $r \to 0$. For example, assuming $\psi(0) \neq 0$, $V'_{lm}\psi \simeq r^l$, and $K \simeq r^{-k}$ at the origin, we must have $k \leqslant 2 + l$ in order that $M(r)$ exists. It will usually be possible to find a solution $K(r)$ of Eq. (III.36) which behaves correctly at the origin.

where

$$M(r) = 2\int_0^r s^2 R_L V R_L \, ds. \tag{III.45}$$

The second-order energy can be written as usual either in the form (see Byers Brown and Hirschfelder, 1963)

$$\varepsilon^{(2)} = -\tfrac{1}{2}\fint_0^\infty [M/sR_L]^2 \, ds \tag{III.46}$$

or

$$\varepsilon^{(2)} = -\tfrac{1}{2}\int_0^\infty M\left[\frac{M - \Gamma}{r^2 R_L^2}\right] dr - \tfrac{1}{2}\sum_j C_j \int_0^\infty \frac{r^2 R_L V R_L}{r - a_j}\, dr, \tag{III.47}$$

where $a_j$ are the zeros of $R_L$ and

$$C_j = M(a_j)/[a_j R_L'(a_j)]^2, \tag{III.48}$$

$$\Gamma(r) = r^2 R_L^2 \sum_j \frac{C_j}{(r - a_j)^2}. \tag{III.49}$$

4. *Second- and Higher-Order Equations*

So far we have only considered the first-order equation. The second-order perturbation equation corresponding to Eq. (III.1) can be obtained from Eq. (II.4) and is

$$(H_0 - \varepsilon)\psi^{(2)} + V'\psi^{(1)} - \varepsilon^{(2)}\psi = 0. \tag{III.50}$$

It has the same form as Eq. (III.1) except that the inhomogeneous term involves $\psi^{(1)}$ which must be known before $\psi^{(2)}$ can be found. To solve Eq. (III.50) we therefore put

$$\psi^{(2)} = G\psi \tag{III.51}$$

and suppose that $\psi^{(1)} = F\psi$ is known. Then by the manipulations described at the beginning of this section we get

$$\nabla\cdot(\psi^2 \nabla G) = 2\psi(V'F - \varepsilon^{(2)})\psi. \tag{III.52}$$

This equation is now of the same form as Eq. (III.8), and can be solved by the same techniques.

The greatest need for explicit forms of the second-order perturbation functions is in order to correct the zeroth-order approximation to a second-order property; this is discussed in Section IV. The search for explicit solutions of the higher-order equations follows the same pattern as that of the first- and second-order equations. However they are not usually of special significance.

## B. Variational Solution

When the unperturbed equation is not separable, or when the partial expansion technique requires an infinite series which only converges slowly, it is nevertheless often possible to obtain a useful variational approximation to the perturbed wave functions. This is indeed the only effective method when the perturbation is due to electron repulsion.

The basis of the variational approach is discussed fully in Section V. There is a variational principle of a very general kind for each order of perturbation which may be derived from the Ritz variation principle for the total energy. In practice it is natural to choose a special form of these principles, of which the prototype is that for the first-order wave function introduced by Hylleraas (1930).

### 1. *Hylleraas Variation Principle for Ground State*

Hylleraas pointed out that for the ground state of a system Eq. (III.1) is equivalent to the variation principle

$$\tilde{\varepsilon}^{(2)} \geqslant \varepsilon^{(2)}, \tag{III.53}$$

where

$$\tilde{\varepsilon}^{(2)} = \langle\tilde{\psi}^{(1)}, (H_0 - \varepsilon)\tilde{\psi}^{(1)}\rangle + \langle\tilde{\psi}^{(1)}, V'\psi\rangle + \langle\psi, V'\tilde{\psi}^{(1)}\rangle \tag{III.54}$$

and $\tilde{\psi}^{(1)}$ is arbitrary; the equality in Eq. (III.53) only holds when the variation function $\tilde{\psi}^{(1)} = \psi^{(1)}$, the true first-order wave function. The principle is easy to prove: by substituting $\tilde{\psi}^{(1)} = \psi^{(1)} + \delta\tilde{\psi}^{(1)}$ in Eq. (III.54) we get

$$\tilde{\varepsilon}^{(2)} - \varepsilon^{(2)} = 2\langle\delta\tilde{\psi}^{(1)}, [(H_0 - \varepsilon)\psi^{(1)} + V'\psi]\rangle + \langle\delta\tilde{\psi}^{(1)}, (H_0 - \varepsilon)\delta\tilde{\psi}^{(1)}\rangle. \tag{III.55}$$

The term in $\delta$ vanishes because of Eq. (III.1) and the term in $\delta^2$ is positive because $\varepsilon$ is the lowest eigenvalue of $H_0$. Clearly the same argument also applies to excited states which are the lowest of each symmetry class of the total Hamiltonian $H = H_0 + \lambda V$.

If the first-order equations cannot be solved analytically it may nevertheless be possible to get a good approximation to $\varepsilon^{(2)}$ and $\psi^{(1)}$ by inserting a trial function $\tilde{\psi}^{(1)}$ in Eq. (III.54) and making $\tilde{\varepsilon}^{(2)}$ stationary with respect to the variation parameters appearing in $\tilde{\psi}^{(1)}$. If the trial function is a linear combination of orthogonal functions $\phi_\alpha$ then $\tilde{\varepsilon}^{(2)}$ has a form similar to Eq. (B.6). This procedure was introduced by Hylleraas and has been used by him (Hylleraas and Midtdal, 1956, 1958) in approximating to the second-order energy in the $1/Z$ expansion of two-electron atoms. This work on He-like systems has been continued to higher orders of perturbation by Scherr and Knight (1963) and is discussed in Section XI.

One of the most important applications of the variational principle is to determine an approximate $\psi^{(1)}$ in order to calculate the first-order corrections to expectation values (see Section IV). In cases where the unperturbed wave function $\psi$ is not known exactly, Eq. (III.54) may still be used to determine an approximate $\psi^{(1)}$ by making $\tilde{\varepsilon}^{(2)}$ stationary, but in such a case $\tilde{\varepsilon}^{(2)}$ is no longer a correct variational approximation to $\varepsilon^{(2)}$. This approach has been used extensively in shielding calculations and is further discussed in Section V (see in particular footnote 12, where the functional $\tilde{\varepsilon}^{(2)}$ is denoted by $\tilde{J}_H$).

*Dirichlet Form of Hylleraas Principle.* If we put $\tilde{\psi}^{(1)} = \tilde{F}\psi$ as in Eq. (III.2) and regard the magnitude of $\tilde{F}$ as a variable, we can minimize $\tilde{\varepsilon}^{(2)}$ explicitly to get a form homogeneous in $\tilde{F}$,

$$\tilde{\varepsilon}^{(2)} = -\frac{\langle\psi, V'\tilde{F}\psi\rangle^2}{\langle\psi, \tilde{F}(H_0 - \varepsilon)\tilde{F}\psi\rangle}. \tag{III.56}$$

The denominator in this expression can be written

$$\langle\psi, \tilde{F}(H_0 - \varepsilon)\tilde{F}\psi\rangle = \langle\psi, \tilde{F}(H_0\tilde{F} - \tilde{F}H_0)\psi\rangle,$$

and if $H_0$ has the form of Eq. (III.5) then

$$\psi\tilde{F}(H_0\tilde{F} - \tilde{F}H_0)\psi = \tfrac{1}{2}\sum_i (\psi\nabla_i\tilde{F})^2 - \tfrac{1}{2}\sum_i \nabla_i\cdot(\tilde{F}\psi^2\nabla_i\tilde{F}).$$

On integrating this expression we get

$$\langle\psi, \tilde{F}(H_0\tilde{F} - \tilde{F}H_0)\psi\rangle = \tfrac{1}{2}\,\langle\psi, \sum_i (\nabla_i\tilde{F})^2\psi\rangle,$$

provided that the surface integrals of $\psi^2\tilde{F}\nabla_i\tilde{F}$ vanish. Equation (III.56) can then be written

$$\tilde{\varepsilon}^{(2)} = -2\,\frac{\langle\psi, V'\tilde{F}\psi\rangle^2}{\langle\psi, \sum_i (\nabla_i\tilde{F})^2\psi\rangle} \geqslant \varepsilon^{(2)}. \tag{III.57}$$

It is clear from this form that the second-order energy for the ground state is always negative.

Prager and Hirschfelder (1963) have recently pointed out that the first-order equation (III.8) is analogous to a $3N$-dimensional Poisson's equation in electrostatics, $F$ playing the role of the electrostatic potential, $\psi^2$ that of a variable dielectric constant, and $-\psi V'\psi/2\pi$ that of the charge density.

The variation principle in the form (III.57) is well-known in electrostatics as the Dirichlet principle for the self-energy of a charge distribution.

A particularly simple general type of variation function which has proved useful in connection with this formula when $V$ is scalar is

$$\tilde{F} = aV' \tag{III.58}$$

which leads to

$$\tilde{\varepsilon}^{(2)} = -2\frac{\langle\psi, (V')^2\psi\rangle^2}{\langle\psi, \sum_i (\nabla_i V)^2\psi\rangle} \geqslant \varepsilon^{(2)}. \tag{III.59}$$

Unfortunately the denominator diverges in the important case of electron repulsion so that $\tilde{\varepsilon}^{(2)} = 0$.

### 2. *Extension of Hylleraas Principle to Excited States*

The usual extension of the variation principle to excited states requires knowledge of the exact perturbed wave functions of the lower states of the same symmetry. Approximate energies and wave functions for the excited states can of course be obtained in the process of minimizing the trial energy expression for the ground state. For trial functions with linear variation parameters the approximate energies are indeed upper bounds to the lower eigenvalues. However, in general, these approximations are unbounded, and the only case in which the approximate energy is always an upper bound to the excited state energy is when it is the lowest state of a given symmetry type. An important advantage of the more restricted variation principle for the second-order energy is that, as shown by Sinanoglu (1961b), it can be fairly easily modified to apply to an excited state if the unperturbed wave functions for the lower states are known.

Consider the variation $\delta\tilde{\varepsilon}_q^{(2)}$ for the excited state $q$ when $\tilde{\varepsilon}_q^{(2)}$ is stationary with respect to changes $\delta\tilde{\psi}_q^{(1)}$:

$$\delta\tilde{\varepsilon}_q^{(2)} = \langle\delta\tilde{\psi}_q^{(1)}, (H_0 - \varepsilon_q)\delta\tilde{\psi}_q^{(1)}\rangle. \tag{III.60}$$

The reason this is not always positive is that the variations will in general contain components $\psi_k$ for $k < q$ which give rise to terms $(\varepsilon_k - \varepsilon_q)$ which are negative. These components are in fact known exactly from perturbation theory, and the variational method suggested by Sinanoglu is to insert them in the first-order trial wave function $\tilde{\psi}_q^{(1)}$ and to vary only that part of $\tilde{\psi}_q^{(1)}$ which is orthogonal to all the lower states. That is, we put

$$\tilde{\psi}_q^{(1)} = \sum_{k<q} \frac{V_{kq}}{\varepsilon_q - \varepsilon_k}\psi_k + \tilde{\chi}_q^{(1)} \tag{III.61}$$

where

$$\langle \psi_k, \tilde{\chi}_q^{(1)} \rangle = 0 \qquad (k < q). \tag{III.62}$$

By substituting Eq. (III.61) into Eq. (III.54) we get

$$\tilde{\varepsilon}_q^{(2)} = \sum_{k<q} \frac{|V_{qk}|^2}{\varepsilon_q - \varepsilon_k} + \langle \tilde{\chi}_q^{(1)}, (H_0 - \varepsilon_q)\tilde{\chi}_q^{(1)} \rangle + 2\langle \tilde{\chi}_q^{(1)}, V'\psi_q \rangle, \tag{III.63}$$

where $V' = V - \varepsilon_q^{(1)}$. Let $\chi_q^{(1)}$ be the exact part of $\psi_q^{(1)}$ orthogonal to $\psi_k$ for $k < q$, and put $\tilde{\chi}_q^{(1)} = \chi_q^{(1)} + \delta\tilde{\chi}_q^{(1)}$. Then by the analog of Eq. (III.55) we have

$$\tilde{\varepsilon}_q^{(2)} - \varepsilon_q^{(2)} = \langle \delta\tilde{\chi}_q^{(1)}, (H_0 - \varepsilon_q)\delta\tilde{\chi}_q^{(1)} \rangle \geqslant 0 \tag{III.64}$$

for variations $\delta\tilde{\chi}_q^{(1)}$ for which

$$\langle \psi_k, \delta\tilde{\chi}_q^{(1)} \rangle = 0 \qquad (k < q). \tag{III.65}$$

Whereas the exact solutions $\psi_q^{(1)}$ of the first-order equations for different states $q$ would yield wave functions orthogonal to the first order in $\lambda$, this is not generally the case for variational approximations. The conditions under which it is true are derived in Section V.

### 3. *Variation Principle for Second-Order Perturbation Equation*

The variation principle of the Hylleraas type, Eq. (III.53), for the second order perturbation function $\psi^{(2)}$ given by Eq. (III.50) is

$$\tilde{\varepsilon}^{(4)} \geqslant \varepsilon^{(4)}, \tag{III.66}$$

where

$$\begin{aligned}\tilde{\varepsilon}^{(4)} = {} & \langle \tilde{\psi}^{(2)}, (H_0 - \varepsilon)\tilde{\psi}^{(2)} \rangle + \langle \tilde{\psi}^{(2)}, V'\psi^{(1)} \rangle + \langle \psi^{(1)}, V'\tilde{\psi}^{(2)} \rangle \\ & - \varepsilon^{(2)}[\langle \tilde{\psi}^{(2)}, \psi \rangle + \langle \psi, \tilde{\psi}^{(2)} \rangle + \langle \psi^{(1)}, \psi^{(1)} \rangle];\end{aligned} \tag{III.67}$$

$\psi^{(1)}$ is the exact solution of Eq. (III.1), and $\tilde{\psi}^{(2)}$ is arbitrary. For cases in which Eq. (III.50) cannot be solved explicitly it is therefore possible to obtain a variational approximation for $\psi^{(2)}$ by making $\tilde{\varepsilon}^{(4)}$ stationary with respect to parameters appearing in the trial function $\tilde{\psi}^{(2)}$. An obvious drawback to this procedure is that it requires an exact $\psi^{(1)}$, and if $\psi^{(1)}$ can be obtained explicitly then so in all likelihood can $\psi^{(2)}$, and the problem is not one requiring the variational approximation. The difficulty can be overcome in principle by adopting the approach of Section VI, which is to reformulate the second-order stage in perturbation theory as a new first-order problem.

## C. Variational Principles for Lower Bounds to the Energy

In this section we shall discuss two other variation principles which, unlike the Ritz principle, give lower bounds to the energy of the ground state. The first of these, due to Temple (1928), applies to all orders of the energy, but has the disadvantage of requiring knowledge of the unperturbed energy of an excited state. The second, which has been discovered recently by Prager and Hirschfelder (1963), is specifically for the second-order energy and does not require knowledge of an excited state.

### 1. *Temple Principle*

This principle (Temple, 1928; Hylleraas, 1961) is based on the inequality for the exact Hamiltonian

$$\langle (H - E_0)\tilde{\Psi}, (H - E_1)\tilde{\Psi}\rangle \geqslant 0, \tag{III.68}$$

where $E_0$ and $E_1$ are the two lowest eigenvalues of $H$ (of a given symmetry) and $\tilde{\Psi}$ is any variation function. By means of the usual perturbation expansion we can deduce a second-order result which may be combined with Eq. (III.53) to give

$$0 \leqslant \tilde{\varepsilon}_0^{(2)} - \varepsilon_0^{(2)} \leqslant \frac{\langle [(H_0 - \varepsilon_0)\tilde{\psi}_0^{(1)} + V'\psi_0]^2\rangle}{\varepsilon_1 - \varepsilon_0}, \tag{III.69}$$

where $\tilde{\varepsilon}_0^{(2)}$ is given by Eq. (III.54). Prager and Hirschfelder (1963) have improved this upper bound further by optimizing with respect to the magnitude of $\tilde{\psi}_0^{(1)}$, which leads to

$$\varepsilon_0^{(2)} \geqslant -\frac{\langle \psi_0, (V')^2\psi_0\rangle}{\varepsilon_1 - \varepsilon_0} + \frac{A_0^2}{B_0} \tag{III.70}$$

where

$$\begin{aligned} A_0 &= \langle \tilde{\psi}_0^{(1)}, V'\psi_0\rangle - \frac{\langle V'\psi_0, (H_0 - \varepsilon_0)\tilde{\psi}_0^{(1)}\rangle}{\varepsilon_1 - \varepsilon_0}, \\ B_0 &= \frac{\langle (H_0 - \varepsilon_0)\tilde{\psi}_0^{(1)}, (H_0 - \varepsilon_0)\tilde{\psi}_0^{(1)}\rangle}{\varepsilon_1 - \varepsilon_0} - \langle \tilde{\psi}_0^{(1)}, (H_0 - \varepsilon_0)\tilde{\psi}_0^{(1)}\rangle. \end{aligned} \tag{III.71}$$

The simpler inequality

$$\varepsilon_0^{(2)} \geqslant -\frac{\langle \psi_0, (V')^2\psi_0\rangle}{\varepsilon_1 - \varepsilon_0} = -\sum_{k \geqslant 1} \frac{|V_{0k}|^2}{\varepsilon_1 - \varepsilon_0} \tag{III.72}$$

follows either by dropping the positive term $A_0^2/B_0$ or by setting $\tilde{\psi}^{(1)} = 0$. It can also be obtained from the exact perturbation expansion (II.20) by approximating the denominators $\varepsilon_k - \varepsilon_0$ by $\varepsilon_1 - \varepsilon_0$ and using the closure relation for the complete unperturbed set $\psi_n$ ; it is originally due to Unsöld (1927). It is interesting to note[8a] that if this approximation is made in the sum (II.17) for the first-order wave function we get the form (III.58),

$$\psi_0^{(1)} \cong -\frac{V'}{\varepsilon_1 - \varepsilon_0}\,\psi_0 . \tag{III.73}$$

The Temple variation principle and the crude fixed lower bound (III.72) suffer from the disadvantage that they require a knowledge of the unperturbed energy $\varepsilon_1$ of the first excited state which is coupled to the ground state by the perturbation $V$. This may not be known.

### 2. *Analog of Thomson's Principle*

The electrostatic analogy mentioned above (Section III, B,1) has recently been fruitfully exploited by Prager and Hirschfelder (1963) to provide a variational lower bound for $\varepsilon_0^{(2)}$ which does not require knowledge of $\varepsilon_1$. The principle in question is the analog of Thomson's principle in electrostatics and may be stated in the form

$$\varepsilon_0^{(2)} \geqslant -\frac{1}{2}\sum_i \langle \psi_0 , \tilde{\mathbf{G}}_i \cdot \tilde{\mathbf{G}}_i \psi_0 \rangle \tag{III.74}$$

where the trial vectors $\tilde{\mathbf{G}}_i$ satisfy the equation

$$\sum_i \boldsymbol{\nabla}_i \cdot (\psi_0^2 \tilde{\mathbf{G}}_i) = -2\psi_0 V' \psi_0 \tag{III.75}$$

and on the boundaries the only requirement on the $\tilde{\mathbf{G}}$ is that

$$\psi_0^2 \tilde{\mathbf{G}}_i = 0. \tag{III.76}$$

The equality in Eq. (III.74) holds if and only if $\tilde{\mathbf{G}}_i = -\boldsymbol{\nabla}_i F$, in which case Eq. (III.74) reduces to Eq. (III.12). The proof is simple. Substitute $\tilde{\mathbf{G}}_i = -\boldsymbol{\nabla}_i F + \delta\tilde{\mathbf{G}}_i$ into Eq. (III.74) to get

$$\begin{aligned} \tilde{\varepsilon}_0^{(2)} = -\frac{1}{2}\sum_i \langle \psi_0 , \tilde{\mathbf{G}}_i \cdot \tilde{\mathbf{G}}_i \psi_0 \rangle &= \varepsilon_0^{(2)} + \sum_i \langle \psi_0 \, , \boldsymbol{\nabla}_i F \cdot \delta\tilde{\mathbf{G}}_i \psi_0 \rangle \\ &- \frac{1}{2}\sum_i \langle \psi_0 , \delta\tilde{\mathbf{G}}_i \cdot \delta\tilde{\mathbf{G}}_i \psi_0 \rangle . \end{aligned} \tag{III.77}$$

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[8a] The authors are indebted to Mr. W. J. Meath for this observation. Lennard-Jones (1930) showed that

$$\psi^{(1)} = \frac{V'\psi_q}{\varepsilon_q - \varepsilon_1} + \sum_j{}' \frac{\varepsilon_j - \varepsilon_1}{\varepsilon_q - \varepsilon_j}\,\frac{V_{jq}\psi_j}{\varepsilon_q - \varepsilon_1}$$

and discussed the conditions under which the terms in the summation can be neglected.

But

$$\psi_0 \boldsymbol{\nabla}_i F \cdot \delta\tilde{\mathbf{G}}_i \psi_0 = \boldsymbol{\nabla}_i \cdot (F \psi_0^2 \delta\tilde{\mathbf{G}}_i) - F \boldsymbol{\nabla}_i \cdot (\psi_0^2 \delta\tilde{\mathbf{G}}_i). \tag{III.78}$$

The second term vanishes by Eq. (III.75) and the integral of the first term by Eq. (III.76). Hence

$$\tilde{\varepsilon}_0^{(2)} = \varepsilon_0^{(2)} - \frac{1}{2} \sum_i \langle \psi_0 , \delta\tilde{\mathbf{G}}_i \cdot \delta\tilde{\mathbf{G}}_i \psi_0 \rangle,$$

and the inequality is proved.

## IV. Expectation Values and Double Perturbation Theory

In this chapter the perturbation theory of expectation values of operators other than the energy is discussed. The most important properties of particular states of a system are of two kinds and can be written as the expectation values of two different kinds of operators.

First-order properties, such as permanent dipole and quadrupole moments, diamagnetic susceptibilities, and charge density at the nucleus, are the straight expectation values of operators $W$, which are usually the sum of one-electron operators. For a system with Hamiltonian $H$ in a state with energy $E$ and normalized eigenfunction $\Psi$, the expectation value of $W$ is simply

$$\langle W \rangle = \langle \Psi, W\Psi \rangle. \tag{IV.1}$$

Such expectation values can be brought within the framework of perturbation theory by introducing a fictitious Hamiltonian

$$\mathscr{H} = H + \mu W$$

with eigenvalues $\mathscr{E}(\mu)$, so that $\mathscr{E}(0) = E$. Then since $W = \partial\mathscr{H}/\partial\mu$, by the Hellmann–Feynman theorem,

$$\begin{aligned} \langle W \rangle &= \langle \Psi, \partial\mathscr{H}/\partial\mu \, \Psi \rangle \\ &= (\partial\mathscr{E}/\partial\mu)_{\mu=0} \, . \end{aligned} \tag{IV.2}$$

Thus $\langle W \rangle$ can be regarded as a first-order perturbation energy $E^{(1)}$ in the perturbation expansion of $\mathscr{E}$:

$$\mathscr{E} = E + \mu E^{(1)} + \mu^2 E^{(2)} + \cdots . \tag{IV.3}$$

Second-order properties include electric polarizabilities, paramagnetic susceptibilities, optical rotary constants, chemical shifts, nuclear spin–spin coupling constants, nuclear shielding constants, and long-range van der Waals interaction constants. These are all essentially second-order energies $E^{(2)}$ associated with the Hamiltonian $\mathscr{H}$ (which in this case will usually have physical significance) and can be written in the form

$$\langle Q\rangle = \tfrac{1}{2}(\partial^2\mathscr{E}/\partial\mu^2)_{\mu=0} = \langle\chi, (W - \langle W\rangle)\Psi\rangle, \tag{IV.4}$$

where $\chi$ is the solution of the equation

$$(H - E)\chi + (W - \langle W\rangle)\Psi = 0. \tag{IV.5}$$

Second-order properties can be written formally as expectation values of operators involving the inverse of $(H - E)$; thus $Q$ can be regarded as the symbolic operator

$$Q = -(W - \langle W\rangle)(H - E)^{-1}(W - \langle W\rangle). \tag{IV.6}$$

Since the exact eigenfunctions $\Psi$ of many-electron atoms and molecules are unknown, the calculation of first- and second-order properties starts with approximate wave functions $\psi$. The approximate expectation values calculated in this way compare unfavorably in accuracy with the energy because, whereas knowledge of an approximate wave function $\psi$ is sufficient to calculate the energy through first-order in the error, this is not true in general for any other operator. The corrections to such approximate expectation values are therefore a matter of importance. The Hamiltonian $H$ can be written in the form

$$H = H_0 + \lambda V,$$

where $H_0$ is the approximate (unperturbed) Hamiltonian corresponding to the approximate wave function $\psi$ $(=\psi^{(0)})$ and $\lambda V$ is the remainder which is responsible for the corrections. Since expectation values can be regarded as perturbation energies associated with an operator $W$, the appropriate tool for calculating the corrections in a systematic manner is a double perturbation theory based on the Hamiltonian

$$\mathscr{H} = H_0 + \lambda V + \mu W. \tag{IV.7}$$

This approach has been used extensively by Dalgarno and his collaborators (Dalgarno and Lewis, 1955; Dalgarno and Stewart, 1958) and is the subject of the present section.

Attention is naturally focused on the leading corrections of first order in the actual or fictitious perturbation parameter $\lambda$. At first sight even these seem impossibly difficult to obtain explicitly for the case in which the perturbation involves the two-electron repulsion terms because they involve perturbed wave functions such as $\psi^{(1)}$ given by Eq. (III.1). Fortunately it is not in fact necessary to find such wave functions in order to evaluate the first-order corrections to expectation values, as the corrections can be expressed entirely in terms of integrals involving only the accessible solutions of first-order perturbation equations with one-electron perturbation terms. The theorem permitting this alternative form has been exploited very thoroughly for atoms by Dalgarno and his collaborators (see Dalgarno and Lewis, 1955; Dalgarno and Stewart, 1958; Dalgarno *et al.*, 1960a), and together with the integrability of the one-electron first-order equations has allowed them to evaluate the leading corrections to the expectation values for a variety of operators. For this reason we refer to the relation as *Dalgarno's interchange theorem*; it is derived in Section IV,B.

Schwartz (1959b) has developed what appears to be a different approach in that he deliberately avoids the use of a Hamiltonian $H_0$, corresponding to the approximate wave function $\psi$, and bases his method on a variation principle (see Section V). However, since he too seeks to calculate $\langle W \rangle$ and $\langle Q \rangle$ correct to the first order in $\Psi - \psi$, the results are equivalent to those of double perturbation theory, as we shall show. It should be emphasized that, as stated in the Introduction, a Hamiltonian $H_0$ can always be constructed and used in the formal development of perturbation theory. An interesting feature revealed by Schwartz's approach is that $H_0$ may then be eliminated from the final formulas if desired.

### A. Double Perturbation Theory

The Rayleigh–Schrödinger perturbation formulas of Section II are easy to generalize to double perturbation problems where the Hamiltonian $\mathscr{H}$ is given by Eq. (IV.7). The basic assumption is that the wave function $\Phi$ and energy $\mathscr{E}$ for the perturbed state can be expanded in a double power series in $\lambda$ and $\mu$[8b],

$$\Phi = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \lambda^n \mu^m \psi^{(n,m)}, \tag{IV.8}$$

$$\mathscr{E} = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \lambda^n \mu^m \varepsilon^{(n,m)}. \tag{IV.9}$$

The resulting perturbation equations for $\psi^{(n,0)}$ and $\varepsilon^{(n,0)}$ are the same as Eqs. (II.3) through (II.10) with $\psi^{(n,0)}$ replacing $\psi^{(n)}$ and $\varepsilon^{(n,0)}$ replacing $\varepsilon^{(n)}$. Similarly, the relations for $\psi^{(0,n)}$ and $\varepsilon^{(0,n)}$ are the same as Eqs. (II.3) through (II.10) with $\psi^{(0,n)}$ replacing $\psi^{(n)}$, $\varepsilon^{(0,n)}$ replacing $\varepsilon^{(n)}$, $W$ replacing

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[8b] For degenerate problems, Eqs. (IV.8) and (IV.9) are not generally valid. See Section IV,E.

$V$, and $W' = W - \varepsilon^{(0,1)}$ replacing $V'$. It is only the mixed perturbation equations which are essentially new, the general member being

$$H_0\psi^{(n,m)} + V\psi^{(n-1,m)} + W\psi^{(n,m-1)} = \sum_{j=0}^{n}\sum_{k=0}^{m}\varepsilon^{(j,k)}\psi^{(n-j,m-k)}. \qquad \text{(IV.10)}$$

In order that $\Phi$ be normalized to unity for all values of $\lambda$ and $\mu$, the perturbed wave functions $\psi^{(j,k)}$ must satisfy the conditions, analogous to Eq. (II.5),

$$\sum_{j=0}^{n}\sum_{k=0}^{m}\langle\psi^{(j,k)}, \psi^{(n-j,m-k)}\rangle = \delta_{n0}\delta_{m0}, \qquad n, m = 0, 1, 2, \ldots . \qquad \text{(IV.11)}$$

A general expression for the mixed order $\varepsilon^{(n,m)}$ can be obtained by multiplying Eq. (IV.10) by $\psi^*$ and integrating over all space,

$$\varepsilon^{(n,m)} = \langle\psi, V\psi^{(n-1,m)}\rangle + \langle\psi, W\psi^{(n,m-1)}\rangle$$
$$- \sum_{j=0}^{n}\sum_{k=0}^{m}\varepsilon^{(j,k)}[1 - \delta_{j0}\delta_{k0} - \delta_{jn}\delta_{km}]\langle\psi, \psi^{(n-j,m-k)}\rangle. \qquad \text{(IV.12)}$$

These double perturbation energies can be expressed in a variety of forms, some of which are discussed in Section IV, B.

*Expectation Values*

The first- and second-order properties $\langle W\rangle$ and $\langle Q\rangle$ associated with an operator $W$ can be expanded in powers of the perturbation parameter $\lambda$, and the coefficients expressed in terms of the perturbation energies $\varepsilon^{(n,m)}$. The general connection can be made by comparing Eqs. (IV.3) and (IV.9), which leads to the expansions

$$E^{(m)} = \sum_{n=0}^{\infty}\lambda^n\varepsilon^{(n,m)}, \qquad m = 0, 1, \ldots . \qquad \text{(IV.13)}$$

The corresponding perturbed wave functions are given by

$$\Psi^{(m)} = \sum_{n=0}^{\infty}\lambda^n\psi^{(n,m)}, \qquad m = 0, 1, \ldots . \qquad \text{(IV.14)}$$

*a. First-Order Properties.* The first-order property $\langle W\rangle$ defined by Eq. (IV.1) can be expanded in powers of $\lambda$ by means of Eq. (IV.14):

$$\langle W\rangle = \sum_{n=0}^{\infty}\lambda^n\sum_{k=0}^{n}\langle\psi^{(k,0)}, W\psi^{(n-k,0)}\rangle \qquad \text{(IV.15a)}$$

$$= \langle\psi, W\psi\rangle + \lambda[\langle\psi^{(1,0)}, W\psi\rangle + \langle\psi, W\psi^{(1,0)}\rangle] + \cdots . \qquad \text{(IV.15b)}$$

In this form the first-order correction involves $\psi^{(1,0)}$, which is the solution of the equation

$$(H_0 - \varepsilon)\psi^{(1,0)} + V'\psi = 0 \tag{IV.16}$$

where $\psi^{(1,0)}$ has been made orthogonal to $\psi$. Equation (IV.15) is useless for explicit calculation if $V$ contains two-particle electron repulsion terms, since Eq. (IV.16) cannot be solved in closed form in this case. Note that since $\langle W\rangle = E^{(1)}$, the corrections in Eq. (IV.15) can also be written in the form

$$\langle W\rangle = \sum_{n=0}^{\infty} \lambda^n \varepsilon^{(n,1)}. \tag{IV.17}$$

*b. Second-Order Properties.* The second-order property $\langle Q\rangle$ defined by Eq. (IV.4) can be expanded in powers of $\lambda$ by means of Eq. (IV.14):

$$\langle Q\rangle = \sum_{n=0}^{\infty} \lambda^n \sum_{k=0}^{n} \langle \psi^{(k,1)}, W\psi^{(n-k,0)}\rangle \tag{IV.18a}$$

$$= \langle \psi^{(0,1)}, W\psi\rangle + \lambda[\langle \psi^{(1,1)}, W\psi\rangle + \langle \psi^{(0,1)}, W\psi^{(1,0)}\rangle] + \cdots, \tag{IV.18b}$$

where $\psi^{(0,1)}$ is the solution of

$$(H_0 - \varepsilon)\psi^{(0,1)} + W'\psi = 0 \tag{IV.19a}$$

and $\psi^{(1,1)}$ is the solution of Eq. (IV.10) with $n = m = 1$,

$$(H_0 - \varepsilon)\psi^{(1,1)} + V'\psi^{(0,1)} + W'\psi^{(1,0)} = \varepsilon^{(1,1)}\psi^{(0,0)}. \tag{IV.20}$$

The initial approximation for $\langle Q\rangle$, given by the first term of Eq. (IV.18b), has the same form as a second-order energy, and requires for its evaluation the solution of Eq. (IV.19a). As discussed in Section III,A, an equation of this type can frequently be solved explicitly when $W$ is a one-particle operator by putting $\psi^{(0,1)} = F\psi$, so that it assumes the form of Eq. (III.3), namely,

$$[H_0, F]\psi + W'\psi = 0. \tag{IV.19b}$$

If $H - H_0 = \lambda V$ is a function of coordinates only, we can go one step further and eliminate $H_0$ to get Schwartz's (1959b) form[9]

$$[H, F]\psi + W'\psi = 0. \tag{IV.19c}$$

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[9] This is similar to, but different from, Eq. (III. 3.4), since here we are dealing with double perturbation theory, and $H$ involves $V$ and not $W$.

As far as the correction terms are concerned, however, Eq. (IV.20) is no easier to solve than Eq. (IV.16). Thus the form (IV.18) is of little practical interest for calculating the correction terms. Note that since $\langle Q \rangle = E^{(2)}$ the corrections may also be written in the form

$$\langle Q \rangle = \sum_{n=0}^{\infty} \lambda^n \varepsilon^{(n,2)}. \tag{IV.21}$$

## B. Dalgarno's Interchange Theorem

The general form of this theorem (Dalgarno and Stewart, 1958) allows one to express the mixed perturbation energies $\varepsilon^{(1,m)}$ entirely in terms of the $W$-perturbed functions $\psi^{(0,m)}$. It applies, without qualifications, only to the case of a nondegenerate unperturbed level; the degenerate case is discussed in Section IV,E. To establish the theorem it is convenient to introduce the Hamiltonian

$$H_* = H_0 + \mu W \tag{IV.22}$$

with eigenfunctions $\chi$ and eigenvalues $E_*$. The perturbation expansions of $\chi$ (normalized) and $E_*$ are given by Eqs. (IV.8) and (IV.9) as

$$\chi = \sum_{m=0}^{\infty} \mu^m \psi^{(0,m)}, \tag{IV.23}$$

$$E_* = \sum_{m=0}^{\infty} \mu^m \varepsilon^{(0,m)}. \tag{IV.24}$$

Let us now regard $\mathscr{H}$ as the single perturbation Hamiltonian

$$\mathscr{H} = H_* + \lambda V. \tag{IV.25}$$

The first-order energy is simply

$$\begin{aligned} E_*^{(1)} &= \langle \chi, V\chi \rangle \\ &= \sum_{m=0}^{\infty} \mu^m \sum_{k=0}^{m} \langle \psi^{(0,m-k)}, V\psi^{(0,k)} \rangle. \end{aligned} \tag{IV.26}$$

But by the definition of $E_*^{(1)}$ it follows from Eq. (IV.9) that

$$E_*^{(1)} = \sum_{m=0}^{\infty} \mu^m \varepsilon^{(1,m)}, \tag{IV.27}$$

and therefore, by comparing Eqs. (IV.26) and (IV.27),

$$\varepsilon^{(1,m)} = \sum_{k=0}^{m} \langle \psi^{(0,m-k)}, V\psi^{(0,k)} \rangle. \tag{IV.28}$$

This proves that the integrals in Eqs. (IV.15) and (IV.18) involving $W\psi^{(1,m)}$ can be interchanged for others involving $V\psi^{(0,m+1)}$, which is the content of the interchange theorem.

*a. First-Order Properties.* By using Eq. (IV.28) for $\varepsilon^{(1,1)}$, the expectation value of $W$ through the first order can be written in the form (Dalgarno and Stewart, 1956b)

$$\langle W\rangle = \langle\psi, W\psi\rangle + \lambda[\langle\psi^{(0,1)}, V\psi\rangle + \langle\psi, V\psi^{(0,1)}\rangle] + \cdots, \tag{IV.29a}$$

where $\psi^{(0,1)}$ is the solution of Eq. (IV.19). By putting $\psi^{(0,1)} = F\psi$ and $\lambda V = H - H_0$, Eq. (IV.29a) can be written in the form derived by Schwartz (1959b)

$$\langle W\rangle = \langle\psi, [W + F(H - \bar{H}) + (H - \bar{H})F]\psi\rangle + O(\lambda^2) \tag{IV.29b}$$

where $F$ is given by Eq. (IV.19c) and, following Schwartz, $\bar{H} = \langle\psi, H\psi\rangle$ has been introduced to free $F$ from the usual orthogonality restriction $\langle\psi, F\psi\rangle = 0$. This is the most useful expression for $\langle W\rangle$ in practice. Since Eq. (IV.19) can usually be solved explicitly, and the integrations in Eqs. (IV.29) are straightforward, $\langle W\rangle$ can now be calculated exactly to the same order of accuracy as the energy (i.e., to order $\lambda^2$).

*b. Second-Order Properties.* In a similar fashion, the use of Eq. (IV.28) for $\varepsilon^{(1,2)}$ allows the second-order property $\langle Q\rangle$ to be written in the form

$$\langle Q\rangle = \langle\psi^{(0,1)}, W\psi\rangle + \lambda[\langle\psi^{(0,2)}, V\psi\rangle + \langle\psi, V\psi^{(0,2)}\rangle + \langle\psi^{(0,1)}, V\psi^{(0,1)}\rangle] + \cdots, \tag{IV.30a}$$

where the function $\psi^{(0,2)}$ is the solution of the second-order single perturbation equation

$$(H_0 - \varepsilon)\psi^{(0,2)} + W'\psi^{(0,1)} - \varepsilon^{(0,2)}\psi = 0. \tag{IV.31a}$$

Schwartz's (1959b) form of Eq. (IV.30a) can be obtained in a similar fashion to Eq. (IV.29b) by putting $\psi^{(0,2)} = G\psi$, etc., and making the additional assumption that $V$ is a function of coordinates only:

$$\langle Q\rangle = \langle\psi, [W'F + G(H - \bar{H}) + (H - \bar{H})G + |F|^2(H - \bar{H})]\psi\rangle + O(\lambda^2). \tag{IV.30b}$$

Equation (IV.31a) can be written in terms of $G$ and $F$, and $H_0$ can be eliminated in favor of $H$, to give the equation quoted by Schwartz:

$$[H, G]\psi + W'F\psi - \varepsilon^{(0,2)}\psi = 0. \tag{IV.31b}$$

Since this equation can also frequently be solved explicitly by the techniques of Section III, the first-order corrections to $\langle Q \rangle$ can be calculated exactly in a large number of cases. This result has been very widely applied to the calculation of the second-order properties of atoms by many authors (see Dalgarno, 1962).

### C. Solution of Perturbation Equations

The methods of solving Eqs. (IV.19) and (IV.31) when $W$ is a one-electron operator have been thoroughly discussed in Section III,A[9a]. These equations correspond to Eqs. (III.1) and (III.50), the only differences being the notational ones: $W' \rightarrow V'$, $\psi^{(0,1)} \rightarrow \psi^{(1)}$, $\psi^{(0,2)} \rightarrow \psi^{(2)}$, $\varepsilon^{(0,2)} \rightarrow \varepsilon^{(2)}$. When explicit solutions for $\psi^{(0,1)}$ and $\psi^{(0,2)}$ cannot be found, various approximate variational techniques can be used. The straightforward method, discussed in Section III,B, is to use the Hylleraas variation principles, Eqs. (III.54) and (III.67). Modifications have also been used (Karplus and Kolker, 1963a) and are discussed briefly in Section XI.

The only cases in which explicit formulas can be given for the corrections are when the equations are one-dimensional or separable. In the one-dimensional case discussed in Section III, A,2, the first-order correction $\varepsilon^{(1,1)}$ can be expressed in a form similar to Eq. (III.26) which applies to ground or excited states, namely,

$$\varepsilon^{(1,1)} = -\oint_a^b \frac{M(z)N(z)}{\psi^2(z)}\, dz, \qquad \text{(IV.32)}$$

---

[9a] Hall (1964) has pointed out that it is not necessary to solve Eq. (IV.19) for each one-electron operator $W$ individually. Rather if one can obtain the correction to the one particle density matrix $\rho(\mathbf{r}, \zeta; \mathbf{r}', \zeta')$, the correction to an expectation value may be found by integration (including summation over the spin $\zeta$). This can be done either by the approach of Schwartz (1959a), extended by Hall (1964), or by the use of double perturbation theory with

$$W = \frac{1}{N} \sum_j \delta(\mathbf{r}_j - \mathbf{r}) \exp[i\mathbf{p}_j \cdot (\mathbf{r}' - \mathbf{r})]\, O_j,$$

where $O_j\,(\zeta, \zeta')$ is an operator which projects out the proper spin component. The expectation value of $W$ may be shown to be the one-particle density matrix. For a representation of this operator as an integral operator see McWeeny and Mizuno (1961). In most cases it will be sufficient to know the correction to the electron density, which may be found using the simpler operator

$$W' = \frac{1}{N} \sum_j \delta(\mathbf{r}_j - \mathbf{r}).$$

where

$$M(z) = 2\int_a^z \psi V'\psi \, d\xi, \tag{IV.33}$$

$$N(z) = 2\int_a^z \psi W'\psi \, d\xi. \tag{IV.34}$$

A similar type of formula can be derived when $H$ and $W$ are separable in the same coordinate system (see Appendix D).

### D. Expansion in Perturbed and Unperturbed Eigenfunctions

In this section the first- and second-order properties $\langle W \rangle$ and $\langle Q \rangle$ are expressed in terms of the perturbed eigenfunctions $\Psi_k$ of $H$ (single perturbation) and in terms of the unperturbed eigenfunctions $\psi_k$ of $H_0$ (double perturbation).

We begin by considering the difference between first- and second-order properties. Whereas the expectation value of $W$ for a particular state $q$ of a system with Hamiltonian $H$ requires only a knowledge of $\Psi_q$, namely,

$$\langle W \rangle_q = \langle \Psi_q, W\Psi_q \rangle, \tag{IV.35}$$

the formal expression for the second-order property $\langle Q \rangle$ in terms of the solutions of $H$ requires the entire spectrum of eigenfunctions and eigenvalues. This can be seen by expanding $\chi$, given by Eq. (IV.5), in terms ot the eigenfunctions $\Psi_k$ and substituting into Eq. (IV.4). The resulting well-known expression has exactly the same form as the second-order energy expansion Eq. (II.20) and is

$$\langle Q \rangle_q = \sum_k{}' \frac{W_{qk}W_{kq}}{E_q - E_k}, \tag{IV.36}$$

where

$$W_{qk} = \langle \Psi_q, W\Psi_k \rangle. \tag{IV.37}$$

The sum is to be taken to include integration over the continuum, and the prime indicates that states with energy $E_q$ are to be omitted.

It is instructive to compare these formally exact expressions with the approximate expressions obtained when $H = H_0 + \lambda V$, and we regard only the spectrum of the unperturbed Hamiltonian $H_0$ as known. By expanding the perturbation functions $\psi^{(0,1)}$ and $\psi^{(0,2)}$ of Eqs. (IV.19) and (IV.31) in terms of the unperturbed functions $\psi_k$ and using Eqs. (II,17), (II.18), (IV.29), and (IV.30) we obtain

$$\langle W\rangle_q = W_{qq}^{(0)} + 2\lambda \sum_k{}' \frac{W_{qk}^{(0)} V_{kq}^{(0)}}{\varepsilon_q - \varepsilon_k} + \cdots, \tag{IV.38}$$

$$\begin{aligned}\langle Q\rangle_q &= \sum_k{}' \frac{W_{qk}^{(0)} W_{kq}^{(0)}}{\varepsilon_q - \varepsilon_k} \\ &\quad + 2\lambda \sum_k{}' \sum_j{}' \frac{(V_{qk}^{(0)} W_{kj}^{(0)} W_{jq}^{(0)} + W_{qk}^{(0)} V_{kj}^{(0)} W_{jq}^{(0)} + W_{qk}^{(0)} W_{kj}^{(0)} V_{jq}^{(0)})}{(\varepsilon_q - \varepsilon_k)(\varepsilon_q - \varepsilon_j)} + \cdots,\end{aligned} \tag{IV.39}$$

where

$$\begin{aligned}W_{qq}^{(0)} &= \langle \psi_q, W\psi_q\rangle, \\ W_{kj}^{(0)} &= \langle \psi_k, W\psi_j\rangle - \delta_{kj}\langle \psi_q, W\psi_q\rangle, \\ V_{kj}^{(0)} &= \langle \psi_k, V\psi_j\rangle - \delta_{kj}\langle \psi_q, V\psi_q\rangle \qquad (\text{all } k, j \text{ except } k = j = q).\end{aligned} \tag{IV.40}$$

The first-order corrections due to the perturbation $V$ are effected through the matrix elements $V_{kj}^{(0)}$ in the terms of order $\lambda$.

There are two important and related second-order properties of electronic systems which we shall consider in more detail to exemplify these formulas. They are the polarizability $\alpha$ of an atom or molecule and the van der Waals constant $C$ for the long-range interaction of two atoms or molecules.

The operator $W$ for the polarizability tensor is the electric dipole moment vector

$$\boldsymbol{\mu} = \sum_s e_s \mathbf{r}_s, \tag{IV.41}$$

where $e_s$, and $\mathbf{r}_s$, are the charge (see footnote 34, Section X) and position of particle $s$, and the summation is over all particles. The static zero-field mean polarizability is defined by

$$\alpha = -(\partial^2 \mathscr{E}/\partial I^2)_{I=0}$$

where $I$ is the electric field intensity. Therefore by Eq. (IV.4) we have $\alpha = \langle Q\rangle$, and hence the mean polarizability for a system in state $q$, given by Eq. (IV.36), can be written (cf. Section X, where $\varepsilon$ is used in the sense of the $E$ in the present section)

$$\alpha_q = \sum_k \frac{f_{qk}}{(E_q - E_k)^2}, \tag{IV.42}$$

where $f_{qk}$ is the mean oscillator strength defined by

$$f_{qk} = \tfrac{2}{3}(E_k - E_q)|\langle \Psi_k, \boldsymbol{\mu}\Psi_q \rangle|^2. \tag{IV.43}$$

If the atom or molecule is isotropic then

$$f_{qk} = 2(E_k - E_q)|(\mu_x)_{qk}|^2 \qquad \text{when} \qquad (\mu_x)_{qk} = \langle \Psi_q, \mu_x \Psi_k \rangle \tag{IV.44}$$

and $\mu_x$ is one of the components of $\boldsymbol{\mu}$.

The zeroth-order approximation $\alpha_q^{(0)}$ to the polarizability of a system based on an approximate wave function $\psi_q^{(0)}$, such as a Hartree–Fock, which takes inadequate account of electron repulsion will be given by Eq. (IV.39), namely.

$$\alpha_q^{(0)} = \sum_k{}' \frac{f_{qk}^{(0)}}{(\varepsilon_q - \varepsilon_k)^2}. \tag{IV.45}$$

The leading correction for the perturbation $V$, which involves the two-particle electron repulsion terms, is given by

$$\alpha_q^{(1)} = 2 \sum_k{}' \sum_j{}' \frac{(\mu_{qk}^{(0)} V_{kj}^{(0)} \mu_{jq}^{(0)} + 2\mu_{qk}^{(0)} \mu_{kj}^{(0)} V_{jq}^{(0)})}{(\varepsilon_q - \varepsilon_k)(\varepsilon_q - \varepsilon_j)} \tag{IV.46}$$

where $V_{kj}^{(0)}$ is defined by Eq. (IV.40) and

$$\mu_{kj}^{(0)} = \langle \psi_k, \mu_x \psi_j \rangle - \delta_{kj} \langle \psi_q, \mu_x \psi_q \rangle. \tag{IV.47}$$

The treatment of the van der Waals constant $C$ is similar (see Section X, C,3). Consider the long-range interaction of two identical atoms A and B in ground $S$ states at distance $R$ apart. The leading term in the multipole expansion of the interaction potential is the two-particle perturbation

$$W = \frac{1}{R^3} (\boldsymbol{\mu}^a \cdot \boldsymbol{\mu}^b - 3\mu_x^a \mu_x^b), \tag{IV.48}$$

where $\boldsymbol{\mu}^a$ and $\boldsymbol{\mu}^b$ are the electric dipole operators for A and B and $\mu_x^a$, $\mu_x^b$ are the components along the molecular axis. $C$ is defined as the coefficient of $R^{-6}$ in the expansion of the interaction energy in powers of $1/R$. The exact expression for $C$ in terms of the atomic eigenfunctions $\Psi_k$ is, therefore,

$$C = \frac{3}{2} \sum_k{}' \sum_j{}' \frac{f_{qk} f_{qj}}{(E_k - E_q)(E_j - E_q)(E_k + E_j - 2E_q)}. \tag{IV.49}$$

However, if, as is the case for all atoms other than hydrogen, approximate atomic wave functions $\psi_k^{(0)}$ are used, then $C$ has correction terms of the same kind as Eq. (IV.39) and involving the same matrix elements.

## E. Interchange Theorems in the Presence of Degeneracy

Thus far our discussion has been limited to situations in which $\varepsilon^{(0,0)}$ is nondegenerate. We now remove this restriction. *We will show that, except for special circumstances, there are no interchange theorems.* More precisely, one cannot, for example, express the expectation value of $W$, correct through first order in $\lambda$, completely in terms of $W$-perturbed wave functions.

To distinguish the members of the degenerate set we will need a further index. Thus we replace $\psi^{(0,0)}$ by $\psi_\alpha^{(0,0)}$ where the $\psi_\alpha^{(0,0)}$ are so chosen that $V$ is "diagonal," i.e., so that $\langle\psi_\alpha^{(0,0)}, V\psi_\beta^{(0,0)}\rangle = 0$, $\alpha \neq \beta$. This of course suffices to determine the $\psi_\alpha^{(0,0)}$ uniquely only in so far as $V$ lifts the degeneracy in first order.

The equation for $\psi_\alpha^{(1,0)}$ then takes the familiar form

$$(H_0 - \varepsilon^{(0,0)})\psi_\alpha^{(1,0)} = -(V - \varepsilon_\alpha^{(1,0)})\psi_\alpha^{(0,0)}, \tag{IV.50}$$

where

$$\varepsilon_\alpha^{(1,0)} = \langle\psi_\alpha^{(0,0)}, V\psi_\alpha^{(0,0)}\rangle.$$

By analogy with what has gone before, one would now guess that the equation for the $W$-perturbed function should take the form

$$(H_0 - \varepsilon^{(0,0)})\chi_\alpha = -W\psi_\alpha^{(0,0)} + \sum_\beta \psi_\beta^{(0,0)}\langle\psi_\beta^{(0,0)}, W\psi_\alpha^{(0,0)}\rangle, \tag{IV.51}$$

where the extra complication is needed in order to make the right-hand side orthogonal to all solutions of the homogeneous equation.

One can now prove by familiar techniques that, through first order in $\lambda$,

$$\begin{aligned}\langle\Psi_\alpha, W\Psi_\alpha\rangle = \langle\psi_\alpha^{(0,0)}, W\psi_\alpha^{(0,0)}\rangle + 2\,\mathrm{Re}\,\lambda\Big[&\langle\chi_\alpha, (V - \varepsilon_\alpha^{(1,0)})\psi_\alpha^{(0,0)}\rangle \\ &+ \sum_{\beta,\beta\neq\alpha} \langle\psi_\alpha^{(0,0)}, W\psi_\beta^{(0,0)}\rangle\langle\psi_\beta^{(0,0)}, \psi_\alpha^{(1,0)}\rangle\Big] + \cdots.\end{aligned} \tag{IV.52}$$

The first term in the square bracket is of the desired form, the second is not. This of course does not prove that further manipulation of the second term will not put it into interchanged form; however, we will make it plausible below that this cannot be done. Before turning to this however let us note that the second term will vanish and hence *we will have an interchange theorem under any of the following circumstances:*

(i) *V causes no mixing in first order*, i.e., $\langle\psi_\beta^{(0,0)}, \psi_\alpha^{(1,0)}\rangle = 0$, $\beta \neq \alpha$. This would be the case, for example, if we were dealing with a purely rotational degeneracy and $V$ were spherically symmetric. Indeed here there would not only be no mixing, but also there would be no splitting. Two other examples are: (1) a spherically symmetric $V$ perturbing the $2s$, $2p$ degeneracy in hydrogen; (2) the $(1s^2 2p)^2P$, $(1s^2, 2s)^2S$ degeneracy in Li, considering the electronic repulsions as a perturbation. Here one would have splitting but no mixing.

(ii) *V causes mixing in first order, but W is diagonal*, i.e., $\langle\psi_\alpha^{(0,0)}, W\psi_\beta^{(0,0)}\rangle = 0$ for those $\beta \neq \alpha$ such that $\langle\psi_\beta^{(0,0)}, \psi_\alpha^{(1,0)}\rangle \neq 0$. This situation is clearly a rather unlikely one, holding for only very special choices of $W$.

(iii) An interchange theorem also exists for the correction to the expectation value when this is *averaged* over the group of states arising from the degenerate level. This is,

$$\sum_\alpha (\Psi_\alpha, W\Psi_\alpha) = \sum_\alpha \langle\psi_\alpha^{(0,0)}, W\psi_\alpha^{(0,0)}\rangle + 2\lambda \operatorname{Re} \sum_\alpha \langle\chi_\alpha, (V - \varepsilon_\alpha^{(1,0)})\psi_\alpha^{(0,0)}\rangle + O(\lambda^2). \quad \text{(IV.53)}$$

This follows from Eq. (IV.52) by summing over the states $\alpha$ and observing that, since $\Psi_\alpha$ and $\Psi_\beta$ are orthogonal and assumed normalized,

$$\langle\psi_\alpha^{(1,0)}, \psi_\beta^{(0,0)}\rangle + \langle\psi_\alpha^{(0,0)}, \psi_\beta^{(1,0)}\rangle = 0.$$

Hence the offending terms in Eq. (IV.52) sum identically to zero.

As we have said, our results so far do not prove the impossibility of deriving a general interchange theorem. However one is readily convinced by examining the offending terms in a special case. Namely, let us suppose that $V$ removes all degeneracy in first order and neither (i) nor (ii) apply. Then the standard expansion techniques applied to the first- and second-order $V$-perturbed equations yield the result that the term in question is equal to

$$\sum_{\beta,\, \beta\neq\alpha} \langle\psi_\alpha{}^{(0,0)}, W\psi_\beta^{(0,0)}\rangle \sum_p{}' \frac{\langle\psi_\beta^{(0,0)}, V\psi_p^{(0,0)}\rangle\langle\psi_p^{(0,0)}, V\psi_\alpha^{(0,0)}\rangle}{(\varepsilon_\alpha^{(1,0)} - \varepsilon_\beta^{(1,0)})(\varepsilon^{(0,0)} - \varepsilon_p^{(0,0)})},$$

and it seems clear that one will not be able to express this completely in terms of $W$-perturbed functions. As a case in point we may note that in the $1/Z$ expansion (see Section XI,A) for atoms one often, because of the degeneracy of hydrogen, encounters two degenerate states of the same angular momentum which are then split and mixed by $V$—for example, the two lowest ${}^1S$ states of beryllium arising from the configurations $1s^2 2s^2$

and $1s^2 2p^2$. For such situations then it appears that one will in general have no interchange theorem to ease the calculation of the expectation value of $W$.

The difficulties in the degenerate case can also be appreciated from another point of view. In the nondegenerate case we derived interchange theorems by use of double perturbation theory. The essential point was that the energy and the wave function could be expanded in a double power series in $\lambda$ and $\mu$ (and that $\delta^{n+1}\mathscr{E}/\delta\mu^n\delta\lambda = \delta^{n+1}\mathscr{E}/\delta\lambda\delta\mu^n$). However for double perturbation theory in the degenerate case, such an expansion is in general not possible. Thus for example if one first puts $\mu = 0$ and then $\lambda = 0$ one must arrive at a degenerate set of wave functions which "diagonalize" $V$, whereas if one first puts $\lambda = 0$ and then $\mu = 0$ one must arrive at a degenerate set of wave functions which "diagonalize" $W$. Since, except for special choices of $W$, these conditions are incompatible it follows that in general a nonanalytic behavior is to be expected at $\lambda = 0$, $\mu = 0$. We should note however that although this discussion of double perturbation theory suggests difficulties we are in fact able to derive interchange theorems under much *weaker* conditions, i.e., (i) and (ii) above, than that $V$ and $W$ be "simultaneously diagonalizable."

In order to approximate the energy $\mathscr{E}$ one can use DEFOPVIM (Section VII) in which $W$ takes the place of $V$ in Eq. (VII.9′); also $\mathscr{H}$ takes the place of $H$ and $\mathscr{E}$ replaces $E(1)$ in Eqs. (VII.13), (VII.14), and (VII.15).

To illustrate double perturbation theory with degeneracy the following example is instructive:

Consider the doubly degenerate first excited state of a doubly perturbed two-dimensional simple harmonic oscillator

$$H_0 = -\frac{1}{2}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + \tfrac{1}{2}(x^2 + y^2)$$

with $V = \frac{1}{2}(x^2 - y^2)$ and $W = xy$. In this case it is easy to show that if $\psi_a$ and $\psi_b$ are two orthogonal degenerate unperturbed wave functions (we dispense with the superscript (0, 0)) such that $\langle\psi_b, V\psi_a\rangle = 0$, then $\langle\psi_b, W\psi_a\rangle \neq 0$. The exact solution may be easily found by observing that the total Hamiltonian

$$H = -\frac{1}{2}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + \tfrac{1}{2}(x^2 + y^2) + \tfrac{1}{2}\lambda(x^2 - y^2) + \mu xy$$

may be written in the form

$$H = -\frac{1}{2}\left(\frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \zeta^2}\right) + \tfrac{1}{2}\omega_-^2 \xi^2 + \tfrac{1}{2}\omega_+^2 \zeta^2,$$

where $\omega_{\pm}^{2}$ are the eigenvalues of the matrix

$$\begin{bmatrix} 1+\lambda & \mu \\ \mu & 1-\lambda \end{bmatrix}$$

and the coordinates $\xi, \zeta$ are rotated through an angle $\alpha$ with respect to $x, y$ given by $\tan 2\alpha = \mu/\lambda$. The exact eigenvalues for the first two excited states are, therefore,

$$E_a = \tfrac{3}{2}\omega_- + \tfrac{1}{2}\omega_+ ,$$

$$E_b = \tfrac{1}{2}\omega_- + \tfrac{3}{2}\omega_+ ,$$

where

$$\omega_{\pm} = \sqrt{1 \pm (\lambda^2 + \mu^2)^{\frac{1}{2}}}.$$

This example shows clearly that $E_a$ and $E_b$ are not analytic functions of $\lambda$ and $\mu$ for the unperturbed condition $\lambda = \mu = 0$ and cannot be expanded in double power series about this point. The correct zeroth-order wave functions are

$$\psi_a = 2\pi^{-\frac{1}{2}} (x \cos\alpha + y \sin\alpha) \exp[-\tfrac{1}{2}(x^2 + y^2)],$$

$$\psi_b = 2\pi^{-\frac{1}{2}} (-x \sin\alpha + y \cos\alpha) \exp[-\tfrac{1}{2}(x^2 + y^2)]$$

and depend through $\alpha$ on the limiting ratio of $\mu/\lambda$ as $\mu$ and $\lambda$ go to zero.

## V. General Connections between Perturbation Theory and the Variational Principle

There are many connections between perturbation theory and the variational principle, some of which have been discussed in the preceding sections. In this section we will explore certain of these connections in more detail.

First we want to emphasize that the relationship between perturbation theory and the variational principle is two-way. Consider some quantity $A$ for which we wish a perturbation expression

$$A = \sum_n \nu^n A^{(n)}$$

where $\nu$ is the order parameter. Then, on the one hand, given a variational principle for $A$, *one can derive variational principles for the individual* $A^{(n)}$. This possibility is obviously of great practical importance. We have already discussed the case $A = E$ in Section III and will discuss it further below. We would note, however, that one can do similar things if $A$ is a scattering phase shift or a scattering amplitude.

On the other hand the perturbation formula for $A^{(0)} + vA^{(1)}$ in fact *provides a variational principle for* $A$ because the mark of the latter is precisely that it yields errors of second order (Makinson and Turner, 1953). We have already had one example of this sort in Section IV in discussing the connection between the double perturbation and Schwartz approaches to the calculation of expectation values. Another, more familiar example (for examples from scattering theory, see Makinson and Turner, 1953) is the following. From first-order perturbation theory we know that $\langle\psi^{(0)}, H\psi^{(0)}\rangle/\langle\psi^{(0)}, \psi^{(0)}\rangle = E + O(v^2)$, whence we infer that $\langle\tilde{\Psi}, H\tilde{\Psi}\rangle/\langle\tilde{\Psi}, \tilde{\Psi}\rangle$ is stationary for first-order variations of $\tilde{\Psi}$ about the true wave function, which is of course correct.[10] As usual, we use tilde to represent trial functions.

## A. Perturbation Theory of the Variational Principle

Let us now consider the case $A = E$ in some detail where, for notational simplicity, we continue to consider only a single perturbation which may be thought of either as $\lambda V$ or $\mu W$. Thus, we consider the Hamiltonian

$$\mathscr{H} = \mathscr{H}_0 + v\mathscr{H}_1$$

and the associated stationary expression $J$ where

$$J \equiv \langle\tilde{\psi}, (\mathscr{H} - \tilde{E})\tilde{\psi}\rangle. \tag{V.1}$$

For *fixed* $\tilde{E}$ one determines the optimal $\tilde{\psi}$ from $\delta J = 0$ and then one *determines* $\tilde{E}$ from $J = 0$. We will symbolize this process by $\delta J = 0$, $J = 0$. To derive variational expressions for individual expansion coefficients we simply insert

$$J = \sum v^n J^{(n)}, \qquad \tilde{\psi} = \sum v^n \tilde{\psi}^{(n)}, \qquad \tilde{E} = \sum v^n \tilde{E}^{(n)}$$

into Eq. (V.1) and equate terms of like power of $v$ to obtain the following sequence of stationary expressions (see also Scherr and Knight, 1963):

$$J^{(0)} \equiv \langle\tilde{\psi}^{(0)}, (\mathscr{H}_0 - \tilde{E}^{(0)})\tilde{\psi}^{(0)}\rangle, \tag{V.2}$$

$$\begin{aligned} J^{(1)} \equiv {} & \langle\tilde{\psi}^{(0)}, (\mathscr{H}_1 - \tilde{E}^{(1)})\tilde{\psi}^{(0)}\rangle + \langle\tilde{\psi}^{(0)}, (\mathscr{H}_0 - \tilde{E}^{(0)})\tilde{\psi}^{(1)}\rangle \\ & + \langle\tilde{\psi}^{(1)}, (\mathscr{H}_0 - \tilde{E}^{(0)})\tilde{\psi}^{(0)}\rangle, \end{aligned} \tag{V.3}$$

$$\begin{aligned} J^{(2)} \equiv {} & \langle\tilde{\psi}^{(0)}, (-\tilde{E}^{(2)})\tilde{\psi}^{(0)}\rangle + \langle\tilde{\psi}^{(0)}, (\mathscr{H}_1 - \tilde{E}^{(1)})\tilde{\psi}^{(1)}\rangle \\ & + \langle\tilde{\psi}^{(1)}, (\mathscr{H}_1 - \tilde{E}^{(1)})\tilde{\psi}^{(0)}\rangle + \langle\tilde{\psi}^{(1)}, (\mathscr{H}_0 - \tilde{E}^{(0)})\tilde{\psi}^{(1)}\rangle \\ & + \langle\tilde{\psi}^{(0)}, (\mathscr{H}_0 - \tilde{E}^{(0)})\tilde{\psi}^{(2)}\rangle + \langle\tilde{\psi}^{(2)}, (\mathscr{H}_0 - \tilde{E}^{(0)})\tilde{\psi}^{(0)}\rangle, \end{aligned} \tag{V.4}$$

$$J^{(3)} \equiv \text{etc.}$$

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[10] Further, by using higher-order perturbation theory one can derive "superstationary" variation principles (see Kikuta, 1954, 1955; Biedenharn and Blatt, 1954; and Section VI).

### 1. *First-Order Variation Principle*

We will now examine the content of each of these stationary expressions in turn. Equation (V.2) is of course the variational expression for the zero-order problem and requires no further comment.

*a. Delves's Variation Principle.* Equation (V.3) is a variational principle for $E^{(1)}$. $J^{(1)}$ is stationary for variations of $\tilde{\psi}^{(1)}$ and $\tilde{\psi}^{(0)}$ about their correct values. Thus $\delta J^{(1)} = 0$, $J^{(1)} = 0$, $J^{(0)} = 0$ can provide approximate $E^{(1)}$, $\psi^{(1)}$, and $\psi^{(0)}$, the latter in general different from the approximate $\psi^{(0)}$ furnished by $\delta J^{(0)} = 0$, $J^{(0)} = 0$. Here $\delta J^{(1)}$ corresponds to the independent variations of both $\tilde{\psi}^{(0)}$ and $\tilde{\psi}^{(1)}$.

Until recently this variation principle has not attracted any attention. The reasons are simple:

(i) In the calculation of the energy levels of an isolated system by perturbation theory ($\mathscr{H}_0 = H_0$, $\nu\mathscr{H}_1 = \lambda V$) one naturally chooses $\mathscr{H}_0$ so that $\psi^{(0)}$ and hence $E^{(1)}$ are known exactly, and one has no need for $J^{(1)}$;

(ii) In the calculation of the effects of external fields ($\mathscr{H}_0 = H$, $\nu\mathscr{H}_1 = \mu W$), very often $E^{(1)} = 0$ by symmetry whence, once again, one has no need for $J^{(1)}$;

(iii) Given, as is usually the case, a definite but approximate $\psi^{(0)}$, i.e., a $\tilde{\psi}^{(0)}$, then $J^{(1)}$ is likely to be of little help in determining an optimal $\psi^{(1)}$ because unrestricted variation of $\tilde{\psi}^{(1)}$ clearly yields an equation for $\tilde{\psi}^{(0)}$ not $\tilde{\psi}^{(1)}$.

However, as has been pointed out recently by Delves (1963a), if we do not know $\psi^{(0)}$ exactly and if one *is* interested in $\langle\psi^{(0)}, H_1\psi^{(0)}\rangle$ for some $H_1$, then this variational principle offers the possibility of an improvement over $\langle\tilde{\psi}^{(0)}, H_1\tilde{\psi}^{(0)}\rangle$. More specifically, the resultant $\tilde{E}^{(1)}$ will be correct through terms of order $\tilde{\psi}^{(0)} - \psi^{(0)}$ and $\tilde{\psi}^{(1)} - \psi^{(1)}$. However, this variational principle has at least two drawbacks.

(1) Even for the ground state it is not a minimal principle, only a stationary principle.[11] Thus what we have termed an improvement may in fact not be one at all, i.e., may not be numerically more accurate, and in particular one does not necessarily improve things by using more elaborate trial functions.

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[11] For the ground state we know $\tilde{E}^{(0)} + \nu\tilde{E}^{(1)} + \cdots \geqslant E^{(0)} + \nu E^{(1)} \cdots$. If now our trial function is accurate to order $\nu^n$, then the left-hand side will be accurate to order $\nu^{2n+1}$ whence we will have

$$\nu^{2n+2}\,\tilde{E}^{(2n+2)} + \cdots \geqslant \nu^{2n+2}\,E^{(2n+2)} + \cdots$$

which implies $\tilde{E}^{(2n+2)} \geqslant E^{(2n+2)}$. In short *we will have minimal principles only for even orders, and then only if we know the lower orders exactly.*

(2) Related to this is the following. We are allowed to vary $\tilde{\psi}^{(0)}$ and $\tilde{\psi}^{(1)}$ independently, and this can lead to peculiar results. In particular we may fix $\tilde{\psi}^{(0)}$ (determined say from $\delta J^{(0)} = 0$, $J^{(0)} = 0$) and vary only the scale of $\tilde{\psi}^{(1)}$ (i.e., we write $\tilde{\psi}^{(1)} = S\phi$ and vary the parameter $S$). One now readily finds that the optimal $\tilde{E}^{(1)}$ is simply $\langle\tilde{\psi}^{(0)}, H_1\tilde{\psi}^{(0)}\rangle$, i.e., no improvement.

*b. Schwartz's Method.* One may regard the Schwartz method (discussed in Section IV and shown there to be equivalent to the Double Perturbation Method) to be a special case of Delves's variation principle in which for *fixed* $\tilde{\psi}^{(0)}$ one restricts the freedom of $\tilde{\psi}^{(1)}$ by requiring that $\tilde{\psi}^{(0)} - \psi^{(0)}$ and $\tilde{\psi}^{(1)} - \psi^{(1)}$ be of the same order, so that the error in $\tilde{E}^{(1)}$ is of order $(\tilde{\psi}^{(0)} - \psi^{(0)})^2$.

This is done in the following way. Writing $\psi^{(1)} = F\psi^{(0)}$ we have the Dalgarno–Lewis equation for $F$:

$$[\mathscr{H}_0, F]\psi^{(0)} = -(\mathscr{H}_1 - \langle\psi^{(0)}, \mathscr{H}_1\psi^{(0)}\rangle)\psi^{(0)}.$$

If now we write $\tilde{\psi}^{(1)} = \tilde{F}\tilde{\psi}^{(0)}$, it is clear that the error in $\tilde{\psi}^{(1)}$ will be of the same order as that in $\tilde{\psi}^{(0)}$ if $\tilde{F}$ satisfies

$$[\mathscr{H}_0, \tilde{F}]\tilde{\psi}^{(0)} = -(\mathscr{H}_1 - \langle\tilde{\psi}^{(0)}, \mathscr{H}_1\tilde{\psi}^{(0)}\rangle)\tilde{\psi}^{(0)}, \tag{V.5}$$

which is the Schwartz condition. As Schwartz notes, one can also derive this equation from a variation principle (see below), which then can be used, if necessary, to effect an approximate solution.

2. *Second-Order Variational Principle*

Equation (V.4) is a variational principle for $E^{(2)}$. In this general form it has not been used though it could have applicability to external field problems where usually one does not know $\tilde{\psi}^{(0)}$ exactly. However, following Schwartz, it is probably better to restrict $\tilde{\psi}^{(1)}$ and $\tilde{\psi}^{(2)}$ or, following Dalgarno, to use double perturbation theory.

If $\psi^{(0)}$ is known exactly, i.e., $\tilde{\psi}^{(0)} = \psi^{(0)}$, $\tilde{E}^{(0)} = E^{(0)}$, $\tilde{E}^{(1)} = E^{(1)}$, then, so far as the numerical value of $J^{(2)}$ and its behavior under variations of $\tilde{\psi}^{(1)}$ are concerned, we may drop the last two terms, whence $\delta J^{(2)} = 0$, $J^{(2)} = 0$ is identical to the Hylleraas minimal [11] principle for $E^{(2)}$ and $\psi^{(1)}$ discussed in Section III, B. An essential point here is that, in contrast to the situation with $J^{(1)}$, free variation of $\tilde{\psi}^{(1)}$ does yield an equation for $\tilde{\psi}^{(1)}$. Similarly, free variation of $\tilde{\psi}^{(n)}$ in $J^{(2n)}$ yields an equation for $\tilde{\psi}^{(n)}$, so that, if one knows the lower orders exactly, one can derive from $J^{(2n)}$ a Hylleraas-like variational principle (Sinanoglu, 1961a; Scherr and Knight, 1963; Sando and Hirschfelder, 1964) which determines an optimal $\tilde{\psi}^{(n)}$ and an upper bound to $E^{(2n)}$.[11]

If on the other hand $\tilde{\psi}^{(0)}$ is only approximate, then the expression $\delta \tilde{J}_H = 0$, where

$$\begin{aligned} \tilde{J}_H = {} & \langle \tilde{\psi}^{(0)}, (\mathscr{H}_1 - \tilde{E}^{(1)})\psi^{(1)} \rangle + \langle \tilde{\psi}^{(1)}, (\mathscr{H}_1 - \tilde{E}^{(1)})\tilde{\psi}^{(0)} \rangle \\ & + \langle \tilde{\psi}^{(1)}, (\mathscr{H}_0 - \tilde{E}^{(0)})\tilde{\psi}^{(1)} \rangle \end{aligned}$$

with $\tilde{E}^{(0)} = \langle \tilde{\psi}^{(0)}, \mathscr{H}_0 \tilde{\psi}^{(0)} \rangle$ and $\tilde{E}^{(1)}$ approximated by $\langle \tilde{\psi}^{(0)}, \mathscr{H}_1 \tilde{\psi}^{(0)} \rangle$, can be used to determine an optimal $\tilde{\psi}^{(1)}$ for a given $\tilde{\psi}^{(0)}$. This $\tilde{\psi}^{(1)}$ can then be used in conjunction with $J^{(1)} = 0$ to yield a variational approximation to $E^{(1)}$.[12] Indeed if we write $\tilde{\psi}^{(1)} = \tilde{F}\tilde{\psi}^{(0)}$ and make the approximation $\tilde{E}^{(0)}\tilde{\psi}^{(0)} \simeq \mathscr{H}_0 \tilde{\psi}^{(0)}$, then this becomes exactly the method of Schwartz. In this connection one should note that free variation of $\tilde{\psi}^{(1)}$ without the approximation $\tilde{E}^{(0)}\tilde{\psi}^{(0)} \simeq \mathscr{H}_0 \tilde{\psi}^{(0)}$ leads to an equation which one can presumably not solve exactly since, by hypothesis, one cannot solve the associated homogeneous equation. On the other hand one may hope to solve Schwartz's Eq. (V.5).

## B. Special Theorems for Variational Wave Functions

### 1. *Orthogonality and Related Theorems*

We could now go on and discuss $J^{(3)}$, etc., but, since no new questions of principle arise and the analysis becomes repetitive, we will terminate the detailed discussion at this point and turn to another question. Thus far we have been concerned with a single state. However, our variational procedures may well provide us with a number of stationary solutions which one would then be tempted to associate with various states. The question then arises—will these several solutions be orthogonal? In what follows we will, among other things, derive sufficient conditions for orthogonality. We believe that they are also necessary conditions if the orthogonality is to be enforced only by the variational principle, i.e., if the solutions in question are not *a priori* orthogonal by construction or because of some symmetry property.

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[12] As has already been remarked in Section III, in many applications $\tilde{J}_H$ has been used as an approximation to $-E^{(2)}$. As is clear from our discussion, and as most authors have realized and mentioned, this is not a variational approximation unless $\tilde{\psi}^{(0)} = \psi^{(0)}$. Of course if one replaces $\mathscr{H}_0$ by $\tilde{\mathscr{H}}_0$, where $\tilde{\psi}_0$ *is* an eigenfunction of $\tilde{\mathscr{H}}_0$, then we have a variational approximation to the second-order energy for the Hamiltonian $\tilde{\mathscr{H}}_0 + \nu\tilde{\mathscr{H}}_1$ (Karplus and Kolker, 1963a). In any case $\tilde{\psi}^{(0)} + \nu^{(}\tilde{\psi}^{1)}$ yields a variational approximation to the *total* energy.

Our basic tool is the observation that, if $\tilde{\psi}_p$ and $\tilde{\psi}_q$ are optimal trial functions, then from $\delta J = 0$ we have (varying $\tilde{\psi}_p$ but not $\tilde{\psi}_p{}^*$)

$$\tilde{E}_p\langle\tilde{\psi}_p, \delta\tilde{\psi}_p\rangle = \langle\tilde{\psi}_p, \mathscr{H}\delta\tilde{\psi}_p\rangle \tag{V.6}$$

and (varying $\tilde{\psi}_q{}^*$ but not $\tilde{\psi}_q$)

$$\tilde{E}_q\langle\delta\tilde{\psi}_q, \tilde{\psi}_q\rangle = \langle\delta\tilde{\psi}_q, \mathscr{H}\tilde{\psi}_q\rangle. \tag{V.7}$$

From now on we will assume $\tilde{E}_p \neq \tilde{E}_q$. Then we have the following *theorem*

(a) If $\delta\tilde{\psi}_p = \eta\tilde{\psi}_q$ and $\delta\tilde{\psi}_q = \eta\tilde{\psi}_p$ are possible variations[13] of the optimal trial functions, then $\tilde{\psi}_p$ and $\tilde{\psi}_q$ are orthogonal.

*Proof:* The proof is immediate. Simply insert the variations into Eqs. (V.6) and (V.7) and subtract to find

$$(\tilde{E}_p - \tilde{E}_q)\langle\tilde{\psi}_p, \tilde{\psi}_q\rangle = 0,$$

which proves the theorem.

From this follow as special cases, for example, the orthogonality of the exact $\psi_p$ and $\psi_q$ and of different solutions of the Rayleigh–Ritz method. It is also of interest to make the following two remarks.

(b) *Generalized Brillouin Theorem.* If $\delta\tilde{\psi}_q = \eta\psi'$ where $\langle\psi', \tilde{\psi}_q\rangle = 0$ is a possible variation of the optimal trial function, then

$$\langle\psi', \mathscr{H}\tilde{\psi}_q\rangle = 0.$$

This is of course an immediate consequence of Eq. (V.7). For $\tilde{\psi}_q$ the optimal unrestricted Hartree–Fock determinant, the allowed $\psi'$ are any linear combination of determinants which differ from $\tilde{\psi}_q$ by any single spin orbital. Thus in this special case our theorem is exactly Brillouin's theorem (Brillouin, 1933–34; Nesbet, 1961).

If now the conditions given in (a) are satisfied, it further follows that not only do the $\tilde{\psi}_p$ resemble excited states in that they are orthogonal, but the $\tilde{E}_p$ in fact yield upper bounds to the energies of excited states.

*Proof:* If the conditions given in (a) are satisfied then, from the theorem we have just proven, we have

$$\langle\tilde{\psi}_p, \mathscr{H}\tilde{\psi}_q\rangle = 0, \qquad p \neq q.$$

Consider $\tilde{\Psi} = \sum a_p\tilde{\psi}_p$ as a new trial function with the $a_p$ as the (linear) variational parameters. The stated result is then an immediate consequence

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[13] Here and in what follows $\eta$ in a general way symbolizes a small quantity. It need not have the same value in different variations. Note also that since $J$ is homogeneous the variations $\delta\tilde{\psi}_p = \eta\tilde{\psi}_p$ and $\delta\tilde{\psi}_q = \eta\tilde{\psi}_q$ are, in effect, always allowed. Thus all conditions are to be understood as being modulo such variations.

of the Hylleraas–Undheim (1930) theorem (see also MacDonald, 1933), since clearly the resulting secular determinant is diagonal with the new variational energies just equal to the $\tilde{E}_p$ again.

(c) *Off-Diagonal Hypervirial Theorems for Variational Wave Functions.* If $\delta\tilde{\psi}_p = i\eta W\tilde{\psi}_q$ and $\delta\tilde{\psi}_q = i\eta W\tilde{\psi}_p$, where $W$ is a Hermitian operator, are allowed variations of the optimal trial functions, then it follows by subtracting Eq. (V.6) and Eq. (V.7) that

$$(\tilde{E}_p - \tilde{E}_q)\langle\tilde{\psi}_p, W\tilde{\psi}_q\rangle = \langle\tilde{\psi}_p, [\mathscr{H}, W]\tilde{\psi}_q\rangle.$$

This generalizes an earlier result of S.T. Epstein and Hirschfelder (1961) which applies to the diagonal case $p = q$.

From this, for example, one can immediately infer, in agreement with other authors (Vetchinkin, 1963, Villars, 1963), that, although all one-electron diagonal hypervirial theorems are satisfied in the unrestricted Hartree–Fock approximation for closed shells, off-diagonal ones are not. That is, if $\tilde{\psi}_q$ is the optimal unrestricted Hartree–Fock determinant and $W$ a one-electron operator, then $\delta\tilde{\psi}_q = i\eta W\tilde{\psi}_q$ is always allowed since it involves at most one-electron excitation [see (b)] and thus the associated diagonal hypervirial theorem $\langle\tilde{\psi}_q, [\mathscr{H}, W]\,\tilde{\psi}_q\rangle = 0$ will be satisfied. (This also follows directly from (b). See Section XI,B). On the other hand, one readily sees that in general $\delta\tilde{\psi}_q = i\eta W\tilde{\psi}_p$ is not allowed since it involves multi-electron excitation.

Returning now to the problem of orthogonality, by expanding everything in powers of $\nu$, we can derive conditions that variational calculations based on $\delta J^{(0)} = \delta J^{(1)} = \delta J^{(2)} \cdots = 0$ yield orthogonality to a certain order. This is of interest, for example, in connection with perturbation theory within the Hartree–Fock formalism (see Section XI) where in effect $\tilde{\psi}^{(0)}, \tilde{\psi}^{(1)}, \ldots$ are the Hartree–Fock approximations to $\psi^{(0)}, \psi^{(1)}, \ldots$.

Since the manipulations are straightforward, we merely quote some of the results.

(d) If $\delta\tilde{\psi}_p^{(0)} = \eta\tilde{\psi}_q^{(0)}$ and $\delta\tilde{\psi}_q^{(0)} = \eta\tilde{\psi}_p^{(0)}$ are allowed variations, then from $\delta J^{(0)} = 0$ we find $\langle\tilde{\psi}_p^{(0)}, \tilde{\psi}_q^{(0)}\rangle = 0$; i.e., we have orthogonality to zero order.

(e) If $\delta\tilde{\psi}_p^{(0)} = \eta\tilde{\psi}_q^{(0)}$ and $\delta\tilde{\psi}_q^{(0)} = \eta\tilde{\psi}_p^{(0)}$ are allowed variations and if $\tilde{\psi}_p^{(0)} = \psi_p^{(0)}$ and $\tilde{\psi}_q^{(0)} = \psi_q^{(0)}$, then from $\delta J^{(1)} = 0$ we find we have orthogonality to first order; i.e., $\langle\tilde{\psi}_p^{(0)}, \tilde{\psi}_q^{(1)}\rangle + \langle\tilde{\psi}_p^{(1)}, \tilde{\psi}_q^{(0)}\rangle = 0$.

(f) If $\delta\tilde{\psi}_p^{(0)} = \eta\tilde{\psi}_q^{(0)}$, $\delta\tilde{\psi}_q^{(0)} = \eta\tilde{\psi}_p^{(0)}$, $\delta\tilde{\psi}_p^{(1)} = \eta\tilde{\psi}_q^{(1)}$, and $\delta\tilde{\psi}_q^{(1)} = \eta\tilde{\psi}_p^{(1)}$ are allowed variations and if $\tilde{\psi}_p^{(0)} = \psi_p^{(0)}$ and $\tilde{\psi}_q^{(0)} = \psi_q^{(0)}$, then from $\delta J^{(2)} = 0$ we find we have orthogonality to second order.

(g) Etc.

As one application of these results, it follows directly in agreement with other authors (Cohen and Dalgarno, 1963b; Layzer, 1963) that, in Hartree–Fock calculations of say the $(1s)^2\ {}^1S$ and $(1s2s)\ {}^1S$ states of He as an expansion in $1/Z$ (Sharma and Coulson, 1962), one will have orthogonality to first order but not in higher orders.

These results, as noted, are based on $\delta J^{(0)} = \delta J^{(1)} = \ldots = 0$. It is also clearly of interest to ask what happens if we use say the Hylleraas variational principle, i.e., $\delta J_p^H = 0$, $\delta J_q^H = 0$ where

$$J_p^H = \langle \psi_p^{(0)}, (\mathscr{H}_1 - E_p^{(1)})\tilde{\psi}_p^{(1)}\rangle + \langle \tilde{\psi}_p^{(1)}, (\mathscr{H}_1 - E_p^{(1)})\psi_p^{(0)}\rangle + \langle \tilde{\psi}_p^{(1)}, (\mathscr{H}_0 - E_p^{(0)})\tilde{\psi}_p^{(1)}\rangle$$

and a similar expression for $J_q^H$.

From $\delta J_p^H = \delta J_q^H = 0$ we then infer

$$0 = \langle \psi_p^{(0)}, (\mathscr{H}_1 - E_p^{(1)})\delta\tilde{\psi}_p^{(1)}\rangle + \langle \tilde{\psi}_p^{(1)}, (\mathscr{H}_0 - E_p^{(0)})\delta\tilde{\psi}_p^{(1)}\rangle$$

and

$$0 = \langle \delta\tilde{\psi}_q^{(1)}, (\mathscr{H}_1 - E_q^{(1)})\psi_q^{(0)}\rangle + \langle \delta\tilde{\psi}_q^{(1)}, (\mathscr{H}_0 - E_q^{(0)})\tilde{\psi}_q^{(1)}\rangle.$$

By use of $\mathscr{H}_0\psi_p^{(0)} = E_p^{(0)}\psi_p^{(0)}$, $\mathscr{H}_0\psi_q^{(0)} = E_q^{(0)}\psi_q^{(0)}$, and $\langle \psi_p^{(0)}, \psi_q^{(0)}\rangle = 0$ we can then immediately derive, by subtracting the two expressions above, the following *theorem*.[14]

(h) If $\delta\tilde{\psi}_p^{(1)} = \eta\psi_q^{(0)}$ and $\delta\tilde{\psi}_q^{(1)} = \eta\psi_p^{(0)}$ are possible variations of the optimal trial functions in the Hylleraas variational principle, then we have orthogonality to first order.

In a similar way we can show:

(i) If $\delta\tilde{\psi}_p^{(1)} = i\eta W\psi_q^{(0)}$ and $\delta\tilde{\psi}_q^{(1)} = i\eta W\psi_p^{(0)}$ are allowed variations in the Hylleraas variation principle, then the off-diagonal hypervirial theorem for $W$ will be satisfied to first order.

(j) If $\delta\tilde{\psi}_p^{(0)} = i\eta W\psi_p^{(0)}$ is an allowed variation in the Hylleraas variation principle, then the hypervirial theorem for $W$ will be satisfied to first order.

## 2. *The Hellmann–Feynman Theorem*

In this section we will discuss the Hellmann–Feynman theorem within the framework of the Hylleraas variation principle.[15] Dropping the state

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[14] A different theorem (with much weaker conditions) is stated by Knight and Scherr (1963), Appendix II, but actually they proved the theorem given here.

[15] For the ordinary variational principle $\delta J = 0$ and hence by implication for $\delta J^{(0)} = \delta J^{(1)} = \cdots = 0$ the problem has already been discussed by Hurley (1954), who shows that a sufficient condition is that the trial function does not depend explicitly on the parameter in question. The necessary condition is that $\delta\tilde{\psi} = \eta(\partial\tilde{\psi}/\partial\sigma)$ be an allowed variation.

subscript, we will show that, if $\delta\tilde{\psi}^{(1)} = \eta(\partial\psi^{(0)}/\partial\sigma)$ is an allowed variation where $\sigma$ is the parameter in question, then the Hellmann–Feynman theorem is satisfied through the first order.

The Hellmann–Feynman theorem states that

$$\frac{\partial E}{\partial\sigma} = \left\langle \Psi, \frac{\partial\mathscr{H}}{\partial\sigma}\Psi \right\rangle \Big/ \langle \Psi, \Psi \rangle.$$

In zero order we have then

$$\frac{\partial E^{(0)}}{\partial\sigma} = \left\langle \psi^{(0)}, \frac{\partial\mathscr{H}_0}{\partial\sigma}\psi^{(0)} \right\rangle,$$

which is certainly true. In first order then we find, by expanding the Hellmann–Feynman theorem,

$$\begin{aligned}\frac{\partial E^{(1)}}{\partial\sigma} = {} & \left\langle \psi^{(0)}, \frac{\partial\mathscr{H}_0}{\partial\sigma}\psi^{(0)} \right\rangle [-\langle \psi^{(0)}, \tilde{\psi}^{(1)} \rangle - \langle \tilde{\psi}^{(1)}, \psi^{(0)} \rangle] \\ & + \left\langle \psi^{(0)}, \frac{\partial\mathscr{H}_0}{\partial\sigma}\tilde{\psi}^{(1)} \right\rangle + \left\langle \tilde{\psi}^{(1)}, \frac{\partial\mathscr{H}_0}{\partial\sigma}\psi^{(0)} \right\rangle \\ & + \left\langle \psi^{(0)}, \frac{\partial\mathscr{H}_1}{\partial\sigma}\psi^{(0)} \right\rangle. \qquad \text{(V.8)}\end{aligned}$$

On the other hand we have $E^{(1)} = \langle \psi^{(0)}, \mathscr{H}_1 \psi^{(0)} \rangle$, whence

$$\begin{aligned}\frac{\partial E^{(1)}}{\partial\sigma} = {} & \left\langle \frac{\partial\psi^{(0)}}{\partial\sigma}, \mathscr{H}_1\psi^{(0)} \right\rangle + \left\langle \psi^{(0)}, \mathscr{H}_1\frac{\partial\psi^{(0)}}{\partial\sigma} \right\rangle \\ & + \left\langle \psi^{(0)}, \frac{\partial\mathscr{H}_1}{\partial\sigma}\psi^{(0)} \right\rangle, \qquad \text{(V.9)}\end{aligned}$$

and the question is: Are these two expressions equal?[16]

We now put $\delta J^H = 0$ with $\delta\tilde{\psi}^{(1)} = \eta(\partial\psi^{(0)}/\partial\sigma)$ and find (varying both $\tilde{\psi}^{(1)}$ and $\tilde{\psi}^{(1)*}$)

$$\begin{aligned}0 = {} & \left\langle \psi^{(0)}, (\mathscr{H}_1 - E^{(1)})\frac{\partial\psi^{(0)}}{\partial\sigma} \right\rangle + \left\langle \frac{\partial\psi^{(0)}}{\partial\sigma}, (\mathscr{H}_1 - E^{(1)})\psi^{(0)} \right\rangle \\ & + \left\langle \frac{\partial\psi^{(0)}}{\partial\sigma}, (\mathscr{H}_0 - E^{(0)})\tilde{\psi}^{(1)} \right\rangle + \left\langle \tilde{\psi}^{(1)}, (\mathscr{H}_0 - E^{(0)})\frac{\partial\psi^{(0)}}{\partial\sigma} \right\rangle. \qquad \text{(V.10)}\end{aligned}$$

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[16] They are of course trivially equal if $\mathscr{H}_0$, and hence $\psi^{(0)}$, is independent of $\sigma$ (for a further discussion of this case see Yaris, 1963a). They are also of course equal if $\tilde{\psi}^{(1)} = \psi^{(1)}$.

We now use

$$\frac{\partial}{\partial\sigma}\langle\psi^{(0)},\psi^{(0)}\rangle=0,$$

and the equation

$$(\mathscr{H}_0-E^{(0)})\frac{\partial\psi^{(0)}}{\partial\sigma}=\left(\frac{\partial E^{(0)}}{\partial\sigma}-\frac{\partial\mathscr{H}_0}{\partial\sigma}\right)\psi^{(0)},$$

which follows from differentiating $\mathscr{H}_0\psi^{(0)}=E^{(0)}\psi^{(0)}$ with respect to $\sigma$, and the zero-order Hellmann–Feynman theorem to write Eq. (V.10) as

$$\begin{aligned}0=&\left\langle\psi^{(0)},\mathscr{H}_1\frac{\partial\psi^{(0)}}{\partial\sigma}\right\rangle+\left\langle\frac{\partial\psi^{(0)}}{\partial\sigma},\mathscr{H}_1\psi^{(0)}\right\rangle\\&-\left\langle\psi^{(0)},\frac{\partial\mathscr{H}_0}{\partial\sigma}\tilde{\psi}^{(1)}\right\rangle-\left\langle\tilde{\psi}^{(1)},\frac{\partial\mathscr{H}_0}{\partial\sigma}\psi^{(0)}\right\rangle\\&+\left\langle\psi^{(0)},\frac{\partial\mathscr{H}_0}{\partial\sigma}\psi^{(0)}\right\rangle[\langle\psi^{(0)},\tilde{\psi}^{(1)}\rangle+\langle\tilde{\psi}^{(1)},\psi^{(0)}\rangle]\end{aligned}$$

which, when inserted into Eq. (V.9), yields Eq. (V.8). Thus the Hellmann–Feynman theorem is satisfied through first order.

## VI. The FOPIM (First-Order Perturbation Iteration Method) and FOP-VIM (First-Order Perturbation-Variation Iterative Method) Fast-Converging Iteration Procedures

As we have discussed in Section II, given the wave function correct to $O(\lambda^n)$ we can compute the energy correct to $O(\lambda^{2n+1})$. Although this is "better" than computing the energy only to $O(\lambda^n)$, this process is not rapidly converging since the energy is only improved two orders in $\lambda$ for each additional order in the wave function. In this section we shall present two procedures which are much more rapidly convergent: the First-Order Perturbation Iteration Method or FOPIM, and a slightly improved version called First-Order Perturbation-Variation Iterative Method or FOP-VIM. In FOPIM, the wave function through the first order is used as the zeroth-order function in the calculation of an improved first-order function. The perturbation potential for this new calculation is proportional to $\lambda^2$. This process can be interated, and each time the new perturbation potential is proportional to the square of the previous perturbation potential

(Hirschfelder, 1963).[17] Thus, after $n$ iterations, the energy is given accurately up to terms of the order of $\lambda$ raised to the $(2)^{n+1}$ power. For example, after five iterations the energy is accurate up to terms of the order of $\lambda^{64}$.

In FOP-VIM, following Dalgarno and Stewart (1961), the perturbed wave function is taken to be the variationally best linear combination of the zeroth order and Rayleigh–Schrödinger first-order functions. This perturbed-variational function is then taken to be the zeroth-order wave function for the calculation of an improved perturbed-variational function. Whereas FOP-VIM may have only a modest advantage over FOPIM for nondegenerate energy levels, we shall show in Section VII that the basic notion of FOP-VIM is very useful for degenerate or almost degenerate energy levels.

We start with a trial wave function $\psi$ which satisfies the Schrödinger equation $H_0\psi = \varepsilon\psi$. The Hamiltonian for the perturbed system is $H = H_0 + \lambda V$. The first-order wave function is $\psi^{(1)} = F\psi$. The expectation value of the energy corresponding to the original trial function is $\mathscr{E}(0)$ as given by Eq. (II.15). The perturbed normalized wave function through the first order is $\Psi(1)$, as given by Eqs. (II.13) and (II.14). The expectation value of the energy corresponding to $\Psi(1)$ is given by $\mathscr{E}(1)$ of Eq. (II.16). Everything up to this point has been discussed in the preceding sections. The following treatment is somewhat novel.

## A. FOPIM

The wave function $\Psi(1)$ satisfies the Schrödinger equation

$$H(1)\Psi(1) = \mathscr{E}(0)\Psi(1), \tag{VI.1}$$

where

$$H(1) = H_0 + \frac{\lambda V + \lambda^2 \varepsilon^{(1)} F}{1 + \lambda F}. \tag{VI.2}$$

The Hamiltonian for the perturbed system is then

$$H = H(1) + \lambda^2 V(1), \tag{VI.3}$$

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[17] There is a variety of other iterative procedures that have been proposed to take advantage of this rapid convergence. The most noteworthy of these are Biedenharn and Blatt (1954), Kikuta, (1954, 1955), and Sack (1963). In addition, Löwdin (1963) has developed an iterative perturbation-variation procedure for solving the perturbed Schrödinger equation by partitioning the secular equation.

where

$$V(1)=\frac{F(V-\varepsilon^{(1)})}{1+\lambda F}. \tag{VI.4}$$

Now we consider the new perturbation problem in which $\Psi(1)$ serves as the zeroth-order wave function and $\lambda^2 V(1)$ is the perturbation potential. Note the $\lambda^2$ plays the same role in the new problem as $\lambda$ plays in the original problem. The new first-order perturbed wave function is

$$\psi^{(1)}(1)=F(1)\Psi(1), \tag{VI.5}$$

where the function $F(1)$ is determined by

$$[F(1), H]\Psi(1)=[V(1)-\varepsilon^{(1)}(1)]\Psi(1). \tag{VI.6}$$

The methods of solving equations of this form are discussed in Section III. The specification of the $F(1)$ is completed by the requirement that

$$\langle\Psi(1), F(1)\Psi(1)\rangle=0. \tag{VI.7}$$

The square norm of $\psi^{(1)}(1)$ is designated as $S(1)$,

$$\langle F(1)\Psi(1), F(1)\Psi(1)\rangle=S(1). \tag{VI.8}$$

Using the first-, second-, and third-order perturbation equations for the new perturbation problem,

$$\varepsilon^{(1)}(1)=\langle\Psi(1), V(1)\Psi(1)\rangle=[\mathscr{E}(1)-\mathscr{E}(0)]/\lambda^2, \tag{VI.9}$$

$$\varepsilon^{(2)}(1)=\langle\Psi(1), V(1)F(1)\Psi(1)\rangle, \tag{VI.10}$$

$$\varepsilon^{(3)}(1)=\langle F(1)\Psi(1), V(1)F(1)\Psi(1)\rangle-\varepsilon^{(1)}(1)S(1). \tag{VI.11}$$

We can now define the second iterated normalized wave function

$$\psi(2)=[1+\lambda^4 S(1)]^{-\frac{1}{2}}[1+\lambda^2 F(1)]\Psi(1). \tag{VI.12}$$

The expectation value of the energy corresponding to $\psi(2)$ is

$$E(2)=\langle\psi(2), H\psi(2)\rangle=\mathscr{E}(1)+\frac{\lambda^4\varepsilon^{(2)}(1)+\lambda^6\varepsilon^{(3)}(1)}{1+\lambda^4 S(1)}. \tag{VI.13}$$

For exactly the same reasons that $\mathscr{E}(1)$ is accurate up to terms of the order of $\lambda^4$, it is apparent that $E(2)$ is accurate up to terms of the order of $\lambda^8$.

The function $\psi(2)$ can now be used as the zeroth-order wave function in a new perturbation calculation. Indeed, after $(n+1)$ iterations we have the normalized wave function

$$\psi(n+1)=[1+\lambda^{2a}S(n)]^{-\frac{1}{2}}[1+\lambda^a F(n)]\psi(n). \tag{VI.14}$$

Here, because of printing difficulties, we use the notation $a = 2^n$. The $S(n)$ is the square norm of $\psi^{(1)}(n)$,

$$\langle F(n)\psi(n), F(n)\psi(n)\rangle = S(n). \tag{VI.15}$$

The function $F(n)$ satisfies the inhomogenous partial differential equation

$$[F(n), H]\psi(n) = [V(n) - \varepsilon^{(1)}(n)]\psi(n) \tag{VI.16}$$

together with the requirement that

$$\langle \psi(n), F(n)\psi(n)\rangle = 0. \tag{VI.17}$$

From the first-, second-, and third-order perturbation equations for this perturbation problem it follows that

$$\varepsilon^{(1)}(n) = \langle \psi(n), V(n)\psi(n)\rangle = [E(n) - E(n-1)]/\lambda^a, \tag{VI.18}$$

$$\varepsilon^{(2)}(n) = \langle \psi(n), V(n)F(n)\psi(n)\rangle, \tag{VI.19}$$

$$\varepsilon^{(3)}(n) = \langle F(n)\psi(n), V(n)F(n)\psi(n)\rangle - \varepsilon^{(1)}(n)S(n). \tag{VI.20}$$

The expectation value of the energy corresponding to $\psi(n+1)$ is

$$E(n+1) = \langle \psi(n+1), H\psi(n+1)\rangle = E(n) + \frac{\lambda^{2a}\varepsilon^{(2)}(n) + \lambda^{3a}\varepsilon^{(3)}(n)}{1 + \lambda^{2a}S(n)}. \tag{VI.21}$$

Since $\lambda^a$ in the present problem plays the same role as $\lambda$ in the original problem, it follows that, since $\mathscr{E}(1)$ is accurate up to terms of the order of $\lambda^4$, the value of $E(n+1)$ is accurate up to terms of the order of $\lambda^{4a}$.

The function $\psi(n+1)$ satisfies the Schrödinger equation

$$H(n+1)\psi(n+1) = E(n)\psi(n+1), \tag{VI.22}$$

where

$$H(n+1) = H(n) + \frac{\lambda^a V(n) + \lambda^{2a}\varepsilon^{(1)}(n)F(n)}{1 + \lambda^a F(n)}. \tag{VI.23}$$

The Hamiltonian for the perturbed system is then

$$H = H(n+1) + \lambda^{2a}V(n+1), \tag{VI.24}$$

where

$$V(n+1) = \frac{F(n)[V(n) - \varepsilon^{(1)}(n)]}{1 + \lambda^a F(n)}. \tag{VI.25}$$

The iteration scheme can then be continued through the next step.

## B. FOP-VIM

The perturbed wave functions can be improved still further with very little effort (Dalgarno and Stewart, 1961)[18]. This involves the coupling of the perturbation and variational techniques. Consider in place of $\Psi(1)$, the normalized function

$$\chi(1) = [1 + \lambda^2\alpha^2 S]^{-\frac{1}{2}}(1 + \lambda\alpha F)\psi. \tag{VI.26}$$

Here $S = \langle F\psi, F\psi\rangle$ and $\alpha$ is a parameter varied to make stationary the energy $E'(1) = \langle\chi(1), H\chi(1)\rangle$. For this optimum value of $\alpha$, the value of $E'(1)$ is given by the secular equation

$$\begin{vmatrix} \mathscr{E}(0) - E'(1) & \lambda^2\varepsilon^{(2)} \\ \lambda^2\varepsilon^{(2)} & -\lambda^2\varepsilon^{(2)} + \lambda^3\varepsilon^{(3)} + \lambda^2 S[\mathscr{E}(0) - E'(1)] \end{vmatrix} = 0. \tag{VI.27}$$

Of the two roots to the secular equation, the only root which has physical significance for our problem corresponds to $E'(1)$ approaching $\mathscr{E}(0)$ as $\lambda$ approaches zero. Thus,

$$E'(1) = \mathscr{E}(0) + \left[\frac{\varepsilon^{(2)} - \lambda\varepsilon^{(3)}}{2S}\right]\left[-1 + \left\{1 + \frac{4\lambda^2 S[\varepsilon^{(2)}]^2}{[\varepsilon^{(2)} - \lambda\varepsilon^{(3)}]^2}\right\}^{-\frac{1}{2}}\right]. \tag{VI.28}$$

The improvement in the energy obtained by this variation of $\alpha$ is given by the expansion in powers of $\lambda$,

$$E'(1) - \mathscr{E}(1) = \lambda^4\frac{[\varepsilon^{(3)}]^2}{\varepsilon^{(2)}} + \lambda^5\left[\frac{[\varepsilon^{(3)}]^3}{[\varepsilon^{(2)}]^2} - 2S\varepsilon^{(3)}\right] + \cdots. \tag{VI.29}$$

The optimum value of $\alpha$ is $[E'(1) - \mathscr{E}(0)]\,[\lambda^2\varepsilon^{(2)}]^{-1}$ or, expanding in powers of $\lambda$,

$$\alpha = 1 + \lambda\frac{\varepsilon^{(3)}}{\varepsilon^{(2)}} + \lambda^2\left[\left(\frac{\varepsilon^{(3)}}{\varepsilon^{(2)}}\right)^2 - S\right] + \cdots. \tag{VI.30}$$

Clearly, in much the same manner as in FOPIM, the $\chi(1)$ can be used as the zeroth-order wave function to generate a new first-order function. The $\chi(1)$ satisfies the Schrödinger equation

$$h(1)\chi(1) = \mathscr{E}(0)\chi(1), \tag{VI.31}$$

where

$$h(1) = H_0 + \frac{\lambda\alpha V + \lambda(1 - \alpha)\varepsilon^{(1)} + \lambda^2\alpha\varepsilon^{(1)}F}{1 + \lambda\alpha F}. \tag{VI.32}$$

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[18] A similar procedure has been used in connection with the Brillouin–Wigner perturbation method by Goldhammer and Feenberg (1956) and by R. C. Young *et al.* (1957).

The Hamiltonian for the perturbed system is then $H = h(1) + \lambda^2 V'(1)$, where

$$V'(1) = [\lambda^{-1}(1-\alpha) + \alpha F][V - \varepsilon^{(1)}][1 + \lambda\alpha F]^{-1}. \qquad \text{(VI.33)}$$

From Eq. (VI.30) it follows that $\lambda^{-1}(1-\alpha)$ is zeroth order in $\lambda$.

## VII. Degenerate or Almost Degenerate Energy Level Perturbations

Nondegenerate perturbation theory becomes inapplicable when two or more energy levels lie close together and interact strongly under the influence of the perturbation. An extension of the FOP-VIM analysis of Section VI suffices to show the explicit effect of some quantum state $k$ on the $q$th state under consideration. Let us form a trial wave function $\Phi_q(1)$ as a linear combination of $\psi_k$ and $\chi_q(1)$ as defined by Eq. (VI.26),

$$\Phi_q(1) = \chi_q(1) + \lambda^2 C\psi_k. \qquad \text{(VII.1)}$$

The constant $C$ can be adjusted so as to optimize the energy

$$\tilde{E}_q = \langle\Phi_q(1), H\Phi_q(1)\rangle / \langle\Phi_q(1), \Phi_q(1)\rangle, \qquad \text{(VII.2)}$$

subject to the condition that, as $\lambda$ approaches zero, $\tilde{E}_q$ approaches $\varepsilon_q$. In this section it is convenient to use the notation $(X)_{ij} = \langle\psi_i, X\psi_j\rangle$. Since $\psi_q^{(1)} = F_q\psi_q$, it follows from Eq. (II.17) that

$$(F_q)_{kq} = (V)_{kq}[\varepsilon_q - \varepsilon_k]^{-1}. \qquad \text{(VII.3)}$$

The constant $C$ corresponding to the physically significant root of the secular equation is

$$C = [\varepsilon_q - \varepsilon_k]^{-2}\left[-\varepsilon_q^{(1)} - \{\varepsilon_q - \varepsilon_k\}\frac{\varepsilon_q^{(3)}}{\varepsilon_q^{(2)}} + (F_q V)_{qk}\right] + \lambda[\cdots] + \cdots. \qquad \text{(VII.4)}$$

Expanding the energy in powers of $\lambda$,

$$\tilde{E}_q = E_q'(1) + \lambda^4[\varepsilon_q - \varepsilon_k]^{-3}\left[-\varepsilon_q^{(1)} - \{\varepsilon_q - \varepsilon_k\}\frac{\varepsilon_q^{(3)}}{\varepsilon_q^{(2)}} + (F_q V)_{qk}\right] + \lambda^5[\cdots] + \cdots. \qquad \text{(VII.5)}$$

Here $E_q'(1)$ is given by Eq. (VI.28). Since $E_q'(1)$ is accurate through terms in $\lambda^3$, it is not surprising that the first corrections to $E_q'(1)$ should be proportional to $\lambda^4$. From Eq. (VII.5) it follows that $\tilde{E}_q > E_q'(1)$ if $\varepsilon_q > \varepsilon_k$ and $\tilde{E}_q < E_q'(1)$ if $\varepsilon_q < \varepsilon_k$. For the ground state or the lowest-energy state of a given symmetry, the energy is lowered by the interaction with every other state. If $|\tilde{E}_q - E_q'(1)| > |E_q'(1) - \mathscr{E}_q(0)|$, the expansion of $\tilde{E}_q$ in powers of $\lambda$ [as given by Eq. (VII.5)] is no longer possible and the nondegenerate perturbation theory becomes inapplicable.

## DE-FOP-VIM

The usual Rayleigh–Schrödinger method can be exceedingly complex and difficult to apply to perturbation problems involving degenerate or almost degenerate energy levels (see Dalgarno, 1961). Greater accuracy and far greater simplicity can be obtained by the following procedure: DE-FOP-VIM, which is FOP-VIM generalized to apply to the degenerate and almost degenerate energy levels (Hirschfelder, 1963).

We may wish to consider the effect of a perturbation either on a particular degenerate energy level or on a tightly packed group of degenerate or almost degenerate energy levels. Since the states corresponding to different energies may interact under the influence of a perturbation, the larger the number of interacting states which are explicitly considered, the greater is the accuracy of the calculations.

The first step in the DE-FOP-VIM is the determination of the "starting" wave functions.[19] For each of the $n_k$ degenerate energy states $\varepsilon_k$ under consideration, we are given a complete set of linearly independent eigenfunctions $\phi_{k1}, \ldots \phi_{kn_k}$ for the unperturbed Hamiltonian $H_0$. Thus, $H_0\phi_{k\beta} = \varepsilon_k\phi_{k\beta}$. The Hamiltonian for the perturbed system is $H_0 + \lambda V$. The "starting" functions are

$$\psi_{k\alpha} = \sum_{\beta=1}^{n_k} a_{\alpha\beta}\phi_{k\beta}. \tag{VII.6}$$

The constants $a_{\alpha\beta}$ are chosen to diagonalize the perturbation matrix so that

$$\langle\psi_{k\alpha}, V\psi_{k\beta}\rangle = \delta_{\alpha\beta}V_{k\alpha;\,k\alpha}. \tag{VII.7}$$

This automatically makes the different $\psi_{k\alpha}$ orthogonal,

$$\langle\psi_{k\alpha}, \psi_{k\beta}\rangle = 0, \quad \alpha \neq \beta. \tag{VII.8}$$

[19] The advantage of determining the "correct zeroth-order" functions $\psi_{k\alpha}$ is that the first-order perturbation energies are obtained at an early stage in the calculations. If, however, one wishes to avoid this step, the $\phi_{k\alpha}$ can be used in place of the $\psi_{k\alpha}$ in Eq. (VII.10) and beyond provided that Eq. (VII.9) is replaced by

$$(H_0 - \varepsilon_k)F_{k\alpha}\phi_{k\alpha} + V\phi_{k\alpha} - \sum_{\beta=1} V_{k\beta;\,k\alpha}\phi_{k\beta} = 0 \tag{VII.9$'$}$$

where $V_{k\beta;\,k\alpha} = \langle\phi_{k\beta}, V\phi_{k\alpha}\rangle$. Equation (VII.9′) follows from the multiplication of Eq. (VII.9) by $a_{\beta\alpha}{}^{-1}$, summing over $\alpha$, and making use of Eq. (VII.6).

If each of the eigenvalues $V_{k\alpha;\,k\alpha}$ of the matrix is different, the degeneracy is removed in the first order of the perturbation, and the choice of the $a_{\alpha\beta}$ is determined to within a phase factor. If, on the other hand, the eigenvalues for the energy matrix are not all different, the $a_{\alpha\beta}$ are not completely specified. For our purposes, in contrast to the usual Rayleigh–Schrödinger treatment, *any choice of the $a_{\alpha\beta}$ compatible with Eq.* (VII.7) *is sufficient.* This is one of the principal simplifications of the DE-FOP-VIM.

Corresponding to a "starting" wave function $\psi_{k\alpha}$ we can define a function $F_{k\alpha}$ such that $F_{k\alpha}\psi_{k\alpha}$ satisfies the first-order equation,

$$(H_0 - \varepsilon_k)F_{k\alpha}\psi_{k\alpha} + [V - V_{k\alpha;\,k\alpha}]\psi_{k\alpha} = 0. \tag{VII.9}$$

The methods for solving equations of this type are discussed in Section III. *Any solution* of Eq. (VII.9) suffices provided that $F_{k\alpha}\psi_{k\alpha}$ satisfies the usual boundary, continuity, and integrability conditions required of a bound state wave function. The fact that

$$G_{k\alpha} = F_{k\alpha} + \sum_{\beta=1}^{n_k} b_{\alpha\beta}\,\psi_{k\beta}/\psi_{k\alpha} \tag{VII.10}$$

for arbitrary constants $b_{\alpha\beta}$ is also a solution to Eq. (VII.9) does not cause us any concern.

Now we are ready to consider the effect of the perturbation on a set of $n = \sum_k n_k$ energy levels $\varepsilon_k$. We fix our attention on those perturbed wave functions $\Psi_q$ whose energies $E_q$ approach the values of the $\varepsilon_k$ in the limit as $\lambda$ approaches zero. The first approximation to $\Psi_q$ can then be written in the form

$$\psi_q(1) = \sum_k \sum_{\alpha=1}^{n_k} [J_{q;\,k\alpha} + \lambda K_{q;\,k\alpha}F_{k\alpha}]\psi_{k\alpha}. \tag{VII.11}$$

The constants $J_{q;\,k\alpha}$ and $K_{q;\,k\alpha}$, are chosen so as to normalize $\psi_q(1)$ and optimize the energy $E_q(1) = \langle\psi_q(1), H\psi_q(1)\rangle$ subject to the condition that $E_q(1)$ approaches the value of one of the $\varepsilon_k$ in the limit as $\lambda$ approaches zero. The optimum values of $E_q(1)$ are given as $n$ of the $2n$ roots of the secular equation

$$\begin{vmatrix} \mathfrak{A} & \mathfrak{B} \\ \mathfrak{B}^+ & \mathfrak{C} \end{vmatrix} = 0, \tag{VII.12}$$

where $\mathfrak{A}$, $\mathfrak{B}$, and $\mathfrak{C}$ are the $n$ by $n$ dimensional submatrices with the elements

$$A_{k\alpha;\,k'\beta} = \langle\psi_{k\alpha}, H\psi_{k'\beta}\rangle - E(1)\langle\psi_{k\alpha}, \psi_{k'\beta}\rangle, \tag{VII.13}$$

$$B_{k\alpha;\,k'\beta} = \langle\psi_{k\alpha}, HF_{k'\beta}\psi_{k'\beta}\rangle - E(1)\langle\psi_{k\alpha}, F_{k'\beta}\psi_{k'\beta}\rangle, \tag{VII.14}$$

$$C_{k\alpha;\,k'\beta} = \langle F_{k\alpha}\psi_{k\alpha}, HF_{k'\beta}\psi_{k'\beta}\rangle - E(1)\langle F_{k\alpha}\psi_{k\alpha}, F_{k'\beta}\psi_{k'\beta}\rangle, \tag{VII.15}$$

and $\mathfrak{B}^+$ is the transpose of $\mathfrak{B}$.

The Löwdin (1963) partitioning technique is particularly well-suited to the solution of such secular equations. The values of the $E_q(1)$ obtained in this manner should be accurate through terms of $O(\lambda^3)$.

The $\psi_q(1)$ can themselves be used as the zeroth-order wave functions for a new perturbation calculation in much the same manner as in the FOPIM or FOP-VIM procedures.

As mentioned in Section IV,E, DEFOPVIM can be used conveniently to calculate the energy in degenerate double perturbation problems.

## VIII. Off-Diagonal Matrix Elements

As we have seen in Section IV, the Dalgarno interchange theorem is often of decisive importance in making practical the calculation of the first-order corrections to the expectation values of one-particle operators. In this section we show that a similar theorem holds for off-diagonal matrix elements.[20]

### A. General Formulation

We wish to compute the matrix element $M = \langle \Psi_p, W\Psi_q \rangle$ correct through first order in $\lambda$. Here $W$ is a Hermitian one-particle operator and $\Psi_p$ and $\Psi_q$ are eigenfunctions of $H = H_0 + \lambda V$ (the formalism can easily be extended to the case where $\Psi_p$ and $\Psi_q$ are eigenfunctions of different Hamiltonians). To this end we introduce the functions $\Phi_p$ and $\Phi_q$ and the numbers $\mathscr{E}_p$ and $\mathscr{E}_q$ defined by the equations[21]

$$H\Phi_p + \mu W\Phi_q = \mathscr{E}_p\Phi_p, \tag{VIII.1}$$

$$H\Phi_q + \mu W\Phi_p = \mathscr{E}_q\Phi_q \tag{VIII.2}$$

and the condition that, as $\mu \to 0$, $\Phi_p \to \Psi_p$ and $\Phi_q \to \Psi_q$.

These conditions, however, do not completely specify our problem. To say that $\Psi_p$ and $\Psi_q$ are eigenfunctions of $H$ with certain eigenvalues does not uniquely determine them, quite apart from questions of degeneracy. The phases of $\Psi_p$ and $\Psi_q$ are still undetermined, and with them the phases of $\mathscr{E}_p$, $\mathscr{E}_q$, and $M$. However, this ambiguity has no physical significance since the phase of a wave function and the phase of the matrix element of a single operator have no physical significance.

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[20] Within the Hartree–Fock formalism this has been shown by Cohen and Dalgarno (1963c). The general result to be derived in this section has also been derived by Borowitz (1964).

[21] Such equations were first discussed by Delves (1963b).

More specifically, what we are usually interested in is the *absolute square* of our matrix element through first order in $\lambda$. Thus, writing

$$M = M^{(0)} + \lambda M^{(1)} + \cdots$$

the quantity of real interest is

$$|M|^2 = |M^{(0)}|^2 + \lambda[M^{(0)*}M^{(1)} + M^{(0)}M^{(1)*}] + \cdots$$

which is independent of phase conventions.

However, we may, if we wish, choose phases in such a way as to simplify calculations without any real loss in generality. We will not do so in this section, but in Section VIII,B it will be convenient to assume that $M^{(0)}$ is real, which in turn [see Eqs. (VIII.7a) and (VIII.7b)] will insure that $\mathscr{E}_p$ and $\mathscr{E}_q$ are real, at least through first order in $\lambda$ and $\mu$, which is all we will actually be interested in. Note that with $M^{(0)}$ real, the quantity of interest is the real part of $M$.

We now carry out a double perturbation expansion through first order in $\lambda$ and $\mu$:

$$\Psi_p = \psi_p^{(0,0)} + \lambda\psi_p^{(1,0)} + \cdots,$$

$$\Phi_p = \psi_p^{(0,0)} + \lambda\psi_p^{(1,0)} + \mu\psi_p^{(0,1)} + \cdots,$$

$$\mathscr{E}_p = \varepsilon_p^{(0,0)} + \lambda\varepsilon_p^{(1,0)} + \mu\varepsilon_p^{(0,1)} + \cdots,$$

and similar equations with $p$ replaced by $q$.

The quantities involved are then further defined by the following differential equations which are a consequence of Eqs. (VIII.1) and (VIII.2):

$$(H_0 - \varepsilon_p^{(0,0)})\psi_p^{(0,0)} = 0, \qquad \text{(VIII.3)}$$

$$(H_0 - \varepsilon_p^{(0,0)})\psi_p^{(1,0)} = -(V - \varepsilon_p^{(1,0)})\psi_p^{(0,0)}, \qquad \text{(VIII.4)}$$

$$(H_0 - \varepsilon_p^{(0,0)})\psi_p^{(0,1)} = -W\psi_q^{(0,0)} + \varepsilon_p^{(0,1)}\psi_p^{(0,0)}. \qquad \text{(VIII.5)}$$

We also have the normalization condition

$$\langle\psi_p^{(1,0)}, \psi_p^{(0,0)}\rangle + \langle\psi_p^{(0,0)}, \psi_p^{(1,0)}\rangle = 0. \qquad \text{(VIII.6)}$$

By taking the scalar product of Eqs. (VIII.4) and (VIII.5) with $\psi_p^{(0,0)}$ we further learn that

$$\varepsilon_p^{(1,0)} = \langle\psi_p^{(0,0)}, V\psi_p^{(0,0)}\rangle, \qquad \text{(VIII.7a)}$$

$$\varepsilon_p^{(0,1)} = \langle\psi_p^{(0,0)}, W\psi_q^{(0,0)}\rangle \equiv M^{(0)}. \qquad \text{(VIII.7b)}$$

There is, of course, a further set of equations with $p$ replaced by $q$. We now want to derive an *interchange theorem*. Through first order in $\lambda$ we have

$$M = M^{(0)} + \lambda[\langle \psi_p^{(1,0)}, W\psi_q^{(0,0)}\rangle + \langle \psi_p^{(0,0)}, W\psi_q^{(1,0)}\rangle] + \cdots .$$

By use of Eqs. (VIII.5) and (VIII.7b) it then follows that

$$\langle \psi_p^{(1,0)}, W\psi_q^{(0,0)}\rangle = -\langle \psi_p^{(1,0)}, (H_0 - \varepsilon_p^{(0,0)})\psi_p^{(0,1)}\rangle + M^{(0)}\langle \psi_p^{(1,0)}, \psi_p^{(0,0)}\rangle,$$

whence from Eq. (VIII.4) we have

$$\langle \psi_p^{(1,0)}, W\psi_q^{(0,0)}\rangle = \langle \psi_p^{(0,0)}, (V - \varepsilon_p^{(1,0)})\psi_p^{(0,1)}\rangle + M^{(0)}\langle \psi_p^{(1,0)}, \psi_p^{(0,0)}\rangle.$$

Similarly we can show that

$$\langle \psi_p^{(0,0)}, W\psi_q^{(1,0)}\rangle = \langle \psi_q^{(0,1)}, (V - \varepsilon_q^{(1,0)})\psi_q^{(0,0)}\rangle + M^{(0)}\langle \psi_q^{(0,0)}, \psi_q^{(1,0)}\rangle.$$

If now we compute $|M|^2$ we readily find, by use of Eq. (VIII.6) and its analog with $p$ replaced by $q$, that

$$\begin{aligned} |M|^2 = |M^{(0)}|^2 + \lambda M^{(0)*}[\langle \psi_p^{(0,0)}, (V - \varepsilon_p^{(1,0)})\psi_p^{(0,1)}\rangle \\ + \langle \psi_q^{(0,1)}, (V - \varepsilon_q^{(1,0)})\,\psi_q^{(0,0)}\rangle] \qquad \text{(VIII.8)} \\ + \text{complex conjugate} + \cdots . \end{aligned}$$

This is the desired theorem. With it we have expressed the first-order corrections completely in terms of functions defined by equations involving only one-electron perturbations. In Section VIII,C we will discuss the further reduction of Eq. (VIII.5) to one-electron equations.

Finally we may remark that in analogy with the discussion centering around Eq. (IV.29b) we may, by writing $\psi_p^{(0,1)} = F_p\psi_p^{(0,0)}$ and $\psi_q^{(0,1)} = F_q\psi_q^{(0,0)}$, eliminate any explicit reference to the unperturbed Hamiltonian $H_0$. The resultant equations are those found by Borowitz (1964).

### B. First-Order Variation Principle

It will be useful for our purposes here to assume that $\mathscr{E}_p$ and $\mathscr{E}_q$ are real. Actually we will need this property only through first order in $\lambda$ and $\mu$, whence we see from Eqs. (VIII.7a) and (VIII.7b) that it is sufficient to assume that $M^{(0)}$ is real. As discussed in the preceding section, this involves no real loss of generality. Also note again that under these circumstances the quantity of interest through order $\lambda$ is the real part of $M$.

From the assumption that $\mathscr{E}_p$ and $\mathscr{E}_q$ are real, it follows that Eqs. (VIII.1) and (VIII.2) can be derived from the variation principle $\delta J = 0$, $J = 0$, where

$$J = \langle \tilde{\Phi}_p, (H - \tilde{\mathscr{E}}_p)\tilde{\Phi}_p \rangle + \langle \tilde{\Phi}_q, (H - \tilde{\mathscr{E}}_q)\tilde{\Phi}_q \rangle + \langle \tilde{\Phi}_p, \mu W \tilde{\Phi}_q \rangle + \langle \tilde{\Phi}_q, \mu W \tilde{\Phi}_p \rangle.$$

If now, in analogy with the discussion in Section V,A, one expands everything in powers of $\mu$:

$$\tilde{\Phi}_p = \tilde{\Psi}_p + \mu \tilde{\Phi}_p^{(1)} + \cdots, \qquad \tilde{\Phi}_q = \tilde{\Psi}_q + \mu \tilde{\Phi}_q^{(1)} + \cdots, \qquad \text{etc.,}$$

one is led, in first order, to a variational principle for the real part of $M$, i.e., the quantity of interest. This variation principle is due to Delves[22] and has all the advantages and disadvantages, already discussed in Section V,A, 1*a*, of his variational principle for diagonal matrix elements.

If further, in analogy with the procedure discussed in Section V,A, 1*b*, one constrains $\tilde{\Phi}_p^{(1)}$ and $\tilde{\Phi}_q^{(1)}$ for *fixed* $\tilde{\Psi}_p$ and $\tilde{\Psi}_q$ in such a way that $\tilde{\Psi}_p - \Psi_p$, $\tilde{\Phi}_p^{(1)} - \Phi_p^{(1)}$, etc., are all of the same order, then, as before, one arrives at results quite equivalent to those of our double perturbation approach (in the "Borowitz form").

## C. Separation of Equations for One-Electron $W$

For $W$ a one-particle operator, we will show that our problem reduces to the solution of one-electron equations in the special case for which $\psi_p^{(0,0)}$ and $\psi_q^{(0,0)}$ are single determinants.

Let us consider then $\psi_p^{(0,0)} = \mathscr{A} \varphi_1(1) \varphi_2(2) \ldots \varphi_N(N)$ and $\psi_q^{(0,0)} = \mathscr{A} \bar{\varphi}_1(1) \varphi_2(2) \ldots \varphi_N(N)$, where $\mathscr{A}$ is the antisymmetrization operator and where we assume $\psi_p^{(0,0)}$ and $\psi_q^{(0,0)}$ differ by only a single spin orbital[23] (the case where they differ by more than one is much simpler in that $\varepsilon_p^{(0,1)} \equiv 0$). Since all the operators in Eq. (VIII.5) are symmetric in the particles, we clearly may write $\psi_p^{(0,1)} = \mathscr{A} \chi_p$, whence, writing out Eq. (VIII.5) in detail, we have

$$(h_1 + h_2 + \cdots - e_1 - e_2 - \cdots)\chi_p = -(w_1 + w_2 + \cdots)\bar{\varphi}_1(1)\varphi_2(2)\cdots + \langle \varphi_1, w_1 \bar{\varphi}_1 \rangle \varphi_1(1)\varphi_2(2)\cdots.$$

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[22] See footnote 21.

[23] We ignore possible complications due to degeneracy. It often is the case that $W$ is "diagonal" in the sense that, given $\psi_p{}^{(0,0)}$, then $\langle \psi_q{}^{(0,0)}, W\psi_p{}^{(0,0)} \rangle$ differs from zero only for one $\psi_q{}^{(0,0)}$ of the degenerate set, and similarly, given $\psi_q{}^{(0,0)}$, a unique $\psi_p{}^{(0,0)}$ is singled out. We also assume $\langle \bar{\varphi}_1, \varphi_1 \rangle = 0$.

Here $H_{0p} = \sum_i h_i$ and $\varepsilon_p^{(0,0)} = \sum_i e_i$. Also we need $h_1 \bar{\varphi}_1(1) = \bar{e}_1 \bar{\varphi}_1(1)$. We now observe that we can write $\chi_p = \chi_{p1} + \chi_{p2}$, where

$$(h_1 + h_2 + \cdots - e_1 - e_2 - \cdots)\chi_{p1} = -w_1\bar{\varphi}_1(1)\varphi_2(2)\cdots + \langle \varphi_1, w_1\bar{\varphi}_1\rangle \varphi_1(1)\varphi_2(2)\cdots$$

and

$$(h_1 + h_2 + \cdots - e_1 - e_2 - \cdots)\chi_{p2} = -(w_2 + w_3 + \cdots)\bar{\varphi}_1(1)\varphi_2(2)\cdots,$$

the essential point being that the right-hand sides of each of the last two equations are orthogonal to the solution of the homogeneous equation, and therefore the equations are consistent.

The reduction to one-electron equations is now immediate, namely,

$$\chi_{p1} = \Delta_1(1)\varphi_2(2)\cdots\varphi_N(N),$$

$$\chi_{p2} = \bar{\varphi}_1(1)\Delta_2(2)\varphi_3(3)\cdots\varphi_N(N) + \bar{\varphi}_1(1)\varphi_2(2)\Delta_3(3)\cdots + \cdots,$$

where

$$(h_1 - e_1)\Delta_1 = -w_1\bar{\varphi}_1 + \langle \varphi_1, w_1\bar{\varphi}_1\rangle\varphi_1,$$

$$(h_2 + \bar{e}_1 - e_1 - e_2)\Delta_2 = -w_2\varphi_2,$$

Further reduction depends on the particular form of $W$. Note also that if $V$ is a one-particle operator (as it is within the Hartree–Fock formalism) then $\chi_{p2}$ does not contribute to the right-hand side of Eq. (VIII.8) and our theory, as it must, becomes identical to that of Cohen and Dalgarno (1963c).

Finally we remark that, as with the diagonal case, variational procedures are available to approximate the solution of Eq. (VIII.5), the stationary expression being just the Hylleraas form

$$J_H = \langle \tilde{\psi}_p^{(0,1)}, (H_0 - \varepsilon_p^{(0,0)})\tilde{\psi}_p^{(0,1)}\rangle + \langle \tilde{\psi}_p^{(0,1)}, W\psi_q^{(0,0)}\rangle + \langle \psi_q^{(0,0)}, W\tilde{\psi}_p^{(0,1)}\rangle - \langle \tilde{\psi}_p^{(0,1)}, \varepsilon_p^{(0,1)}\psi_p^{(0,0)}\rangle - \langle \varepsilon_p^{(0,1)}\psi_p^{(0,0)}, \tilde{\psi}_p^{(0,1)}\rangle.$$

## IX. Time-Dependent Perturbation Theory

Recently,[24–28] attention has been directed to the possibility of using the

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[24] Schwartz and Tieman (1959) and Schwartz (1961): calculations of the Lamb shift in hydrogen.

[25] Mavroyannis and Stephen (1962): variation principle for polarizability given in an appendix.

[26] Karplus (1962): variation principles stated.

[27] Karplus and Kolker (1963b): contains among other things a review of the literature and a detailed derivation of variational principles for electric and magnetic polarizabilities.

[28] Yaris (1963b, 1964): time-dependent variation-perturbation theory is developed in a way which looked rather different from but is equivalent to the more usual approach as, say, given in Karplus and Kolker (1963b).

techniques which we have been discussing, such as the closed form solution of the perturbation equations, the variational approximations, and so on, for the solution of time-dependent problems. The time-dependent perturbation problems, relevant to the properties of atoms and molecules, which have been studied most are those involving oscillating electric and/or magnetic fields. In such cases the first-order properties associated with the perturbation average to zero and only the steady-state values of the second-order properties are usually of interest. These include the frequency-dependent electric polarizability, magnetic susceptibility, optical rotary constant, and so on. In this section we shall confine our attention to this type of perturbation.

### A. General Formalism

We consider a system described by a Hamiltonian $H$ which is subject to a time-dependent perturbation of the form

$$\mu\mathscr{W} = \mu(W e^{-i\omega t} + W^{+} e^{i\omega t}), \tag{IX.1}$$

where $W^{+}$ is the Hermitian conjugate of $W$.[29] We assume that the solution $\Phi$ of the time-dependent Schrödinger equation

$$(H + \mu\mathscr{W})\Phi = i\dot{\Phi} \tag{IX.2}$$

may be expanded as a perturbation series in the parameter $\mu$,

$$\Phi = \Phi^{(0)} + \mu\Phi^{(1)} + \cdots, \tag{IX.3}$$

and attempt to determine $\Phi^{(1)}$. By inserting Eq. (IX.3) into Eq. (IX.2) and equating terms of like powers of $\mu$, we readily find that

$$H\Phi^{(0)} = i\dot{\Phi}^{(0)}, \tag{IX.4a}$$

$$H\Phi^{(1)} + \mathscr{W}\Phi^{(0)} = i\dot{\Phi}^{(1)}. \tag{IX.4b}$$

The solution of Eq. (IX.4a) is of course

$$\Phi^{(0)} = \Psi e^{-iEt}, \tag{IX.5a}$$

where

$$H\Psi = E\Psi. \tag{IX.5b}$$

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[29] The solution of problems involving a more general time dependence is discussed by Karplus and Kolker (1963b) and Yaris (1963b, 1964).

Throughout Section IX, $E$ is $E/\hbar$, and the units are chosen so that $\hbar = 1$. Inserting this into Eq. (IX.4b) and using Eq. (IX.1), we see that the steady-state solution of Eq. (IX.4b), which is usually the one of interest, can be written in the form

$$\Phi^{(1)} = \Psi_- e^{-i(E+\omega)t} + \Psi_+ e^{-i(E-\omega)t},$$

where $\Psi_+$ and $\Psi_-$ satisfy the time-independent first-order perturbation equations

$$(H - E - \omega)\Psi_- = -W\Psi, \tag{IX.6a}$$

$$(H - E + \omega)\Psi_+ = -W^+\Psi. \tag{IX.6b}$$

*Solution of Perturbation Equations*

Equations (IX.6a) and (IX.6b) are to be compared with the first-order perturbation Eq. (IV.5) for the time-independent case, from which they differ only in the occurrence of the frequency $\omega$. There are, as usual, three possible methods of solution.

*a. Expansion in Unperturbed Eigenfunctions.* The formal solution of the equations in terms of the eigenfunctions $\Psi_p$ of $H$ (the solution given in all the text books) is always possible and is

$$\Psi_- = -\sum_p \Psi_p \frac{\langle \Psi_p, W\Psi \rangle}{E_p - E - \omega}, \tag{IX.7a}$$

$$\Psi_+ = -\sum_p \Psi_p \frac{\langle \Psi_p, W^+\Psi \rangle}{E_p - E + \omega}. \tag{IX.7b}$$

However the solutions in this form are not particularly useful unless the sums terminate or are very rapidly convergent.

*b. Explicit Solution.* It may be possible to directly exhibit solutions of Eqs. (IX.6a) and (IX.6b) in closed form. This was first done by Podolsky[30] (1928) for the polarizability of atomic hydrogen. The main difficulty is that, because of the occurrence of the frequency $\omega$, the solutions $\Omega_\pm$ of the homogeneous equation

$$(H - E \pm \omega)\Omega_\pm = 0$$

are not proper eigenfunctions of $H$. This makes the explicit solutions of Eqs. (IX.6a) and (IX.6b) more difficult to find than that of Eq. (III.1), which corresponds to $\omega = 0$.

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[30] This same problem was solved again recently using Laplace transform techniques by Karplus and Kolker (1963b), by Mittleman and Wolf (1963) (with applications to the coherent scattering of light), and by Adamov *et al.* (1963).

The first step is to reduce Eqs. (IX.6a) and (IX.6b) to one-dimensional form, either by separation or by partial expansion. If the corresponding homogeneous equation can be solved, the first-order functions $\Psi_\pm$ can then be found by integrating over the homogeneous solutions, as in Section III,A,3 (for details see Morse and Feshbach, 1953).

*c. Approximate Variational Solution.* Approximate solutions may be obtained by noting that Eqs. (IX.6a) and (IX.6b) can be replaced by the variational principles

$$\delta\tilde{L}_- = 0, \qquad \delta\tilde{L}_+ = 0,$$

where[31] the real second-order quantities $\tilde{L}_\pm$ are given by

$$\tilde{L}_- = \langle\tilde{\Psi}_-, (H - E - \omega)\tilde{\Psi}_-\rangle + \langle\tilde{\Psi}_-, W\Psi\rangle + \langle\Psi, W^+\tilde{\Psi}_-\rangle,$$

$$\tilde{L}_+ = \langle\tilde{\Psi}_+, (H - E + \omega)\tilde{\Psi}_+\rangle + \langle\tilde{\Psi}_+, W^+\Psi\rangle + \langle\Psi, W\tilde{\Psi}_+\rangle.$$

The optimal values of $\tilde{L}_\pm$ then furnish variational approximations to their exact values which are

$$L_- = \langle\Psi, W^+\Psi_-\rangle, \tag{IX.8a}$$

$$L_+ = \langle\Psi, W\Psi_+\rangle. \tag{IX.8b}$$

The quantities of physical interest are usually the combinations

$$L = L_+ + L_-,$$

which may be expanded by using Eqs. (IX.7a) and (IX.7b) to give

$$L = -2\sum_p \frac{(E_p - E)\langle\Psi, W^+\Psi_p\rangle\langle\Psi_p, W\Psi\rangle}{(E_p - E)^2 - \omega^2}.$$

For example, when $W$ is the $x$ component of the dipole moment operator, $-L$ is the frequency-dependent polarizability $\alpha_{xx}(\omega/2\pi)$ [see Section X, Eq. (X.18)].

We should remark also that not only are $\tilde{L}_\pm$ stationary, they may also have minimal properties (Karplus and Kolker, 1963b). To see this we write

$$\tilde{\Psi}_\pm = \Psi_\pm + \delta\tilde{\Psi}_\pm.$$

Then using Eq. (IX.6) we find

$$\tilde{L}_\pm = L_\pm + \langle\delta\tilde{\Psi}_\pm, (H - E \pm \omega)\delta\tilde{\Psi}_\pm\rangle.$$

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[31] These expressions differ from those given by Karplus and Kolker (1963b). It is not necessary to introduce "adjoint wave functions" for first-order calculations.

Now if $E$ is the ground state energy, then $\langle \delta\tilde{\Psi}_{\pm}, (H-E)\delta\tilde{\Psi}_{\pm}\rangle \geq 0$ and of course $\langle \delta\tilde{\Psi}_{\pm}, \omega\delta\tilde{\Psi}_{\pm}\rangle \geq 0$. Thus we have $\tilde{L}_{+} \geq L_{+}$ for all $\omega$, and $\tilde{L}_{-} \geq L_{-}$ for those values of $\omega$ such that $\delta\tilde{\Psi}_{-}$ is orthogonal to states of energy less than $E+\omega$. This orthogonality can be arranged by having the contribution of these states to $\tilde{\Psi}_{-}$ be exactly in accord with Eq. (IX.7a), and by similar "partial orthogonalities" we can, just as in the time-independent case of Section III,B,2, derive inequalities for excited states.

Few applications have been made so far of these variational formulations to problems of interest in theoretical chemistry, but many are promised (Karplus and Kolker, 1963b).

## B. Double Perturbation Theory

Thus far we have assumed that $\Psi$ is known exactly, but this will usually not be the case. Hence it would appear profitable to develop a double perturbation theory to enable us, as in the time-independent problem, to systematically correct for the inaccuracies in our approximation to $\Psi$. In what follows we write down a few of the basic equations and prove an interchange theorem.

Denoting our approximation to $\Psi$ by $\psi^{(0)}$ and introducing the associated Hamiltonian $H_0$, we have

$$H = H_0 + \lambda V, \qquad E = E^{(0)} + \lambda E^{(1)} + \cdots,$$
$$\Psi = \psi^{(0)} + \lambda\psi^{(1)} + \cdots, \qquad \Psi_{\pm} = \psi_{\pm}^{(0)} + \lambda\psi_{\pm}^{(1)} + \cdots,$$

where, as in Section II,

$$\begin{aligned}(H_0 - E^{(0)})\psi^{(0)} &= 0,\\ (H_0 - E^{(0)})\psi^{(1)} &= -(V - E^{(1)})\psi^{(0)},\end{aligned} \tag{IX.9}$$
$$E^{(1)} = \langle \psi^{(0)}, V\psi^{(0)}\rangle, \quad \text{and} \quad \operatorname{Re}\langle \psi^{(0)}, \psi^{(1)}\rangle = 0.$$

The perturbation equations for $\psi_{+}^{(0)}$ and $\psi_{+}^{(1)}$ are[32]

$$(H_0 - E^{(0)} + \omega)\psi_{+}^{(0)} = -W^{+}\psi^{(0)}, \tag{IX.10}$$

$$(H_0 - E^{(0)} + \omega)\psi_{+}^{(1)} = -W^{+}\psi^{(1)} - (V - E^{(1)})\psi_{+}^{(0)}; \tag{IX.11}$$

the equations for $\psi_{-}^{(0)}$ and $\psi_{-}^{(1)}$ are similar with $-\omega$ replacing $\omega$ and $W$ replacing $W^{+}$.

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[32] Equation (IX.10) and the corresponding one for $\psi_{-}^{(0)}$ can of course be derived from variational principles exactly similar in form to $\delta L_{\pm} = 0$ but with $\Psi$ replaced by $\psi^{(0)}$, $H - E$ replaced by $H_0 - E^{(0)}$, etc. Karplus and Kolker (1963c) have used these principles to derive zero-order approximations to the polarizabilities of He and $H_2$; for $\psi^{(0)}$ they used Hartree-Fock type functions.

*Interchange Theorem*

Since $W$ is usually a one-particle operator and $V$ is a two-particle operator, it is clearly of interest to establish an interchange theorem. We will now show that $L_+$ can, to first order in $\lambda$, be written entirely in terms of functions defined by equations involving only $W$ and not $V$; a similar result can be proven for $L_-$.

To first order in $\lambda$ we have

$$L_+ = \langle\psi^{(0)}, W\psi_+^{(0)}\rangle + \lambda\langle\psi^{(0)}, W\psi_+^{(1)}\rangle + \lambda\langle\psi^{(1)}, W\psi_+^{(0)}\rangle + \cdots.$$

The zero-order term is already of the desired form. Further, by use of Eqs. (IX.10) and (IX.11),

$$\begin{aligned}\langle\psi^{(0)}, W\psi_+^{(1)}\rangle &= \langle W^+\psi^{(0)}, \psi_+^{(1)}\rangle = -\langle(H_0 - E^{(0)} + \omega)\psi_+^{(0)}, \psi_+^{(1)}\rangle \\ &= \langle\psi_+^{(0)}, W^+\psi^{(1)}\rangle + \langle\psi_+^{(0)}, (V - E^{(1)})\psi_+^{(0)}\rangle.\end{aligned}$$

The second term here is also of the desired form, so we are left to deal with

$$\langle\psi_+^{(0)}, W^+\psi^{(1)}\rangle + \langle\psi^{(1)}, W\psi_+^{(0)}\rangle = 2\,\mathrm{Re}\langle\psi^{(1)}, W\psi_+^{(0)}\rangle.$$

To this end we define $\theta_+$ by

$$(H_0 - E^{(0)})\theta_+ = -W\psi_+^{(0)} + \eta\psi^{(0)}, \tag{IX.12}$$

where $\eta = \langle\psi^{(0)}, W\psi_+^{(0)}\rangle$ is real since, by use of Eq. IX.10),

$$\eta^* = \langle\psi_+^{(0)}, W^+\psi^{(0)}\rangle = -\langle\psi_+^{(0)}, (H_0 - E^{(0)} + \omega)\psi_+^{(0)}\rangle,$$

which is certainly real. With this definition and Eq. (IX.9) we have

$$\begin{aligned}\langle\psi^{(1)}, W\psi_+^{(0)}\rangle &= -\langle\psi^{(1)}, (H_0 - E^{(0)})\theta_+\rangle + \eta\langle\psi^{(1)}, \psi^{(0)}\rangle \\ &= \langle\psi^{(0)}, (V - E^{(1)})\theta_+\rangle + \eta\langle\psi^{(1)}, \psi^{(0)}\rangle;\end{aligned}$$

whence

$$2\,\mathrm{Re}\langle\psi^{(1)}, W\psi_+^{(0)}\rangle = 2\,\mathrm{Re}\langle\psi^{(0)}, (V - E^{(1)})\theta_+\rangle$$

since $\mathrm{Re}\langle\psi^{(1)}, \psi^{(0)}\rangle = 0$. Finally, then, we have

$$\begin{aligned}L_+ = \langle\psi^{(0)}, W\psi_+^{(0)}\rangle &+ \lambda\langle\psi_+^{(0)}, (V - E^{(1)})\psi_+^{(0)}\rangle + \lambda\langle\psi^{(0)}, (V - E^{(1)})\theta_+\rangle \\ &+ \lambda\langle\theta_+, (V - E^{(1)})\psi^{(0)}\rangle,\end{aligned}$$

which is of the desired form. Similarly,

$$\begin{aligned}L_- = \langle\psi^{(0)}, W^+\psi_-^{(0)}\rangle &+ \lambda\langle\psi_-^{(0)}, (V - E^{(1)})\psi_-^{(0)}\rangle \\ &+ \lambda\langle\psi^{(0)}, (V - E^{(1)})\theta_-\rangle + \lambda\langle\theta_-, (V - E^{(1)})\psi^{(0)}\rangle\end{aligned}$$

where

$$(H_0 - E^{(0)})\theta_- = -W^+\psi_-^{(0)} + \langle\psi^{(0)}, W^+\psi_-^{(0)}\rangle\psi^{(0)}. \tag{IX.13}$$

We conclude by noting that if we cannot solve Eq. (IX.12) for $\theta_+$ exactly we have available, as usual, a variational principle from which we may derive approximate solutions, namely, $\delta\mathscr{L}_+ = 0$, with

$$\mathscr{L}_+ = \langle\tilde{\theta}_+, (H_0 - E^{(0)})\tilde{\theta}_+\rangle + \langle\tilde{\theta}_+, W\psi_+^{(0)}\rangle + \langle\psi_+^{(0)}, W^+\tilde{\theta}_+\rangle$$
$$-\eta\langle\tilde{\theta}_+, \psi^{(0)}\rangle - \eta\langle\psi^{(0)}, \tilde{\theta}_+\rangle.$$

Similarly, we may approximate the solution to Eq. (IX.13) by use of $\delta\mathscr{L}_- = 0$, where

$$\mathscr{L}_- = \langle\tilde{\theta}_-, (H_0 - E^{(0)})\tilde{\theta}_-\rangle + \langle\tilde{\theta}_-, W^+\psi_-^{(0)}\rangle + \langle\psi_-^{(0)}, W\tilde{\theta}_-\rangle$$
$$-\eta'\langle\tilde{\theta}_-, \psi^{(0)}\rangle - \eta'\langle\psi^{(0)}, \tilde{\theta}_-\rangle$$

and

$$\eta' = \langle\psi^{(0)}, W^+\psi_-^{(0)}\rangle.$$

## X. Sum Rules and the Calculation of Sums

In the preceding sections, our emphasis has been on avoiding and bypassing the standard formulas of perturbation theory with their infinite summations. In their place, we have substituted expressions of the form $\langle\psi_q, Q\psi_q\rangle$, where $Q$ is to be determined *exactly* by the solution of some differential equation or *approximately* by means of some variational principle. These formulas have been presented as alternatives to the sums, but they can be considered equally well as evaluations of the sums—that is, as *sum rules.*

In this section we wish to explore in some detail the significance of sums of the form

$$G_k(\omega) = \sum_j{}'(\varepsilon_q + \omega - \varepsilon_j)^k\langle\psi_q, W\psi_j\rangle\langle\psi_j, A\chi\rangle \tag{X.1}$$

and their evaluation in the form $\langle\psi_q, Q_k(\omega)\psi_q\rangle$. The equality

$$\langle\psi_q, Q_k(\omega)\psi_q\rangle = G_k(\omega)$$

is then a sum rule. In Eq. (X.1), $k$ may be a positive or negative integer, $\omega$ is a constant, $W$ and $A$ are operators, and $\chi$ is a given function as, for example, $\psi_q$. The primed sigma indicates summation over all of the discrete energy states and integration over the continuum but excludes the state (or states) with energy $\varepsilon_q$.

As an example, we consider the derivation and application of the family of oscillator strength sum rules.

## A. General Techniques for Evaluating Sums

Let us examine carefully the general techniques which Dalgarno (1963) has given for the evaluation of the $G_k(\omega)$.

For $k$ positive, obviously

$$\begin{aligned} G_k(\omega) &= \sum_j{}' \langle \psi_q, W(\varepsilon_q + \omega - H_0)^k \psi_j \rangle \langle \psi_j, A\chi \rangle \\ &= \langle \psi_q, W(\varepsilon_q + \omega - H_0)^k A\chi \rangle - \omega^k \langle \psi_q, W\psi_q \rangle \langle \psi_q, A\chi \rangle. \end{aligned} \tag{X.2}$$

If the state $q$ is degenerate with the set of wave functions $\psi_{qi}$, then the second term in Eq. (X.2) should read

$$-\omega^k \sum_i \langle \psi_q, W\psi_{qi} \rangle \langle \psi_{qi}, A\chi \rangle. \tag{X.3}$$

For $k$ negative, we are limited to a consideration of operators $W$ which are Hermitian with respect to $\psi_q$ and all of the $\psi_j$. In order to evaluate the sum, we must solve the differential equation for a real function $F$,

$$[(\varepsilon_q + \omega - H_0)^{|k|} F - \omega^{|k|} \langle \psi_q, F\psi_q \rangle] \psi_q = [W - \langle \psi_q, W\psi_q \rangle] \psi_q. \tag{X.4}$$

We further require that $H_0$ be Hermitian[33] with respect to $F\psi_q$. Then, it is evident that

$$(\varepsilon_q + \omega - \varepsilon_j)^{|k|} \langle \psi_q, F\psi_j \rangle = \langle \psi_q, W\psi_j \rangle. \tag{X.5}$$

Thus, with $k$ negative,

$$\begin{aligned} G_k(\omega) &= \sum_j{}' \langle \psi_q, F\psi_j \rangle \langle \psi_j, A\chi \rangle \\ &= \langle \psi_q, FA\chi \rangle - \langle \psi_q, F\psi_q \rangle \langle \psi_q, A\chi \rangle. \end{aligned} \tag{X.6}$$

If the state $q$ is degenerate with the set of wave functions $\psi_{qi}$, then the second term in Eq. (X.6) is

$$-\sum_i \langle \psi_q, F\psi_{qi} \rangle \langle \psi_{qi}, A\chi \rangle. \tag{X.7}$$

Dalgarno has found it useful to study $G_k(\omega)$ as a function of both $k$ and $\omega$ (see Section X,C). Some of the values of $G_k(\omega)$ are known empirically, and this helps to estimate the values of others. Since the derivative

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[33] If the Hamiltonian includes delta functions as explained in Appendix C, the Hamiltonian is generally Hermitian. If the Laplacian operator in $H_0$ has the usual form without delta functions, there are many cases where $H_0$ is not Hermitian. For example, for the hydrogen atom, if $\psi_q$ and $\psi_j$ are $S$-state wave functions and $p_r = (\hbar/i)r^{-1}\, \partial/\partial r(r \quad )$ is the radial momentum operator:

$$\langle \psi_q, H_0 p_r \psi_j \rangle - \langle H_0 \psi_q, p_r \psi_j \rangle = h(\psi_q{}^* \psi_j)_{r=0}.$$

of $G_k(\omega)$ with respect to the parameter $\omega$ is equal to the sum of the derivatives of the terms on the right-hand side of Eq. (X.1),

$$dG_k(\omega)/d\omega = kG_{k-1}(\omega). \tag{X.8}$$

As a result, all of the functions $G_{-k}(\omega)$, where $k$ is positive, can be expressed as derivatives of $G_{-1}(\omega)$,

$$G_{-1-k}(\omega) = \frac{(-1)^k}{k!}\frac{d^k}{d\omega^k}G_{-1}(\omega). \tag{X.9}$$

If $\omega = 0$, the sum rules may be stated in a somewhat simpler form in terms of the $k$th repeated commutator

$$[H_0, F]_k \equiv [H_0, [H_0, \dots [H_0, [H_0, F]] \dots ]]. \tag{X.10}$$

If $H$ and $W$ are Hermitian, we have the hypervirial theorem (or the Heisenberg equation of change),

$$\langle\psi_q, [H_0, W]_k\psi_j\rangle = (\varepsilon_q - \varepsilon_j)^k\langle\psi_q, W\psi_j\rangle. \tag{X.11}$$

Thus, for $\omega = 0$ and $k$ positive, in place of Eq. (X.2),

$$G_k(0) = \langle\psi_q, [H_0, W]_k A\chi\rangle. \tag{X.12}$$

For $G_{-k}(0)$ with $k$ positive, it is easy to verify that Eq. (X.4) may be written in the form

$$(-1)^k[H_0, F]_k\psi_q = [W - \langle\psi_q, W\psi_q\rangle]\psi_q. \tag{X.13}$$

Salem (1962) has found an interesting sum rule corresponding to $G_{-1}(0)$ with $W = \partial H/\partial\mu$ and $\chi = \psi_q$. According to S. T. Epstein (1954) and Byers Brown (1958),

$$\left\langle\psi_q, \frac{\partial H}{\partial\mu}\psi_j\right\rangle = (\varepsilon_j - \varepsilon_q)\left\langle\psi_q, \frac{\partial\psi_j}{\partial\mu}\right\rangle. \tag{X.14}$$

It follows that

$$\sum_j{}' \frac{\langle\psi_q, A\psi_j\rangle\left\langle\psi_j, \frac{\partial H}{\partial\mu}\psi_q\right\rangle + \left\langle\psi_q, \frac{\partial H}{\partial\mu}\psi_j\right\rangle\langle\psi_j, A\psi_q\rangle}{\varepsilon_j - \varepsilon_q}$$
$$= \left\langle\psi_q, \frac{\partial A}{\partial\mu}\psi_q\right\rangle - \frac{\partial}{\partial\mu}\langle\psi_q, A\psi_q\rangle. \tag{X.15}$$

This sum rule has a wide range of applicability depending upon the choice of the parameter $\mu$ and the operator $A$. For example, $\mu$ might be taken to be the strength of an external field, an interatomic separation, or the mass or electric charge on a nucleus.

### B. Sum Rules for Oscillator Strengths

There is a family of summations involving oscillator strengths which provide an excellent example of the application of the sum rules.[34] Different members of the family correspond to different physical properties. Let us introduce the family by means of a discussion of the index of refraction.

According to the Clausius–Mosotti relation, in a gas with number density $d$ where all of the molecules are in state $q$, the index of refraction $\eta$ for light of frequency $\nu$ is given by (Hirschfelder *et al.*, 1954, p.889)

$$(\eta^2 - 1)/(\eta^2 + 2) = (4\pi/3)\, d\alpha(\nu). \tag{X.16}$$

Here $\alpha(\nu)$ is the mean value of $\alpha_{xx}(\nu)$, $\alpha_{yy}(\nu)$, and $\alpha_{zz}(\nu)$, the diagonal elements of the frequency-dependent polarizability tensor,

$$\alpha(\nu) = \tfrac{1}{3}[\alpha_{xx}(\nu) + \alpha_{yy}(\nu) + \alpha_{zz}(\nu)]. \tag{X.17}$$

In the limit as $\nu$ becomes zero, $\alpha(\nu)$ becomes the usual average polarizability $\alpha$.

From time-dependent perturbation theory (see Section IX), it is easy to show that

$$\alpha_{xx}(\nu) = a_0^3 \sum_j{}' \frac{f(x)_{qj}(e^2/a_0)^2}{(\varepsilon_q - \varepsilon_j)^2 - h^2\nu^2}. \tag{X.18}$$

Here $f(x)_{qj}$ is the oscillator strength corresponding to a transition from state $q$ to state $j$ under the influence of $x$-polarized electric dipole radiation,

$$f(x)_{qj} = 2\,\frac{(\varepsilon_j - \varepsilon_q)\langle\psi_q, \mu_x\psi_j\rangle\langle\psi_j, \mu_x\psi_q\rangle}{(e^2/a_0)(ea_0)^2}. \tag{X.19}$$

Here $\mu_x$ is the $x$ component of the dipole moment,[35] $\mu_x = \sum_i e_i x_i$, where $e_i$ is the charge and $x_i$ the coordinate of the $i$th particle, and the summation

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[34] Levinger (1960, Chapter I) has an excellent treatment of these sum rules and their significance.

[35] As Bethe (1937, p.222) has shown, the dipole moment should be defined with coordinates relative to the center of mass, $x_c = \Sigma m_i x_i/M$, where $m_i$ is the mass of the $i$th particle and $M$ is the total mass of the system. If we let the total charge on the system be $C = \Sigma e_i$, then

$$\mu_x = \sum_i e_i(x_i - x_c) = \sum_i e_i x_i - Cx_c = \sum_i e_i^* x_i.$$

Thus, the "usual" definition for the dipole moment suffices if $C = 0$. However, if the system has a net charge, each of the $e_i$ should be replaced by an effective charge $e_i^* = e_i - Cm_i/M$.

is extended over all of the charged particles in the system including nuclei. The mean oscillator strength for the $q$ to $j$ transition is

$$f_{qj} = \tfrac{1}{3}[f(x)_{qj} + f(y)_{qj} + f(z)_{qj}]. \tag{X.20}$$

The oscillator strengths are important since each one has independent physical significance and can be independently measured.

Many physical properties of an atom or molecule can be expressed in terms of the summations[36]

$$S_k(x) = \sum_j{}' (\varepsilon_j - \varepsilon_q)^k f(x)_{qj} (e^2/a_0)^{-k} \tag{X.21}$$

or letting

$$S_k = \tfrac{1}{3}[S_k(x) + S_k(y) + S_k(z)],$$
$$S_k = \sum_j{}' (\varepsilon_j - \varepsilon_q)^k f_{qj} (e^2/a_0)^{-k}. \tag{X.22}$$

$S_k(x)$ can also be written in the form

$$S_k(x) = 2(-1)^{k+1} \sum_j{}' \frac{(\varepsilon_q - \varepsilon_j)^{k+1} \langle \psi_q, \mu_x \psi_j \rangle \langle \psi_j, \mu_x \psi_q \rangle}{(e^2/a_0)^{k+1} (e a_0)^2}. \tag{X.23}$$

Throughout the remainder of Section X, we use atomic units (energy $\sim e^2/a_0$ and length $\sim a_0$). This choice of units does not effect the values of the oscillator strengths which are dimensionless.

The family of $S_k$ corresponding to integer values of $k$ ranging from minus infinity through $k = 2$ provides an interesting group of *sum rules.* The values of $S_k$ vary smoothly with $k$ and (for systems with finite electron density at the nuclei) approach infinity at $k = 2.5$. Thus, Dalgarno and Kingston (1960) have found that for the ground state, $q = 0$, the $S_k(x)$ can be approximated with considerable accuracy by the expression

$$S_k(x) = n[(\varepsilon_1 - \varepsilon_0) + a(2.5 - k)^{-1} + b(2.5 - k)^{-2}]^k. \tag{X.24}$$

Here $n$ is the number of electrons in the atom or molecule, "1" is the first excited state with nonvanishing oscillator strength, and the constants $a$ and $b$ are adjusted to make Eq. (X.24) correct for two selected values of $k$ (usually $k = -1$ and $k = -2$). Thus, a detailed knowledge of the individual oscillator strengths may frequently not be required for the determination of a physical property.

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[36] Note that Dalgarno's $S_k$ are equal to $(2)^k$ times our $S_k$ since Dalgarno uses the Rydberg $(e^2/2a_0)$ as his unit of energy. Also note that his binding energies are the negative of our $\varepsilon_p$ and $\varepsilon_j$.

Dalgarno and his colleagues (see Dalgarno, 1960b, 1963; Dalgarno and Lynn, 1957; Dalgarno and Kingston, 1958, 1960; and Dalgarno and Ewart, 1962) have discussed the various sum rules corresponding to different values of $k$ and showed their applications to atomic problems. The difficult derivations of the sum rules for $k = 2$ and 3 were developed by Vinti (1932a). Let us consider the properties of the summations corresponding to different values of $k$. We shall carry out the derivations in considerable detail, as it is important that the results be applicable to molecules as well as to atoms.

1. $k = -3$: *Norm of a First-Order Perturbation Wave Function*

The first-order perturbation wave function corresponding to a perturbation potential $\mu_x$ can be written in the spectral form

$$\psi_q^{(1)} = \sum_j{}'(\varepsilon_q - \varepsilon_j)^{-1}\langle\psi_j, \mu_x\psi_q\rangle\psi_j. \tag{X.25}$$

Thus, comparing with Eq. (X.23),

$$\langle\psi_q^{(1)}, \psi_q^{(1)}\rangle = \tfrac{1}{2}S_{-3}(x). \tag{X.26}$$

2. $k = -2$: *Polarizability*

From Eq. (X.18), it follows directly that

$$\alpha_{xx}(0) = S_{-2}(x). \tag{X.27}$$

3. $k = -1$: *Size or Approximate Polarizability*

Again, from Eq. (X.23) it follows that[37]

$$S_{-1}(x) = 2\langle\psi_q, \mu_x^2\psi_q\rangle - 2[\langle\psi_q, \mu_x\psi_q\rangle]^2. \tag{X.28}$$

The dipole moment for a system of $n$ electrons and an arbitrary number of nuclei is[35]

$$\mu_x = -\left(1 + \frac{mC}{M}\right)\sum_j x_j + \sum_\alpha\left(Z_\alpha - \frac{m_\alpha C}{M}\right)x_\alpha. \tag{X.29}$$

Here $x_j$ and $x_\alpha$ are the electronic and nuclear coordinates, respectively; $Z_\alpha$ and $m_\alpha$ are the atomic number and mass of the $\alpha$th nucleus; $m$ is the electron mass; $M$ is the total mass of the system; and $C$ is the total charge on the system, $C = (\sum_\alpha Z_\alpha) - n$. If we let a bar over a variable indicate

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[37] For degeneracy problems see Eq. (X.3).

its expectation value corresponding to the wave function $\psi_q$, then Eq. (X.28) becomes

$$\begin{aligned} S_{-1}(x) = 2n\left(1+\frac{mC}{M}\right)^2 \{\overline{x_1^2} - (\bar{x}_1)^2 + (n-1)[\overline{x_1 x_2} - (\bar{x}_1)^2]\} \\ - 4n\left(1+\frac{mC}{M}\right)\sum_\alpha \left(Z_\alpha - \frac{m_\alpha C}{M}\right)[\overline{x_1 x_\alpha} - \bar{x}_1 \bar{x}_\alpha] \qquad \text{(X.30)} \\ + 2\sum_\alpha \sum_\beta \left(Z_\alpha - \frac{m_\alpha C}{M}\right)\left(Z_\beta - \frac{m_\beta C}{M}\right)[\overline{x_\alpha x_\beta} - \bar{x}_\alpha \bar{x}_\beta]. \end{aligned}$$

This expression for $S_{-1}(x)$ is closely related to $\tilde{\alpha}_{xx}(0)$, the Kirkwood–Vinti (see Kirkwood, 1932; Vinti, 1932b; Hirschfelder, 1935; Hirschfelder *et al.*, 1954, p. 946; Dalgarno, 1962) approximation to the polarizability. Indeed, if we neglect the small nuclear contributions and the small (or zero) $mC/M$,

$$\tilde{\alpha}_{xx}(0) = [S_{-1}(x)]^2/n'. \qquad \text{(X.31)}$$

Here $n'$ is best interpreted as the number of electrons in the outer shell. Insofar as the Kirkwood–Vinti approximation to the polarizability is accurate,

$$S_{-2}(x) \doteq [S_{-1}(x)]^2/n'. \qquad \text{(X.32)}$$

For the hydrogen atom in its ground state, $S_{-2}(x) = 4.5$ and $S_{-1}(x) = 2$, so that Eq. (X.32) gives $4.5 \doteq 4.0$.

4. $k = 0$: *Reiche–Thomas–Kuhn Sum Rule*

From Eq. (X.23),

$$\begin{aligned} S_0(x) &= 2\sum_j{}' (\varepsilon_j - \varepsilon_q)\langle\psi_q, \mu_x\psi_j\rangle\langle\psi_j, \mu_x\psi_q\rangle \\ &= \sum_j{}' \langle\psi_q, \mu_x\psi_j\rangle\langle\psi_j, [H_0, \mu_x]\psi_q\rangle - \sum_j{}' \langle\psi_q, [H_0, \mu_x]\psi_j\rangle\langle\psi_j, \mu_x\psi_q\rangle \\ &= \langle\psi_q, [\mu_x, [H_0, \mu_x]]\psi_q\rangle. \qquad \text{(X.33)} \end{aligned}$$

The Hamiltonian for the system (in atomic units) is

$$H_0 = -\tfrac{1}{2}\sum_i \Delta_i - \tfrac{1}{2}\sum_\alpha \left(\frac{m}{m_\alpha}\right)\Delta_\alpha + U_0(\mathbf{r}_1, \ldots, \mathbf{r}_n; \mathbf{r}_\alpha, \ldots) - H_c. \qquad \text{(X.34)}$$

Here $H_c$ is the kinetic energy of the system as a whole,

$$H_c = -\frac{1}{2M}\left(\sum_i \nabla_i + \sum_\alpha \nabla_\alpha\right)\cdot\left(\sum_i \nabla_i + \sum_\alpha \nabla_\alpha\right). \qquad \text{(X.35)}$$

It is easy to show that $H_c$ commutes with $\mu_x$, as defined by Eq. (X.29), and that

$$[H_0, \mu_x] = \sum_i \frac{\partial}{\partial x_i} - \sum_\alpha \frac{mZ_\alpha}{m_\alpha} \frac{\partial}{\partial x_\alpha} + \frac{mC}{M}\left(\sum_i \frac{\partial}{\partial x_i} + \sum_\alpha \frac{\partial}{\partial x_\alpha}\right). \qquad \text{(X.36)}$$

If the nuclei were held fixed, the derivatives with respect to $x_\alpha$ would not appear. Using Eqs. (X.29) and (X.33), it follows that

$$S_0(x) = n + \sum_\alpha \left(\frac{m}{m_\alpha}\right) Z_\alpha^2 - \frac{mC^2}{M}. \qquad \text{(X.37)}$$

Thus, we have derived the Reiche–Thomas–Kuhn sum rule (see Kuhn, 1925; Bethe, 1933; Condon and Shortley, 1935; Levinger, 1960, Chapter I):

$$\sum_j{}' f_{qj} = n + \sum_\alpha \left(\frac{m}{m_\alpha}\right) Z_\alpha^2 - \frac{mC^2}{M} = S_0. \qquad \text{(X.38)}$$

If the nuclei were artificially held fixed (indicated by fn) then the Reiche–Thomas–Kuhn sum rule would have reduced to the usual form

$$\sum_j{}' (f_{qj})_{\text{fn}} = n = (S_0)_{\text{fn}}. \qquad \text{(X.39)}$$

### 5. $k = 1$: *Momentum Correlation or Isotopic Shift of Atomic Energy Levels*

Starting with Eq. (X.23),

$$\begin{aligned} S_1(x) &= -2 \sum_j{}' \langle \psi_q, [H_0, \mu_x]\psi_j\rangle\langle \psi_j, [H_0, \mu_x]\psi_q\rangle \\ &= -2\langle \psi_q, [H_0, \mu_x][H_0, \mu_x]\psi_q\rangle. \end{aligned} \qquad \text{(X.40)}$$

Using Eq. (X.36), and assuming that $\psi_q$ is a function of the relative coordinates of the electrons and nuclei,

$$\begin{aligned} S_1(x) &= -2\left\langle \psi_q, \left[\sum_{i,k} \frac{\partial^2 \psi_q}{\partial x_i \partial x_k} - 2 \sum_{i,\alpha} \frac{mZ_\alpha}{m_\alpha} \frac{\partial^2 \psi_q}{\partial x_i \partial x_\alpha} + \sum_{\alpha,\beta} \frac{m^2 Z_\alpha Z_\beta}{m_\alpha m_\beta} \frac{\partial^2 \psi_q}{\partial x_\alpha \partial x_\beta}\right]\right\rangle \\ &= 2\left\langle \psi_q, \left[\sum_i p_{x_i} - \sum_\alpha \frac{mZ_\alpha}{m_\alpha} p_{x_\alpha}\right]^2 \psi_q\right\rangle. \end{aligned} \qquad \text{(X.41)}$$

This expression for $S_1(x)$ involves the momentum correlations.

$S_1(x)$ can also be expressed in the form,

$$\begin{aligned} S_1(x) &= \sum_j{}' \langle \psi_q, \mu_x \psi_j\rangle\langle \psi_j, [H_0, [H_0, \mu_x]]\psi_q\rangle \\ &\quad + \sum_j{}' \langle \psi_q, [H_0, [H_0, \mu_x]]\psi_j\rangle\langle \psi_j, \mu_x \psi_q\rangle \\ &= \langle \psi_q, \{\mu_x[H_0, [H_0, \mu_x]] + [H_0, [H_0, \mu_x]]\mu_x\}\psi_q\rangle. \end{aligned} \qquad \text{(X.42)}$$

Since $[H_0, \mu_x]$, as given by Eq. (X.36), only involves the momenta and not the coordinates, and since all of the momenta commute with each other,

$$\begin{aligned}[H_0, [H_0, \mu_x]] &= [U_0, [H_0, \mu_x]] \\ &= -\sum_i \frac{\partial U_0}{\partial x_i} + \sum_\alpha \frac{mZ_\alpha}{m_\alpha} \frac{\partial U_0}{\partial x_\alpha}. \end{aligned} \tag{X.43}$$

Here we have assumed that $U_0$ is a function only of the relative coordinates. Thus,

$$S_1 = +\frac{2}{3}\left\langle \psi_q, \boldsymbol{\mu}\cdot\left[-\sum_i (\nabla_i U_0) + \sum_\alpha \frac{mZ_\alpha}{m_\alpha}(\nabla_\alpha U_0)\right]\psi_q\right\rangle. \tag{X.44}$$

The greatest interest is attached to the fixed nucleus problems where

$$(S_1)_{\text{fn}} = \frac{2}{3}\left\langle \psi_q, \sum_{j,k} \mathbf{r}_j\cdot(\nabla_k U_0)\psi_q\right\rangle. \tag{X.45}$$

For molecules,

$$U_0 = -\sum_{\alpha, j} Z_\alpha r_{\alpha j}^{-1} + \sum_{i>j} r_{ij}^{-1} + \sum_{\alpha>\beta} Z_\alpha Z_\beta r_{\alpha\beta}^{-1}, \tag{X.46}$$

so that,

$$\sum_k \partial U_0/\partial x_k = \sum_\alpha Z_\alpha \sum_k (x_k - x_\alpha) r_{\alpha k}^{-3}. \tag{X.47}$$

As a result,

$$(S_1)_{\text{fn}} = \frac{2}{3}\sum_\alpha Z_\alpha\left\langle \psi_q, \sum_k \left[\frac{1}{r_{\alpha k}} + \frac{(\mathbf{r}_k - \mathbf{r}_\alpha)}{r_{\alpha k}^3}\cdot\left\{\mathbf{r}_\alpha + \sum_{l\neq k} \mathbf{r}_l\right\}\right]\psi_q\right\rangle. \tag{X.48}$$

For an atomic state, if $\varepsilon_q$ is calculated assuming that the nucleus is held fixed, then the energy taking the nuclear motion into account is $\varepsilon_q + G_q$. Hughes and Eckart (1930) and Vinti (1940) showed that

$$G_q = 3(m/M)(S_1)_{\text{fn}}. \tag{X.49}$$

### 6. $k = 2$: *Charge Density at the Nuclei and Radiative Transition Probabilities*

Again from Eq. (X.23),

$$\begin{aligned} S_2(x) &= \sum_j{}' \langle \psi_q, [H_0, [H_0, \mu_x]]\psi_j\rangle\langle\psi_j, [H_0, \mu_x]\psi_q\rangle \\ &\quad -\sum_j{}' \langle \psi_q, [H_0, \mu_x]\psi_j\rangle\langle\psi_j, [H_0, [H_0, \mu_x]]\psi_q\rangle \\ &= \langle \psi_q, [[H_0, [H_0, \mu_x]]\,[H_0, \mu_x]]\psi_q\rangle \\ &\quad - \langle \psi_q, [H_0, \mu_x]\,[H_0, [H_0, \mu_x]]\,\psi_q\rangle. \end{aligned} \tag{X.50}$$

Using Eqs. (X.36) and (X.43), and recognizing that both $\psi_q$ and $U_0$ are functions of the relative coordinates,

$$S_2 = \frac{1}{3}\left\langle \psi_q, \left[\left(\sum_j \nabla_j - 2\sum_\alpha \frac{mZ_\alpha}{m_\alpha}\nabla_\alpha\right)\cdot\sum_i \nabla_i U_0 \right.\right. \\ \left.\left. + \sum_\alpha\sum_\beta \frac{m^2 Z_\alpha Z_\beta}{m_\alpha m_\beta}\nabla_\alpha\cdot\nabla_\beta U_0\right]\psi_q\right\rangle. \tag{X.51}$$

It is easy to show that the only nonvanishing terms are

$$S_2 = -\frac{1}{3}\sum_i\sum_\alpha \left\langle \psi_q, \left[Z_\alpha \Delta_i\left(\frac{1}{r_{\alpha i}}\right) + \frac{m^2 Z_\alpha^3}{m_\alpha^2}\Delta_\alpha\left(\frac{1}{r_{\alpha i}}\right)\right]\psi_q\right\rangle. \tag{X.52}$$

But in accordance with Appendix C,

$$\Delta_i(r_{\alpha i}^{-1}) = -r_{\alpha i}^{-2}\,\delta_+(r_{\alpha i}) = \Delta_\alpha(r_{\alpha i}^{-1}). \tag{X.53}$$

Thus,[38] letting $\rho_q(\mathbf{r}_\alpha)$ be the absolute value of the electron density (Löwdin, 1959) at the nucleus $\alpha$,

$$S_2 = \frac{4\pi}{3}\sum_\alpha Z_\alpha \rho_q(\mathbf{r}_\alpha)\left[1 + \frac{m^2 Z_\alpha^2}{m_\alpha^2}\right]. \tag{X.54}$$

For fixed nuclei, the nuclear mass can be considered to be infinite.

Clinton (1961) has made a very interesting interpretation of $S_2$. Let $P_{j\to k}$ be the probability of a spontaneous transition with the emission of a photon from a state of energy $\varepsilon_j$ to a state of lower energy $\varepsilon_k$. To the electric dipole radiation approximation, we have (Bethe and Salpeter, 1957)

$$P_{j\to k} = (3/4\pi)(\varepsilon_j - \varepsilon_k)^2 f_{kj}. \tag{X.55}$$

Therefore, since $f_{kj} = -f_{jk}$,

$$S_2 = \frac{4\pi}{3}\left[\sum_{j=q+1}^{\infty} P_{j\to q} - \sum_{j=0}^{q-1} P_{q\to j}\right] \tag{X.56}$$

Or, by virtue of Eq. (X.54),

$$\sum_{j=q+1}^{\infty} P_{j\to q} - \sum_{j=0}^{q-1} P_{q\to j} = \sum_\alpha Z_\alpha \rho_q(\mathbf{r}_\alpha). \tag{X.57}$$

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[38] Byers Brown (1958) derived $(S_2)_{\text{fn}}$ by considering the force constants for a molecule. If $E_q$ is the energy of the molecule as a function of the nuclear coordinate, he obtained

$$\sum_\beta\sum_\alpha \nabla_\alpha\cdot\nabla_\beta E_q = 4\pi\sum_\alpha Z_\alpha\rho_q(\mathbf{r}_\alpha) - 3(S_2)_{\text{fn}}$$

which is identically zero since $E_q$ is invariant with respect to translations.

There are three interesting conclusions that may be drawn from Eq. (X.57):

(a) If a state $q$ has zero electron density at the nuclei,

$$\sum_{j=q+1}^{\infty} P_{j\to q} = \sum_{j=0}^{q-1} P_{q\to j}. \tag{X.58}$$

(b) The ground state of any molecular system cannot have zero electron density at all of its nuclei unless radiative transitions from *all* other states of the system are forbidden.

(c) The natural line breadth $b_{q0}$ of a transition from a state $q$ to the ground state is

$$b_{q0} = \sum_{j=0}^{q-1} P_{q\to j} = \sum_{j=q+1}^{\infty} P_{j\to q} - \sum_{\alpha} Z_\alpha \rho_q(\mathbf{r}_\alpha). \tag{X.59}$$

7. $k = 3$: *Infinite for S-State Wave Functions*

From Eq. (X.23),

$$S_3(x) = 2 \sum_j{}' \langle \psi_q, [H_0, [H_0, \mu_x]]\psi_j\rangle\langle\psi_j, [H_0, [H_0, \mu_x]]\psi_q\rangle \tag{X.60}$$

$$= 2\langle \psi_q, [H_0, [H_0, \mu_x]]^2 \psi_q\rangle. \tag{X.61}$$

And from Eq. (X.43),

$$S_3 = \frac{2}{3}\left\langle \psi_q, \left[-\sum_i \nabla_i U_0 + \sum_\alpha \frac{mZ_\alpha}{m_\alpha}\nabla_\alpha U_0\right]^2 \psi_q\right\rangle. \tag{X.62}$$

Using Eqs. (X.46) and (X.47), we obtain a lengthy formula for the $S_3$. For fixed nuclei, this reduces to give

$$\begin{aligned}(S_3)_{\text{fn}} &= \sum_\alpha Z_\alpha^2 n \langle \psi_q, r_{\alpha 1}^{-4}\psi_q\rangle \\ &\quad + 2\sum_\alpha Z_\alpha^2 \sum_{j>k} \left\langle \psi_q, \frac{(\mathbf{r}_j - \mathbf{r}_\alpha)\cdot(\mathbf{r}_k - \mathbf{r}_\alpha)}{r_{\alpha j}^3 r_{\alpha k}^3}\psi_q\right\rangle \\ &\quad + 2\sum_{\alpha>\beta} Z_\alpha Z_\beta \sum_{j,k}\left\langle \psi_q, \frac{(\mathbf{r}_j - \mathbf{r}_\alpha)\cdot(\mathbf{r}_k - \mathbf{r}_\beta)}{r_{\alpha j}^3 r_{\beta k}^3}\psi_q\right\rangle.\end{aligned} \tag{X.63}$$

The first sum in Eq. (X.63) becomes infinite if $\rho_q(\mathbf{r}_\alpha)$ is not zero for any of the nuclei. Thus, for $S$-state atoms, $(S_3)_{\text{fn}}$ is infinite. If, on the other hand, $\rho_q(\mathbf{r}_\alpha) = 0$ for all of the nuclei, the value of $(S_3)_{\text{fn}}$ is finite.

8. *Values of* $S_k$

Table I gives values of $S_k$ which have been determined for H, H$^-$, and He. Dalgarno and Kingston (1960) solved a recursive set of differential equations to determine the values of $S_{-k}$ for the ground state of H. The

TABLE I

VALUES OF $S_k = \Sigma'_j (\varepsilon_j - \varepsilon_q)^k f_{qj} (e^2/a_0)^{-k}$

| Atom | H | | H$^-$ | He | He | He |
|---|---|---|---|---|---|---|
| $k$ | 1$s$ | % discrete | $1^1S$ | $1^1S$ | $2^1S$ | $2^3S$ |
| 2.5 | ∞ | (0) | ∞ | ∞ | ∞ | ∞ |
| 2 | 1.333333 | (6.8) | 44.12 | 485.2 | 348.4 | 353.6 |
| 1 | 0.666667 | (33.7) | 4.04 | 16.34 | 11.48 | 11.62 |
| 0 | 1.0 | (56.5) | 2.0 | 2.0 | 2.0 | 2.0 |
| −1 | 2.0 | (71.7) | 13.2 | — | — | — |
| −2 | 4.5 | (81.4) | 62. | — | — | — |
| −3 | 10.75 | (87.7) | — | — | — | — |
| −4 | 26.583333 | (91.8) | — | — | — | — |
| −5 | 67.173610 | (94.4) | — | — | — | — |
| −6 | 172.188079 | (96.2) | — | — | — | — |

figures in parentheses are the percentage contribution by the discrete states, as calculated by Inokuti (1964). The $S_k$ for H$^-$ were determined by Dalgarno and Ewart (1962); the values of $S_k$ for the three states of He are given by Dalgarno and Kingston (1958).

## C. Application of the Sum Rules

Let us consider in detail a few of the applications of the sum rules. References to additional applications are given in Section XI.

### 1. *Index of Refraction*

The index of refraction can be expressed in terms of a fast-converging sequence of constants times the $S_{-k}$, provided that the wave length $\lambda$(Å) of the incident light is sufficiently long that $h\nu < |\epsilon_q - \epsilon_j|$ for all states $j$. If we let $b = 10^{-16}[hc/(e^2/a_0)]^2 = 2.0760 \times 10^5$, then $[h\nu/(e^2/a_0)]^2 = b/\lambda^2$. Thus, for this long wave length light, Eq. (X.18) can be expanded into the form

$$\alpha_{xx}(\nu) = a_0^3 \sum_j{}' \frac{f(x)_{qj}}{(\varepsilon_q - \varepsilon_j)^2} \sum_{k=0}^{\infty} \left[\frac{b}{\lambda^2(\varepsilon_q - \varepsilon_j)^2}\right]^k . \qquad \text{(X.64)}$$

Making use of Eqs. (X.16), (X.17), and (X.22), it follows that

$$\frac{\eta^2 - 1}{\eta^2 + 2} = (4\pi/3)\, d a_0^3 [S_{-2} + (b/\lambda^2) S_{-4} + (b/\lambda^2)^2 S_{-6} + \cdots]. \qquad \text{(X.65)}$$

Equation (X.24) provides a convenient way of estimating the $S_{-k}$ (provided that the state $q$ is the ground state). The two constants in this equation are determined from either experimental or calculated values of the polarizability ($S_{-2}$) and the expectation value of $[\sum_i \mathbf{r}_i]^2$ (which gives $S_{-1}$). It was in this manner that Dalgarno and Kingston (1960) calculated the index of refraction (and the related Verdet constants) for He, Ne, Ar, Kr, and Xe. The agreement with experimental data was excellent.

### 2. *Average Excitation Energy in High-Energy Collisions*

Another use of the $S_k$ is in the calculation of the average excitation energy $I$ which is used in the Bethe theory (see Mott and Massey, 1949) to calculate the range-versus-energy relations for high-energy particles passing through targets. Dalgarno (1960b) showed that

$$\begin{aligned} \log_e(I) &= \sum_j{}' f_{qj} \log_e(\varepsilon_j - \varepsilon_q) \Big/ \sum_j{}' f_{qj} \\ &= \left[\frac{d}{dk} \log_e(S_k)\right]_{k=0} . \end{aligned} \tag{X.66}$$

He then used a four-constant generalization of Eq. (X.24) to approximate $S_k$. The resulting values of $I$ are in excellent agreement with experiment for the ground states of H, He, Li, and Be.

### 3. *Intermolecular Dispersion Energies*

Landau and Lifshitz (1958, 1960) consider a simple mathematical identity which makes it possible to use sum rule techniques for the calculation of intermolecular dispersion energies,

$$\frac{1}{a+b} = \frac{2}{\pi} \int_0^\infty \frac{ab\, d\omega}{(a^2+\omega^2)(b^2+\omega^2)} . \tag{X.67}$$

For example, consider the usual London (electric dipole) dispersion energy between two atoms $a$ and $b$,

$$E_{ab}^{(\text{dis})} = -C(a_0/R)^6(e^2/a_0), \tag{X.68}$$

where $R$ is the interatomic separation. If the atoms are in the states $q$ and $s$, respectively, and we let $a_{jq} = \varepsilon(a)_j - \varepsilon(a)_q$ and $b_{ks} = \varepsilon(b)_k - \varepsilon(b)_s$, then the usual expression [see Section IV,B and Eq. (IV.49)] for the constant $C$ is

$$C = \frac{3}{2} \sum_j{}' \sum_k{}' \frac{f(a)_{qj} f(b)_{sk}}{a_{jq} b_{ks}(a_{jq} + b_{ks})}, \tag{X.69}$$

where $f(a)_{qj}$ and $f(b)_{sk}$ are the oscillator strengths of $a$ and $b$, respectively. Because of the term $(a_{jq} + b_{ks})$ in the denominator, the double summation cannot be factored into two single sums and the sum rule techniques applied. However, Mavroyannis and Stephen (1962) showed that, using Eq. (X.67), Eq. (X.69) can be rewritten in the form [39a]

$$C = \frac{3}{\pi} \int_0^\infty B_a(\omega) B_b(\omega)\, d\omega, \tag{X.70}$$

where

$$B_a(\omega) = \sum_j{}' \frac{f(a)_{qj}}{a_{jq}^2 + \omega^2} \tag{X.71}$$

and

$$B_b(\omega) = \sum_k{}' \frac{f(b)_{qj}}{b_{jq}^2 + \omega^2}. \tag{X.72}$$

In the notation of Eq. (X.18), $B(\omega) = \alpha(i\omega/h)$, the polarizability for an imaginary angular frequency $\omega$.

For each of the molecules, the functions $B(\omega)$ are well-behaved and can be determined with the use of the sum rule techniques.[39b] From Eq. (X.19), the definition of the oscillator strengths, $B(\omega)$ can be written in the form

$$B(\omega) = \frac{2}{3} \sum_j{}' \frac{(\varepsilon_j - \varepsilon_q)\langle \psi_q, \boldsymbol{\mu}\psi_j \rangle \cdot \langle \psi_j, \boldsymbol{\mu}\psi_q \rangle}{(\varepsilon_j - \varepsilon_q)^2 + \omega^2}, \tag{X.73}$$

where $\boldsymbol{\mu}$ is the vector dipole moment. From Eq. (X.11),

$$(\varepsilon_j - \varepsilon_q)\langle \psi_q, \boldsymbol{\mu}\psi_j \rangle = \langle \psi_q, [\boldsymbol{\mu}, H_0]\psi_j \rangle. \tag{X.74}$$

Furthermore, we can define a vector function $\mathbf{F}(\omega)$ which satisfies the partial differential equation

$$\{[H_0, [H_0, \mathbf{F}(\omega)]] + \omega^2[\mathbf{F}(\omega) - \langle \psi_q, \mathbf{F}(\omega)\psi_q \rangle]\}\psi_q = (\boldsymbol{\mu} - \langle \psi_q, \boldsymbol{\mu}\psi_q \rangle)\psi_q, \tag{X.75}$$

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[39a] Actually, Mavroyannis and Stephen used a field theory approach to the intermolecular forces and obtained Eq. (X.70) first, then showed that it is equivalent to Eq. (X.69). Linder (1962) and Linder and Hoernschmeyer (1964) have obtained similar results using Kramer's fluctuating reaction field techniques.

[39b] The $\alpha(i\omega/h)$ can be determined much more easily by the time-dependent perturbation methods of Section IX. Here $i\dot{\Phi} = [H_0 + W\exp(-\omega t)]\Phi$ where, to the first approximation, $\Phi = [\psi + (\phi + i\theta)\exp(-\omega t)]\exp(-i\varepsilon_q t)$. The real and the imaginary first-order equations are then

$$(H_0 - \varepsilon_q)\phi - \omega\theta + W\psi = 0 \quad \text{and} \quad (H_0 - \varepsilon_q)\theta + \omega\phi = 0.$$

It follows that

$$\phi = \sum_j \psi_j \langle \psi_j, W\psi_q \rangle (\varepsilon_q - \varepsilon_j)[(\varepsilon_q - \varepsilon_j)^2 + \omega^2]^{-1}.$$

Thus, $\alpha_{xx}(i\omega/h) = -2\langle \psi, W\phi \rangle$ where $W = \mu_x - \langle \psi, \mu_x\psi \rangle$. The two coupled equations correspond to a factorization of Eq. (X.75).

so that

$$\langle \psi_j, \mathbf{F}(\omega)\psi_q \rangle = \frac{\langle \psi_j, \boldsymbol{\mu}\psi_q \rangle}{(\varepsilon_j - \varepsilon_q)^2 + \omega^2}. \tag{X.76}$$

Equation (X.73) then becomes, with the use of Eqs. (X.74) and (X.76),

$$\begin{aligned} B(\omega) &= \frac{2}{3} \sum_j{}' \langle \psi_q, [\boldsymbol{\mu}, H_0]\psi_j \rangle \cdot \langle \psi_j, \mathbf{F}(\omega)\psi_q \rangle \\ &= \frac{2}{3} \langle \psi_q, [\boldsymbol{\mu}, H_0] \cdot \mathbf{F}(\omega)\psi_q \rangle. \end{aligned} \tag{X.77}$$

Or, if we restrict ourselves to the electronic Hamiltonian, Eq. (X.33), and use Eq. (X.34),

$$B(\omega) = -\frac{2}{3} \sum_{l=1}^{n} \langle \psi_q, \nabla_l \cdot [\mathbf{F}(\omega)\psi_q] \rangle. \tag{X.78}$$

Here $n$ is the number of electrons in the molecule. Equations (X.77) and (X.78) are new and have not been applied to any specific example.

There are two limits in which the value of $B(\omega)$ is known:

(1) for $\omega = 0$, using Eq. (X.27),

$$B(0) = S_{-2} = \alpha, \text{ the mean polarizability;} \tag{X.79}$$

(2) in the limit as $\omega \to \infty$,

$$\omega^2 B(\omega) = S_0 = n, \text{ the number of electrons in the molecule.} \tag{X.80}$$

Mavroyannis and Stephen (1962) use Eqs. (X.79) and (X.80) to give a simple approximation to $B(\omega)$,

$$\tilde{B}(\omega) = n\alpha(n + \alpha\omega^2)^{-1}. \tag{X.81}$$

This leads to the approximate expression for $C$,

$$\tilde{C} = \frac{3}{2} \frac{\alpha_a \alpha_b}{(\alpha_a/n_a)^{\frac{1}{2}} + (\alpha_b/n_b)^{\frac{1}{2}}}. \tag{X.82}$$

For the interaction of two hydrogen atoms in their ground state, this gives $\tilde{C} = 7.16$, whereas the exact calculated value is $C = 6.50$. For rare gas atoms through Xe, the value of $C$ seems to agree within 30–40% with the experimental Lennard-Jones potential parameter. A somewhat better approximation for $B(\omega)$ [and, hence, of $C$] is obtained by explicitly evaluating the first few terms in $B(\omega)$ and approximating the remainder,

$$\tilde{B}(\omega) = \sum_{j=1}^{k}{}' \frac{f_{qj}}{(\varepsilon_j - \varepsilon_q)^2 + \omega^2} + \frac{J_k}{K_k + \omega^2}. \tag{X.83}$$

Here the constants $J_k$ and $K_k$ are adjusted so as to satisfy the two limiting conditions, Eqs. (X.79) and (X.80), and have values which depend upon $k$, the number of terms considered explicitly. Thus, for the two hydrogen atoms, considering the $1s \to 2p$, $1s \to 3p$, and $1s \to 4p$ transitions explicitly, Mavroyannis and Stephen (1962) obtained $\tilde{C} = 6.66$, a big improvement.

Mavroyannis and Stephen (1962) also determined the magnetic dipole dispersion interaction energy terms which are usually neglected. Letting $\mathbf{M}$ be the magnetic dipole operator,

$$\mathbf{M} = \frac{e}{2mc} \sum_l \mathbf{r}_l \times \mathbf{p}_l. \tag{X.84}$$

There are three types of magnetic dipole dispersion interaction terms,

$$U_2 = -\frac{4}{3R^6} \sum_j{}' \sum_k{}' \frac{[\langle \psi_q, \boldsymbol{\mu}\psi_j \rangle \cdot \langle \psi_j, \mathbf{M}\psi_q \rangle]_a [\langle \psi_s, \boldsymbol{\mu}\psi_k \rangle \cdot \langle \psi_k, \mathbf{M}\psi_s \rangle]_b}{(a_{jq} + b_{ks})}, \tag{X.85}$$

$$U_3 = \frac{2}{9R^4} \sum_j{}' \sum_k{}' \frac{a_{jq} b_{ks}}{\hbar^2 c^2} \left[ \frac{|\langle \psi_q, \boldsymbol{\mu}\psi_j \rangle|_a^2 |\langle \psi_s, \mathbf{M}\psi_k \rangle|_b^2}{a_{jq} + b_{ks}} + \frac{|\langle \psi_q, \mathbf{M}\psi_j \rangle|_a^2 |\langle \psi_s, \boldsymbol{\mu}\psi_k \rangle|_b^2}{a_{jq} + b_{ks}} \right], \tag{X.86}$$

$$U_4 = -\frac{2}{3R^6} \sum_j{}' \sum_k{}' \frac{|\langle \psi_q, \mathbf{M}\psi_j \rangle|_a^2 |\langle \psi_s, \mathbf{M}\psi_k \rangle|_b^2}{a_{jq} + b_{ks}}. \tag{X.87}$$

$U_2$ corresponds to an interaction energy between two optically active molecules. If one of the molecules is replaced by its mirror image, the sign of $U_2$ changes. Thus $U_2$ may be important in biological specificities. The values of $U_2$, $U_3$, and $U_4$ are generally smaller than $-C/R^6$. However, the same sum rule techniques could be used to express these magnetic dispersion interaction terms as are considered here for the electric dipole dispersion interaction.

At extremely large separations, $R > hc|a_{qj}|^{-1}$ or $hc|b_{sk}|^{-1}$ for any $j$ or $k$, relativistic corrections become important. Mavroyannis and Stephen (1962) and also Dzialoshinskii (1957) give the interaction terms at large separations. Of particular interest is the behavior of resonant collisions at large separations, where Stephen (1964) found that the interaction energy varies as $R^{-1}\exp(-bR)$ where $b$ is a constant. Indeed, for resonant collisions, the correction to the Born–Oppenheimer approximation under some conditions may be large enough to make the concept of intermolecular forces unusable.

## XI. Applications

In the preceding sections we have been mainly concerned with the basic *formalism* of perturbation theory. In this section we present an annotated bibliography of recent *applications* of perturbation theory to atomic and molecular problems, these applications, for the most part, being ones which make use of the "new techniques" which we have discussed in the previous Sections. We have left our bibliography quite incomplete in the general areas of electrical and magnetic effects. However the calculation of atomic polarizabilities and shielding factors has recently been reviewed by Dalgarno (1962), and the calculation of the magnetic susceptibilities of molecules has for our purposes recently been reviewed by Karplus and Kolker (1963a; see also Hoyland and Parr, 1963).

Since many of the papers have reference to the $1/Z$ method and the Hartree–Fock approximation, it will be useful to discuss these before we proceed.

### A. The $1/Z$ Expansion (Hylleraas, 1930)[40] and the Shielding Approximation (Layzer, 1959; Dalgarno and Stewart, 1960b) for Atoms

In the $1/Z$ expansion $\lambda V$ is taken to be the Coulomb interaction between the electrons. To see that for an atom this is indeed an expansion in powers of $1/Z$, we have only to note that, if in the standard nonrelativistic Hamiltonian we make the canonical transformation $\mathbf{r}_i \to \mathbf{r}_i/Z$, $\mathbf{p}_i \to Z\,\mathbf{p}_i$, then we find that

$$\frac{H}{Z^2} = \sum_i \left(\frac{p_i^2}{2m} - \frac{e^2}{r_i}\right) + \frac{1}{Z}\sum_{i>j}\frac{e^2}{r_{ij}},$$

which proves the assertion. In many papers, what we have considered as a canonical transformation is duplicated by a change of units and $H/Z^2$ is

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[40] See also Sinanoglu (1961c), where the equations for $\psi^{(1)}$, $E^{(1)}$, $E^{(2)}$, and $E^{(3)}$ are analyzed in detail with special emphasis on the physical interpretation of the quantities which appear. For an extension to relativistic systems see Layzer and Bachall (1962).

in effect taken as the Hamiltonian in those units. The $1/Z$ method offers a convenient method of surveying an entire isoelectronic sequence.

In a similar way the shielding approximation, in which one identifies $\lambda V$ with $-(Z-\zeta)\sum_i e^2/r_i + \sum_{(i>j)} e^2/r_{ij}$ (for the numerical value of $\zeta$ see below), can be shown to be an expansion in powers of $(Z-\zeta)/\zeta$ and $1/\zeta$.

Actually, however, one need not make separate calculations for the shielding approximation (Dalgarno and Stewart, 1960b). It can be derived from the $1/Z$ expansion. Namely, the exact average value of any operator which is not itself an explicit function of $\zeta$ must be independent of $\zeta$. Call this average $A(Z)$. Then all one need do is take the series for this furnished by the $1/Z$ procedure, reexpand it around $Z=\zeta$, and regroup the terms according to powers of $(Z-\zeta)/\zeta$ and $1/\zeta$.[41] We should note however that this procedure is purely formal. For numerical work to avoid rounding-off errors, etc., it will often be desirable to carry out the shielding approximation directly. [We are indebted to G. G. Hall for this remark. See also Fröman and Hall (1961).]

We have said that exact expressions are independent of $\zeta$. However if we just work, say, through the first order, which in practice is often the case if the zero-order term does not vanish, then in general there will be a dependence on $\zeta$ (incidentally there is no $\zeta$ dependence of the energy if we go to second order). Then the question arises: how do we choose $\zeta$? A numerically very satisfactory procedure (Dalgarno and Stewart, 1960b) is to choose that value of $\zeta$ (different for different properties) which makes the first-order correction vanish, i.e., one chooses the stationary value for the particular property in question.

### B. Perturbation Theory and the Hartree–Fock Approximation for Atoms

For simplicity we will discuss only the case of completely closed shells (i.e., closed in the principal quantum number), so that $\Psi_{\mathrm{HF}}$ is a single determinant and the equations have a simple Hamiltonian form. Otherwise, for example, we have the complication of several determinants

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[41] For recent empirical and semiempirical investigations of the $1/Z$ expansion and the shielding approximation, see for example: Crossley and Coulson (1963), Kaufman (1962), Edie and Rohrlich (1962a,b), Scherr *et al.* (1962), Scherr and Silverman (1962), Hall and Rees (1962), Linderberg and Shull (1960), Holøien (1960), Edlén (1960), Johnson and Rohrlich (1959). Analytical expressions and tables of the Slater $F$ and $G$ integrals using screened hydrogenic orbitals are given by Naqvi and Victor (1964). They also use Layzer's method for calculating the optimum screening constants and resulting physical properties of atoms up to Cs.

and/or off-diagonal Lagrange multipliers.[42] However it is true in any case, of course, that a consistent expansion of the relevant quantities which appear in the equations determining the orbitals leads to a well-defined set of equations which can be solved successively. Further, for these equations one can prove interchange theorems, Fröman-like theorems [see (5) below], etc.

As with the exact wave function (see Section XI,A), one derives the $1/Z$ expansion by treating the electron–electron interaction as a perturbation. In the preceding chapters we have assumed that the perturbation is linear in the perturbation parameter. This is, of course, not true in the present application, because within the Hartree–Fock formalism the electron–electron interaction involves the wave function in a nonlinear way. This complicates the algebra but involves no new points of principle: $\psi_{\mathrm{HF}}^{(n)}$ determines $E_{\mathrm{HF}}^{(2n+1)}$, interchange theorems can be proven, variational principles can be derived, etc.

An important feature of the completely closed shell problem is that $H_0$ is nondegenerate, whereas away from completely closed shells $H_0$ is usually nonrotationally degenerate (recall the $l$ degeneracy of the hydrogen atom) and the particular choice of zero-order function singled out by the Hartree–Fock (HF) method is then usually not the correct one, i.e., the one which makes the perturbation diagonal within the degenerate set. For the case of completely closed shells, however, $\mathrm{H}_0$ is nondegenerate, whence we have

$$\Psi_{\mathrm{HF}} = \Psi\left(1 + O\left(\frac{1}{Z}\right)\right). \qquad \text{(XI.1)}$$

Confining ourselves then to this, the simplest case, we have further the following useful theorems [as will be clear if in a general way $\Psi_{\mathrm{HF}} = \Psi\ (1 + O(\lambda))$, then most of the theorems which follow will be true with $1/Z$ replaced by $\lambda$]:

(1) Since $\Psi_{\mathrm{HF}}$ is a variational approximation to $\Psi$, it follows immediately from Eq. (XI.1) that $E_{\mathrm{HF}} = E(1 + O(1/Z^2))$; i.e., the correlation energy begins with $E^{(2)} - E_{\mathrm{HF}}^{(2)}$.[43]

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[42] The unrestricted Hartree–Fock (UHF) method, for example, maintains the Hamiltonian form but at a price (cf. Nesbet (1961)). We will not discuss the UHF method explicitly except to note that in general theorems (3), (4), and (5) below hold with $\Psi_{\mathrm{HF}}$ replaced by $\Psi_{\mathrm{UHF}}$. Also theorems (1) and (2) hold if $\Psi_{\mathrm{UHF}} = \Psi[1 + O(1/Z)]$, i.e., if $\Psi$ is a single determinant in the limit as $Z \to \infty$.

[43] Away from completely closed shells this is no longer necessarily true (see Layzer, 1959; Linderberg and Shull 1960). For a detailed discussion of $E^{(2)} - E_{\mathrm{HF}}^{(2)}$, see Layzer (1963).

(2) From the Brillouin theorem,[44] which tells us that the first-order corrections in Eq. (XI.1) involve no one-particle excitations, it follows that if $W$ is a one-particle operator[45] then[46]

$$\langle \Psi_{\mathrm{HF}}, W\Psi_{\mathrm{HF}} \rangle = \langle \Psi, W\Psi \rangle \left(1 + O\left(\frac{1}{Z^2}\right)\right).$$

(3) From the Brillouin theorem in the form $\langle \Psi', H\Psi_{\mathrm{HF}} \rangle$ where $\Psi'$ is a determinant which differs from $\Psi_{\mathrm{HF}}$ by a single spin orbital [see also Section V,B,1,*b*], it follows that the hypervirial theorem is satisfied for any one-electron operator $W$,[47] i.e., that

$$\langle \Psi_{\mathrm{HF}}, [H, W]\Psi_{\mathrm{HF}} \rangle = 0,$$

since $W\Psi_{\mathrm{HF}}$ can be written as a sum of $\Psi_{\mathrm{HF}}$ and various $\Psi'$ [see also Section V, B,1,*c*].

(4) Since in varying $J$ one does not require any special dependence of the trial function on parameters, it follows from Hurley's general result (1954)[48] that $\Psi_{\mathrm{HF}}$ satisfies various Hellmann–Feynman theorems. Clearly this conclusion is *not* restricted to the case of completely closed shells.

(5) If we denote the orbital energies by $\varepsilon_i$ then, by use of the virial theorem and the Hellmann–Feynman theorem for $\partial E_{\mathrm{HF}}/\partial Z$, one can prove (Fröman, 1958) that

$$(n+1)E_{\mathrm{HF}}^{(n)} = 2\sum_i \varepsilon_i^{(n)}.$$

[44] Brillouin (1933–34) and Møller and Plesset (1934). In the latter paper $\Psi_{\mathrm{HF}}$ is used as a zero-order approximation for $\Psi$ and a formal perturbation calculus is developed with $\lambda V = H - H_{\mathrm{HF}}$. For a detailed exposition of the first-order theory with special attention to the physical interpretation of the various quantities which appear, see also Sinanoglu (1961d).

[45] If we take for $W$ that operator whose expectation value is the one-electron density matrix (see footnote 9a, Section IV,C), then we have the result that for completely closed shells: the occupied Hartree-Fock spin orbitals equal natural spin orbitals to $O(1/Z^2)$. See also Nazaroff and Hirschfelder (1963) and Kutzelnigg (1963).

[46] This was proven for a large class of $W$'s by Møller and Plesset (1934) by showing that the electron charge density is given correctly through $O(1/Z)$. More general proofs have been given by Hall (1961) and by Cohen and Dalgarno (1961b). See also Goodisman (1963a) and Goodisman and Klemperer (1963). Away from completely closed shells the theorem is no longer necessarily true (see Cohen and Dalgarno (1963a).

[47] Away from closed shells one may readily discover which hypervirial theorems are satisfied by using the method of S. T. Epstein and Hirschfelder (1961) and determining those $W$'s for which $\delta\Psi_{\mathrm{HF}} = i\eta W\Psi_{\mathrm{HF}}$ is an allowed variation. In particular, since a uniform change of radial scale is always allowed, it follows that the usual virial theorem will be satisfied.

[48] See also Goodisman (1963b). For more special proofs see Stanton (1960) and Hall (1961).

We conclude our discussion by noting that, although we have been explicitly talking in a "Hamiltonian wave function language," it is also possible, following McWeeny (1962; also Adams, 1962), to do everything via the density matrix.

We now turn to the bibliography.

## C. Energy Levels of Isolated Systems

### 1. *The* $1/Z$ *Expansion for He-like Ions*

(1) Scherr and Knight (1963). Using Hylleraas-like variational principles (see Section V), they calculated the wave function to sixth order and the energy to thirteenth order for the ground states. They use elaborate Hylleraas-like trial functions and claim eight- to nine-place accuracy. The results suggest that the series converges for $Z \geq 0.78$. As mentioned in the Introduction, the series is known to converge for some range of $Z$. Internal checks are provided by the virial theorem and the Hellmann–Feynman theorem for $\partial E/\partial Z$. Expectation values of various operators are given in Scherr and Knight (1964). This work supersedes that reported earlier (Scherr and Knight, 1962).

(2) Knight and Scherr (1963). Elaborate Hylleraas-like trial functions and also configuration-interaction type trial functions are used in the Hylleraas variational principle to calculate the wave function to first order, and hence the energy to third order, for various low-lying excited states. Eight-place accuracy is claimed. First-order corrections to the expectation values of various operators are also calculated.

(3) Perrin and Stewart (1963). Configuration-interaction type wave functions are used in the Hylleraas variational principle to calculate $E^{(2)}$ for various excited states. Calculations are less accurate than in Knight and Scherr (1963).

(4) Sharma and Coulson (1962). Same as Knight and Scherr (1963) above but with less elaborate Hylleraas-type trial functions.

(5) Schwartz (1962). Calculation of $E^{(2)}$ for the ground state using the Hylleraas variational principle. Trial functions of both the Hylleraas and the configuration-interaction type are used to compare the merits of the two approaches

(6) Somerville and Stewart (1962).

Much the same as Schwartz (1962).

### 2. *Hartree–Fock as Zero-Order Approximation*

(7) Kahas and Nesbet (1963). Some estimates of $\Psi - \Psi_{\mathrm{HF}}$ for Li and LiH.

(8) Kelly (1963). $\varepsilon^{(2)}$ and $\varepsilon^{(3)}$, augmented by a selective summation of higher-order effects, are evaluated for Be using expansions in terms of unperturbed eigenfunctions. These expansions are particularly simple to evaluate because, as Kelly shows, the virtual Hartree–Fock states all lie in the continuum, whence the sums are in fact integrals which are readily obtained numerically. Very promising results are found for the correlation energy. In a subsequent paper, Kelly and Sessler (1963) analyze the nature of the "selective summation" in more detail.

(9) A. W. Weiss and Martin (1963). $\varepsilon^{(2)}$ and $\varepsilon^{(3)}$ are calculated for He by using the Hylleraas variational principle. The error in the energy is greater than that for the corresponding $1/Z$ expansion, but expectation values are better for the Hartree–Fock basis than for the hydrogenic.

(10) S. T. Epstein (1964). Alternative choices for the Hartree-Fock Hamiltonian are discussed.

### 3. *The United Atom Expansion*

Bingel (1959, 1963) has proposed a perturbation treatment of diatomic and polyatomic molecules based on the united atom. The perturbation potential is taken to be

$$V = \sum_i \frac{Z}{r_i} - \sum_\alpha \sum_i \frac{Z_\alpha}{r_{\alpha i}},$$

where $Z = \sum_\alpha Z_\alpha$ is the atomic number of the united atom, and $r_{\alpha i}, r_i$ are the distances of the $i$th electron from nucleus $\alpha$. and from the center of nuclear charge. The results of Rellich and Kato discussed in Section XII prove that such a treatment is convergent for small $Z$. Bingel has expanded the first-order perturbation energy in powers of the internuclear distances $R$ through terms in $R^3$ in the general case, and has expressed the coefficients of $R^2$ and $R^3$ in terms of the charge density at the center of the united atom and related properties.

The difficulty of a series expansion in powers of $R$ has been discussed by Steiner (1961) and confirmed in detail by Byers Brown and Steiner (1963, 1964) for the case of one-electron diatomic molecules, such as the hydrogen molecule-ion. These authors show that:

(a) Bingel's analysis gives an incorrect result for the coefficient of $R^3$ in the electronic energy;

(b) the electronic energy $W(R)$ is not an analytic function of $R$ at $R = 0$, but has the form

$$W(R) = W_0 + R^2W_2 + R^3W_3 + R^4W_4 + R^5W_5 + R^5(\log R)W_5' + \cdots,$$

where the $W_n$ are independent of $R$.

(11) Buckingham and Duparc (1962). Variational treatments for the very short-range interaction energy of H + H and He + He are described, and the electronic energy is expanded as a polynomial in $R$. The value of $W_2$ is given approximately by Bingel's formula, but $W_3$ appears to be twice as large as that predicted by Bingel. Nevertheless the united atom nuclear cusp condition, used by Bingel (1963) to relate $W_2$ and $W_3$, is approximately satisfied by the variational wave functions.

(12) Duparc and Buckingham (1964). The work in (11) is extended to the system H + He. The results are similar to those in (11), and it is shown that $W_2$ and $W_3$ satisfy approximately the relation $W_3 = -ZW_2$ found by Byers Brown and Steiner (1963) for the one-electron case.

(13) Hauk *et al.* (1963). A single-center perturbation method is proposed for obtaining the first-order wave functions of hydrides of the type $XH_n$. The first-order perturbation equations are solved in closed form starting from a single-center Slater determinant. References to earlier single-center calculations are given.

### 4. *Long-Range Forces between Atoms*

Various properties of one-electron diatomic molecular ions have been calculated with the unperturbed system consisting of an electron and a nucleus [but see items (14) and (19) below]. Quite high-order (asymptotic) expansions have been found in powers of $1/R$ where $R$ is the nuclear separation.

(14) Robinson (1961). Attempts at a more symmetric approach to $H_2^+$.

(15) Robinson (1958). $E^{(2)}$ for various states of $H_2^+$ is determined without prior expansion in $1/R$ by use of spheroidal coordinates. Earlier authors used spherical coordinates exclusively. The results contain errors (see Dalgarno and Stewart, 1960c).

(16) Dalgarno and Lynn, (1957b). Expansion of $E^{(2)}$ in powers of $1/R$ is carried out after the perturbation calculation, so that the asymptotic character of this expansion is clearly displayed.

(17) Dalgarno and Stewart (1957). The $2p\pi$ state of $HeH^{2+}$.

(18) Dalgarno and Stewart (1956b). The $1s\sigma$ and $2p\sigma$ states of $HeH^{2+}$.

(19) Dalgarno and Lynn (1956). A more symmetric form of perturbation theory is applied to $H_2^+$.

(20) Dalgarno and Lewis (1956). Ground state of $H_2^+$ and some comments on $H_2$. It is pointed out that convergence of the perturbation theory they have used is poor because the actual problem is degenerate whereas $H_0$ is not.

(21) Musher (1963). The differential equation for $\psi^{(1)}$ is solved approximately for the dipole–dipole interaction between well-separated atoms. The van der Waals energy and various expectation values are calculated.

(22) Dahler and Hirschfelder (1956). Treatment of long-range interactions especially for asymmetrical molecules. Careful treatment of degeneracy problems.

(23) Aono (1958). Frequently charge transfer forces cannot be neglected by comparison with dispersion forces.

### D. Expectation Values

#### 1. *Double Perturbation Theory and the 1/Z Expansion; also the Shielding Approximation for the Ground State of the Helium Sequence*

(1) Dalgarno and Stewart (1960b).
(2) Dalgarno and Stewart (1960a).
(3) Dalgarno and Stewart (1958).

#### 2. *The Schwartz—Method for He-like Ions*

(4) R. J. Weiss (1963). Properties of the ground state and first excited state are calculated. Because of the choice of $\tilde{\psi}^{(0)}$, the method becomes essentially identical to the first-order screening approximation with a particular choice of $\zeta$.

(5) Schwartz (1959b). Properties of the ground state are calculated. Because of the choice of $\tilde{\psi}^{(0)}$, what are calculated in effect are various $E^{(1,1)}$ and $E^{(1,2)}$ in the shielding approximation with a particular value of $\zeta$.

#### 3. *Long-Range Expansions for One-Electron Diatomic Molecular Ions*

(see also C4 above).

(6) Dalgarno and Stewart (1960c). Various oscillator strengths of $HeH^{2+}$ are calculated.

(7) Dalgarno *et al.* (1960b). The hyperfine structure of $H_2{}^+$.

### E. Time-Dependent Perturbation Theory

References are all given in Section IX.

### F. Perturbation Theory within the Hartree–Fock Approximation

The papers which follow are concerned with the properties of isolated atoms. For a discussion of atoms in external fields, polarizability, etc., we refer again to Dalgarno's review (1962). Unless otherwise noted, it is always a $1/Z$ expansion which has been used.

(1) Dalgarno (1960a). An upper bound for $E^{(2)}$ is calculated variationally for He.

(2) Linderberg (1961). $\psi^{(1)}$ and the energy up to third order are calculated for some two-, three- and four-electron states. $\psi^{(1)}$ is found as an expansion in Laguerre functions.

(3) Cohen and Dalgarno (1961a). $\psi^{(1)}$ and $E^{(2)}$ for the He ground state are found in closed form.

(4) Cohen and Dalgarno (1961c). The $1/Z$ expansion formalism is developed in detail, including interchange theorems, and applied to the He and Be isoelectronic sequences. The expectation values of several one-electron operators are calculated through first order. The shielding approximation is also used.

(5) Sharma and Coulson (1962). $\psi^{(1)}$ is found for various two-electron states. Linderberg's (1961) expansion technique is used.

(6) Perrin and Stewart (1963). Same problem as Sharma and Coulson (1962), but $\psi^{(1)}$ is found only approximately.

(7) Sharma (1962). The $1/Z$ perturbation method is developed for the unrestricted Hartree–Fock approximation and applied to Li.

(8) Cohen and Dalgarno (1963c). Low-lying states of the Li sequence are discussed. $E^{(2)}$ and various expectation values are calculated. An interchange theorem for off-diagonal matrix elements (see Section VIII) is proven and applied.

(9) Cohen (1963). Following up the work of Cohen and Dalgarno (1961a), $\psi^{(1)}$ is found in closed form for $1s$, $2s$, and $2p$ atomic orbitals.

## XII. Existence and Convergence of the Perturbation Series (by Theodore W. Palmer)

The object of this section is to review the rigorous mathematical theory developed by Rellich[49], Kato,[50] and others[51] in order to justify the use of perturbation theory and to determine its scope and limitations. Before

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[49] The pioneering research by Rellich is reported in a series of five papers (Rellich, 1936a,b, 1939, 1940, 1942). An introduction to this theory is contained in a later publication (Rellich, 1953a). For reviews of subsequent work, see Rellich, 1952, 1953b, and 1955.

[50] The most complete discussion of perturbed operators in Hilbert space with various applications to quantum mechanics is by Kato (1951a). An abridged version of the theory is also available (Kato, 1949b, 1950). Various related questions are treated in the other papers of Kato listed in the references.

[51] See Friedrichs (1948, 1963), Heinz (1951), Ikebe and Kato (1962), Sz. Nagy (1947), Schröder (1953), Titchmarsh (1958), Speisman (1957). Perturbation theory is treated from a different mathematical viewpoint in Primas (1961) and Murray (1962).

proceeding, however, it will be well to review briefly the important and perhaps unfamiliar mathematical concepts involved. These may be introduced by discussing the nature of the Schrödinger (nonrelativistic) Hamiltonian operator $H$ for an $N$-particle atom, molecule, or crystal which has the form

$$H = -\sum_i \frac{1}{2m_i} \nabla_i^2 + \sum_{i>j}\sum \frac{e_i e_j}{r_{ij}}, \tag{XII.1}$$

where $e_i$ and $m_i$ are the charge and mass of the $i$th particle. Indeed, since the determination and interpretation of the spectrum and eigenfunctions of $H$ is one of the most fundamental problems of quantum chemistry, and since either the whole or a part of $H$ is the most common choice for an unperturbed Hamiltonian, a discussion of the mathematical properties of $H$ is a necessary preliminary to any discussion of perturbation theory.

## A. Mathematical Properties of *H*

A careful study of the properties of the operator $H$ must begin with a description of the set of functions on which it operates. To gain mathematical rigor, it is convenient to formulate the problem within the theory of Hilbert space.[52] We may realize the abstract separable Hilbert space $\mathfrak{H}$ as the set of all square-integrable complex valued functions $\phi$ on the configuration space of $H$. Then it is clear that the operator $H$ of Eq. (XII.1) is unbounded and cannot be defined on all of $\mathfrak{H}$, since there are functions $\phi$ in $\mathfrak{H}$ with arbitrarily small norm $\|\phi\| \equiv \langle\phi, \phi\rangle^{\frac{1}{2}}$ for which $\|H\phi\|$ is arbitrarily large or infinite.

In general an *operator* $A$ in Hilbert space assigns a unique element $A\phi$ to each element $\phi$ in a subset $\mathfrak{D}_A$ of $\mathfrak{H}$ called the *domain* of $A$. Different choices of the domain give rise to different operators. Thus, before $H$ can be considered as a well-defined operator in Hilbert space, we must specify the domain on which it operates. This is a clear-cut and tractable problem which replaces the much more difficult choice of boundary and differentiability conditions in the theory of differential equations.

In this section, as in any discussion of quantum mechanics, we require all operators $A$ to be *linear*. Thus $\mathfrak{D}_A$ must be a linear manifold, and $A(a\phi + b\psi) = aA\phi + bA\psi$ for all $\phi, \psi$ in $\mathfrak{D}_A$ and all complex numbers $a,b$.

Entirely too little is known about an operator unless it is at least defined on a *dense* domain, i.e., one which contains arbitrarily good approximations to any function in $\mathfrak{H}$. Beyond this basic requirement, which we assume

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[52] Further information on the concepts outlined in this section may be obtained from the classic books of Stone (1951) and von Neumann (1955).

for all operators in this section, the theory depends on successfully extending the domain, so that the operator is self-adjoint in the sense defined below.

Suppose there is a sequence of functions $\phi_n$ in the domain of an operator $A$, and that both of the sequences $\phi_n$ and $A\phi_n$ converge in the mean. It is reasonable to expect that the domain of $A$ may be extended to include the limit $\phi$ of the sequence $\phi_n$, with $A\phi$ defined as the limit of $A\phi_n$. When $A$ is *Hermitian*, i.e., when $\langle A\phi, \psi\rangle = \langle\phi, A\psi\rangle$ for all $\phi, \psi$ contained in $\mathfrak{D}_A$, then this is actually possible, and the resulting operator is still Hermitian. If the domain of an operator $A$ is enlarged by the inclusion of all such extensions, then the new operator is called the *closure* of $A$. An operator which is equal to its own closure is called *closed*.

Most closed Hermitian operators can still be extended in infinitely many ways. The various extensions have different eigenvalues and eigenfunctions, and thus correspond to different operators in the physical sense as well as in the strict mathematical sense. Those Hermitian operators which possess a unique "complete"[53] set of eigenfunctions are exactly the self-adjoint operators. An operator $A$ is called *self-adjoint* if, whenever $\psi$ and $\chi$ satisfy $\langle A\phi, \psi\rangle = \langle\phi, \chi\rangle$ for all $\phi$ in $\mathfrak{D}_A$, then $\psi$ is contained in $\mathfrak{D}_A$ and $A\psi = \chi$. Thus, a Hermitian operator is self-adjoint if its domain has been extended so far that it includes, and therefore equals, the domain of its adjoint. A self-adjoint operator is closed, since obviously no further extension could remain Hermitian, and thus the closure must be the operator itself. Since the closure of an operator is a uniquely defined extension, an operator with self-adjoint closure can often play the role of a self-adjoint operator. Such an operator is called *essentially self-adjoint*.

A Hermitian operator $A$ for which a real number $e$ exists such that $\langle A\phi, \phi\rangle \geq e\langle\phi, \phi\rangle$ for all $\phi$ in $\mathfrak{D}_A$ is said to be bounded below or *half-bounded*. Study of the corresponding quadratic form $\langle A\phi, \phi\rangle$ leads to the definition of a self-adjoint extension of $A$ called the Friedrichs extension (for further details see Friedrichs, 1934). Even when $A$ is not essentially self-adjoint, and thus has infinitely many self-adjoint extensions, the Friedrichs extension is unique. Thus in some cases half-bounded Hermitian operators may also substitute for their self-adjoint Friedrichs extension.

With this introduction we can discuss an important paper of Kato (1951b) in which he proves that operators of a general type, including the

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[53] By a "complete" set of eigenfunctions we mean that the operator belongs to a resolution of the identity. For a definition and discussion of this concept see von Neumann (1955, especially Chapter II, Sections 8 and 9).

Hamiltonian operator $H$ of Eq. (XII.1), are essentially self-adjoint when defined on any reasonable domain. Explicitly, the domain is merely required to contain the dense linear manifold generated by products of Hermite orthogonal functions of the Cartesian coordinates of configuration space. The proof depends on writing $H$ as $T + U$, where $T$ is the kinetic and $U$ the potential energy operator. The domain $\mathfrak{D}_c$ of the closure $T_c$ of $T$ can be easily characterized in terms of functions in momentum space, where $T_c$ is clearly self-adjoint. A Fourier transform changes these momentum functions back into functions in configuration space. It is then proved that numbers $a'$ and $b'$ can be found such that

$$\|U\phi\| \leq a'\|\phi\| + b'\|T_c\phi\| \qquad \text{(XII.2)}$$

for all $\phi$ in $\mathfrak{D}_c$. In fact, no matter how small a positive number is chosen for $b'$, a number $a'$ can be found for which the inequality is true. It follows from this inequality that $H = T + U$ is defined on $\mathfrak{D}_c$ and is self-adjoint there.

This is not the place to pursue the generalizations and many important consequences of this paper. The interested reader should consult the very readable original work of Kato (1951b), and also Ikebe and Kato (1962), and Kato (1951c, 1952, 1956). Results which are important for perturbation theory will be mentioned as required.

### B. Perturbation Series

The Rayleigh–Schrödinger perturbation series are defined in Section II. The formal procedure followed there leaves unanswered questions about the properties and interpretation of the series. The study of perturbed operators in Hilbert space shows some cases in which it can be proved that the series converge to eigenvalues and eigenfunctions of the perturbed operators. In many other cases these power series define analytic functions inside circles of convergence with nonzero radii. These functions can usually be analytically continued along the real axis to the desired value of the perturbation parameter, and the resulting values are again eigenvalues or eigenfunctions of the perturbed operator. We will describe both of these situations as *regular* perturbation. There are also cases in which it is possible to show that partial sums are asymptotic approximations to discrete eigenvalues and eigenfunctions, or to the ghosts left behind when these have disappeared into the continuous spectrum. These asymptotic approximations are sometimes useful even if there are only a finite number of well-defined finite terms in the series.

### 1. *Regular Perturbation*[54]

We will consider operators of the form

$$H(\lambda) = \sum_{n=0}^{\infty} \lambda^n H_n = H_0 + \lambda H_1 + \lambda^2 H_2 + \cdots, \tag{XII.3}$$

where all of the $H_n$ are Hermitian and $\lambda$ takes on only real values. Thus this theory may apply to any perturbation problem in which the perturbation parameter $\lambda$ can be chosen so that the perturbed operator is such a power series. Operators which depend on a parameter in a nonanalytic fashion do not seem to have been extensively studied.

Rather than give the most general conditions under which the perturbation series has a nonzero radius of convergence, we will mention two sufficient conditions[55] which seem to cover most applications in quantum chemistry. Rellich (1939) has shown that the first condition is only slightly more restrictive than the most general hypotheses.

*Condition* 1: *The operator* $H_0$ *is self-adjoint on* $\mathfrak{D}$, *each* $H_n$ *is Hermitian on a domain containing* $\mathfrak{D}$, *and there exist nonnegative constants a,b,c, such that*

$$\|H_n\phi\| \leq c^{n-1}\{a\|\phi\| + b\|H_0\phi\|\} \tag{XII.4}$$

*for all* $\phi$ *in* $\mathfrak{D}$ *and all* $n \geq 1$.

*Condition* 2: *The operators* $H_n$ *are Hermitian on the same domain* $\mathfrak{D}$, *and there are real constants a,b,c, and e, with b,c nonnegative, such that*

$$e\langle\phi, \phi\rangle \leq \langle H_0\phi, \phi\rangle, \tag{XII.5}$$

$$|\langle H_n\phi, \phi\rangle| \leq c^{n-1}\{a\langle\phi, \phi\rangle + b\langle H_0\phi, \phi\rangle\} \tag{XII.6}$$

*for all* $\phi$ *in* $\mathfrak{D}$ *and all n.*

When Condition 1 is satisfied we take $H(\lambda)$ to be the operator defined by Eq. (XII.3) on $\mathfrak{D}$ for $|\lambda| < (b + c)^{-1}$. When Condition 2 is satisfied we must choose $H(\lambda)$ to be the Friedrichs extension of the half-bounded, but possibly non–self-adjoint, operator defined by Eq. (XII.3) on $\mathfrak{D}$ for $|\lambda| < (b + c)^{-1}$. In both cases $H(\lambda)$ will be self-adjoint where defined.

The form of the inequalities Eq. (XII.4) and Eq. (XII.6) is dictated by the need for convergence, by the unboundedness of $H_0$ and $H_n$, and by the

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[54] Rellich (1936a) discusses regular perturbation for bounded operators. Rellich (1939, 1940, 1942, 1953a), Kato (1949b, 1951a), Sz. Nagy (1947), Schröder (1953), and Speisman (1957) all discuss regular perturbation for unbounded operators, although the last two sources deal only with operators of the form $H_0 + \lambda H_1$.

[55] Condition 1 is discussed in all of the papers mentioned in footnote 54 except that of Speisman. Condition 2 is taken from Kato (1951a).

possibility that $H_0$ may have many eigenfunctions with small or zero eigenvalues. One or all of these conditions can often be proved in quantum mechanical perturbation problems. But first let us examine the consequences of these conditions.

*a. Theorem on Regular Perturbation.* Let Condition 1 or Condition 2 be fulfilled, and let $H(\lambda)$ be the appropriate unique self-adjoint extension of $\sum_{n=0}^{\infty} \lambda^n H_n$.

(I) Let $E$ be an isolated nondegenerate eigenvalue of $H_0$. Then there exists a $\rho > 0$ such that:

(*i*) for $|\lambda| < \rho, H(\lambda)$ has a nondegenerate eigenvalue $E(\lambda)$ such that $E(0) = E$, and a corresponding eigenfunction $\Psi(\lambda)$;

(*ii*) both $E(\lambda)$ and $\Psi(\lambda)$ can be expanded in power series convergent for $|\lambda| < \rho$.

(II) Let $E$ be the only point of the spectrum of $H_0$ in the interval $(E - d, E + d)$ and let $E$ be an eigenvalue with finite degeneracy[56] $g$. For each $d'$ with $0 < d' < d$, there exists a $\rho$ greater than zero such that:

(*i*) for $|\lambda| < \rho$ there are exactly $g$ eigenvalues $E_j(\lambda)$ (counting multiplicity) of $H(\lambda)$ in the interval $(E - d', E + d')$;

(*ii*) each of these eigenvalues, together with a complete set of their eigenfunctions, $\Psi_j(\lambda)$, can be expanded in a power series convergent for $|\lambda| < \rho$.

(III) In either of the above cases the eigenvalues $E_j(\lambda)$ and eigenfunctions $\Psi_j(\lambda)$ can be continued analytically as functions of $\lambda$ on a region containing the interval of the real axis for which $H(\lambda)$ is defined and on which $E_j(\lambda)$ does not become a point of the continuous spectrum or an eigenvalue of infinite degeneracy of $H(\lambda)$.

This theorem justifies the Rayleigh–Schrödinger perturbation series formulas for regular perturbation. The analytic character of the eigenvalues and eigenfunctions, which usually extends along the real axis far beyond the radius of convergence, guarantees a smooth transition between unperturbed and perturbed states.

Rough quantitative information can also be drawn from these conditions.[57] Lower bounds for the radii of convergence of the series and

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[56] The theorem is still valid when $g$ is allowed to take on the value zero. This is interpreted to mean that there is no point of the spectrum in the interval.

[57] Rellich (1940) contains the first estimates in the general unbounded case. The most direct proofs are in Kato (1951a) and Sz. Nagy (1947), but the different formulas obtained by Schröder (1953) and Speisman (1957) may be superior in some cases when $H_0 + \lambda H_1$ is considered.

upper bounds for the size of individual terms depend on the constants $a,b,c,d$, and $E$. Because of the very general nature of the theory, and the crude methods used in its applications to specific examples, these bounds are probably very poor. When $\lambda$ is smaller than the radius of convergence, estimates of the error

$$\left| E(\lambda) - \sum_{n=0}^{N} \lambda^n E^{(n)} \right|$$

can be given but these are not useful in practical problems.

(*b*) *Applications.* All the applications of perturbation theory to quantum chemistry involve the operator $H$ of Eq. (XII.1) or some part of it. The most important cases are those in which the perturbation contains the electron repulsion terms or the difference between many-center and one-center Coulomb potentials. These cases correspond to a division of $H$ into the form

$$H = H_0 + \lambda H_1, \tag{XII.7}$$

where

$$H_0 = T + U_0, \qquad H_1 = U - U_0,$$

and $\lambda = 1$ is the value of interest. Neither the unperturbed potential $U_0$ nor the perturbation $H_1$ contains singularities worse than Coulomb poles. Kato (1951b) has proved that $U_0$ and $H_1$ each satisfy an inequality of the type of Eq. (XII.2), and a little algebraic manipulation shows that a number $a$ can always be found so that

$$\|H_1\phi\| \leq a\|\phi\| + b\|H_0\phi\| \tag{XII.8}$$

for arbitrarily small positive values of $b$. Therefore, Condition 1 is satisfied, and hence the operator $H_0 + \lambda H_1$ is defined and self-adjoint for all real values of $\lambda$, and its eigenvalues and eigenfunctions are analytic wherever they do not intersect the continuous spectrum.

This conclusion applies in particular to the well-known $1/Z$ expansion for atoms, which has been so widely used in the recent developments. The transformation of the Schrödinger equation into the form Eq. (XII.7) with $\lambda = 1/Z$ is given in Section XI. As noted above, the radii of convergence guaranteed by the general theory are usually quite poor. Even in the particular case of a two-electron atom, Kato (1951a, p. 170) has only been able to prove that for the lowest state the $1/Z$ expansion converges for $Z > 7.6$ (which corresponds physically to the oxygen cation $0^{6+}$). However the detailed calculations of Scherr and Knight (1963), going as far as the term in $(1/Z)^{13}$ in the energy expansion, suggest that the series converges for $Z = 0.78$, which includes the negative hydrogen ion $H^-$.

### 2. *Asymptotic Perturbation Series*

The theory of regular perturbation does not include all applications. In particular there are cases when only a finite number of terms of the perturbation series are well-defined and finite. Kato (1951a) has developed a theory of asymptotic perturbation series which provides criteria for the usefulness of perturbation theory in some nonregular cases. For a regular perturbation series the errors divided by $\lambda^M$,

$$\left|E(\lambda) - \sum_{n=0}^{M} \lambda^n E^{(n)}\right| \Big/ \lambda^M$$

and

$$\left\|\phi(\lambda) - \sum_{n=0}^{M} \lambda^n \phi^{(n)}\right\| \Big/ \lambda^M,$$

approach zero as $\lambda$ approaches zero. We denote this by calling the errors $O(\lambda^M)$. It is this behavior of the partial sums of the perturbation series which Kato generalizes. The rather complicated hypotheses and conclusions of this theory are best summarized by Kato's statement "roughly speaking, perturbation method gives correct results in the sense of asymptotic expansions as long as the necessary quantities are calculated by operations in Hilbert space." The results are based on Kato's generalized variational method (Kato, 1949a).

### 3. *Perturbations Leading to a Continuous Spectrum*

Another application of perturbation theory is to problems like the Stark effect in which a discrete level of $H_0$ "disappears into the continuum" with the application of the perturbation $H_1$. The theory of the Auger effect and the calculation of the Lamb shift for the excited states of atoms furnish other examples.

Here then one not only has the question: In what sense, if any, is perturbation theory convergent? One also would like to know: What is perturbation theory actually calculating since the discrete level no longer exists?

Physically the answer to the last question is clear; one is calculating the position of a metastable level. However it is only recently that Kato (1951a) and Titchmarsh (1958) have given mathematically more precise answers to these questions. In effect what they have done is to give conditions on $H_0$ and $H_1$ such that a well-defined metastable state will appear in the neighborhood of the original discrete state of $H_0$ and such that the average energy of this state is correctly calculated by perturbation theory.

Mathematically such states reveal themselves in several related ways.

(a) Let us for simplicity assume that the spectrum of $H(\lambda)$ for $\lambda > 0$ is completely continuous. Then no energy would seem distinguished. If, however, one examines the Green's function of $H(\lambda)$ as a function of the complex variable $z$, then one finds that, in addition to having a branch line along the real axis corresponding to the continuous spectrum of $H(\lambda)$, it has poles near the real axis. These poles approach the real axis and represent the discrete states of $H_0$ as $\lambda$ approaches zero. Perturbation theory calculates the real parts of these poles and, clearly, regions of the continuous spectrum near these poles *are* distinguished. The real part of the pole is the position of the metastable state.

(b) In spite of the continuous nature of the spectrum, the spectrum is effectively more concentrated in the regions of the real axis near the poles of the Green's function. Namely, if one expands an arbitrary function in terms of the eigenfunctions of $H$, one finds that contributions to the expansion will, in general, be particularly large from regions which include the metastable states, and these contributions persist as $\lambda$ approaches zero.

(c) Wave packets formed by superposing eigenstates of $H$ from a small region including the metastable states are quite well-localized, this localization persisting as $\lambda$ approaches zero. This is not true if the small region does not contain a metastable state.

The last property would seem to make contact with what one intuitively thinks of as a metastable state. Also, the pole of the Green's function is reminiscent of Gamow's complex eigenvalues in the theory of $\alpha$ decay. To complete the connection we note that the localization referred to in (c) does not of course persist for all time. Rather, one can show that it decays with a well-defined lifetime (see for example Hohler, 1958, and Petzold, 1959), this lifetime being determined by the imaginary part of the poles of the Green's function. With this, the identification is clearly complete.

Property (c) allows Kato to apply the theory of asymptotic perturbation series to this problem. The operators defining the first $M$ terms of the perturbation series are required to be defined at least on a manifold consisting essentially of the functions which are zero outside of a given bounded set which represents the region of the physical problem. Then the functions belonging to a small finite interval of the continuous spectrum near the $M$th partial sum of a perturbed eigenvalue can be expanded in terms of the $M$th partial sums of the corresponding perturbed eigenfunctions, and this expansion is complete up to $O(\lambda^M)$.

# Appendix A.
# Algebraic Manipulations for Obtaining Perturbation Energies

## I. Derivation of High-Order Perturbation Energy Formulas

A sequence of algebraic manipulations is required in order to derive Eqs. (II.8) and (II.12) for the higher-order perturbation energies. We assume that both $V$ and $H_0$ are Hermitian. Because of the Hermitian property of $H'_0$ and the zeroth-order perturbation relation $H'_0\psi = 0$,

$$\langle\psi, H'_0\psi^{(n)}\rangle = 0. \tag{A.1}$$

Thus, multiplying Eq. (II.4) by $\psi^*$ and integrating over space leads to Eq. (II.8). Other functional forms for $\varepsilon^{(n)}$ are obtained from the following identities. Making use of the Hermitian property of both $V'$ and $H'_0$ together with Eqs. (II.3) and (II.4) in which $n$ is replaced by $(n-1)$,

$$\begin{aligned}\langle\psi, V'\psi^{(n-1)}\rangle &= -\langle\psi^{(1)}, H'_0\psi^{(n-1)}\rangle \\ &= \langle\psi^{(1)}, V'\psi^{(n-2)}\rangle - \sum_{j=2}^{n-1}(1, n-1-j)\varepsilon^{(j)}.\end{aligned} \tag{A.2}$$

Similarly, using Eq. (II.4) with $n = k$ and again with $n$ replaced by $(n-k)$,

$$\begin{aligned}\langle\psi^{(k-1)}, V'\psi^{(n-k)}\rangle &= -\langle\psi^{(k)}, H'\psi^{(n-k)}\rangle + \sum_{j=2}^{k}(k-j, n-k)\varepsilon^{(j)} \\ &= \langle\psi^{(k)}, V'\psi^{(n-1-k)}\rangle + \sum_{j=2}^{k}(k-j, n-k)\varepsilon^{(j)} \\ &\quad - \sum_{j=2}^{n-k}(k, n-k-j)\varepsilon^{(j)}.\end{aligned} \tag{A.3}$$

Using Eq. (A.2) together with the normalization condition Eq. (II.5), Eq. (II.8) leads to the result

$$\varepsilon^{(n)} = \langle\psi^{(1)}, V'\psi^{(n-2)}\rangle - \sum_{j=2}^{n-2}\varepsilon^{(j)}\{(0, n-j) + (1, n-j-1)\}. \tag{A.4}$$

Combining Eq. (A.4) with Eq. (A.3), in which $k = 2$, and making use of the normalization condition Eq. (II.5),

$$\begin{aligned}\varepsilon^{(n)} &= \langle\psi^{(k)}, V'\psi^{(n-1-k)}\rangle - \sum_{j=k+1}^{n-k}\sum_{s=0}^{k}\varepsilon^{(j)}(s, n-j-s) \\ &\quad - \sum_{j=2}^{k}\sum_{s=k+1-j}^{k}\varepsilon^{(j)}(s, n-j-s).\end{aligned} \tag{A.5}$$

The form of Eq. (A.5) remains invariant when we apply the recursion relation Eq. (A.3) with successively larger values of $k$. Thus we conclude that Eq. (A.5) is valid provided that $k \geq 2$ and $2k + 1 \leq n$. Replacing $n$ by $2n$ and letting $k = n - 1$ leads to Eq. (II.12a); whereas replacing $n$ by $2n + 1$ and letting $k = n$ gives Eq. (II.12b).

## 2. Energy Expectation for Truncated Wave Functions

The expectation value $\mathscr{E}(n)$ can be written as the ratio $\mathscr{E}(n) = B(n)[D(n)]^{-2}$ where

$$B(n) = \sum_{j=0}^{n} \sum_{k=0}^{n} \lambda^{j+k} \langle \psi^{(j)}, H\psi^{(k)} \rangle.$$

The calculation of the $B(n)$ is facilitated by the recursion relation

$$B(n) = B(n-1) + \lambda^{2n} \langle \psi^{(n)}, H\psi^{(n)} \rangle + \sum_{j=0}^{n-1} \lambda^{n+j} \{ \langle \psi^{(n)}, H\psi^{(j)} \rangle + \langle \psi^{(j)}, H\psi^{(n)} \rangle \}. \tag{A.6}$$

The perturbation equations can be written

$$\begin{aligned} H\psi &= \lambda V\psi + \varepsilon\psi, \\ H\psi^{(k)} &= \lambda V\psi^{(k)} - V\psi^{(k-1)} + \sum_{j=0}^{k} \varepsilon^{(j)} \psi^{(k-j)}. \end{aligned} \tag{A.7}$$

The calculation of the $B(n)$'s is then made with the help of Eqs. (II.8), (A.4), and (A.5). We then obtain

$$\mathscr{E}(n) = \sum_{k=0}^{2n+1} \lambda^k \varepsilon^{(k)} - \lambda^{2n+2} A(n)[D(n)]^{-2}, \qquad n = 2, 3, \ldots, \tag{A.8}$$

where

$$A(2) = \varepsilon^{(2)}(2,2) + [\varepsilon^{(3)} + \lambda\varepsilon^{(4)} + \lambda^2\varepsilon^{(5)}][(1,2) + (2,1) + \lambda(2,2)] \tag{A.9}$$

$$\begin{aligned} A(3) = {} & \varepsilon^{(2)}(3,3) + \varepsilon^{(3)}[(3,2) + (2,3) + \lambda(3,3)] \\ & + \left\{ \sum_{k=4}^{7} \lambda^{k-4} \varepsilon^{(k)} \right\} [(1,3) + (2,2) + (3,1) + \lambda\{(2,3) + (3,2)\} \\ & + \lambda^2(3,3)] \end{aligned} \tag{A.10}$$

$$\begin{aligned} A(n) = {} & (n,n) \sum_{k=2}^{n} \varepsilon^{(k)} \lambda^{k-2} + [(n, n-1) + (n-1, n)] \sum_{k=3}^{n} \varepsilon^{(k)} \lambda^{k-3} \\ & + \sum_{k=0}^{n-4} \sum_{l=0}^{k+2} (n-l, n+l-2-k) \sum_{j=0}^{n-k-4} \varepsilon^{(k+4+j)} \lambda^j \\ & + \sum_{k=1}^{n} \lambda^{k-1} \sum_{l=0}^{n-k} (n-l, k+l) \sum_{j=0}^{n-1} \varepsilon^{(n+1+j)} \lambda^j, \qquad n = 4, 5, \ldots. \end{aligned} \tag{A.11}$$

# Appendix B.

## Expansion in Terms of Arbitrary Complete Set

In this appendix we present the formulas which result when the first-order wave function is expanded in terms of an arbitrary complete set of functions $\phi_\alpha$ belonging to the same space as the eigenfunctions of the unperturbed Hamiltonian $H_0$. The use of convenient discrete complete sets of functions goes back to P. Epstein (1926), Lennard-Jones (1930), and Hylleraas (1928), and is common nowadays; for example, see Löwdin and Shull (1955), Hirschfelder and Löwdin (1959). Their application to perturbation theory has been formalized by Blinder (1960).

Consider the expansion of the first-order wave function for the state $q$,

$$\psi_q^{(1)} = \sum_\alpha \langle \phi_\alpha, \psi_q^{(1)} \rangle \phi_\alpha. \tag{B.1}$$

The coefficients may be obtained by substituting in Eq. (III.1), multiplying by $\phi_\beta^*$, and integrating to get

$$\sum_\beta (H_{\alpha\beta} - S_{\alpha\beta}\varepsilon_q)\langle \phi_\beta, \psi_q^{(1)} \rangle + (V_{\alpha q} - S_{\alpha q}\varepsilon_q^{(1)}) = 0, \tag{B.2}$$

where

$$H_{\alpha\beta} = \langle \phi_\alpha, H_0 \phi_\beta \rangle,$$

$$S_{\alpha\beta} = \langle \phi_\alpha, \phi_\beta \rangle,$$

$$V_{\alpha q} = \langle \phi_\alpha, V\psi_q \rangle, \qquad \varepsilon_q^{(1)} = V_{qq} = \langle \psi_q, V\psi_q \rangle. \tag{B.3}$$

Hence

$$\langle \phi_\alpha, \psi_q^{(1)} \rangle = -\sum_\beta (H_{\alpha\beta} - \varepsilon_q S_{\alpha\beta})^{-1}(V_{\beta q} - V_{qq}S_{\beta q}). \tag{B.4}$$

It is interesting to note, as Blinder (1960) points out, that the same coefficients are obtained from the Hylleraas variation principle, Eq. (III.50), if the trial function $\tilde{\psi}_q^{(1)}$ is chosen to be a linear combination of the $\phi$'s with variable coefficients. The function $\psi_q^{(1)}$, defined by Eqs. (B.1) and (B.4), is not in general orthogonal to $\psi_q$ since

$$\langle \psi_q, \psi_q^{(1)} \rangle = -\sum_\alpha \sum_\beta S_{q\alpha}(H_{\alpha\beta} - \varepsilon_q S_{\alpha\beta})^{-1}(V_{\beta q} - V_{qq}S_{\beta q}) \tag{B.5}$$

does not, in general, vanish. However, it is always possible to add an arbitrary amount of $\psi_q$ to $\psi_q^{(1)}$ so that they become orthogonal. The second-order energy can be obtained by substituting Eqs. (B.1) and (B.4) into Eq. (II.7), and is

$$\varepsilon^{(2)} = -\sum_\alpha \sum_\beta (V_{q\alpha} - V_{qq}S_{q\alpha})(H_{\alpha\beta} - \varepsilon_q S_{\alpha\beta})^{-1}(V_{\beta q} - V_{qq}S_{\beta q}). \tag{B.6}$$

The procedure therefore requires the inversion of a matrix and a double summation. However this extra labor is often repaid by rapid convergence of the sum. It is naturally convenient to choose the set $\phi$ to be orthogonal so that $S_{\alpha\beta} = \delta_{\alpha\beta}$. An additional simplification which is frequently used is to choose one member of the set, say $\phi_q$, to be the unperturbed wave function $\psi_q$.

## Appendix C.

## The Use of Delta Functions in the Laplacian and Momentum Operators

Frequently a lack of Hermitian behavior occurs for generalized momentum operators and for many of the other physical operators which occur in quantum mechanics. The reason seems to be *mathematical* rather than *physical.* Delta functions can be used to extend the Hermitian domain of the Laplacian and the momentum operators (see Sec. 12.A). A well known example is $\nabla.\nabla(r^{-1}) = -r^{-2}\delta_+(r)$ where $\delta_+(r)$ is defined by Eq. (C.2).

Consider a set of generalized orthogonal coordinates $(q_1, q_2, q_3)$ with the metric scale factors $h_1, h_2, h_3$ so that the Jacobian of the transformation from Cartesian to generalized coordinates is $h = h_1 h_2 h_3$. The range of definition of $q_j$ extends from $a_j$ to $b_j$. The unit vector in the direction of increasing $q_j$ is $\hat{q}_j$. Difficulties in the definition of the quantum mechanical operators occur at those points where $\hat{q}_j$ is ill-defined and the transformation from Cartesian to the generalized coordinates is not one-to-one. Generally such points occur at either the upper or the lower bounds of definition of the generalized coordinates. A careful consideration of the mathematical problems led Robinson and Hirschfelder (1963) to assert that the Laplacian operator is properly written in the form

$$\nabla\cdot\nabla = \sum_{j=1}^{3}\left[h^{-1}\frac{\partial}{\partial q_j}\left(hh_j^{-2}\frac{\partial}{\partial q_j}\right) + \{\delta_+(q_j - a_j) - \delta_-(b_j - q_j)\}h_j^{-2}\frac{\partial}{\partial q_j}\right] \tag{C.1}$$

Here the $\delta_+$ and the $\delta_-$ are similar to the Dirac delta functions and are defined by:

$$\begin{aligned} &\int_{a_j}^{t} U(q_j)\delta_+(q_j - a_j)\,dq_j = U(a_j), \qquad a_j \leqslant t \leqslant b_j, \\ &\int_{t}^{b_j} U(q_j)\delta_-(b_j - q_j)\,dq_j = U(b_j), \qquad a_j \leqslant t \leqslant b_j. \end{aligned} \tag{C.2}$$

In much the same manner, the operator for the momentum conjugate to $q_j$ can be written

$$p_j = (\hbar/i)\left[h^{-1/2}\frac{\partial}{\partial q_j}(h^{1/2} \quad ) + \tfrac{1}{2}\delta_+(q_j - a_j) - \tfrac{1}{2}\delta_-(b_j - q_j)\right]. \tag{C.3}$$

However, it is difficult to interpret the square or cube of $p_j$. On this account, Robinson and Lewis (1963) suggest defining the momentum operator in terms of a "finite" Fourier transform. Defining $F(k)$ as

$$F(k) = (2\pi)^{-1/2}\int_a^b \exp(ik\xi)\psi(\xi)h^{1/2}\,d\xi, \tag{C.4}$$

then

$$p_j\psi(q_j) = \lim_{k\to\infty}(2\pi h)^{-1/2}\int_{-k}^{k}\exp(ikq_j)kF(k)\,dk, \qquad a_j \leqslant q_j \leqslant b_j. \tag{C.5}$$

In spherical coordinates, $h = r^2 \sin\theta$ goes to zero as $r$ approaches zero. As a result, the delta function terms very seldom contribute to the physical equations. However, in confocal elliptic coordinates, which are frequently used for molecular problems, the volume element does not approach zero in the limits of integration of one of the variables, and the delta function terms are often needed.

## Appendix D.

## Solution of Separable Perturbation Equations in Generalized Coordinates

In this appendix we discuss the separation and subsequent perturbation expansion of the three-dimensional Schrödinger equation for a perturbed system with a separable potential $U$ (see Section III,A,2,c).

Let the original Schrödinger equation in orthogonal generalized coordinates $q_1, q_2, q_3$ be

$$-\frac{1}{2}\sum_i\left[\frac{1}{h}\frac{\partial}{\partial q_i}\left(\frac{h}{h_i^2}\frac{\partial\Psi}{\partial q_i}\right)\right] + U\Psi = \mathrm{E}\Psi, \tag{D.1}$$

where $h_1, h_2, h_3$ are the metric scale factors and $h = h_1h_2h_3$. Here the Dirac-type delta function term discussed in Appendix C is not required.

Under certain well-known conditions discussed in detail by Morse and Feshbach (1953), the equation separates and we can put

$$\Psi = \prod_i \Psi_i(q_i). \tag{D.2}$$

The condition on the potential $U$ for separability is

$$U = \sum_i U_i(q_i)/h_i^2, \tag{D.3}$$

and a condition on the coordinates for separability is that $h/h_i^2$ is equal to a function $g_i(q_i)$ times a function of the other coordinates. The separated equations are then

$$-\frac{1}{2g_i}\frac{d}{dq_i}\left(g_i\frac{d\Psi_i}{dq_i}\right) + U_i\Psi_i = \left(\sum_j S_{ij}C_j\right)\Psi_i, \tag{D.4}$$

where $S_{ij}$ are the elements of the Stäckel determinant $S$ and the $C_j$ are constants. The Stäckel elements $S_{i1}, S_{i2}, S_{i3}$ are functions of $q_i$ only and are defined so that

$$\sum_i S_{ij}/h_i^2 = \delta_{j1} \tag{D.5}$$

and the Robertson condition

$$h = gS \tag{D.6}$$

are satisfied, where $g = g_1 g_2 g_3$. The energy is $E = C_1$ and $C_2, C_3$ are separation constants.

Let $U^{(0)}$ be the unperturbed potential and $V$ the separable perturbation potential, so that

$$U_i = U_i^{(0)} + \lambda V_i, \tag{D.7}$$

and put

$$H_i^{(0)} = -\frac{1}{2g_i}\frac{d}{dq_i}\left(g_i\frac{d}{dq_i}\right) + U_i^{(0)}, \tag{D.8}$$

$$\Psi_i = \psi_i + \lambda\psi_i^{(1)} + \lambda^2\psi_i^{(2)} + \cdots, \tag{D.9}$$

$$C_i = C_i^{(0)} + \lambda C_i^{(1)} + \lambda^2 C_i^{(2)} + \cdots. \tag{D.10}$$

Then the various orders of Rayleigh–Schrödinger perturbation equations are

$$[H_i^{(0)} - \mathscr{E}_i^{(0)}]\psi_i = 0, \tag{D.11a}$$

$$[H_i^{(0)} - \mathscr{E}_i^{(0)}]\psi_i^{(1)} + [V_i - \mathscr{E}_i^{(1)}]\psi_i = 0, \tag{D.11b}$$

$$[H_i^{(0)} - \mathscr{E}_i^{(0)}]\psi_i^{(2)} + [V_i - \mathscr{E}_i^{(1)}]\psi_i^{(1)} - \mathscr{E}_i^{(2)}\psi_i = 0, \tag{D.11c}$$

where $\mathscr{E}_i^{(n)} = \sum_j S_{ij}\, C_j^{(n)}$.

By multiplying by $\psi_i$, integrating over the range $(a_i, b_i)$ of $q_i$, and assuming that the separated Hamiltonian operators are Hermitian, we get

$$\sum_j \{S_{ij}\}\, C_j^{(0)} = \{H_i^{(0)}\}, \tag{D.12a}$$

$$\sum_j \{S_{ij}\}\, C_j^{(1)} = \{V_i\}, \tag{D.12b}$$

$$\sum_j \{S_{ij}\}\, C_j^{(2)} = \{F_i(V_i - \mathscr{E}_i^{(1)})\} \tag{D.12c}$$

where the curly brackets are defined by

$$\{X\} = \iiint \psi^* X \psi g \, dq_1\, dq_2\, dq_3, \tag{D.13}$$

and we have put

$$\psi_i^{(1)} = F_i \psi_i. \tag{D.14}$$

It is convenient to normalize the $\psi_i$ so that

$$\int_{a_i}^{b_i} \psi_i^* \psi_i g_i \, dq_i = 1.$$

The various orders of the energy are obtained by eliminating the constants $C_2$ and $C_3$ to get

$$\varepsilon^{(0)} = \sum_i \{H_i^{(0)}\}\{\bar{S}_{i1}\}/\{S\}, \tag{D.15a}$$

$$\varepsilon^{(1)} = \sum_i \{V_i\}\{\bar{S}_{i1}\}/\{S\}, \tag{D.15b}$$

$$\varepsilon^{(2)} = \sum_i \{F_i(V_i - \mathscr{E}_i^{(1)})\}\{\bar{S}_{i1}\}/\{S\}, \tag{D.15c}$$

where $\bar{S}_{ij}$ is the cofactor of $S_{ij}$ in $S$. Note that the equations through the first order are identical with those obtained from the equation

$$\varepsilon^{(0)} + \lambda\varepsilon^{(1)} = \frac{\langle \psi, (H^{(0)} + \lambda V)\psi \rangle}{\langle \psi, \psi \rangle}. \tag{D.16}$$

This follows from the nature of the Stäckel determinant; thus the normalizing integral is

$$\langle\psi, \psi\rangle = \iiint |\psi_1\psi_2\psi_3|^2 h \, dq_1 \, dq_2 \, dq_3$$
$$= \det(\{S_{ij}\}). \tag{D.17}$$

The perturbation equation of any order can be solved directly by quadrature. Thus, substituting Eq. (D.14) into Eq. (D.11b) and assuming that $\psi_i$ is real, we get the first-order equation in the one-dimensional form discussed in Section III,A,2,

$$\frac{d}{dq_i}\left(g_i\psi_i^2 \frac{dF_i}{dq_i}\right) = 2\psi_i g_i(V_i - \mathscr{E}_i^{(1)})\psi_i . \tag{D.18}$$

By integrating once we get

$$g_i\psi_i^2 \frac{dF_i}{dq_i} = M_i(q_i) = 2\int_{a_i}^{q_i} \psi_i g_i(V_i - \mathscr{E}_i^{(1)})\psi_i \, dq_i , \tag{D.19}$$

and again we get

$$F_i(q_i) = F_i(a_i) + \int_{a_i}^{q_i} (M_i/g_i\psi_i^2) \, dq_i . \tag{D.20}$$

For excited states the wave function factor $\psi_i$ may possess nodes in the interval $(a_i, b_i)$. In such a case the integration in Eq. (D.20) must be taken along a contour C in the complex plane which avoids the zeros of $\psi_i$. Alternatively, the singularities in the integrand may be removed by subtracting out the poles, as discussed in Section III,A,2,b. For any state the second-order energy given by Eq. (D.15c) may be written in the form

$$\varepsilon^{(2)} = -\frac{1}{2}\sum_i \left[\oint_{a_i}^{b_i} (M_i^2/g_i\psi_i^2) \, dq_i\right] \{\bar{S}_{i1}\}/\{S\}, \tag{D.21}$$

or the alternative form corresponding to Eq. (III.32).

## Appendix E.

## Solution of Perturbation Equation by Spherical Harmonic Expansion

Consider the important case mentioned in Section III,A,3, in which the unperturbed potential is spherically symmetric so that the unperturbed wave function $\psi$ is an eigenfunction of angular momentum

$$\psi = R_L(r)Y_{LM}(\theta, \varphi), \tag{E.1}$$

where $Y_{LM}$ is a normalized spherical harmonic. We shall confine our treatment to the solution of the first-order equation (III.1) since the higher-order equations are of the same form.

The first step is to expand the perturbation term $V'(r,\theta,\varphi)$ in terms of the angular eigenfunctions,

$$V' = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} V'_{lm}(r) Y_{lm}(\theta, \varphi). \tag{E.2}$$

The inhomogeneous term in Eq. (III.1) can then also be expanded in terms of the spherical harmonics,

$$V'\psi = R_L(r) \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} V_{lm}(r) Y_{lm}(\theta, \phi), \tag{E.3}$$

where

$$V_{lm}(r) = \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{+\lambda} \langle Y_{lm}, Y_{LM} Y_{\lambda\mu} \rangle V'_{\lambda\mu}(r) \tag{E.4}$$

and $\langle Y_{lm}, Y_{LM} Y_{\lambda\mu} \rangle$ is given in terms of the Clebsch–Gordon or Wigner coefficients by (see Hirschfelder *et al.*, 1954, p. 910.)

$$\langle Y_{lm}, Y_{LM} Y_{\lambda\mu} \rangle = \left[ \frac{(2L+1)(2\lambda+1)}{4\pi(2l+1)} \right]^{1/2} S^{L\lambda}_{l00} S^{L\lambda}_{lM\mu} \delta_{m,M+\mu}.$$

The next step is to express $\psi^{(1)}$ (not $F$) as a partial expansion in terms of the spherical harmonics

$$\psi^{(1)} = R_L(r) \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} F_{lm}(r) Y_{lm}(\theta, \varphi). \tag{E.5}$$

When the expansions (E.3) and (E.5) are substituted into Eq. (III.1) and the harmonic components are separated out, we obtain the set of ordinary inhomogeneous differential equations for the unknown functions $F_{lm}(r)$,

$$\frac{d}{dr}\left( r^2 R_L^2 \frac{dF_{lm}}{dr} \right) + [L(L+1) - l(l+1)] R_L^2 F_{lm} = 2r^2 R_L V_{lm} R_L. \tag{E.6}$$

Note that if the perturbation $V$ is spherically symmetric, the terms $V_{lm}$ all vanish except for $l = L$, $m = 0$, and in this case the single equation (E.6) is of the one-dimensional form discussed in Section III,A,2, and can be solved immediately by quadrature.

In the general case it will usually be more convenient to solve Eq. (E.6) with $V'_{\lambda\mu}(r)$ in the inhomogeneous term and to combine the solutions, say $F^{l}_{\lambda\mu}(r)$, to obtain the $F_{lm}$:

$$F_{lm}(r) = \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{+\lambda} \langle Y_{lm}, Y_{LM} Y_{\lambda\mu} \rangle F^{l}_{\lambda\mu}(r). \tag{E.7}$$

If $G_l(r)$ is the solution of the homogeneous equation

$$\frac{d}{dr}\left(r^2 R_L^2 \frac{dG_l}{dr}\right) + [L(L+1) - l(l+1)]R_L^2 G_l = 0 \tag{E.8}$$

corresponding to Eq. (E.7), we put

$$F_{\lambda\mu}^l = G_l f_{\lambda\mu}^l \tag{E.9}$$

and solve for $f_{\lambda\mu}^l$ by quadrature. The solution for $F_{\lambda\mu}^l$ may then be written in a form similar to Eq. (III,41),

$$F_{\lambda\mu}^l(r) = G_l(r)\left\{f_{\lambda\mu}^l(0) + \oint_0^r [M_{\lambda\mu}^l / s^2 R_L^2 G_l^2]\, ds\right\}, \tag{E.10}$$

where the integral is in the complex $s$ plane if necessary, to avoid the zeros of $R_L$ and $G_l$ [cf. Eqs. (III.25) and (III.41)], and

$$M_{\lambda\mu}^l(r) = 2\int_0^r s^2 G_l R_L V'_{\lambda\mu} R_L\, ds. \tag{E.11}$$

The second-order energy can be expressed in terms of sums over the Clebsch–Gordon coefficients and integrals involving products of the functions $M_{\lambda\mu}$:

$$\varepsilon^{(2)} = -\frac{1}{2}\sum_{l}\sum_{\lambda}\sum_{\lambda'}\sum_{\mu,m}\langle Y_{\lambda\mu}Y_{LM},\, Y_{lm}\rangle\langle Y_{lm},\, Y_{LM}Y_{\lambda'\mu}\rangle \oint_0^\infty \left[\frac{M_{\lambda\mu}^l M_{\lambda'\mu}^l}{s^2 G_l^2 R_L^2}\right] ds. \tag{E.12}$$

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