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EDITED BY

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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 computers to solve the wave equations and achieve its results. Its goals are great, but perhaps the new field can better boast of its conceptual framework than of its numerical accomplishments. It provides a unification of the natural sciences that was previously inconceivable, and the modern development of cellular biology shows that the life sciences are now, in turn, using the same basis. "Quantum biology" is a new field which describes the life processes and the functioning of the cell on a molecular and submolecular level.

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

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

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.

January, 1967 PER-OLOV LÖWDIN

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Approximate Hartree-Fock Calculations on Small Molecules

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I. Introduction

The Molecular Hartree–Fock Approximation

For singlet ground states, the molecular Hartree–Fock approximation consists of a variational calculation to find a Slater determinant that minimizes the electronic energy, expressed as the mean value of the molecular Hamiltonian with fixed internuclear coordinates. For other states, the traditional Hartree–Fock method would use as a trial function the linear combination of Slater determinants needed to form a wave function with specified spin or spatial point group quantum numbers. It can easily be shown (e.g., Nesbet, 1961) that the N orthonormal orbitals of a Hartree–Fock single determinant must satisfy equations

$$\mathscr{H}_0\phi_i = \varepsilon_i\phi_i \tag{1}$$

where $\mathscr{H}_0$ is an integrodifferential operator that contains terms dependent on the density function

$$\rho(1, 1') = \sum_{i=1}^{n} \phi_i^*(1)\phi_i(1'). \tag{2}$$

Hence Eqs. (1), while formally resembling one-particle Schrödinger equations, are actually nonlinear. For molecules, the Hartree–Fock equations involve partial differential and integral operators with several independent variables. As such, the equations are intractable to the standard methods of numerical analysis.

As a consequence of developments of computational technique, it has been possible in recent years to compute molecular Hartree–Fock wave functions that compare well in accuracy with the corresponding functions for atoms. There are three important elements in this work. First, the matrix Hartree–Fock method, originally proposed by Roothaan (1951) and by Hall (1951) in the context of the molecular LCAO approximation, replaces Eqs. (1) by the corresponding linear equations, with $\mathscr{H}_0$ replaced by its matrix elements in a specified basis of atomic orbitals, and ϕ replaced by the vector representing the linear expansion of a molecular orbital function in the same atomic orbital basis. The partial differential equations are replaced by matrix equations whose elements are constructed from multidimensional definite integrals. Second, it was recognised by Boys (1950a) that accurate molecular wave functions require the use of orbital basis sets much more general than those considered in the LCAO approximation, where only a single basis orbital is used for each independent occupied orbital in the component atoms. Third, the introduction of electronic digital computers has made possible the enormously complex calculations required to implement the matrix Hartree–Fock method in an orbital basis sufficiently complete to produce quantitative results. The efficient organization and programming of these calculations has been an essential prerequisite to the results discussed here.

This article will review results obtained by this method for molecules containing more than two or three electrons. This excludes the smallest molecules, for which special methods can be used to give results of high accuracy. The improvement in results obtained in going from simple LCAO calculations to a reasonable approximation to a true Hartree–Fock calculation has been substantial. For this reason, LCAO results will not be discussed here, but the reader is referred to a review by Allen and Karo (1960) and to papers by Ransil (1960) and Mulliken (1962).

II. Computational Technique

A. Choice of Orbital Basis

Computer programs for solution of the matrix Hartree–Fock equations have been described in detail elsewhere (Nesbet, 1954, 1963; Roothaan and Bagus, 1963). For molecular calculations, a general orbital basis is selected. Matrix elements of the one- and two-electron operators in the Hamiltonian must be computed in this basis as input data for the matrix calculation. By far the most difficult and time-consuming part of the over-all calculation is the computation of two-electron integrals of the electronic Coulomb repulsion, since the number of these integrals increases as the fourth power of the order of the orbital basis set. These integrals represent the classical electrostatic interaction energy of two charge distributions, each formed by the product of two basis orbitals. For obvious physical and practical reasons, the basis orbitals are most often chosen to have simple functional forms when expressed in spherical polar coordinates about some atomic nucleus in a molecule. If this is so, each elementary charge density can be associated with either one or two atoms, and each electrostatic integral involves basis orbitals from as many as four different atoms. The basis sets used in molecular calculations represent various compromises between the conflicting demands of rapid convergence and ease of evaluation of multicenter integrals.

It has been known for some time that the radial factor of an atomic Hartree–Fock orbital can be expressed to high accuracy as a linear combination of a small number of exponential radial functions multiplied by powers of r. General rules for choosing the exponents of single functions of this kind, as a qualitative approximation to Hartree–Fock orbitals, were proposed by Slater (1930), and many LCAO calculations have been carried out using basis orbitals with exponents determined by Slater's rules. In the work described here, the number of basis orbitals used is considerably larger than the bare minimum needed to provide one basis orbital for each orbital occupied in the ground state configuration of every atom in a given molecule. The term LCAO will be used here only in reference to calculations with minimal basis sets, either with Slater orbitals or with more complicated functions, including actual ground state atomic Hartree–Fock orbitals. In general, LCAO calculations have led to unsatisfactory results, due to the rigidity of the basis set. The strong electrostatic field in a molecule distorts the atomic valence orbitals in the sense of changing their radial functional form or of modifying their angular dependence. When orbital basis sets are used that are capable of representing such distortion, in addition to the superposition of orbitals already described in the LCAO molecular orbital approximation, significant improvements result. This is most clearly documented in the case of the HF molecule, which will be discussed below. The most important practical implication of this is that any calculation intended to give quantitative results must produce very large numbers of electrostatic integrals.

1. *Gaussian Basis Orbitals*

It was proposed by Boys (1950a) that Gaussian functions, of the form $\exp(-\alpha r^2)$ multiplied by polynomials in x, y, z, be used for molecular calculations. These are the only known functions for which the general four-center integral reduces to a closed form expressible in terms of standard functions. Simple calculations show that more Gaussians than exponential functions are required for similar accuracy in expanding an atomic Hartree–Fock orbital. A matrix Hartree–Fock calculation on CH_4 and the carbon atom (Nesbet, 1954, 1960a) with Gaussian basis orbitals was one of the first molecular calculations to use an extended basis set, in this case two or three basis functions for each atomic orbital on carbon. This work established the feasibility of calculations of the kind considered here, but the basis set was inadequate to give any clear indication of what might be expected from a molecular Hartree–Fock approximation. More recent work by Krauss (1963) on CH_4 and $NH_4{}^+$ has shown that a Gaussian basis set roughly twice as large as that used earlier is capable of approaching the true Hartree–Fock function. Systematic calculations on atoms by Huzinaga (1965) and on atoms and small molecules by Reeves and Harrison (1963), Harrison (1964), and Reeves and Fletcher (1965) have formulated rules for choosing a Gaussian basis expected to lead to molecular calculations of useful accuracy. An interesting result of this work is the conclusion that powers of r^2 should *not* be included as factors of Gaussian radial functions, since expansions of atomic orbitals converge more rapidly without them. This fact greatly simplifies the analysis needed in deriving integral formulas by the method originally proposed by Boys (1950a).

Especially when powers of r^2 are omitted, calculations with Gaussian orbitals become studies in sophisticated data handling, since relatively simple arithmetic is performed on long lists of numbers. These difficulties are apparently less severe than the numerical analysis problem of efficient evaluation of three- and four-center integrals with exponential basis orbitals, so Gaussian basis orbitals have been used for several calculations on polyatomic molecules that will be discussed in Section IV, below.

2. *Exponential Basis Orbitals*

Exponential orbitals are used whenever possible in order to limit the size of the basis set. For atoms the electrostatic integrals are trivial, since they can be computed by a simple formula (Boys, 1950b). For diatomic molecules the problem is very much more difficult, but simplifications result from axial symmetry (which immediately removes two of the six quadratures in a two-particle integral) and from the possibility of using spheroidal coordinates (Ruedenberg, 1951). An efficient method of evaluating two-center electrostatic integrals has been described and programmed by Harris (1960). A number of the matrix Hartree–Fock calculations discussed here have been carried out with a computer program (Nesbet, 1960b) whose detailed structure is based on unpublished work by Merryman (1959). These programs are designed so that the dominant computational step is weighted by the second rather than the fourth power of the number of basis functions. Arbitrary orbital quantum numbers can be used, since this is essential to achieve the angular and radial polarization effects that account for the qualitative difference between LCAO and true Hartree–Fock wave functions. A similar but improved and highly efficient program has recently been put into service (Wahl *et al.*, 1964).

A program of comparable efficiency, applicable to linear polyatomic molecules, has been written by McLean (1960), and used for calculations on both diatomic and polyatomic molecules. The method used involves explicit computation of a one-particle potential function, followed by two-dimensional numerical quadrature of the product of this potential and the other one-particle charge density (product of two basis orbitals). The special method for diatomic molecules, mentioned above, combines one-dimensional numerical quadrature with summation of an infinite but rapidly convergent series.

No method has as yet been implemented that would make efficient use of exponential basis functions for nonlinear molecules.

3. *One-Center Expansion*

In principle, every molecular orbital could be expanded as a linear combination of basis orbitals all on one center. In practice, this converges too slowly to be useful except for central hydrides, XH_n. Recent work by Moccia (1962, 1964a,b,c) has shown that this method is practicable. This work includes calculations on several nonlinear molecules containing too many electrons to be amenable to Gaussian orbitals: SiH_4, PH_3, PH_4^+, H_2S.

B. Computation of One-Electron Properties

An unrestricted Hartree–Fock wave function (Nesbet, 1955, 1961) has the remarkable property that mean values of one-particle operators are stable up to the second order of many-particle perturbation theory (Møller and Plesset, 1934). This is an important reason for trying to obtain a reasonably valid Hartree–Fock function when the object is to compute physical properties of a molecule.

Table I contains data on electric dipole and quadrupole moments. The agreement with experiment is very good for the wave functions expected to be closest to true Hartree–Fock functions. This is especially true for the diatomic hydrides. The computed moments are obtained as

TABLE I

GROUND STATE ELECTRIC DIPOLE AND QUADRUPOLE MOMENTS

Molecule	Reference	μ_e (D)[a]		$(d\mu/dr)_e$ (D/Å)		Q_e (10^{-26}esu)[b]	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
LiH	Ebbing (1962)	−5.99	−5.828	−2.47	−2.0	—	—
	Kahalas and Nesbet (1963)	−5.888	—	—	—	—	—
HF	Clementi (1962)	1.984	1.818	1.7	0.954	—	—
	Nesbet (1962)	1.827	—	1.029	—	—	—
	Moccia (1964a)	2.097	—	—	—	—	—
LiF	McLean (1963b)	6.30	6.284	—	—	—	—
BeO	Yoshimine (1964)	7.29	—	—	—	—	—
BH	Stevens and Lipscomb (1965a)	1.585	—	—	—	—	—
CO	Nesbet (1964a)	0.361	−0.112	3.834	2.97	−1.806	±1.63
	Huo (1965)	0.181	—	4.89	—	−2.20	—
BF	Nesbet (1964a)	−0.617	—	4.882	—	−4.382	—
	Huo (1965)	−1.04	—	5.56	—	−4.58	—
F_2	Wahl (1964)	—	—	—	—	0.886	—
CO_2	McLean (1963a)	—	—	—	—	−2.503	−3
H_2O	Moccia (1964c)	2.085	1.850	—	—	—	—
NH_3	Moccia (1964b)	1.51	1.48	—	—	—	—
HCl	Nesbet (1964b)	1.488	1.081	1.788	±1.00	3.957	—
	Moccia (1964a)	2.166	—	—	—	—	—

[a] The polarity of the dipole moment is given as positive if the effective net charge on the heaviest atom is negative.

[b] The quadrupole moment is computed with respect to the center of mass, assuming the most common nuclear species.

mean values of the appropriate operator taken with an approximate Hartree–Fock wave function.

Quantities such as electric polarizability or magnetic susceptibility represent the response of a system to an applied field. If a new ground state Hartree-Fock function is computed for each value of the applied field, the mean value of the interaction energy should be stable up to second order just as static one-particle properties are for an unmodified Hartree–Fock function. But the polarizability or susceptibility is expressed as just such a mean value. This implies that the perturbed Hartree–Fock theory (Peng, 1941; Dalgarno, 1959) should give good results for such quantities. To implement this requires, in addition to the basic programs for matrix Hartree–Fock calculations, programs to evaluate matrix elements of the special one-particle operators that occur in electromagnetic interactions (Pitzer *et al.*, 1962), and a program to solve the system of inhomogeneous equations arising from the perturbed Hartree–Fock equations in a fixed orbital basis (Stevens *et al.*, 1963). Results of computations, by this method, of magnetic susceptibility and nuclear screening in several molecules are summarized in Table II. The agreement with experiment is in general very good.

TABLE II

GROUND STATE MAGNETIC CONSTANTS OF DIATOMIC MOLECULES[a]

Molecule (AB)		LiH	Li_2	FH	F_2	BH
χ (ppm)	Calc.	−7.630	−28.94	−10.27	−10.617	18.16
	Obs.	—	—	−8.6	—	—
σ_A (ppm)	Calc.	90.15	98.58	404.65	−199.7	−264.43
	Obs.	—	—	—	−210.1	—
σ_B (ppm)	Calc.	26.45	—	28.11	—	22.55
	Obs.	—	—	27.9	—	—
C_A (kc/sec)	Calc.	9.45	0.240	336.0	152.0	496.4
	Obs.	9.92	—	±305	157	—
C_B (kc/sec)	Calc.	−9.15	—	−69.97	—	−8.5
	Obs.	−10.1	—	±71	—	—
μ_J/J (nm)	Calc.	−0.6677	0.1100	0.738	−0.101	−8.17
	Obs.	−0.654	0.10797	0.7392	−0.121	—

[a] Data from Stevens *et al.* (1963) and Stevens and Lipscomb (1964a,b,c, 1965a,b).

C. Molecular Energy Levels

The molecular orbital theory originated as an extension to molecules of the Bohr atomic theory. Quantum numbers characterizing molecular symmetry can be used to designate a set of orbital functions ordered by energy. Observed electronic energy levels can be assigned to definite molecular orbital configurations obtained by distributing the available number of electrons among the orbital functions. When used quantitatively, the Hartree–Fock approximation is to some extent in conflict with this simple *Aufbauprinzip*. The Hartree–Fock equations are different for every electronic state, and no unique set of Hartree–Fock orbitals can be defined for the collection of states of interest in molecular spectroscopy.

In principle, a separate Hartree–Fock calculation should be carried out for each electronic state of interest. This has been done only for a few molecular states, in particular, for excited states of N_2^+ (Cade *et al.*, 1966). As a working compromise, unoccupied orbitals obtained as excited eigenvectors of the ground state matrix Hartree–Fock equations have been used to construct excited state electronic wave functions. When several functions obtained in this way have the same molecular quantum numbers, it is sometimes necessary to diagonalize the matrix of the electronic Hamiltonian over this set of wave functions in order to resolve degeneracies or near degeneracies. This will be referred to as a limited configuration interaction (CI) calculation. When configurations differ by only a single orbital such a calculation is a first-order approximation to a Hartree–Fock calculation (Nesbet, 1955).

Another, and more serious, difficulty in deriving electronic energy levels from Hartree–Fock calculations is the systematic error due to the inability of a Hartree–Fock function to represent the spatial correlation between a pair of electrons. If correlation energy is defined as the difference between the Hartree–Fock energy of a given state and the true eigenvalue of the nonrelativistic Hamiltonian for that state, it is found that correlation energy differences between different electronic excited states of the same molecule are not negligible. The net correlation energy difference between a molecule at internuclear equilibrium and the corresponding separated atoms can be a substantial fraction of the molecular dissociation energy. In N_2, for example, roughly half of the dissociation energy, $D_e = 9.90$ eV, comes from the net correlation energy difference (Nesbet, 1964a). While some success has been achieved in attempting to develop an empirical theory of ground state correlation energies, there is not yet sufficient data for an adequate understanding of correlation energy differences between excited states.

In order to understand changes of correlation energy that result from electronic excitation or from changes of internuclear distances, it has been found useful to hypothesize, in a localized orbital representation of occupied Hartree–Fock orbitals (Lennard–Jones, 1949, 1952), that correlation energy is insensitive to changes of molecular structure that maintain the number and spatial relationship of electron pairs (Clementi, 1963a,b; Nesbet, 1962, 1964a) in a given molecular orbital configuration. Especially for singly bonded diatomic molecules, this hypothesis leads to a very good empirical estimate of the net correlation energy correction to computed Hartree–Fock ground state dissociation energies (Nesbet, 1965a). As a corollary to this hypothesis, significant changes of correlation energy with internuclear distance should be attributed to the crossing of molecular orbital configuration energy curves or hypersurfaces rather than to changes within a given configuration. The crossing of ionic and neutral configurations that occurs for $R > r_e$ for most stable diatomic molecules (unless the ground state molecular orbital configuration is compatible with the separated neutral atoms) has an effect that increases with R near r_e. It follows from this that the computed Hartree–Fock ω_e should be greater than the observed value, the anharmonicity $\omega_e x_e$ should be less than that observed, and the Hartree–Fock r_e should be less than that observed, since configuration interaction must pull the Hartree–Fock potential curve down as R increases beyond r_e (Nesbet, 1962).

III. Diatomic Molecules

A. Hydrides

The hydrogen fluoride molecule provides a very clear example of the importance of the distortion or polarization of the constituent atoms forming a molecule, an effect that can be described within the molecular Hartree–Fock approximation only by going beyond the LCAO idea of constructing molecular orbitals by superposition of atomic valence orbitals. A calculation by Karo and Allen (1959) on the ground state of HF is a classical example of the LCAO theory: the basis orbitals are taken to be ground state atomic Hartree–Fock orbitals. As a consequence, the total molecular energy is very good, −99.96338 atomic units (27.211 eV) at nuclear equilibrium, as compared with −99.48360 au for Slater orbitals and with the experimental energy, −100.53301 au. However, this total energy improvement has little effect on the computed dissociation energy obtained by subtracting atomic ground state energies computed in the same approximation, to give 1.56 eV for atomic Hartree–Fock orbitals, compared with 1.37 eV for Slater orbitals. The experimental D_e is 6.08 eV. If the Slater orbital exponents are varied in both atom and molecule to give the best energy, amounting to an independent change of scale for each basis orbital in the molecule, the total energy at equilibrium is -99.53614 au (Ransil, 1960) and the dissociation energy is 2.56 eV.

It is known from matrix Hartree–Fock calculations for atoms that the shape of the outer part of a radial Hartree–Fock orbital is difficult to determine, because it has only a small effect on the total atomic energy. Conversely, it is to be expected that the shape of atomic valence orbitals can easily be modified by neighboring atoms in a molecule. Changes of functional form more complicated than a change of scale can only be represented by increasing the number of basis functions in a molecular matrix Hartree–Fock calculation beyond those considered in the LCAO approximation. The first results with computer programs written for the purpose of examining such questions showed a very striking increase in the computed dissociation energy of HF. With an orbital basis set capable of representing radial distortion, by including several radial functions for each atomic orbital, and angular distortion, by including higher spherical harmonics than those present in the atomic valence shells, the dissociation energy was computed to be 4.41 eV, corresponding to a total molecular energy of -99.99106 au (Nesbet, 1960b). This result for the dissociation energy has been shown to be insensitive to further improvements in the basis set. A basis set that allows an improved representation of the fluorine atom gives $D_e = 4.11$ eV, total $E = -100.0571$ (Nesbet, 1962). An independent calculation with a different basis set, intended to be a close approximation to the true Hartree–Fock function, gives $D_e = 4.05$ eV, $E = -100.0575$ au (Clementi, 1962).

An empirical estimate can be made of the net correlation energy contribution to D_e (Nesbet, 1965a). The Hartree–Fock electronic configuration at equilibrium should dissociate with very little change in electronic structure into $F^- + H^+$. Thus the correlation energy on this Hartree–Fock potential curve should be that of F^-. The actual ground state dissociates into F + H, so the correlation energy in the limit of separated atoms is that of neutral F in its ground state. The difference in correlation energy between F^- and F is -2.01 eV (Clementi, 1963a,b), and this quantity should be a good estimate of the net correlation energy difference between HF at nuclear equilibrium and the separated atoms. If D_e is 4.11 or 4.05 eV in the Hartree–Fock approximation, total D_e should be 6.12 or 6.06 eV, respectively. This is in quantitative agreement with the observed value, 6.08 eV.

The two best approximate Hartree–Fock wave functions mentioned above (Nesbet, 1962; Clementi, 1962) have been analyzed by Kern and Karplus (1964), who give difference contour maps of the electronic density functions and compute the forces acting on the nuclei appropriate to each wave function. They conclude that the wave function of Clementi, who used fewer basis orbitals but varied the orbital exponents more systematically, is significantly less satisfactory by the criterion of net forces on the nuclei, which must be equal and opposite for a true Hartree–Fock function. Computed values of electric dipole moment and dipole moment derivative (Table I) are also in closer agreement with experiment for the larger basis set.

A recent calculation by Harrison (1964) has shown that Gaussian basis orbitals can give comparable results to those mentioned above. With nine s and five p Gaussian functions on F, and three s and one p Gaussian function on H, $E = -100.01785$ au was computed at $R = 1.75\ a_0$.

A calculation by the one center method (Moccia, 1964a) gives $E = -100.00529$ au at computed r_e, $1.728\ a_0$. The dipole moment, 2.097 D, is comparable to values computed with exponential basis orbitals on each atom.

Calculations at three internuclear distances about the ground state equilibrium (Nesbet, 1962) indicate that the valence orbital configurations $(4\sigma/1\pi)$ and $(4\sigma/3\sigma)$ lead to repulsive states $^1\Pi$, $^3\Pi$, and $^3\Sigma^+$. The molecular orbital state $^1\Sigma^+$ from $(4\sigma/3\sigma)$ must cross the ground state configuration. Since this crossing will be resolved by configuration interaction, leading to the observed ground $X^1\Sigma^+$ state and an excited $V^1\Sigma^+$ state, it is possible to estimate the excitation energy and r_e value for the V state. These values are given in Table III, and are in qualitative agreement with experiment. Since the potential energy minimum for the V state arises from a curve-crossing, the corresponding dipole moment function should be very unusual (Nesbet, 1965a). It should have a *minimum* value near r_e, just the mirror image of the ground state function, since in the V state the molecular orbital configuration changes at r_e from neutral to ionic, dissociating into ions.

Because LiH has only four electrons, it has been studied by a number of different methods which, unlike the matrix Hartree–Fock approximation, cannot easily be applied to larger systems. The most accurate calculation on LiH (Browne and Matsen, 1964) uses a linear combination of antisymmetrized four electron functions, constructed from nonorthogonal orbitals, as a trial function in a variational calculation. Earlier references are given in this paper. The computed total energy E at nuclear equilibrium

TABLE III

SPECTROSCOPIC CONSTANTS OF DIATOMIC MOLECULES

Molecule and state	Reference	T_e (cm^{-1})		r_e (Å)		ω_e (cm^{-1})	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
HF, X $^1\Sigma^+$	Nesbet (1962)	—	—	0.892	0.917	4055	4138.5
	Clementi (1962)	—	—	0.920	0.917	—	—
	Harrison (1964)	—	—	0.920	0.917	—	—
V $^1\Sigma^+$	Nesbet (1962)	60,500	84,771	1.85	2.09	—	—
HF$^+$, $^2\Pi$	Nesbet (1962)	143,900	127,200	—	—	—	—
$^2\Sigma^+$	Clementi (1962)	153,800	137,000	—	—	—	—
	Nesbet (1962)	169,060	137,000	—	—	—	—
HCl, X $^1\Sigma^+$	Nesbet (1964b)	—	—	1.333	1.2746	2498	2989.7
V $^1\Sigma^+$	Nesbet (1964b)	72,500	76,221	~2.3	2.43	—	—
HCl$^+$, $^2\Pi$	Nesbet (1964b)	108,200	104,050	1.381	1.3152	—	—
$^2\Sigma^+$	Nesbet (1964b)	129,300	133,100	1.622	1.5138	—	—
N_2, X $^1\Sigma_g{}^+$	Nesbet (1964a)	—	—	1.072	1.094	2722	2359.6
	Cade *et al.* (1966)	—	—	1.065	1.094	2730	2359.6
A $^3\Sigma_u{}^+$	Nesbet (1965b)	44,356	49,308	1.243	1.287	1865	1460.6
$^3\Delta_u$	Nesbet (1965b)	52,740	—	1.245	—	1858	—
B' $^3\Sigma_u{}^-$	Nesbet (1965b)	61,124	65,431	1.247	1.281	1852	1517.7
a' $^1\Sigma_u{}^-$	Nesbet (1965b)	61,124	67,324	1.247	1.270	1852	1530.0
B $^3\Pi_g$	Nesbet (1965b)	65,908	58,998	1.193	1.213	1974	1735.4
w $^1\Delta_u$	Nesbet (1965b)	66,523	71,293	1.242	1.263	1873	1548.0
a $^1\Pi_g$	Nesbet (1965b)	81,579	68,619	1.211	2.221	1863	1694.1
$N_2{}^+$, A $^2\Pi_u$	Cade *et al.* (1966)	123,700	134,460	1.129	1.176	2313	1902.8
X $^2\Sigma_g{}^+$	Cade *et al.* (1966)	140,090	125,597	1.098	1.116	2461	2207.2
B $^2\Sigma_u{}^+$	Cade *et al.* (1966)	160,040	151,184	1.024	1.075	3102	2419.8
CO, X $^1\Sigma^+$	Nesbet (1964a)	—	—	1.118	1.128	2352	2169.8
	Huo (1965)	—	—	1.101	1.128	2431	2169.8
a $^3\Pi$	Nesbet (1965b)	48,702	48,688	1.188	1.209	1968	1739.3
a' $^3\Sigma^+$	Nesbet (1965b)	57,744	55,823	1.302	1.352	1654	1230.7
d $^3\Delta$	Nesbet (1965b)	63,692	62,299	1.308	1.396	1627	1137.8
e $^3\Sigma^-$	Nesbet (1965b)	69,617	65,340	1.314	1.393	1597	1094.0
I $^1\Sigma^-$	Nesbet (1965b)	69,617	66,185	1.314	1.416	1597	1045
$^1\Delta$	Nesbet (1965b)	72,997	—	1.313	—	1596	—
A $^1\Pi$	Nesbet (1965b)	75,807	65,075	1.260	1.235	1385	1515.6
CO$^+$, X $^2\Sigma^+$	Nesbet (1965b)	124,400	113,051	1.105	1.115	1751	1562.1
A $^2\Pi$	Nesbet (1965b)	137,130	133,784	1.234	1.244	2332	2214.2

TABLE III—contd.

Molecule and state	Reference	T_e (cm^{-1})		r_e (Å)		ω_e (cm^{-1})	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
BF, $X\ {}^1\Sigma^+$	Nesbet (1964a)	—	—	1.272	1.265	1414	1402.1
	Huo (1965)	—	—	1.246	1.265	1496	1402.1
$a\ {}^3\Pi$	Nesbet (1965b)	25,174	—	1.318	1.309	1369	1323.6
$A\ {}^1\Pi$	Nesbet (1965b)	57,459	51,157	1.328	1.305	1293	1265.0
BF$^+$, $X\ {}^2\Sigma^+$	Nesbet (1965b)	90,292	88,500	1.221	—	1663	—
$A\ {}^2\Pi$	Nesbet (1965b)	146,982	—	1.633	—	1038	—
LiF, $X\ {}^1\Sigma^+$	McLean (1963b)	—	—	1.528	1.564	1134	964.1
BeO, $X\ {}^1\Sigma^+$	Yoshimine (1964)	—	—	1.290	1.331	1808	1487.3
F_2, $X\ {}^1\Sigma^+$	Wahl (1964)	—	—	1.33	1.42	1257	919.0

is -8.0561 au (experimental value -8.0703 au). Computed spectroscopic constants and dipole moment are in excellent agreement with experiment.

Ebbing (1962) has carried out a matrix Hartree–Fock calculation on LiH followed by an extensive configuration interaction calculation, using basis orbitals in the form of exponentials of spheroidal (elliptical) coordinates (ξ, η, ϕ) multiplied by powers of ξ and η. Exponential atomic orbitals can be expressed as simple linear combinations of these elliptical coordinate functions, but the converse statement is not true, and the added flexibility of independent choice of exponent for $\exp(-\alpha\xi)$ and $\exp(-\beta\eta)$ is intended to decrease the number of basis orbitals needed. For atomic orbitals β must be equal to $\pm\alpha$.

Ebbing computes Hartree–Fock energy -7.98506 au and total energy -8.04128 au, as well as the electric dipole moment and dipole moment derivative (Table I). Correlation effects are analyzed in terms of the inner and outer electronic shells ($1\sigma^2$ and $2\sigma^2$, respectively) and compared with the known correlation energy of atomic ions, Li^+ and H^-, respectively. From this comparison it is clear that the total correlation energy of LiH at equilibrium is nearly equal to that of the separated ions. The intershell correlation energy is estimated to be -0.002 au, or -0.05 eV. Here the shells are described in terms of canonical Hartree–Fock orbitals, and a linear transformation to localized orbitals (Lennard Jones, 1949, 1952) could reduce the intershell term even further.

An approximate Hartree–Fock calculation on LiH, with extensive configuration interaction, was carried out with the principal purpose of computing a reliable value of the electric field gradient q at the Li nucleus (Kahalas, 1961; Kahalas and Nesbet, 1961, 1963). Exponential atomic basis orbitals were used. It is found that including a $3d\sigma$(Li) orbital in the basis set has an important effect on the computed value of q, an operator of $d\sigma$ symmetry. The effect of this basis orbital on the total energy is negligible (0.01 %) and the change of electric dipole moment is relatively small (1.0 %). The computed value of $(q/2e)$ at $R = 3.02\, a_0$ is $-0.0200\, a_0{}^{-3}$ without the $3d\sigma$ orbital, changing to -0.0167 when the $3d\sigma$ orbital is included. The $3d\sigma$ exponent was determined by minimizing the electronic energy. Configuration interaction was found to have a very small effect, changing the computed $(q/2e)$ to $-0.0166\, a_0{}^{-3}$ at the computed r_e. This result has been verified by Browne and Matsen (1964), who compute $(q/2e) = -0.0173\, a_0{}^{-3}$. When these results are combined with the experimental quadrupole coupling constant (eqQ/h) of Li^7 in LiH (Wharton *et al.*, 1962), they lead to a prediction of the nuclear quadrupole moment Q of Li^7, which has not been measured directly. The molecular electric dipole moment obtained in the Hartree–Fock approximation is in good agreement with experiment (Table I).

Kahalas and Nesbet (1963) obtain a Hartree–Fock dissociation energy of 1.44 eV. If this is combined with an empirical estimate of the net correlation energy, 1.03 eV from a comparison of $Li^+ + H^-$ with $Li + H$, as suggested by Ebbing's results (1962), this gives $D_e = 2.47$ eV, close to the experimental D_e, 2.52 eV (Nesbet, 1965a).

A calculation on BH of accuracy comparable to the work described above has been carried out by Stevens and Lipscomb (1965a). Predicted values of magnetic constants are listed in Table II.

A calculation has been carried out on HCl (Nesbet, 1964b), with a basis set that is comparable to earlier work on HF (Nesbet, 1960b). The basis set does not include d orbitals, which might be expected to have a significant effect on computed one electron properties. The molecular electric quadrupole moment, listed in Table I, and its computed derivative were used by Sharma (1965) to compute the integrated absorption coefficient of the pressure induced Q branch in the vibration rotation absorption spectrum of HCl admixed with inert gases. The results agree well with available experimental data. Calculated excitation energies obtained from the ground state approximate Hartree–Fock calculation are included in Table III. The $V\,{}^1\Sigma^+$ state is analogous to the corresponding state in HF, discussed above. The total energy calculated at $R = 2.4085\, a_0$ is $E = -459.80374$ au, 1 au below the energy reported by Moccia (1964c) for an extended one-center orbital basis. The dipole moment calculated by Moccia is included in Table I. The Cl(^2P) atomic energy calculated with the orbital basis used for HCl (Nesbet, 1964b) is -459.20317 au, to be compared with the Hartree–Fock value (Clementi, 1965), -459.48179 au.

B. N_2, CO, and BF

These molecules have the ground state configuration $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4$ for CO and BF, and $1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2 2\sigma_u{}^2 3\sigma_g{}^2 1\pi_u{}^4$ for the homopolar symmetry of N_2. The electronic excited states of these molecules have been the subject of thorough experimental studies. Approximate Hartree–Fock calculations on the ground states, using two exponential basis orbitals for each atomic orbital, were carried out on N_2 (Richardson, 1961) and on CO (Lefebvre-Brion *et al.*, 1960, 1961), at only one internuclear distance. This work was extended by including $d\sigma$ and $d\pi$ orbitals in comparable calculations on N_2, CO, and BF at five internuclear distances (Nesbet, 1964a). Electric moments computed in this work are listed in Table I. The sum of computed dissociation energy and estimated net correlation energy is in reasonable agreement with experiment, but there is some indication of systematic correlation effects due to interaction between localized pairs of electrons in different parts of the effective triple bond in these molecules, or due to the $2s$-$2p$ degeneracy in the Be-like positive ion left when these molecules are separated while maintaining the number and relationship of electron pairs.

Calculations intended to converge very closely to the true Hartree–Fock wave function have been reported for CO and BF (Huo, 1965) and for N_2 (Cade *et al.*, 1966). Approximate Hartree–Fock calculations on the low-lying states of the positive ions were included in this work. A number of results for electric moments and spectroscopic constants are listed in Tables I and III.

There is an apparent conflict between computed and observed values of the electric dipole moment of CO (Table I). There is some question that the experimental sign of this quantity has yet been definitely determined (Nesbet, 1964a). The dipole moment computed by Huo (1965) would be compatible with an experimental moment of the observed magnitude but with positive sign. However, in an earlier calculation with an extended basis set (Lefebvre-Brion *et al.*, 1963) computed $\mu_e = 0.244\ D$ was reduced to $0.117\ D$ by configuration interaction. It would be necessary to examine correlation corrections to Huo's result before concluding that the computed sign is definitely positive.

The electronic excited states of CO have been studied in a series of calculations with orbital basis sets augmented compared with earlier LCAO calculations. In general, the molecular orbital configurations obtained by replacing an occupied 5σ or 1π orbital by the lowest orbital (2π) unoccupied in the matrix Hartree–Fock calculation for the ground state correspond to observed valence excited states. However, the $^1\Sigma^+$ state of the configuration $1\pi^3 2\pi$ has very high energy unless atomic orbitals with higher principal quantum number than 2 are included in the orbital basis set (Lefebvre-Brion *et al.*, 1960). When such orbitals are included, the lowest excited $B\,^1\Sigma^+$ state is found to belong to a series of molecular Rydberg states (Lefebvre-Brion *et al.*, 1964). In this work, the Hamiltonian matrix is diagonalized over a set of configurations all differing by one orbital, with a positive molecular ion configuration as a fixed core. Energies computed relative to the limiting positive ion state are in close agreement with observed molecular Rydberg series. Because of this generally close agreement, it was suggested that the state known as $E\,^1\Sigma^+$ might have been misidentified, since the only computed state with corresponding energy and quantum defect is a $^1\Pi$ state. This has recently been confirmed experimentally, and this state should be designated as $E\,^1\Pi$ (Tilford *et al.*, 1965). The $^1\Sigma^+(1\pi^3 2\pi)$ valence state lies above the ionization limit and could not be distinguished from the underlying continuum, except possibly as a scattering resonance.

This work has been extended to molecular Rydberg states in NO, BF, and N_2 (Lefebvre-Brion and Moser, 1965a,b). In general the agreement with observed energy levels is sufficiently close that exceptions can be attributed to misidentification of observed levels.

The valence excited states of N_2, CO, and BF have been computed in the simplest molecular orbital model (Nesbet, 1965b), using molecular orbitals computed in an approximate Hartree–Fock calculation on the ground state. Excitation energies are computed for states constructed by replacing one occupied Hartree–Fock orbital by the lowest unoccupied matrix Hartree–Fock orbital (2π for CO, BF; $1\pi_g$ for N_2), then taking linear combinations of single determinants to construct functions of definite molecular symmetry and spin. Some results for spectroscopic constants are listed in Table III. Relatively large shifts of molecular orbital configurations with respect to each other are expected as a consequence of correlation energy differences, but the order of states within a configuration should be correct, and this is found to be in agreement with experiment. This kind of calculation can indicate the general location of excited states and give an estimate of spectroscopic constants ω_e and B_e, as an aid to a precise experimental identification, but more quantitative predictions will require more elaborate calculations, including a reliable computation of correlation energy differences. In the case of BF, it is found that all valence states of the configuration ($1\pi^3 2\pi$) lie at or above the first ionization limit, so these states are not expected to be distinguishable from the electronic continuum. This is in agreement with the fact that the only observed valence excited states in BF can be identified as $^{3,1}\Pi$ of the configuration ($1\pi^4 5\sigma 2\pi$).

C. C_2, BN, BeO, and LiF

The ground state configuration of these molecules is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4$ or $1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2 2\sigma_u{}^2 1\pi_u{}^4$ for C_2. However, for C_2 the lowest unoccupied σ orbital ($3\sigma_g$) competes with the highest occupied π orbital ($1\pi_u$), and a $^3\Pi_u$ state of molecular orbital configuration ($1\pi_u{}^3 3\sigma_g$) lies very close to the $^1\Sigma_g{}^+$ ground state. Approximate Hartree–Fock calculations with large basis sets have been carried out on the $^1\Sigma^+$ ground states of LiF (McLean, 1963b, 1964) and of BeO (Yoshimine, 1964). Computed electric dipole moments are listed in Table I and spectroscopic constants in Table III. An empirical estimate of the molecular correlation energy indicates that the computed LiF energy is within 0.2 eV of the true Hartree–Fock energy. In terms of dissociation energy, computed D_e in the Hartree–Fock approximation is 4.03 eV, estimated net correlation energy is 1.96 eV, to give an estimated total of 5.99 eV, exactly equal to the experimental D_e (McLean, 1963b).

The valence excited states of C_2 and BN have been studied by Fougere (1965). For C_2, all molecular orbital configurations constructed by placing the six electrons outside of a $1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2$ core into all combinations of six orbitals from the set ($2\sigma_u$, $3\sigma_g$, $3\sigma_u$, $1\pi_u$, $1\pi_g$) were included in a limited configuration interaction calculation (Fougere and Nesbet, 1966). This set of Slater determinants reduces to several hundred independent states, capable of describing all molecular states that separate into atoms in their ground state configuration ($1s^2 2s^2 2p^2$). Molecular orbitals were obtained at nine internuclear distances by approximate Hartree–Fock calculations on a single electronic state, different at different values of R in order to produce orbitals appropriate to the neutral atomic ground state at large R. The best orbital basis set consisted of two exponential orbitals for each atomic orbital, with an additional $3d\sigma$ and $3d\pi$ on each atom. The close relationship between spectroscopic constants of computed and observed states was used to predict constants for a number of unobserved states, by means of a statistical regression analysis. Basis orbitals capable of describing molecular Rydberg states were not included in this work.

D. Other Diatomics

A calculation on F_2 intended to converge closely to a true Hartree–Fock function has been reported by Wahl (1964). The computed Hartree–Fock dissociation energy is negative, but this is in agreement with a simple empirical estimate of the net correlation energy in F_2, which turns out to be greater than the observed dissociation energy. The ground state molecular orbital configuration energy curve has a well-defined minimum, and computed spectroscopic constants are in reasonable agreement with experiment (Table III).

The ground state of TiO has been experimentally identified as $^3\Delta$, in conflict with a simple ligand-field model, which predicts a $^3\Sigma^-$ state of configuration δ^2 (Berg and Sinanoğlu, 1960). Carlson and Moser (1963) used orbitals obtained by an LCAO ground state calculation to construct a number of molecular orbital valence state wave functions. This work indicated that the molecular ground state should be $^3\Delta$, from configuration $\delta\sigma$, with low-lying states $^1\Delta(\delta\sigma)$ and $^1\Sigma^+(\sigma^2)$, in agreement with states observed spectroscopically. This work was confirmed by Carlson and Nesbet (1964), who extended the basis set to include $4p\sigma$ and $4p\pi$ orbitals on Ti and $3d\pi$ on O, with exponents of all valence orbitals determined variationally. Calculations at three internuclear distances were used to determine spectroscopic constants. Empirical correlation energy corrections were estimated for the lowest molecular states.

For weakly interacting atoms, the molecular orbital theory can be used to examine the effective Heisenberg exchange interaction coupling the atomic spins S. As an example of this theory a calculation was carried out on Mn_2 at three internuclear distances, using an orbital basis consisting of a minimal exponential atomic basis plus $4p$ orbitals (Nesbet, 1964c). The equilibrium internuclear distance r_e is found to lie in a range in which most of the molecular valence orbitals are of atomic form, a result expected for magnetic materials. In these circumstances a number of states of different total spin lie close together. Relative spacing is determined by the effective Heisenberg exchange integral J, which can be computed by perturbation theory, taking spin-dependent configuration interation into account. The computed value of $4S^2J$ at the computed r_e (2.88 Å) is -0.0082 eV, equivalent to 95.2°K, which may be compared with Curie temperatures in transition metals. This molecule, which contains fifty electrons, is the largest yet studied by *ab initio* methods.

IV. Polyatomic Molecules

A. Central Hydrides

A number of these molecules have been studied by the one-center method (Moccia, 1964a,b,c). This work includes several molecules (SiH_4,

PH_3, H_2S) for which no comparable work is available by other methods. The total energy computed for HCl (Section III, A) compares unfavorably with approximate Hartree–Fock energies computed for the atoms and for the diatomic molecule, using exponential basis orbitals on both atoms. The computed dipole moment (Table I) is also in poor agreement with experiment. However, the dipole moments computed for smaller molecules (NH_3, H_2O) are much closer to the experimental values (Table I).

The calculation by Moccia (1964a) on CH_4 used the matrix Hartree–Fock method with a large basis set of one-center exponential functions. The computed energy is -39.87 au. This result compares very favorably with an earlier calculation (Albasiny and Cooper, 1961) in which the traditional Hartree–Fock method (numerical integration) was used to solve the coupled equations for radial functions in the expansion of CH_4 molecular orbitals in terms of spherical harmonics up to $l = 3$. The energy computed by this method is -39.90 au. Moccia obtains values of equilibrium internuclear distances and bond angles that are, in general, in good agreement with experiment.

Calculations on CH_4 and NH_4^+, using a large basis set of Gaussian orbitals, have been reported by Krauss (1963). The computed energy of CH_4 at nuclear equilibrium is -40.1668 au, 0.27 au below the best result obtained by the one-center method. These calculations are expected to give close approximations to the molecular Hartree–Fock functions. These calculations have been extended to a study of internuclear distances and bond angles in hydride molecules or ions with central B, C, N, and O atoms (Krauss, 1964). The results are in good agreement with existing experimental values.

As part of an exploratory project on the use of Gaussian basis orbitals, Reeves and Harrison (1963) carried out a matrix Hartree–Fock calculation on CH_4 with five s orbitals on C, two s orbitals on H, and one p orbital on C. Because of the use of only one p orbital this basis set is not likely to give a consistent approximation to a Hartree–Fock function.

B. Linear Polyatomic Molecules

The computer program for molecular integrals in linear polyatomic molecules written by McLean (1960) has been used for several matrix Hartree–Fock calculations, including the calculation by Clementi (1962) on HF. Several calculations on CO_2, with various basis orbital sets, all at one internuclear distance, are reported by McLean (1963a). Limitations in the computer programs used restricted the number of basis orbitals so that the valence orbitals of all three atoms could not be represented to equal accuracy. One exponential orbital was used for each atomic 1*s* and 2*s*, one for the central C 2*pσ*, and one basis orbital for each atomic 2*pπ*. This set was augmented for one series of calculations by adding two 2*pσ* orbitals for each O atom, an additional C 2*pσ*, and two 3*dσ* for the C atom. In another calculation, these orbitals were replaced by a single 2*pσ* and 3*dπ* on each O atom, and two additional 2*pπ* orbitals on C. Because the *σ* orbital set could be augmented only at the expense of the *π* orbitals, and vice versa, these calculations probably give an unbalanced representation of the molecular charge density (Mulliken, 1962). Since comparable calculations were not made on the separated atoms, no estimate of the dissociation energy is given. The ground state calculation at one internuclear distance gives the computed molecular quadrupole moment listed in Table I.

Similar calculations were carried out on N_3^- and NO_2^+ (Clementi and McLean, 1963), on C_3 (Clementi and McLean, 1962a), and on HF_2^- (Clementi and McLean, 1962b). The basis sets were similar to those used for CO_2, and were subject to the same limitations. All calculations were for one nuclear conformation of the molecular ground state, so no spectroscopic constants could be computed.

C. Other Molecules

Moskowitz and Harrison (1965) report approximate Hartree–Fock calculations on ethylene (C_2H_4), using several basis sets of Gaussian orbitals. The largest basis set used included carbon atom orbitals that give a ground state matrix Hartree–Fock energy of −37.61922 au, compared with the atomic Hartree–Fock energy, −37.6886 au (Clementi, 1965). No spherical harmonics higher than *p* for the C orbitals or *s* for the H orbitals are included in the molecular basis set. Vertical excitation energies are computed both in the simple molecular orbital approximation and with limited configuration interaction (a two-by-two matrix for the two ^1A_g states constructed from *π* valence orbitals). The computed excitation energies of excited $\pi \rightarrow \pi^*$ states $^3B_{3u}$ and $^1B_{3u}$ are, respectively, 4.318 and 10.433 eV, compared with experimental excitation energies, 4.8 and 7.6 eV. The computed vertical ionization potential, 10.352 eV, is close to the experimental value, 10.52 eV. The computed Hartree–Fock dissociation energy is 0.6185 au. A series of calculations with a relatively small basis were carried out on twisted conformations of C_2H_4. The computed twisting frequency is 1168 cm^{-1}, compared with the experimental value, 1027 cm^{-1}. Calculations with small basis sets for various CC and CH distances gave well-defined energy minima for distances in reasonable agreement with experiment.

Comparable calculations on C_2, ethylene, and acetylene (C_2H_2) have been carried out by Moskowitz (1965). Ground state Hartree–Fock energies are computed at the experimental nuclear equilibrium. These results are used to estimate the net correlation energy in the CC double bond to be between 0.057 and 0.096 au, and the net correlation energy in the triple bond to be between 0.103 and 0.147 au.

V. Discussion

The results shown in Tables I and II indicate that the molecular Hartree–Fock approximation can produce accurate values of one-electron properties. A number of predictions of quantities not yet measured experimentally are included in these tables.

The spectroscopic data in Table III shows, in general, good qualitative agreement with experiment with regard to the identification of observed states, but large systematic errors remain in computed values of T_e and ω_e. These quantities will be affected by the two chief shortcomings of present calculations, first, failure to carry out individual Hartree–Fock calculations for each separate state, and second, neglect of correlation energy. From the results of Cade *et al.* (1966), who report independent Hartree–Fock calculations for several states of $N_2{}^+$, yet still find the $^2\Pi_u$ and $^2\Sigma_g{}^+$ states in the wrong order (Table III), it appears that large discrepancies arise from correlation energy differences between different states. The variation of correlation energy with internuclear distance also affects ω_e.

Ground state dissociation energies can in many cases (discussed above) be accounted for by adding an empirical molecular net correlation energy into the computed Hartree–Fock dissociation energy. This work has not yet been extended to an adequate treatment of correlation energy differences between excited states.

Successful calculation of ground state properties has only been possible with orbital basis sets, in the matrix Hartree–Fock method, that are capable of representing the most important effects of distortion or polarization of atomic valence orbitals in a molecular environment. This requires some flexibility in the representation of each valence orbital, inclusion of unoccupied atomic valence orbitals, and inclusion of polarizing orbitals with radial factors similar to atomic valence orbitals but with higher angular quantum numbers.

Calculations of the molecular ground state at one internuclear distance give at best the various measurable one-electron properties. A comparable calculation on the separated atoms gives an estimate of the Hartree–Fock dissociation energy. If calculations are carried out at three or more internuclear distances it is possible, most importantly, to verify the existence of an equilibrium conformation, and then to compute molecular geometry. Computation of excited molecular orbital configuration energies gives information that is at least qualitatively useful in identifying excited states observed spectroscopically.

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Single-Center Molecular Wave Functions

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I. Introduction

In principle the problem of finding nonrelativistic molecular wave functions for a fixed nuclear framework was solved in the 1920's, when Schrödinger formulated his, now famous, differential equation:

$$\mathscr{H}\Psi_0 = W_0\Psi_0. \tag{1}$$

The zero subscripts denote exact solutions, $\mathscr{H}$ is the quantum mechanical Hamiltonian operator for the system to be investigated, and Ψ_0 is its electronic wave function in the stationary state of energy W_0. For nearly all systems Eq. (1) is mathematically difficult to solve and for the past forty years quantum chemists have been mainly concerned with alleviating the mathematical problem. Much effort has been put into this work because, when Ψ_0 is known, other electronic properties can be readily found.

One of the most common lines of approach has been to use the variational theorem. This theorem states that if we calculate

$$W = \int \Psi^* \mathscr{H} \Psi \, d\tau \Big/ \int \Psi^* \Psi \, d\tau \tag{2}$$

for some chosen wave function Ψ of a given symmetry, then, $W \geq W_0$, where W_0 is the lowest exact solution of Eq. (1) in which Ψ_0 is of the same symmetry as Ψ. The procedure which uses this theorem, called the variational method, is to choose some form of Ψ which is dependent on one or more parameters and then to minimize W as a function of these parameters. Ψ will then be the best wave function, from an energy point of view, for the form chosen. Much will depend, however, on the functional form of Ψ, both with regard to the amount of labor involved and to the accuracy of the final result.

Commonly one chooses a trial function Ψ which is a linear combination of some finite set of functions Φ_i,

$$\Psi = \sum_{i=1}^{N} c_i \Phi_i. \tag{3}$$

The required minimization of W with respect to the coefficients c_i then leads to N simultaneous homogeneous linear equations:

$$\sum_{j=1}^{N} c_j (H_{ij} - S_{ij} W) = 0, \qquad i = 1, 2, \ldots, N. \tag{4}$$

The quantities

$$H_{ij} = H_{ji}^* = \int \Phi_i^* \mathscr{H} \Phi_j \, d\tau \tag{5}$$

$$S_{ij} = S_{ji}^* = \int \Phi_i^* \Phi_j \, d\tau \tag{6}$$

can be found from the chosen Φ_i and the known $\mathscr{H}$. This is called the linear variational method, and the condition that there exists a nontrivial solution to Eq. (4) is that the determinant

$$|(H_{ij} - S_{ij} W)| = 0. \tag{7}$$

This equation has N roots and the lowest one will converge on W_0 as more independent basis functions, Φ_i, are introduced. Once the roots are known, Eq. (4) and the normalization condition will allow us to obtain the coefficients c_i.

In order to satisfy the Pauli principle, each basis function must be antisymmetric with respect to the interchange of any two electrons; this may be accomplished by writing Φ_i as a Slater determinant[1]:

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[1] For the purposes of discussion it is assumed that we are dealing with a singlet state and that each orbital is doubly occupied.

$$\Phi_i = (n!)^{-1/2} \begin{vmatrix} \phi_1(1) & \bar{\phi}_1(1) & \phi_2(1) \ldots & \bar{\phi}_{n/2}(1) \\ \phi_1(2) & \bar{\phi}_1(2) & \phi_2(2) & \bar{\phi}_{n/2}(2) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_1(n) & \bar{\phi}_1(n) & \phi_2(n) \ldots & \bar{\phi}_{n/2}(n) \end{vmatrix} \tag{8}$$

$$= |\,\phi_1(1) \quad \bar{\phi}_1(2) \quad \phi_2(3) \ldots \bar{\phi}_{n/2}(n)\,|\,.$$

In this determinant each of n electrons is placed in a one-electron spin orbital, ϕ_i, where no bar implies spin α and a bar implies spin β. Each ϕ_i is a function of the coordinates of the one electron and may also depend on one or more parameters which can be chosen to minimize the lowest root of Eq. (7). The important decision which now has to be made concerns the choice of the functional form of ϕ_i.

First one must decide whether to locate the orbitals, ϕ_i, on a single center (hereafter referred to as single-center functions) or, as in the Linear Combination of Atomic Orbitals Molecular Orbital method, on many centers (multicenter functions); this article will deal exclusively with the former choice. The method of using only single-center functions has also been called "the one-center method," "the central field approximation," "the central orbital approach," and "the united atom method."

The principle behind the single-center method is that any molecular wave function can be expanded in terms of functions about any one single convenient point. It was in 1933 that Mulliken first suggested this approach and since that time over eighty papers have been published in the field. The advantage of the method is that, though many more terms are needed in the wave function than in the conventional methods, the integrals of Eq. (5) and Eq. (6) are all single-center integrals and are all tractable, whereas those for multicenter functions are, at best, difficult to evaluate. As Löwdin (1957) has said, by using the single-center method one, in effect, replaces the solution of a secular equation of lower order and complicated matrix elements with a secular equation of high order having simple matrix elements. In other words a mathematically difficult problem is replaced by a simple but tedious one, and as such is ideally suited for modern high-speed digital computers. It is true that, in the single-center model, the basic set of orbitals has no natural association with the problem itself, but after obtaining the total wave function one may transform the result to another basic set which is directly associated with the problem under consideration.

The method is suited for a basic set of complicated orbitals, though in the past not much advantage has been taken of this fact, and it is ideal for finding, analytically, the energy derivatives with respect to nuclear coordinates.

The method will be most satisfactory for those molecules which are of high, and close to spherical, symmetry because the addition of functions having higher angular terms will then be small. Methane, with its tetrahedral symmetry, should be particularly good in this respect, for in the expansion of the potential due to the nuclei at any point:

$$V(r, \theta, \phi) = -\sum_{L=0}^{\infty} \sum_{M=-L}^{L} \frac{4\pi}{2L+1} Y_{LM}(\theta, \phi) \sum_{\alpha} Z_{\alpha} \left(\frac{r_<^L}{r_>^{L+1}} \right) Y_{LM}^*(\theta_\alpha, \phi_\alpha) \quad (9)$$

where the subscript α denotes each nucleus, the terms with $L = 1, 2, 5$ vanish. If, in the wave function, one includes harmonics up to l then terms up to $L = 2l$ must be included in Eq. (9), so that a wave function containing up to f harmonics is equivalent to taking the first six terms in Eq. (9) and a purely spherical function is equivalent to taking the first three terms.

In the single-center method, the wave function will be poorest close to the off-center nuclei, where certain cusp conditions are difficult to fulfill. However this disparity will be least when the charge on the off-center nuclei is small, and it is for this reason that the hydrides (XH_n), with the orbital center on the heavy nucleus (X), are the most suitable molecules for single-center calculations.

Single-center functions should be very good for excited states, where the average distance of the electrons from the nuclei is much greater than the nuclear separation and where the numerical magnitude of the wave function close to the nuclei is small.

If only single excitations are used to form Φ_i, Eq. (8), from Φ_1, the energy will probably tend to converge to the Hartree–Fock value, but if other than single excitations are included, then some of the correlation energy will be achieved.

In the next section the method will be applied to a simple example and in Sections III and IV applications of the method will be reviewed. Section V will deal with refinements and future prospects.

Throughout this paper, wherever it is possible, atomic units have been used: 1 au (length) = 0.52915 Å, 1 au (energy) = 27.210 eV.

II. Method of Calculation

As far as outlining the method of calculation, we will restrict ourselves to the use of Slater-type orbitals for ϕ_i, that is:

$$\phi_i(1) = (2\zeta_i)^{n_i+1/2}[(2n_i)!]^{-1/2} r_1^{n_i-1} \exp(-\zeta_i r_1) Y_{l_i m_i}(\theta_1, \phi_1) s(1). \quad (10)$$

Here, n_i and ζ_i are the nonlinear variable parameters, the n_i may be restricted to integers if one wishes, the $Y_{l_i m_i}$ are normalized spherical harmonics, $s(1)$ is the spin function (α or β) for electron 1, and r_1, θ_1, and ϕ_1 are the polar coordinates of electron 1 with respect to the chosen center. These orbitals will be chosen to be orthogonal by the Schmidt method; other choices for ϕ_i and methods of orthogonalization will be considered in Sections III and IV.

As an example we will treat the ammonia molecule, for which the Hamiltonian is

$$\mathscr{H} = \sum_{i=1}^{10} -\tfrac{1}{2}\nabla_i^2 + \sum_{i=1}^{10} \frac{-7}{r_i} + \sum_{i=1}^{10} \sum_{\alpha=1}^{3} -\frac{1}{r_{\alpha i}} + \sum_{i \leq j}^{10} \frac{1}{r_{ij}} + \sum_{\alpha=1}^{3} \frac{7}{R_\alpha} + \sum_{\alpha \leq \beta}^{3} \frac{1}{R_{\alpha\beta}}. \tag{11}$$

These terms, in order, are the kinetic energy operator and the nitrogen-electron, proton-electron, electron-electron, nitrogen-proton, and proton-proton potential energy operators. For the sake of simplicity we will assume a single determinantal wave function for the ten electrons, i.e.,

$$\Psi = \Phi_1 = |\phi_s(1)\bar{\phi}_s(2)\phi_{s^*}(3)\bar{\phi}_{s^*}(4)\phi_{p_x}(5)\bar{\phi}_{p_x}(6)\phi_{p_y}(7)\bar{\phi}_{p_y}(8)\phi_{p_z}(9)\bar{\phi}_{p_z}(10)|. \tag{12}$$

The Slater orbitals will be centered on the nitrogen nucleus; it is usual to choose the heavy nucleus as the center in XH_n-type molecules and the center of symmetry in molecules where all the nuclei are equivalent. Explicitly, the orbitals being used are of the form:

$$\begin{aligned} \phi_s &\sim r^{n_s - 1} \exp(-\zeta_s r) \\ \phi_{s^1} &\sim r^{n_{s^1} - 1} \exp(-\zeta_{s^1} r) \\ \phi_{p_x} &\sim r^{n_{px} - 1} \exp(-\zeta_{p_x} r) \sin\theta \cos\phi \\ \phi_{p_y} &\sim r^{n_{py} - 1} \exp(-\zeta_{p_y} r) \sin\theta \sin\phi \\ \phi_{p_z} &\sim r^{n_{pz} - 1} \exp(-\zeta_{p_z} r) \cos\theta \\ \phi_{s^*} &= (\phi_{s^1} - S\phi_s)/(1 - S^2)^{1/2} \end{aligned} \tag{13}$$

where $S = \int \phi_s \phi_{s^1}\, d\tau$.

As all these orbitals are normalized and mutually orthogonal, the overlap integral, S_{11}, will be unity and there will be a single energy root, $W = H_{11}$ [see Eq. (7)].

The rules governing the reduction of integrals involving determinants to integrals involving orbitals are the same as those used in atomic problems, and in this case we have:

$$H_{11} = \sum_{i=1}^{10} I_i' + \sum_{i \leq j}^{10} (J_{ij}' - K_{ij}') + \sum_{\alpha=1}^{3} \frac{7}{R} + \sum_{\alpha \leq \beta}^{3} \frac{1}{R_{\alpha\beta}} \tag{14}$$

where the primes indicate that spins are included and

$$I_i' = \int \phi_i^*(1)\left[-\frac{1}{2}\nabla_1{}^2 - \frac{7}{r_1} - \sum_{\alpha=1}^{3}\frac{1}{r_{\alpha 1}}\right]\phi_i(1)\, d\tau_1 \cdot S(1) = I_i \cdot S\ (1)$$

$$J_{ij}' = \iint \phi_i^*(1)\phi_j^*(2)[1/r_{12}]\phi_i(1)\phi_j(2)\, d\tau_1\, d\tau_2 \cdot S(1)S(2)$$

$$= J_{ij} \cdot S(1)S(2)$$

$$K_{ij}' = \iint \phi_i^*(1)\phi_j^*(2)[1/r_{12}]\phi_j(1)\phi_i(2)\, d\tau_1\, d\tau_2 \cdot S(1)S(2)$$

$$= K_{ij} \cdot S(1)S(2).$$

$S(1)$ is, for example, the integral over spin coordinates for the spin functions on electron 1 and is unity if both spin functions are the same; otherwise it is zero.

We therefore have:

$$\begin{aligned} W = H_{11} &= 2I_s + 2I_{S^*} + 2I_{p_x} + 2I_{p_y} + 2I_{p_z} \\ &+ J_{ss} + J_{s^*s^*} + J_{p_xp_x} + J_{p_yp_y} + J_{p_zp_z} \\ &+ 2(2J_{ss^*} - K_{ss^*}) + 2(2J_{sp_x} - K_{sp_x}) + 2(2J_{sp_y} - K_{sp_y}) \\ &+ 2(2J_{sp_z} - K_{sp_z}) + 2(2J_{s^*p_x} - K_{s^*p_x}) + 2(2J_{s^*p_y} - K_{s^*p_y}) \\ &+ 2(2J_{s^*p_z} - K_{s^*p_z}) + 2(2J_{p_xp_y} - K_{p_xp_y}) + 2(2J_{p_xp_z} - K_{p_xp_z}) \\ &+ 2(2J_{p_yp_z} - K_{p_yp_z}). \end{aligned}$$

Each of the one-electron integrals, I_i, is composed of three parts, a kinetic energy term:

$$I_i^T = \int \phi_i^*(1)\left[-\frac{1}{2}\nabla_1{}^2\right]\phi_i(1)\, d\tau_1,$$

a nitrogen-electron potential energy term:

$$I_i^N = \int \phi_i^*(1)\left[-\frac{7}{r_1}\right]\phi_i(1)\, d\tau_1$$

and a proton-electron potential energy term:

$$I_i^P = \int \phi_i^*(1)\left[\sum_{\alpha=1}^{3}\frac{1}{r_{\alpha 1}}\right]\phi_i(1)\, d\tau_1.$$

Evaluation of I_i^T and I_i^N is straightforward and leads to the expressions:

$$I_i^T = \zeta_i^2 [n_i + 2l_i(l_i + 1)]/[2n_i(2n_i - 1)]$$

and

$$I_i^N = -7\zeta_i/n_i.$$

To evaluate I_i^P, we must first expand the three distances, between an electron and each proton, in spherical harmonics about the nitrogen nucleus as in Eq. (9). I_i^P is then a series of terms each of which is a product of three integrals which are of the form

$$\int_0^\infty r_1^{2n_i} \exp(-2\zeta_i r_1)\,(r_<^L/r_>^{L+1})\,dr_1,$$

$$\int_0^\pi \Theta_{l_i m_i}^2(\theta_1)\Theta_{LM}(\theta_1)\sin\theta_1\,d\theta_1,$$

and

$$\int_0^{2\pi} \Phi_{m_i}^2(\phi_1)\Phi_M(\phi_1)\,d\phi_1,$$

where $r_<$ and $r_>$ are the lesser and greater of the two distances: electron-origin and nucleus-origin; the spherical harmonics $Y_{lm}(\theta, \phi)$ have been written as the product $\Theta_{lm}(\theta)\Phi_m(\phi)$.

For the general case, when one is dealing with noninteger n_i, the radial integral reduces to gamma and incomplete gamma functions (see Joy and Parr, 1958). These become factorials, $A_k(\rho)$ and $B_k(\rho)$ functions for integer n_i. The theta integral may be expressed as a Condon and Shortley C^k coefficient and the third integral evaluated on inspection.

The two-electron integrals, J_{ij} and K_{ij}, may also, after expansion of $1/r_{12}$ in spherical harmonics, be written as a series of terms each of which is a product of six integrals, i.e., over r_1, r_2, θ_1, θ_2, ϕ_1, and ϕ_2. It is here that the great advantage of the single-center method is felt; had we put our atomic orbitals on different centers no such simple expansion would have been possible. The radial integrals can be evaluated in terms of incomplete beta functions (or as a polynomial for integer n_i, see Roothaan and Bagus, 1963), and the angular integrals as before.

The nuclear-nuclear potential energy terms can be found immediately if the molecular geometry of ammonia is known. We can therefore evaluate $W = H_{11}$, in terms of gamma, incomplete gamma, and incomplete beta functions and C^k coefficients, for any set of n_i and ζ_i.

The next part of the problem is to find a set of n_i and ζ_i which will give the lowest possible value to W. Modern digital computers enable us to do this with speed and accuracy in a straightforward manner by a method known as "Pattern Search." This method was first formulated by Hooke and Jeeves (1961) and later refined by Ludwig (1962). To explain the procedure, let us consider the minimization of W with respect to just one parameter which we will call n. The first step is to guess some value of n, say x, and calculate an original W (Step 1). We then change n to $x + \alpha\Delta$, where Δ is some chosen decrement less than x, and calculate W for $\alpha = +1$ and -1 (Step 2). We retain the value for α which gives a W value lower than the original one; if with α either $+1$ or -1 no lower value is found we reduce the size of Δ and repeat Step 2. Usually this is not the case and we then change the value of the parameter by $2\alpha\Delta$, α having the value which previously lowered W. That is, having decided the best direction in which to go, we now go twice as far in that direction (Step 3). We now return to Step 1 and continue cycling through Steps 2 and 3 until Δ is less than the desired accuracy for n.

The procedure can be generalized for more than one parameter and certain refinements incorporated, but in principle it is as outlined above. Such a direct minimum search method has the important advantage that the cycle can be interrupted at any time and the "best" parameters at that moment are given; the cycle can then be started up later with these values as input data.

To summarize this section: one first chooses the form of the wave function and the structural parameters, one then reduces W to integrals over orbitals and these integrals to their radial and angular components, and finally one chooses parameters such as to minimize W.

The results for ammonia for the model as outlined here will be discussed in the next section.

III. Simple Wave Functions[2]

By simple it is meant that the wave function is a single determinant composed of just one atomic orbital for each electron; for example for a ten-electron case one might have $\Psi = |1s^2 2s^2 2p_x{}^2 2p_y{}^2 2p_z{}^2|$ and the orbitals could be Slater type, Fock–Petrashen, or hydrogenlike. This is, in fact, the situation studied in some detail in the previous section.

Hartmann and his co-workers (Hartmann, 1947; Hartmann and Gliemann, 1958, 1959; Hartmann and Grein, 1959) have studied $CH_5{}^+$,

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[2] In this section and the next, all results given will include the corrections made by later workers of errors in the original papers and with each reference the source of the correction will be found.

CH_4, CD_4, $NH_4{}^+$, $CH_3{}^-$, NH_3, and $OH_3{}^+$ by approximating Ψ still further; they have reduced the charge on the heavy nucleus (the orbital center) by two units and considered only the outer eight electrons, i.e., $\Psi = |2s^2 2p_x{}^2 2p_y{}^2 2p_z{}^2|$. By taking hydrogenlike atomic orbitals with all exponents equal to the same value (Z_0) an equation for the energy of the eight electrons (E) in terms of Z_0 and the bond distances (R) results. Minimization of E with respect to Z_0 and R enables E, R, Z_0, vibrational frequencies, and diamagnetic susceptibilities to be determined. This method has been remarkably successful, as applied by Lampe and Futrell (1963), in predicting the proton affinities of molecules as well as bond lengths (see Table I). In general the wave functions used in this method have been spherically symmetric though in one paper, Hartmann and Gliemann (1959), a polarization factor was introduced into the orbitals which was different for different orbitals, thus allowing for the nonspherical symmetry of $CH_3{}^-$, NH_3, and $OH_3{}^+$.

TABLE I

PROTON AFFINITIES AND BOND DISTANCES BY THE HARTMANN METHOD

A	$P(A)$ (eV)		R (Å)	
	Calc.	Obs.	Calc.	Obs.
CH_4	6.994	>4.95	1.157	1.091
NH_3	10.367	>7.45	1.035	1.015
H_2O	7.532	>7.25	0.936	0.958
HF	3.937	—	0.879	0.917
CH_3	5.829	5.04	—	—
NH_2	8.417	7.95	—	—
OH	5.032	6.10	0.952	0.971
F	0.416	2.70	—	—
NH^+	—	—	1.062	1.035
H_3O^+	—	—	0.980	1.00

In 1953 Bernal proposed the use of Fock–Petrashen (1934) orbitals in single-center methods; these are essentially Slater-type orbitals but with a particular orthogonalization of the $2s$ to the $1s$ orbital, i.e., $1s \sim e^{-\alpha r}$, $2s \sim [1 - (\alpha + \beta)r/3]\, e^{-\beta r}$, and $2p_z \sim re^{-\gamma r} \cos \theta$. He calculated the total energies of CH_4 and $NH_4{}^+$ taking into account all ten electrons. As dictated by symmetry, he kept the same exponent (γ) for all three p orbitals;

hence the total wave function was spherically symmetric. Banyard and March (1956) similarly treated H_2O and NH_3 and also calculated the X-ray scattering factors. For NH_3 these authors (1957) computed the total energy allowing p orbital exponents to be different, but found little gain in energy for such a nonspherical wave function. Banyard (1960, 1961) has also calculated the radial diamagnetic susceptibilities of CH_4, NH_3, and H_2O, using the formula $\chi_r = -0.7923 \int_0^\infty 4\pi r^2 \rho(r) r^2 dr$, where $\rho(r)$ is the radial density distribution. Banyard and Hake (1964, 1965) have applied the method to the eighteen-electron system of H_2S with reasonably successful results and also to PH_2^-, PH_3, and PH_4^+; the proton affinity of phosphine is found to be 236 kcal/mole (experimental, ~209).

Using Bernal's method Higuchi (1959) has obtained 7.5 eV for the proton affinity of methane, and Rosenfeld (1964) has shown that H_4O^{++} is unstable relative to $H_3O^+ + H^+$ by 40–60 kcal/mole, having in fact an energy of -75.314 au.

In Hungary Gaspar *et al.* (1958, 1962a) have calculated energies, bond distances, and proton affinities for HF, OH^-, OH, H_2O, and H_3O^+, using Fock–Petrashen orbitals. It is interesting to note that, though nonspherical functions were used, a lower energy was obtained for H_2O with $H\hat{O}H = 180°$ than with $H\hat{O}H = 104°27'$ and for H_3O^+ with $H\hat{O}H = 120°$ than with $H\hat{O}H = 106°46'$; this shows that within this simple approximation the nuclear repulsions dominate and that the prediction of bond angles with such a model is not possible. Gaspar *et al.* (1962b) state that allowance for nonsphericity makes a significant difference to the energy, in contradiction to Banyard and March (1957); however, they based this statement on a faulty comparison. They compared B.M.s energy for H_2O for a spherical function and $H\hat{O}H = 105°$ with their energy for a nonspherical function but with $H\hat{O}H = 180°$, obtaining a difference of 0.113 au. A comparison for the same bond angle gives a difference of only 0.03 au.

For BH_4^-, CH_4, and NH_4^+ the two methods, Hartmann's with one orbital exponent and Bernal's with three, have been comparatively studied by Grein (1962), and some of his results are given in Table II. These results show that the single-exponent functions are almost as good as the triple-exponent functions, implying that it is nearly correct to consider the nuclei as completely screened by the 1s electrons.

Funabashi and Magee (1957) determined the energies and ionization potentials for H_2, H_2O, and CH_4 using hydrogenlike wave functions with variation of the parameters: ζ_{1s} and ζ_{2p} (ζ_{2s} was related to ζ_{1s} through the

TABLE II

GREIN'S COMPARISON OF THE HARTMANN AND BERNAL METHODS

Property	BH_4^-			CH_4			NH_4^+		
	Hartmann	Bernal	Obs.	Hartmann	Bernal	Obs.	Hartmann	Bernal	Obs.
R (au)	2.505	2.208	2.37	2.186	1.971	2.065	2.003	1.835	1.96
E (au)	−25.864[a]	−26.112	—	−39.048[b]	−39.349	−40.522	−55.331[c]	−55.684	—
χ_r (10^{-6}cm^3/mole)	−54.55	−44.0	—	−31.43	−26.35	−26.70	−19.8	−16.97	−19.4
ω_1 (cm^{-1})	2189	—	2270	3009	—	2914	3600	—	3033
ω_2 (cm^{-1})	1073	1295	1065	1315	1536	1526	1494	1711	1685
ω_3 (cm^{-1})	2907	3506	2270	3577	4133	3020	3784	4258	3134
ω_4 (cm^{-1})	2022	2440	1080	2470	2866	1306	2656	3008	1397

[a] In order to make a proper comparison, the fourth and fifth ionization potentials of boron, as given by Moore (1958), have been added to Hartmann's eight-electron energy (−3.834 au).

[b] Fifth and sixth ionization potentials of carbon added to Hartman's energy (−6.64 au).

[c] Sixth and seventh ionization potentials of nitrogen added to Hartmann's energy (−10.54 au).

orthogonality condition); their results were inferior to those obtained using Bernal's method.

For NH_3, H_2O, and HF, Bishop *et al.* (1963) have compared the results of Banyard and March, Funabashi and Magee, and Gaspar *et al.* with their own, which were based on Slater-type orbitals orthogonalized by the Schmidt process. Within this framework a number of models were examined, and as an example we will consider NH_3. For a spherical wave function, with integer principal quantum numbers (n_i) and centered on the nitrogen nucleus, the energy was -55.4022 au; a further lowering could be obtained by allowing n_i to become noninteger (lowering = 0.2019 au) or the wave function to become nonspherical (lowering = 0.0022 au) or both (0.2026 au). This final result could be further improved by 0.0004 au by allowing the orbital center to move off the nitrogen nucleus by 0.0004 au. The small decrease in energy due to nonsphericity bears out the results of Banyard and March, while the movement of the orbital center off the heavy nucleus also leads to an insignificant improvement; however the inclusion of noninteger principal quantum numbers leads to a considerable decrease in energy. In all cases the energies were lower than those of the workers mentioned previously, and for this improved minimization and use of Schmidt orthogonalized Slater-type orbitals is responsible.

Agreement between calculated and observed bond distances (R) and breathing force constants (k) is quite good, as witnessed by Table III.

TABLE III

BOND DISTANCES AND FORCE CONSTANTS FOR NH_3, H_2O, and HF[a]

Property	NH_3		H_2O		HF	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
R (au)	1.921	1.916	1.792	1.810	1.712	1.733
k (md/Å)	24.64	21.78	21.62	16.63	11.58	9.67

[a] After Bishop *et al.* (1963).

Hoyland and Lampe (1962) have used the same model to calculate the relative energies of $CH_3{}^+$, CH_3, CH_4, and $CH_5{}^+$ and the proton affinity of methane, with good success, obtaining 7.26 eV for the latter quantity; and Bishop and Hoyland (1963) have studied the first-row diatomic hydrides. The model has also been used by Pulay and Török (1964) for the

SiH_4 molecule, and the bond distance, energy, diamagnetic susceptibility, and breathing force constant are all found to an accuracy comparable to that in Table III.

The simplicity, and in some cases accuracy, of a spherically symmetric wave function for XH_n molecules has led Hauk *et al.* (1963) to construct a perturbation theory for these molecules which takes cognizance of this fact. They consider the actual wave function as this spherical "puff," with the concomitant spherical shell proton potential, suitably distorted near the proton sites. Using the Schrödinger perturbation method, they solve directly the differential equations which result from the introduction of the perturbation into the Schrödinger equation. The prescription for the calculation of approximate ground state molecular energies and wave functions for the first-row hydrides has been given.

IV. Complex Wave Functions

Here we will consider those wave functions not discussed in the previous section. The simple wave function can be improved by using a single determinant and determining the one-electron atomic orbitals (ϕ_i) by numerical techniques (the Hartree–Fock procedure) or by replacing each atomic orbital with a linear combination of Slater-type orbitals (all on a single center). Either of these methods will produce an energy whose lower bound is the Hartree–Fock energy. Alternatively, the single determinant of the last section may be replaced by a linear combination of determinants, and if these determinants differ in more than one atomic orbital it will be possible to obtain an energy lower than the Hartree–Fock energy, as some correlation energy will be included.

A. With Numerical Radial Functions

Many workers in England have adopted the Hartree or Hartree–Fock techniques to determine the radial parts of single-center wave functions. This work was originated by Buckingham *et al.* (1941) in what was, strictly speaking, the first single-center paper. They determined, amongst other properties, the energy of methane using a Hartree self-consistent field scheme and thereby neglecting exchange terms; originally the binding energy was given as 0.70 au, however, the correction of an error gives a negative binding energy. An identical calculation was made by Bernal and Massey (1954) for NH_4^+, but the binding energy was not published. Carter (1956) made the obvious and necessary improvement on the calculations by including exchange terms (Hartree–Fock method) and also considered, to some extent, the inclusion of nonspherical components in the wave function (as was not done by Buckingham *et al.*). Though both methane and silane were treated, only the binding energy of the latter, −0.35 au, was given.

It was not until 1958 that this numerical approach was treated rigorously; in that year Mills (1958) found the HF SCF wave functions for methane. Having first determined the spherical component of the wave function, he used a perturbation technique to include the next higher (f) harmonics. Unfortunately, following scepticism by Saturno and Parr (1960), his numerical procedure has been shown by Albasiny and Cooper (1961) to be too approximate for determining the spherical component, and Mills (1961) himself has noted an error in the determination of the f harmonics.

More recently Albasiny and Cooper (1961, 1963a) have solved numerically the six differential equations that arise in a HF SCF treatment of BH_4^-, CH_4, and NH_4^+ if one uses orbitals on a single center up to and including f harmonics; as was shown in Section I, this is effectively the same as an expansion of the field due to the nuclei up to sixth-order terms. The results obtained are extremely good, as is shown by Table IV.

A similar and very thorough numerical treatment has been given, by Cohen and Coulson (1961) and by Cohen (1962), for the ground and excited states of the hydrogen molecular ion. The purpose of these workers was not to find just a very accurate wave function, which anyway already existed, but rather to study the convergence properties of single-center expansions and to produce functions without the two major defects of expansions in Slater-type orbitals, namely, failure to reflect singularities (or cusps) at the nuclear positions and the introduction of a singularity at the center of expansion (this is, of course, no fault if the center is chosen on one of the nuclei). For the ground state, the total wave function was written as

$$\Psi = \sum_{s=0}^{n} f_{2s}(r) P_{2s}(\cos \theta),$$

where the radial components were determined numerically from the differential equations resulting from the application of Eq. (1) and the P_{2s} were the Legendre polynomials; r and θ were the coordinates of the single electron, the coordinate center being at the molecular midpoint. The inclusion of s, d, g, and i harmonics, a nuclear separation of 2.0 au, and extrapolation of the numerical techniques gave an electronic energy of −1.09994 au which is within 0.25% of the exact value. The spherical approximation (s component only and known as the s limit) gave −1.0185 au,

TABLE IV

PROPERTIES OF BH_4^-, CH_4, AND NH_4^+

Property	BH_4^-			CH_4			NH_4^+		
	A and C[a]	Bishop[b]	Obs.	A and C[c]	Bishop[d]	Obs.	A and C[a]	Bishop[b]	Obs.
R (au)	2.240	2.288	2.372	2.013	2.014	2.05	1.915	1.904	1.954
E (au)	−26.615	−26.530	−27.205	−39.894	−39.844	−40.522	−56.306	−56.270	−56.842
k (md/Å)	15.6	16.8	—	25.0	25.8	23.5	29.6	32.8	—
χ_r (10^{-6}cm^3/mole)	−45.1	—	—	−27.8	—	−26.7	−19.0	—	−20.6
α_{xx} (10^{-24}cm^3)[e]	15.00	—	—	5.98	—	2.6	2.95	—	—

[a] Albasiny and Cooper (1963a,b).

[b] Bishop (1963b)

[c] Albasiny and Cooper (1961).

[d] Bishop (1963a).

[e] Polarizabilities as corrected in Albasiny and Cooper (1963b).

in good agreement with Howell and Shull (1959) and other workers (see Part B of this section). For the excited states, as one might expect, the results were even better and effectively exact.

The value of the *s* limit given by Cohen and Coulson for the ground state of H_2^+ is in sharp disagreement with the value of Chen (1958a), who obtained -1.059616 au. Chen based his numerical solution on the Tibbs–Wannier potential problem; this potential is that of a Coulomb field with cut off and thus identical to the spherical approximation of H_2^+. It would appear therefore that only a numerical error would account for the difference between his value and that of other workers, and this in fact is the case as has been shown by Hauk and Parr (1965).

B. With Analytical Radial Functions

In the field of more exact calculations using analytical orbitals a great deal of work has been done on the two simplest molecules, H_2^+ and H_2, work which was stimulated by Matsen's paper, published in 1953, on H_2^+ and Huzinaga's work in 1956 and 1957a. It was in connection with their work on the hydrogen molecule that Joy and Parr (1958) suggested that the use of Slater-type orbitals with noninteger principal quantum numbers (n_i) would be of particular importance for single-center calculations. Of course, many years before, when Slater gave his rules for determining n_i and ζ_i, the n_i for $n_i > 3$ were noninteger; what Joy and Parr now suggested was that all n_i should be noninteger with values taken to minimize the total energy. The improvement in energy that could be obtained with this extra flexibility was considered to be due essentially to a gain in more peaking of the wave function at the off-center nuclei.

For a Slater orbital, of the form $r^{n-1}e^{-\zeta r}Y_{lm}(\theta, \phi)$, the radial distribution function is proportional to $r^{2n}e^{-2\zeta r}$, and this function is maximum when $r = n/\zeta$; the distance between this point and the point (towards the origin) where the distribution function is $1/e$ of its maximum, we can consider as the half band width (l) and as a measure of the amount of peaking of the orbital. Simple algebra gives us the equation

$$\ln(1-k) = -k - 0.5n^{-1} \tag{15}$$

where k is defined by $l = k(n/\zeta)$; solution of this equation for different n values is given in Table V.

In most single-center calculations one desires that the orbitals should peak at the off-center nuclei, which requires that n/ζ be roughly equal to the origin-nuclei distance and to some extent fixes the n/ζ ratio. It is therefore only through k that the half band width can be varied, and Table V shows

TABLE V

SOLUTION OF EQ. (15)

n	1	2	3	4	5	6	7	∞
k	0.70	0.55	0.47	0.42	0.38	0.35	0.33	0

that the higher n, the smaller k and hence l become; in other words, peaking is directly related to n and optimum peaking requires optimum n values. For high n, peaking will be most pronounced.

An alternative measure of peaking is the average square fractional deviation of r from its average value, and this can be shown to be $1/(2n + 1)$ for a Slater-type orbital (Ludwig and Parr, 1961). Thus an increase in n lowers the deviation of r from its average value and thereby increases peaking.

This idea was applied to the hydrogen molecule with considerable success, Joy and Parr (1958) and Bishop (1963a), for a seven-term wave function centered at the molecular midpoint:

$$\begin{aligned}\Psi &= c_1|ss^{\mathrm{I}}| + c_2|s^{\mathrm{II}}s^{\mathrm{III}}| + c_3|s^{\mathrm{IV}}d_0| \\ &\quad + c_4|s^{\mathrm{V}}g_0| + c_5|p_0p_0| + c_6|p_{+1}p_{-1}| + c_7|p_0{}^{\mathrm{I}}f_0|.\end{aligned}$$

The total energy was calculated to be -1.1605 au (experimental: -1.175 au), the bond distance 1.38 au (1.40 au), and the force constant 6.33 md/Å (5.75 md/Å). The last two quantities were found by Bishop from the evaluation of the energy for three different nuclear separations.

Hoyland and Parr (1963) have used this seven-term function to evaluate the magnetic susceptibility of hydrogen. They did this via a variation method designed to take advantage of the simplicity of single-center wave functions. In order to obtain the paramagnetic part of the susceptibility, two additional perturbation terms were added to the wave function. The paramagnetic part was found to be 0.49×10^{-6} emu and the diamagnetic -4.01×10^{-6} emu, compared with the experimental values of 0.085×10^{-6} and -4.11×10^{-6} emu, respectively. (In all cases the origin of the vector potential was at the expansion center.) These numbers are disappointing and this is probably because the electron density given by this wave function is too spherical. A second calculation was therefore made using one of the protons as the expansion center, the unperturbed function having nine terms (and producing a total energy of -1.137 au) and the perturbation function seven terms. Results from this function gave good over-all agreement: paramagnetic and diamagnetic components were 0.75×10^{-6}

and -4.80×10^{-6} emu (experimental: 0.85×10^{-6} and -4.88×10^{-6} emu). The paramagnetic and diamagnetic components of the nuclear magnetic shielding constants were also calculated with this function and found to be -0.59×10^{-5} and 3.26×10^{-5} emu (experimental: -0.56×10^{-5} and 3.22×10^{-5} emu).

Ludwig and Parr (1961) have applied the concept of nonintegral quantum numbers to the Legendre polynomials themselves and in place of the normal d orbital have taken one whose angular part is $(\cos^2 \theta)^{l/2} - (l+1)^{-1}$ where l is noninteger. The idea was to allow for arbitrary peakedness in the angular part of the wave function as well as in the radial part. With a two-term function

$$\Psi = c_1|ss| + c_2|sd|$$

for hydrogen, they found that for $l = 2$ the total energy was -1.1022 and for $l = 3.278$ (the optimum value of l) it was -1.1104; the experimental value is -1.175 au. These results show the importance of angular peakedness, at least, when Ψ is composed of a small number of terms.

Shull and his co-workers, following a suggestion by Shull and Löwdin (1955), have used associated Laguerre functions of order $(2l + 2)$ for the radial terms in expansions for H_2^+ (Howell and Shull, 1959) and H_2 (Shull and Hagstrom, 1956; and Hagstrom and Shull, 1959). The results led these authors to a despondency which was not shared by people using Slater orbitals. In fact Joy and Handler (1965a) have succeeded in obtaining lower energies for H_2^+ with only half the number of terms used by Howell and Shull. The best electronic energy the latter obtained was -1.095633 au for a function composed of six s, five d, and four g type terms.

For H_2 a wave function of forty-four terms led to a total energy of -1.16141 au, that is 98.9% of the observed value, and corresponds to 92.8% of the binding energy. The advantage of Slater orbitals with nonintegral n_i is seen when one compares this value with the -1.1605 au given by Bishop (1963a) with only seven terms, though it should be pointed out that this latter function has twenty-four nonlinear parameters through which the energy is minimized; however, if a good minimization technique is available, this is not a problem.

Houser *et al.* (1963) and Joy and Handler (1965a,b) have recently made a thorough analysis of the convergence of single-center expansions for H_2^+, using Slater-type orbitals. The former showed that the s limit could be reached with only six s functions and that convergence was rapidly achieved; a similar fast convergence on adding higher angular terms was also observed. Wave function plots showed, as was to be expected, that the angular terms were, essentially, improving the wave function near the nuclei. What is unusual about their results is that a second d, a second g, or a second i function gave little improvement, particularly as Joy and Handler found an energy of -1.098928 au for a two s + two d + one g + one i function, compared with a value given by Houser *et al.* for a function containing one less d function of -1.09670 au. It would appear that the latter authors did not make a thorough enough search of the energy surface to obtain their n_i and ζ_i for the second orbitals of each type. Joy and Handler have shown that the n_i for such orbitals are quite large—for d orbitals $n \sim 10$—though this is not surprising when one realizes that large n_i increase the density at the nuclei, just where it is needed most.

In their second paper on the convergence in single-center expansions for H_2^+, Joy and Handler (1965b) report that the convergence is l^{-4} over-all and exponential for a given l (harmonic). It would be nice if these two results could be applied to many-electron problems, but so far we have no way of telling. The best energy values obtained by Joy and Handler were, for a four s + four d + two g + two i + two k function, for integer n_i: -1.101206 au and for noninteger n_i: -1.101214 au, compared with the exact result: -1.10263 au. Boorstein and Goodisman (1963) have similarly investigated H_2^+ using hydrogenic wave functions.

The representation of the electronic charge in the neighborhood of off-center nuclei has been investigated by Turner *et al.* (1964a) for the particularly simple problem of an off-center expansion of a 1s hydrogen atom wave function. Using a 1s ($n = 1$) function as the leading term, in order that a nonzero, noninfinite value of Ψ be given at the expansion point itself, a second s function, and one of each of the higher Slater orbitals (with noninteger n_i), they estimated the energy for three distances, between nucleus and expansion center (R): -0.49521 ($R = 0.7$ au), -0.48969 ($R = 1.4$ au), and -0.48466 ($R = 2.0$ au). They indicated that at least two or three Slater orbitals of a given symmetry should be used in single-center expansions; this would seem to agree with Joy and Handler and not with Houser *et al.* (1963) though it is always possible that H is a less favorable case than H_2^+.

One very direct method of improving single-center wave functions near the off-center nuclei is to add in orbitals which exist only near and are centered at such positions. One can do this and yet not defeat the whole purpose of single-center calculations if the range of such additional orbitals is small enough that they do not overlap with each other. Then, only two-center integrals appear and these, because of the small range, can be evaluated numerically. This has been applied with considerable success by Bishop (1964) who used an additional orbital on each nucleus: $\psi = (15/2\pi P^5)^{1/2}(P - \rho)$, $\rho < P$ and $\psi = 0$, $\rho \geq P$, where ρ was the distance from the nuclear position (where the orbital was centered) and P was a constant which was determined by minimizing the total molecular energy. For the hydrogen molecular ion, inclusion of such a function on each of the two protons decreased the electronic energy of a "best" five-term combination of Slater-type orbitals from -1.09670 to -1.09944 au (exact: -1.10262 au), with a similar improvement in the wave function itself. It would therefore seem that this idea is worth pursuing for other molecules.

Stuart and Matsen (1964), using a thirty-term orbital product centered on the helium nucleus and composed of Slater orbitals, have calculated, for the ground state of the HeH^+ molecular ion, the energy, bond distance, and vibrational frequency. Their values: -2.9691 au, 1.464 au, and 3184 cm^{-1}, respectively, compare favorably with both a James–Coolidge type calculation and a two-center calculation.

The molecules BH_4^-, NH_4^+ (Bishop, 1963b), and CH_4 (Bishop, 1963a) have all been investigated using a wave function of the type first proposed by Saturno and Parr (1960). This wave function consisted of five determinants, of which the first corresponded to a spherical distribution and the other four differed from it in only one orbital:

$$\Psi = c_1|s^2s^{*2}p^6| + c_2|s^2s^{*2}p^5d| + c_3|s^2s^*fp^6| + c_4|s^2s^{*2}p^5f^1| + c_5|s^2s^{*2}p^5g|.$$

All the one-electron orbitals were of the Slater type with noninteger n_i and, by evaluating the energy for different bond lengths, the equilibrium energy, bond lengths, and breathing force constants were determined. In Table IV the results are compared with those of Albasiny and Cooper and it can be seen that there is very satisfactory over-all agreement. The proton affinity of ammonia was predicted to be 0.362 au, where the experimental lower limit is 0.277 au. A complete description of the distribution of electrons in methane, using this five-term wave function, has been given by Turner *et al.* (1964b). By comparison with the C + 4H system, it is seen that considerable electronic charge is drawn from the carbon into the carbon-hydrogen bonds and, if one thinks of the molecule circumscribed by a cube, a small amount of charge is withdrawn from the unoccupied corners. However the weakness of single-center distributions is shown by the fact that the charge is rather diffuse throughout the interior and does not possess the pronounced directional character of LCAO SCF distributions. This diffuse character is caused by the compromise one is forced to make in putting some charge around the hydrogen nucleus and some at the distance from the carbon nucleus which is appropriate to a normal carbon atom. Turner *et al.* also calculated the octupole moment of methane from the formula

$$(7)^{-1/2}\int r^3T_3(\theta, \phi)\Omega(r, \theta, \phi)r^2\, dr\, d\Omega,$$

where $T_3(\theta, \phi)$ is the third-order tetrahedral harmonic and Ω the charge distribution; they found the value 12.9 $e\cdot a_0{}^3$, where the experimental value is estimated to be 9.2 to 18.5 $e\cdot a_0{}^3$.

Bratoz and Allavena (1962) and Allavena and Bratoz (1963) have used a linear combination of thirteen determinants to obtain the infrared spectrum of ammonia and a combination of eight determinants to obtain the infrared spectrum of water. The force constants used in determining these spectra were obtained by analytically differentiating the energy. In this differentiation of the variational parameters only the coefficients (c_i) of the determinants were considered to be dependent on the molecular geometry; the exponents of the Slater orbitals (centered on the heavy nucleus) were kept at fixed values. Not all of the determinants were of A_1 symmetry; some were of a symmetry type which only became "active" under vibration.

Due to a fortuitous cancellation of approximations, that is, not taking a complete set of determinants and not allowing for dependence of orbital exponents on the nuclear coordinates, striking results were obtained as is witnessed by Table VI.

The strength of this method, however, lies in the fact that the vibrational frequencies are determined solely and directly from the ground state wave

TABLE VI

DETERMINATION OF VIBRATIONAL FREQUENCIES[a]

	H_2O		NH_3	
	Calc.	Obs.	Calc.	Obs.
ω_1 (cm^{-1})	3665	3825	3860	3506
ω_2 (cm^{-1})	1793	1654	1310	1022
ω_3 (cm^{-1})	3772	3936	4110	3577
ω_4 (cm^{-1})	—	—	1910	1691

[a] Allavena *et al.* (1963) and Bratoz *et al.* (1962).

functions. Errors which arise in interpolation methods for determining force constants and which could be important when dealing with small interaction force constants do not appear in this method.

Many years before Bratoz's work Platt (1950) had presented two hypotheses which had led to an excellent account of bond distances and force constants in diatomic hydrides, namely, that (*i*) the bond distance is near the radius in the neutral united atom at which the effective nuclear charge is unity, and (*ii*) the force constant is approximately given by $k = 4\pi e^2 \rho_{eq}$, where ρ_{eq} is the density of the electrons in the united atom at this radius. It can be shown, Bratoz *et al.* (1960), that this is equivalent to the Bratoz approach in the approximation of a totally spherical wave function and identical to the method of Longuet-Higgins and Brown (1955), where that method applies to breathing force constants. The latter authors obtained all the force constants of the XH_n hydrides in terms of ρ_{eq}, this quantity being found empirically from one known vibrational frequency.

The alternative to a linear combination of determinants is a single determinant for which each orbital is itself a linear combination of atomic orbitals; the lower limit to the energy of such a wave function is, of course, the Hartree–Fock value. This approach has been used by Koide *et al.* (1957) for CH_4, by Allen (1958) for HF, and by Moccia (1962, 1964) for CH_4, NH_3, H_2O, HF, SiH_4, PH_3, H_2S, HCl, NH_4^+, and PH_4^+. Koide, using Fock–Petrashen orbitals up to *f* harmonics, obtained an energy of -39.80 au for methane, a result inferior to both Albasiny's and Bishop's value. Allen, also including *f* harmonics, obtained -99.9147 au (experimental: -100.5278) for the energy and 2.28D (experimental: 1.74D) for the dipole moment of HF in a calculation similar to the one of Moccia, which will be described next.

Perhaps the greatest justification, certainly in the quality and the extent of the results, for single-center expansions has come from the work of Moccia. Using the Roothaan SCF method to determine the correct linear combinations of atomic orbitals and energy minimization to determine the orbital exponents (n_i had integral values only), he was able to calculate bond distances, angles, dipole moments, ionization potentials, and molecular energies for a whole range of molecules to a high degree of accuracy (see Table VII).

To some extent the success of his work is due to the inclusion of a large number of Slater-type orbitals (in some cases twenty-one) and inclusion of up to *f* harmonics. There are two points of disagreement, however, between his results and those of Albasiny and Cooper and those of Bishop; the

TABLE VIIa

Results of Moccia[a]

Property		CH_4	NH_4^+	NH_3	H_2O	HF
R_e (X—H)	Calc.	2.08	1.990	1.928	1.814	1.728
	Exptl.	2.067	1.96	1.912	1.810	1.7328
H—X—H	Calc.	Tetr.	Tetr.	108°54′	106°32′	—
	Exptl.	Tetr.	Tetr.	106°48′	105°3′	—
μ (au)	Calc.	—	—	0.5949	0.8205	0.825
	Exptl.	—	—	0.583	0.728	0.716
First I.P.	Calc.	0.5042	0.9412	0.4147	0.4954	0.6429
	Exptl.	0.4774	—	0.386	0.463	0.5795
E_{Total}	Calc.	−39.86597	−56.21769	−55.97482	−75.92244	−100.0053
	Exptl.	−40.522	−56.86	−56.562	−76.46	−100.48

[a] All results are in atomic units.

TABLE VIIb

Results of Moccia[a]

Property		SiH_4	PH_4^+	PH_3	H_2S	HCl
R_e (X—H)	Calc.	2.787	2.750	2.672	2.509	2.404
	Exptl.	2.76	2.68	2.678	2.525	2.409
H—X—H	Calc.	Tetr.	Tetr.	89°48′	89°24′	—
	Exptl.	Tetr.	Tetr.	93°10′	92°13′	—
μ (au)	Calc.	—	—	0.4610	0.6789	0.8524
	Exptl.	—	—	0.217	0.362	0.413
First I.P.	Calc.	0.4391	0.7551	0.3671	0.3506	0.4850
	Exptl.	0.448	—	0.371	0.384	0.462
E_{Total}	Calc.	−290.1024	−341.5493	−341.3960	−397.5891	−458.8378
	Exptl.	−292.141	—	−343.42	−400.81	−462.81

[a] All results are in atomic units.

latter find an agreement on the bond lengths of CH_4 and NH_4^+ but differ from Moccia, in both cases by about 0.07 au. Also Moccia's energy for NH_4^+ is higher than that of Bishop whereas for CH_4 it is lower. As Bishop used the same program for both molecules, changing only the nuclear charge, and presumably Moccia did the same, it is hard to account for this disagreement.

Joshi, continuing Moccia's work at the University of Chicago, has recently completed extensive calculations for NH_3 and NH. By writing a computer program specifically for XH_3-type molecules with C_{3v} symmetry, he has been able to include twenty-five symmetry-adapted basis functions with harmonics up to *h*. The bond length, angle, total energy, dipole moment, and first ionization potential of ammonia are reported as 1.867 au, 109.342°, −56.084 au, 0.5993 au, and 0.4155 au, respectively. The energy value is superior to Moccia's; however, the inclusion of higher harmonics, rather surprisingly, gives a poorer bond angle. The potential barrier to umbrella inversion is found to be 0.0411 au, compared with the experimental value of 0.0092 au. It is possible that a difference in correlation energy between planar and nonplanar ammonia is responsible for this poor result.

For NH, using twenty-four basis functions (16σ and 8π), he obtained all but 1.96 eV of the total Hartree–Fock energy, a considerable achievement.

This work is continuing for the eight-electron systems: BeH_3^-, BH_3, CH_3^+, and NH_3^{++}, and also for the equilateral triangular H_3^+ molecule, functions centered on the middle of the triangle.

V. General Remarks

It would appear from the results given in Sections III and IV that many properties are well accounted for by a single-center wave function composed of a limited number of terms and in some cases by a wave function which is just a single term of the kind considered in Section II. Such properties are the bond distances, ionization potentials, breathing force constants, X-ray scattering factors, and relative energies. Properties having an angular dependence, however, are not so well treated, and the reason for this is twofold: (*i*) The radial component of the wave function is usually much better than the angular component as it has been optimized through its parameters (n_i and ζ_i); the angular part, on the other hand, has been rigidly approximated by a limited series of spherical harmonics. (*ii*) The electronic energy depends more critically on bond lengths than on angles; this is seen from the fact that the first term in any expansion is $Y_{00}(\theta_a\phi_a)$ and this function is angle-independent.

The rest of this section will be concerned with the improvement and extension of the single-center method.

A. Choice of Parameters

From a technical point of view, the method by which the nonlinear parameters (n_i and ζ_i) are optimized is of the utmost importance, and it is the author's opinion that the "Pattern Search Method" as developed by Ludwig and outlined in Section II is the best method that is now available. This method is particularly useful for scanning the whole energy surface and is adept at changing the direction of the search as more information is gained in contrast with the method of "Steepest Descents." It is probably in their use of the two different techniques that Joy and Handler obtained better results for H_2^+ than Houser *et al.*

A decision which always arises when one is adding more and more terms to a single-center expansion is whether one should add higher angular components or more terms with the same angular components but with different n_i and ζ_i. The only results which can help us to answer this question are those for H_2^+, where it would seem that at least two terms for each different harmonic should be included and seldom are more than three required. This would also seem to be implied by Moccia's results, though he did not give the energy changes for term by term addition. But for most molecules the answer must come from a trial and error approach. However one can be certain that it is better to properly optimize each ζ_i (and to a lesser extent each n_i) rather than add many terms to the expansion to make up for the shortcomings of ill-adjusted exponents.

There seems to be some divergence of opinion as to the need for large n values in single-center orbitals; Moccia finds only low values for H_2O and HF whereas Joy and Handler found, particularly for the second orbital of a given harmonic, very large values for H_2^+. As large n values improve the wave function at the off-center nuclei, it would seem that the energy contribution from this part of the wave function is only important when one is seeking very high accuracy, as in the H_2^+ case. Also, the importance of satisfying the cusp conditions at these off-center nuclei will depend on the molecule being treated; it is obviously less important for HF, where most of the charge is on the fluorine and not near the proton, than for H_2^+, where most of the charge is on the proton.

The use of noninteger n_i in Slater-type orbitals would seem to be important if one is dealing with a single (or limited number) term function; the energy gained is then worthwhile, but if one has a large number of terms as is possible for, say, H_2^+ then the utility of noninteger n_i disappears. One advantage which, however, remains is that the computer program for optimizing the nonlinear parameters can treat both n_i and ζ_i exactly alike if the n_i are noninteger. A special problem arises if the $1s$ type orbital has a noninteger n value, because then the wave function will be either zero or infinite at the center of expansion, depending on whether n is greater or less than unity. Though often energy is gained by allowing this to happen, it is a displeasing feature and may well affect certain calculated properties adversely. It would therefore seem to be better to use a value of unity for the 1*s* type orbital, a value it would reach anyway if enough terms were taken in the expansion.

A final fact to be noted about the nonlinear parameters is that the ratio, n_i/ζ_i, usually varies linearly with bond distance, as is to be expected since it measures the position of maximum peaking. This allows one to make a good guess at the right ratio for any particular bond distance, provided the ratio is known at two other bond distances.

B. Analytical Determination of Derivatives

The method introduced by Bratoz and Allavena (1962), BA, for finding molecular force constants from single-center wave functions will only be successful if many terms are included in the wave function. The reason for this is that they only considered the *linear* variational parameters, the c_i of Eq. (3), to be dependent on the molecular geometry and assumed that the orbital exponents (ζ_i) were fixed. It is apparent that, for a wave function made up of a limited number of determinants, variation of the nonlinear parameters will be important and should be considered.

The BA method can be extended to include this feature and still retain its analytic character in the following way. Let us consider the simple example of evaluating d^2E/dR^2 for a single determinantal wave function, i.e., $E = H_{11}$ and where, say, R is a bond distance. We have

$$E = E(R, \zeta_1, \zeta_2, \ldots, \zeta_n),$$

$$\frac{dE}{dR} = \frac{\partial E}{\partial R} + \sum_{i=1}^{n} \left(\frac{\partial E}{\delta \zeta_i}\right)\left(\frac{d\zeta_i}{dR}\right),$$

and

$$\frac{d^2E}{dR^2} = \frac{\partial^2 E}{\partial R^2} + \sum_{i=1}^{n} \left(\frac{\partial^2 E}{\partial R \partial \zeta_i}\right)\left(\frac{d\zeta_i}{dR}\right) + \sum_{i=1}^{n} \left[\frac{d}{dR}\left(\frac{\partial E}{\partial \zeta_i}\right)\right]\left(\frac{d\zeta_i}{dR}\right) + \sum_{i=1}^{n} \left(\frac{\partial E}{\partial \zeta_i}\right)\left(\frac{d^2\zeta_i}{dR^2}\right).$$

If ζ_i are chosen to minimize the energy then

$$\frac{\partial E}{\partial \zeta_i} = 0, \qquad i = 1, 2, \ldots, n \tag{16}$$

and as this is true for all R values,

$$\frac{d}{dR}\left(\frac{\partial E}{\partial \zeta_i}\right) = 0, \qquad i = 1, 2, \ldots, n. \tag{17}$$

Using these equations we obtain:

$$\frac{d^2E}{dR^2} = \frac{\partial^2 E}{\partial R^2} + \sum_{i=1}^{n} \left(\frac{\partial^2 E}{\partial R \partial \zeta_i}\right)\left(\frac{d\zeta_i}{dR}\right) \tag{18}$$

where BA would have had only the first term on the right-hand side. The $d\zeta_i/dR$ may be obtained by expanding Eq. (17):

$$\frac{\partial^2 E}{\partial R \partial \zeta_i} + \sum_{k=1}^{n} \left(\frac{\partial^2 E}{\partial \zeta_i \partial \zeta_k}\right)\left(\frac{d\zeta_k}{dR}\right) = 0, \qquad i = 1, 2, \ldots, n.$$

The derivatives $\partial^2 E/\partial R \partial \zeta_i$ and $\partial^2 E/\partial \zeta_i \partial \zeta_k$ in this equation can be found analytically and values determined once the parameters for the molecule in its equilibrium configuration are known. Using these values and solving the n equations we are able to obtain the $d\zeta_i/dR$ for use in Eq. (18).

This extension should strengthen the BA approach as we are still able to evaluate force constants from knowledge of the molecular geometry and wave function for just the equilibrium nuclear framework. Such an analytic approach is superior to the numerical method of finding force constants, whereby a number of molecular energies are calculated for different nuclear positions and to these an energy surface fitted. The small differences in energy for changes in nuclear geometry make the latter method highly suspect.

C. Use of Fock–Petrashen Orbitals

The use of Fock–Petrashen (1934) orbitals in single-center methods was originated by Bernal (1953) and has been continued by, amongst others, Banyard and Gaspar (see Section III). These orbitals differ from the Slater type in that they are already orthogonalized; for example, the 1*s* and 2*s* orbitals are of the form $e^{-\alpha r}$ and $[1 - (\alpha + \beta)r/3]e^{-\beta r}$, respectively. This type of orthogonalization is different from that usually applied to Slater orbitals, namely Schmidt orthogonalization, where, after simplicification, the 1*s* and 2*s* orbitals are of the form $e^{-\alpha r}$ and $[re^{-\beta r} - 24\alpha^3 e^{-\alpha r}/(\alpha + \beta)^4]$, respectively.

Both of these forms are contained in the general expression:

$$1s \sim e^{-\alpha r}$$

$$2s \sim (r - a)e^{-\beta(r-a)} + be^{-\alpha(r-a)}$$

where

$$b = [a - 3/(\alpha + \beta)]e^{a(\beta - \alpha)}[2\alpha/(\alpha + \beta)]^3,$$

for when $a = 0$ one has the Schmidt form and when $a = 3/(\alpha + \beta)$ one has the Fock–Petrashen form. Writing the orbitals in this general way is instructive because it shows that the Fock–Petrashen 2*s* orbital can be obtained from the Schmidt orthogonalized orbital by moving vectorially every point of the latter through an amount $a = 3/(\alpha + \beta)$.

Earlier work by Bishop *et al.* (1963) on NH_3, H_2O, and HF has shown that, if orbitals are allowed to move off the heavy nucleus, they only do so by a very small amount and the optimum movement, as far as the energy criterion is concerned, is of the order of 10^{-4} au. So that one would expect that, by moving every point of a 2*s* orbital vectorially through a distance $3/(\alpha + \beta)$, a quantity usually of the order 10^{-1} au, much poorer results would be obtained.

A direct comparison, however, between the Bishop *et al.* work and that using Fock–Petrashen orbitals is not possible as in the former case the 2*p* orbitals were also allowed to move off the heavy nucleus (moving a 1*s* orbital makes no difference as normalization always corrects the change) and because of the difference between a lateral translation and a vectorial translation. The problem was investigated afresh by Bishop (1965). For this study the H_2O molecule was used, bond distance: 1.81 au, bond angle: 105°, with the simple spherical approximation, namely, a single determinant: $|1s^2 2s^2 2p^6|$ with orbitals having integer n_i and the *p* orbitals having the same exponent, γ. Three sets of results were obtained: (*i*) when the energy was minimized with respect to the three exponents α, β, and γ and to a (general case); (*ii*) the same as before but a was fixed at $3/(\alpha + \beta)$ (Fock–Petrashen case); and (*iii*) as (*ii*) but a was fixed at zero (Schmidt case). These results are given in Table VIII.

TABLE VIII

TOTAL ENERGIES FOR H_2O USING DIFFERENT ORBITALS

	(*i*) General	(*ii*) Fock–Petrashen	(*iii*) Schmidt
α	7.669	7.716	7.667
β	2.154	2.626	2.136
γ	1.901	1.884	1.901
a	0.016	0.290	0.0
E (au)	−75.1950	−75.0064	−75.1948

It is seen that the optimum value of a, 0.016 au, is much closer to zero than to 0.290 au, and so it is to be expected, as it is found, that Schmidt results are better than Fock–Petrashen results. The general 2*s* function can also be obtained from the Schmidt 2*s* function by the addition to the latter of a second 1*s* orbital whose exponent is β, so the results also give the information that the mixing in of a second 1*s* orbital of fixed exponent leads to an energy improvement of 0.0002 au.

In the light of these results, it is recommended that Schmidt orthogonalized Slater orbitals should always be used in preference to Fock–Petrashen orbitals.

D. Truncation

Parr (1964) has suggested that some form of balanced truncation might be useful in the further development of single-center methods. He argues that when wave functions are expanded in a limited (truncated) series of harmonics, one, in effect, truncates the electron-electron and electron-nuclear potentials of interaction and one perhaps should similarly truncate the nuclear-nuclear terms in order to produce the maximum cancellation of errors. The author has investigated this idea for a five-term methane wave function with a bond distance of 2.0 au. The nuclear energy is of the form

$$12 + 3 \sum_{l=0}^{k} P_l\left(-\frac{1}{3}\right), \tag{19}$$

where the P_l are Legendre polynomials and k is the highest harmonic to be included. The nuclear-electronic and electronic-electronic terms are both found, as usual, by using the r_{12}^{-1} expansion [see Eq. (9)]. For this particular molecule and wave function L values of 0, 3, 4, 6, and 7 are involved in the nuclear-electronic expansion and 0, 1, 2, 3, 4, and 5 in the electronic-electronic expansion. In Table IX are given electronic energies (maximum

TABLE IX

TRUNCATED EXPANSIONS FOR METHANE

k	Electronic energy	Nuclear energy	Total energy
0	−52.3840	15.0	−37.3840
1	−53.0809	14.0	−39.0809
2	−53.3397	13.0	−40.3397
3	−53.6147	14.2222	−39.3925
4	−53.6661	14.2593	−39.4069
5	−53.6665	13.2593	−40.4072
6	−53.6791	13.8395	−39.8396
7	−53.6816	14.3374	−39.3441
8	−53.6816	13.5185	−40.1631

L value is k) and nuclear energies [maximum l value is k, see Eq. (19)] for different k values.

In the spirit of this suggestion, one should perhaps only compare energies for $k = 0$, 3, and 4, as only for these values are all three potential terms identically truncated, but even so there does not seem to be any significant improvement over more conventional approaches and the loss of the use of the variational theorem is a further drawback.

E. Kim–Parr Method

Recently Kim (1965) has used the Integral Hellman–Feynmann Theorem (Kim and Parr, 1964) in conjunction with the single-center perturbation method of Hauk *et al.* (1963) to obtain molecular energies and force constants for CH_4, NH_3, and H_2O. The IHF theorem states that

$$\Delta E = E_x - E_y = \langle \Phi_x \,|\, \mathscr{H}_y - \mathscr{H}_x \,|\, \Phi_y \rangle / \langle \Phi_x \,|\, \Phi_y \rangle$$

where

$$\mathscr{H}_x \Phi_x = E_x \Phi_x \qquad \text{and} \qquad \mathscr{H}_y \Phi_y = E_y \Phi_y$$

and $\mathscr{H}_x$ and E_x are, respectively, the Hamiltonian and electronic energy for a molecule in static nuclear configuration x and $\mathscr{H}_y$ and E_y the same for a configuration y. This theorem is used in the Kim–Parr approach by considering the x state to be a molecule with a completely spherical nuclear potential (so-called molecular puff) and the y state to be the molecule with its real nuclear potential. To calculate ΔE they have taken Φ_x to be the symmetric single-center wave functions given by Bishop *et al.* (1963) and Φ_y to be the Hauk perturbed wave functions. Their results are summarized in Table X.

These results in themselves are interesting and ΔE is obviously a useful energy improvement, but what is perhaps more valuable is that the variation in ΔE with angle (α) was studied. For NH_3, ΔE was found to be a minimum for $\alpha = 107°$, an excellent result, whereas for H_2O the minimum was at 127°, i.e., 22° off the observed angle. It is well-known that the change in energy with angular variation for H_2O is very small and this no doubt accounts for the latter result being so poor; however more molecules will have to be investigated before one can really say whether this method is going to be useful for predictions of angular geometry. The barrier to inversion in NH_3 was found to be of the right order, 0.0137 au, compared with the observed value of 0.0093 au and, in general, the force constants are quite good; however, K_{RR} for CH_4 seems to be out of line.

TABLE X

KIM–PARR RESULTS[a]

Property		CH_4	NH_3	H_2O
Bond length (R)		2.00	1.9161	1.787
Bond angle (α)		Tetr.	106°46′	105°
E_1[b]		−39.4273	−55.4022	−75.1993
ΔE[c]		−0.4672	−0.5410	−0.3287
E_2[d]		−39.8945	−55.9432	−75.5280
Experimental energy		−40.522	−56.562	−76.465
K^e_{RR}	Calc.	37.1671	24.7128	17.32
	Exptl.	23.47	21.7788	16.65
$K_{\alpha\alpha}/R^2_{eq}$	Calc.	—	3.3106	0.8009
	Exptl.	—	1.5187	0.768
$K_{R\alpha}/R_{eq}$	Calc.	—	0.9976	0.2199
	Exptl.	—	1.3092	0.506

[a] Results are in atomic units except for force constants which are in md/Å.

[b] Energy of approximate molecular puff, integer n_i (Saturno and Parr, 1960; Bishop *et al.*, 1963).

[c] IHF energy increment.

[d] $E_2 = E_1 + \Delta E$.

[e] Potential function defined as:

$$2V = a + bR + c\alpha + K_{RR}R^2 + 2K_{R\alpha}R\alpha + K_{\alpha\alpha}\alpha^2.$$

F. Future Applications

Prospects for the single-center method are encouraging, and in the future it is to be expected that more, and even complex, molecules will be studied. Certainly work will be done to obtain single-center functions which produce some of the electron correlation energy; so far only hydrogen has been so treated.

An application of the method to hydrocarbons is also possible, and some pioneering work in this field has been accomplished by Chen (1958b). A full-scale treatment, using a many-term wave function, for the He-He repulsive potential would also be interesting. Huzinaga's early attack on this problem (1957b), using single-center techniques, gave rather poor results, but more recently Miller and Present (1963), using a two-term configuration: $|1s^2 2s^2| + |1s3d_\sigma 2s^2|$, found good results for internuclear distances less than 0.6 au. With more terms, good agreement should be found for distances up to 1.0 au.

Finally, the area which most clearly should be investigated is that of excited states. Little has been so far accomplished; yet, as mentioned previously, it is here that the single-center approach should be most accurate.

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Molecular Orbital Theory

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I. Introduction

This chapter deals with the formal problem of reducing molecular orbital calculations to expressions involving one- and two-electron integrals over the spatial coordinates, with coefficients determined by the group-theoretical properties of the spin functions and the electronic permutations. This problem is encountered, for example, when one undertakes to write the expectation value of the Hamiltonian for a given antisymmetrized spin-orbital product, and in that particular case the answer is well-known. We shall be particularly interested in discussing wave functions which are constructed to be eigenfunctions of the spin, and shall consider the reduction of expressions not only for the energy and other spin-free one- and two-electron operators, but also for general one- and two-electron spin-

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dependent operators, such as the spin density or the Fermi contact interaction.

The construction of many-electron spin eigenfunctions has received study ever since the early days of quantum mechanics. Serber (1934a,b) showed how irreducible matrix representations of the symmetric group could be used to combine a spatial-orbital product and its permutations to form spin eigenfunctions. Similar work was done independently by Yamanouchi, who published his results first in Japanese and later (Yamanouchi, 1938) in English. This work was extended and more fully described by Kotani *et al.* (1955). Recently Matsen (1964) has reported a systematic way of discussing the role played by spin in many-particle quantum mechanical systems. The general formalism for handling many-electron spin eigenfunctions is only needed when not all the electrons are assigned to doubly occupied spatial orbitals, and as a result relatively few calculations embodying the Serber–Yamanouchi techniques have been carried out. However, these techniques are most useful in open-shell calculations, and the author (Harris, 1960) has found them invaluable. Section II of this chapter describes the matrix representation method and shows how it may be applied to calculate matrix elements of both spin-free and spin-dependent operators.

The matrix representation method in general generates more than one eigenstate of given total spin and its z component, so that its use normally results in a manifold of such states. As the number of electrons increases, the number of eigenstates and the complexity of computation go up rapidly unless offsetting simplifications are introduced. The most effective simplifications are double occupancy of the spatial orbitals and at least partial orbital orthogonalization. We accordingly give in Section III a detailed discussion of the effects of double occupancies (closed shells), and we consider the extent to which orthogonalizations can be carried out on a given orbital product without thereby altering the wave function. Explicit formulas are given for matrix elements of both spin-free and spin-dependent operators for states involving electrons both in and out of closed shells.

A powerful alternative to the use of double occupancies to reduce the complexities of molecular orbital problems is the use of an arbitrary single member of the manifold of spin eigenstates. If this member is chosen suitably, considerable partial orthogonalization can be carried out. Such a method enables us to partake of the advantages available from the assignment of different orbitals to electrons of different spins (Slater, 1953). We show how a spin-projected single-determinantal wave function based on different spatial orbitals for different spins, as formulated by Löwdin

(1955a,b), Pauncz (1962), and Pauncz *et al.* (1962), can be related to the matrix representation method, and we show how to calculate expectation values of both spin-free and spin-dependent operators. The discussion of spin-free operators parallels that of Pauncz *et al.*, but we believe the treatment of spin-dependent operators is new and affords the possibility of avoiding dubious approximations in the calculation of spin densities and other spin-dependent quantities in open-shell systems.

This chapter does not explicitly discuss the problem of determining the single-configurational wave function of minimum energy. This, the Hartree–Fock problem, has been discussed for closed-shell systems by Roothaan (1951). Roothaan's work also contains references to the earlier literature. For open-shell systems the theory stands at a less definitive stage, at least as far as actual calculations are concerned. By using wave functions which are antisymmetrized spin-orbital products but not necessarily spin eigenfunctions, the closed-shell Hartree–Fock theory has been formally extended to open-shell situations. This approach is exemplified by the spin-polarized Hartree–Fock theory as formulated by Pople and Nesbet (1954), and discussed further by Nesbet (1961) (see also Roothaan, 1960). Nesbet (1963) also discussed the extensions of the conventional Hartree–Fock theory resulting when the convenient but artificial requirement of definite orbital symmetries is dropped along with the restriction to closed shells.

An approach more in line with the development presented in this chapter would be the optimization of the energy for a spin eigenfunction such as the spin-projected single determinant discussed in Section IV. This, the *extended* Hartree–Fock theory, has been discussed by Löwdin (1955b, 1960), but has not seen extensive use, due to apparent computation difficulties. One study is, however, provided by the work of Pratt (1956) on Li. It is this author's opinion that the Hartree–Fock problem is not inherently much more difficult with a spin-projection than without one, as in either case the antisymmetrizing projection forces the consideration of all permutations not excluded by orthogonality conditions. We therefore look toward the possibility that in the future more calculations will use true spin eigenfunctions for calculating the energy and the expectation values of other operators, both spin-dependent and spin-free.

II. Spin and Antisymmetry

A. Preliminaries

We consider a general molecular system which includes n electrons and N nuclei. The ith electron will be described by a set of spatial coordinates $\mathbf{r}_i$ and by spin coordinates $\boldsymbol{\sigma}_i$. We use the nonsubscripted symbols $\mathbf{r}$ and $\boldsymbol{\sigma}$

to denote collectively the spatial and spin coordinates of all electrons 1 through n. Nucleus i will be described by coordinates $\mathbf{R}_i$, and will have charge $+eZ_i$. Interparticle distances will be represented by double subscripts: r_{ij} and R_{ij} stand for $|\mathbf{r}_i - \mathbf{r}_j|$ and $|\mathbf{r}_i - \mathbf{R}_j|$, respectively. A wave function for the n electrons of this system will be designated $\Psi(\mathbf{r}, \boldsymbol{\sigma})$. We shall use $\Phi(\mathbf{r})$ or $\Xi(\mathbf{r})$ to stand for n-electron functions of the spatial coordinates separately, while $\Theta(\boldsymbol{\sigma})$ will stand for an n-electron spin function.

One of our aims will be to find approximate solutions to the electronic Schrödinger equation

$$\mathscr{H}\Psi(\mathbf{r}, \boldsymbol{\sigma}) = E\Psi(\mathbf{r}, \boldsymbol{\sigma}). \tag{1}$$

We use script letters to designate operators; in Eq. (1) $\mathscr{H}$ is the Hamiltonian operator. We shall mainly consider problems in which $\mathscr{H}$ can be approximated with the neglect of relativistic, spin-dependent, nuclear-structure-dependent, and magnetic effects. The remaining, first-order contributions to $\mathscr{H}$ are simply the kinetic energies of all particles and the Coulomb energy of their electrostatic interaction. In writing Eq. (1) we have also made the further approximation of the separability of the electronic and nuclear motion according to Born and Oppenheimer (1927), and therefore we assume the nuclear positions $\mathbf{R}_i$ to be given. Subject to the above limitations, E is the total energy, for stationary nuclei, if the Hamiltonian is written in the form

$$\begin{aligned} \mathscr{H} = &-\frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla_i{}^2 - \sum_{i=1}^{n}\sum_{j=1}^{N}\frac{Z_je^2}{R_{ij}} \\ &+ \sum_{j=2}^{n}\sum_{i=1}^{j-1}\frac{e^2}{r_{ij}} + \sum_{j=2}^{N}\sum_{i=1}^{j=1}\frac{Z_iZ_je^2}{|\mathbf{R}_i - \mathbf{R}_j|}. \end{aligned} \tag{2}$$

The solutions to Eq. (1) must also satisfy the Pauli exclusion principle (Pauli, 1925), which requires that they be antisymmetric in the coordinates of the n electrons. This requirement is met only if $\Psi(\mathbf{r}, \boldsymbol{\sigma})$ satisfies the condition

$$\mathscr{A}\Psi(\mathbf{r}, \boldsymbol{\sigma}) = \Psi(\mathbf{r}, \boldsymbol{\sigma}) \tag{3}$$

in which $\mathscr{A}$, the antisymmetrizing operator, is an idempotent projector defined as $\mathscr{A} = (n!)^{-1}\Sigma_p\varepsilon_p\mathscr{P}$, where $\mathscr{P}$ is the operator which causes a particular permutation of the electron coordinates (both spatial and spin), ε_p is the parity of the permutation (-1 if the permutation requires an odd number of pairwise interchanges, $+1$ otherwise), and the sum is over all

$n!$ permutations of the n sets of electronic coordinates. It may be remarked that Eq. (3) is equivalent to the requirement

$$\mathscr{P}\Psi(\mathbf{r}, \boldsymbol{\sigma}) = \varepsilon_p \Psi(\mathbf{r}, \boldsymbol{\sigma}), \qquad \text{all permutations } \mathscr{P}, \tag{4}$$

as may be seen by applying any permutation $\mathscr{P}$ to Eq. (3) and observing that $\mathscr{P}\mathscr{A} = \varepsilon_p \mathscr{A}$.

Occasionally we will need to refer separately to permutations of either the spatial or spin coordinates. Letting $\mathscr{P}_r$ and $\mathscr{P}_\sigma$ refer to spatial and spin permutations, respectively, we have the obvious relation $\mathscr{P} = \mathscr{P}_r \mathscr{P}_\sigma$. Combining this relationship with the definition of $\mathscr{A}$, we obtain the useful identity

$$\mathscr{A}\mathscr{P}_r = \varepsilon_p \mathscr{A}\mathscr{P}_\sigma^{-1}. \tag{5}$$

B. Spin Functions

Because we are considering $\mathscr{H}$ in an approximation such that it is independent of the spin, the operators for the square of the total spin, $\mathscr{S}^2$, and its z component, $\mathscr{S}_z$, both commute with $\mathscr{H}$. Since $\mathscr{S}^2$ and $\mathscr{S}_z$ also commute with each other, it is possible to choose a complete set of eigenfunctions of $\mathscr{H}$ which are also simultaneous eigenfunctions of $\mathscr{S}^2$ and $\mathscr{S}_z$. To study the eigenfunctions of $\mathscr{S}^2$ and $\mathscr{S}_z$ we shall examine the n-electron spin function space. Since the spin space for a single electron is spanned by two spin functions, which we denote α and β (with $\mathscr{S}_z$ eigenvalues of $+\hbar/2$ and $-\hbar/2$, respectively), the spin space of n electrons will be spanned by 2^n functions which can be written in terms of $\alpha(\boldsymbol{\sigma}_i)$ and $\beta(\boldsymbol{\sigma}_i)$, for $i = 1, \dots n$. We denote a set of functions which span the spin space $\Theta_i(\boldsymbol{\sigma})$, $i = 1, \dots 2^n$. A simple way of choosing the functions $\Theta_i(\boldsymbol{\sigma})$ is as simple products:

$$\begin{aligned}
\Theta_1(\boldsymbol{\sigma}) &= \alpha(\boldsymbol{\sigma}_1)\, \alpha(\boldsymbol{\sigma}_2) \cdots \alpha(\boldsymbol{\sigma}_n) \\
\Theta_2(\boldsymbol{\sigma}) &= \beta(\boldsymbol{\sigma}_1)\, \alpha(\boldsymbol{\sigma}_2) \cdots \alpha(\boldsymbol{\sigma}_n) \\
\Theta_3(\boldsymbol{\sigma}) &= \alpha(\boldsymbol{\sigma}_1)\beta(\boldsymbol{\sigma}_2) \cdots \alpha(\boldsymbol{\sigma}_n) \\
&\;\vdots \\
\Theta_{2n}(\boldsymbol{\sigma}) &= \beta(\boldsymbol{\sigma}_1)\, \beta(\boldsymbol{\sigma}_2) \cdots \beta(\boldsymbol{\sigma}_n).
\end{aligned}$$

It is more useful to choose the $\Theta_i(\boldsymbol{\sigma})$ in such a way that each $\Theta_i(\boldsymbol{\sigma})$ is a pure spin state, i.e., an eigenfunction of $\mathscr{S}^2$ and $\mathscr{S}_z$. This is clearly possible since the $\Theta_i(\boldsymbol{\sigma})$ span the entire spin space and the operators $\mathscr{S}^2$ and $\mathscr{S}_z$ commute. Then each $\Theta_i(\boldsymbol{\sigma})$ can be classified according to its total spin and spin magnetic quantum numbers S and M_s, corresponding to the eigenvalues $S(S+1)\hbar^2$ and $M_s\hbar$ for the operators $\mathscr{S}^2$ and $\mathscr{S}_z$, respectively. Well-known methods exist for the construction of a complete set of pure spin states for an n-spin system (see, for example, Kotani *et al.*, 1955).

The complete set of pure spin states will in many cases contain more than one spin function for given S and M_s. For example, there are two different three-electron doublet states with positively directed spin (i.e., states with $S = \frac{1}{2}$, $M_s = +\frac{1}{2}$), which may be chosen as follows:

$$\Theta_1(\boldsymbol{\sigma}) = 2^{-1/2}(\alpha\beta\alpha - \beta\alpha\alpha) = 2^{-1/2}(\alpha\beta - \beta\alpha)\alpha,$$

$$\Theta_2(\boldsymbol{\sigma}) = 2^{-1/2}(\alpha\alpha\beta - \alpha\beta\alpha) = 2^{-1/2}\alpha(\alpha\beta - \beta\alpha).$$

Whenever we suppress arguments referring to individual electrons, they may be assumed to be taken in ascending order, so that in the above equations $\alpha\beta\alpha$ means $\alpha(\boldsymbol{\sigma}_1)\beta(\boldsymbol{\sigma}_2)\alpha(\boldsymbol{\sigma}_3)$, etc. We may interpret $\Theta_1(\boldsymbol{\sigma})$ as describing a state in which the spins of electrons 1 and 2 are coupled to form a pair of oppositely directed spins, while $\Theta_2(\boldsymbol{\sigma})$ describes a state in which the spins of electrons 2 and 3 are coupled. The other possible coupling, that of electrons 1 and 3, does not describe a third state because it yields a spin function which is linearly dependent upon $\Theta_1(\boldsymbol{\sigma})$ and $\Theta_2(\boldsymbol{\sigma})$. States such as these, with common values of S and of M_s, cannot be distinguished in their spin properties, but may be classified according to their α and β ordering, for example with the aid of a branching diagram.

Using a complete set of pure spin states $\Theta_i(\boldsymbol{\sigma})$, $i = 1, \ldots 2^n$, we may write the most general n-electron function of both spatial and spin coordinates in the form

$$\Psi(\mathbf{r}, \boldsymbol{\sigma}) = \sum_{i=1}^{2^n} \Phi_i(\mathbf{r})\Theta_i(\boldsymbol{\sigma}). \tag{6}$$

If we now require $\Psi(\mathbf{r}, \boldsymbol{\sigma})$ to be a pure spin state, the right-hand side of Eq. (6) must be limited to terms all of whose $\Theta_i(\boldsymbol{\sigma})$ have a common eigenvalue of $\mathscr{S}^2$ and a common eigenvalue of $\mathscr{S}_z$. Letting d stand for the number of such terms, which we have already observed may be greater than unity, Eq. (6) may be reduced to

$$\Psi(\mathbf{r}, \boldsymbol{\sigma}) = \sum_{i=1}^{d} \Phi_i(\mathbf{r})\Theta_i(\boldsymbol{\sigma}), \tag{7}$$

where $\Psi(\mathbf{r}, \boldsymbol{\sigma})$ and the $\Theta_i(\boldsymbol{\sigma})$ are all eigenfunctions of given S and M_s. The spatial functions $\Phi_i(\mathbf{r})$ are thus far unrestricted.

C. Antisymmetry Conditions

Further restrictions may be placed on the wave function $\Psi(\mathbf{r}, \boldsymbol{\sigma})$ of

Eq. (7) by insisting that it satisfy the antisymmetry requirement given in Eq. (4). Applying a permutation $\mathscr{P}$ to both sides of Eq. (7), we have, using $\mathscr{P}_r$ and $\mathscr{P}_\sigma$,

$$\mathscr{P}\Psi(\mathbf{r}, \boldsymbol{\sigma}) = \sum_{i=1}^{d} [\mathscr{P}_r\Phi_i(\mathbf{r})][\mathscr{P}_\sigma\Theta_i(\boldsymbol{\sigma})]. \tag{8}$$

Because $\mathscr{P}_\sigma$ commutes with both $\mathscr{S}^2$ and $\mathscr{S}_z$, the quantity $\mathscr{P}_\sigma\Theta_i(\boldsymbol{\sigma})$ appearing in Eq. (8) must be an eigenfunction of $\mathscr{S}^2$ and $\mathscr{S}_z$ with the same quantum numbers S and M_s as $\Theta_i(\boldsymbol{\sigma})$ itself. Since the functions $\Theta_i(\boldsymbol{\sigma})$, $i = 1, \dots d$ are the complete set of functions with these quantum numbers, $\mathscr{P}_\sigma\Theta_i(\boldsymbol{\sigma})$ must be a linear combination of $\Theta_1(\boldsymbol{\sigma})$, $\Theta_2(\boldsymbol{\sigma})$, ... $\Theta_d(\boldsymbol{\sigma})$. This fact is expressed by the equation

$$\mathscr{P}_\sigma\Theta_i(\boldsymbol{\sigma}) = \sum_{j=1}^{d} V_{ji}(P)\Theta_j(\boldsymbol{\sigma}), \tag{9}$$

where the coefficients $V_{ji}(P)$ depend of course upon the permutation $\mathscr{P}$. Substituting Eq. (9) into Eq. (8), the expression for $\mathscr{P}\Psi(\mathbf{r}, \boldsymbol{\sigma})$ becomes

$$\mathscr{P}\Psi(\mathbf{r}, \boldsymbol{\sigma}) = \sum_{i=1}^{d} \sum_{j=1}^{d} V_{ji}(P)[\mathscr{P}_r\Phi_j(\mathbf{r})]\Theta_i(\boldsymbol{\sigma}). \tag{10}$$

On the other hand, $\mathscr{P}\Psi(\mathbf{r}, \boldsymbol{\sigma})$ is, according to Eq. (4), equal to $\varepsilon_p\Psi(\mathbf{r}, \boldsymbol{\sigma})$, which may be written in the form

$$\mathscr{P}\Psi(\mathbf{r}, \boldsymbol{\sigma}) = \varepsilon_p\Psi(\mathbf{r}, \boldsymbol{\sigma}) = \varepsilon_p \sum_{j=1}^{d} \Phi_j(\mathbf{r})\Theta_j(\mathbf{r}). \tag{11}$$

The right-hand sides of Eqs. (10) and (11) are equivalent only if the coefficients of corresponding spin functions $\Theta_i(\boldsymbol{\sigma})$ are equal. This condition is

$$\varepsilon_p\Phi_j(\mathbf{r}) = \sum_{i=1}^{d} V_{ji}(P)[\mathscr{P}_r\Phi_i(\mathbf{r})], \qquad j = 1, \dots d. \tag{12}$$

The set of linear equations described by Eq. (12) can be inverted to give $\mathscr{P}_r\Phi_i(\mathbf{r})$ in terms of the set of $\Phi_j(\mathbf{r})$, provided that the coefficient matrix $\mathrm{V}(P) = \{V_{ji}(P)\}$ is nonsingular. This is indeed the case, as may be seen by observing that the set of matrices $\mathrm{V}(P)$, for all $\mathscr{P}$, constitute a matrix representation of the permutation group of order n. This means that the matrix $\mathrm{V}(P^{-1})$ will be the inverse of $\mathrm{V}(P)$. We invert Eq. (12) by multiplying both sides by $V_{kj}^{-1}(P)$ and summing over j. Doing this for each k from 1 to d, we obtain the set of equations

$$\sum_{j=1}^{d} \varepsilon_p V_{kj}^{-1}(P)\Phi_j(\mathbf{r}) = \mathscr{P}_r\Phi_k(\mathbf{r}), \qquad k = 1, \dots d. \tag{13}$$

Another way of expressing Eq. (13) is to write that the functions $\Phi_k(\mathbf{r})$ must transform under permutation as

$$\mathscr{P}_r\Phi_k(\mathbf{r}) = \sum_{j=1}^{d} U_{jk}(P)\Phi_j(r), \qquad k = 1, \dots d, \tag{14}$$

with

$$U_{jk}(P) = \varepsilon_p V_{kj}^{-1}(P). \tag{15}$$

Equations (14) and (15) tell us that the transformation properties of the spatial functions $\Phi_k(\mathbf{r})$ can be deduced from those of the spin functions $\Theta_i(\boldsymbol{\sigma})$. We therefore need to know how to find the matrices $\mathbf{V}(P)$. This task is easiest if we choose the $\Theta_i(\boldsymbol{\sigma})$ orthonormal. In that case we may take the scalar product of both sides of Eq. (9) with $\Theta_k(\boldsymbol{\sigma})$, obtaining

$$V_{ki}(P) = \langle\Theta_k(\boldsymbol{\sigma})\,|\,\mathscr{P}_\sigma\Theta_i(\boldsymbol{\sigma})\rangle. \tag{16}$$

If the spin functions $\Theta_i(\boldsymbol{\sigma})$ are known, Eq. (16) provides an explicit construction of the matrices $\mathbf{V}(P)$. Moreover, the orthonormality makes $\mathbf{V}(P)$ a unitary matrix, so that $V_{kj}^{-1}(P) = V_{jk}^{*}(P)$, and Eq. (15) may be rewritten in the matrix form

$$\mathbf{U}(P) = \varepsilon_p\mathbf{V}^{*}(P). \tag{17}$$

Equation (17) shows that $\mathbf{U}(P)$ is also unitary.

Normally we do not have available a set of functions $\Phi_j(\mathbf{r})$ satisfying Eq. (14), but instead we have a single function $\Phi_0(\mathbf{r})$ from which we would like to construct a set of functions $\Phi_j(\mathbf{r})$. The construction is made by taking suitable linear combinations of the permutations of $\Phi_0(\mathbf{r})$. As we shall see, a set of functions $\Phi_j(\mathbf{r})$ may be generated from a given $\Phi_0(\mathbf{r})$ in d different ways, which we distinguish by a superscript, so that we write $\Phi_j{}^i(\mathbf{r})$ to indicate the function $\Phi_j(\mathbf{r})$ in the ith set of functions produced from $\Phi_0(\mathbf{r})$. The functions $\Phi_j{}^i(\mathbf{r})$ may be obtained as follows:

$$\Phi_j{}^i(\mathbf{r}) = \sum_{\mathscr{Q}} U_{ji}^{*}(Q)\mathscr{Q}_r\Phi_0(\mathbf{r}), \qquad i = 1, \dots d. \tag{18}$$

Here $\mathscr{Q}$ is a permutation, and the sum is over all $\mathscr{Q}$.

We may confirm the validity of Eq. (18) by verifying that it leads to the relationships required by Eq. (14). Starting from Eq. (18), we form the expression appearing on the right side of Eq. (14). We have

$$\sum_{j=1}^{d} U_{jk}(P)\Phi_j{}^i(\mathbf{r}) = \sum_{j=1}^{d} U_{jk}(P)\sum_{\mathscr{Q}} U_{ji}^{*}(Q)\mathscr{Q}_r\Phi_0(\mathbf{r}), \qquad i, k = 1, \dots d. \tag{19}$$

Using the fact that $\mathbf{U}$ is unitary, and a representation matrix, we write $U_{jk}(P) = U^{-1}_{jk}(P^{-1}) = U^*_{kj}(P^{-1})$, thereby enabling Eq. (19) to be rewritten

$$\sum_{j=1}^{d} U_{jk}(P)\Phi_j{}^i(\mathbf{r}) = \sum_{\mathscr{Q}} \sum_{j=1}^{d} U^*_{kj}(P^{-1})U^*_{ji}(Q)\mathscr{Q}_r\Phi_0(\mathbf{r}), \qquad i, k = 1, \ldots d. \tag{20}$$

Next we use matrix multiplication and the representation property of the matrices $\mathbf{U}$ to replace $\sum_{j=1}^{d} U^*_{kj}(P^{-1})U^*_{ji}(Q)$ by $U^*_{ki}(P^{-1}Q)$:

$$\sum_{j=1}^{d} U_{jk}(P)\Phi_j{}^i(\mathbf{r}) = \sum_{\mathscr{Q}} U^*_{ki}(P^{-1}Q)\mathscr{Q}_r\Phi_0(\mathbf{r}), \qquad i, k = 1, \ldots d. \tag{21}$$

Finally, we observe that, because the $\mathscr{Q}$ summations are over all elements of a group, the operator $\mathscr{Q}$ may within the summation be replaced by $\mathscr{P}\mathscr{Q}$ without affecting the value of the sum. Doing so gives the result

$$\begin{aligned} \sum_{j=1}^{d} U_{jk}(P)\Phi_j{}^i(\mathbf{r}) &= \sum_{\mathscr{Q}} U^*_{ki}(Q)\mathscr{P}_r\mathscr{Q}_r\Phi_0(\mathbf{r}) \\ &= \mathscr{P}_r \sum_{\mathscr{Q}} U^*_{ki}(Q)\mathscr{Q}_r\Phi_0(\mathbf{r}), \qquad i, k = 1, \ldots d. \end{aligned} \tag{22}$$

Notice that, when we replaced Q by PQ in the argument of U^*_{ki}, we obtained $P^{-1}PQ$, which we simplified to Q. The last expression on the right of Eq. (22) is, using Eq. (18), just $\mathscr{P}_r\Phi_k{}^i(\mathbf{r})$, thereby completing the demonstration that Eq. (18) causes Eq. (14) to be satisfied.

Each of the d different ways of making the functions $\Phi_j(\mathbf{r})$ will generally lead to a different function $\Psi(\mathbf{r}, \boldsymbol{\sigma})$. Letting $\Psi^i(\mathbf{r}, \boldsymbol{\sigma})$ stand for the wave function made from the ith set of functions $\Phi_j(\mathbf{r})$, we have, using Eqs. (7) and (18),

$$\Psi^i(\mathbf{r}, \boldsymbol{\sigma}) = \sum_{j=1}^{d} \sum_{\mathscr{Q}} U^*_{ji}(Q)\mathscr{Q}_r\Phi_0(\mathbf{r})\Theta_j(\boldsymbol{\sigma}), \qquad i = 1, \ldots d. \tag{23}$$

The most general function $\Psi(\mathbf{r}, \boldsymbol{\sigma})$ derivable from $\Phi_0(\mathbf{r})$ and its permutations will be a linear combination of all these $\Psi^i(\mathbf{r}, \boldsymbol{\sigma})$,

$$\Psi(\mathbf{r}, \boldsymbol{\sigma}) = \sum_{i=1}^{d} c_i\Psi^i(\mathbf{r}, \boldsymbol{\sigma}). \tag{24}$$

Equations (23) and (24) describe one way of constructing antisymmetric wave functions. An alternative way to construct such functions is by the formula

$$\Psi^i(\mathbf{r}, \boldsymbol{\sigma}) = n!\mathscr{A}\Phi_0(\mathbf{r})\Theta_i(\boldsymbol{\sigma}), \qquad i = 1, \ldots d. \tag{25}$$

Because $\mathscr{S}^2$ and $\mathscr{S}_z$ commute with $\mathscr{A}$, the wave function defined by

Eq. (25) has the desired spin properties. We may rearrange Eq. (25) by introducing the definition of $\mathscr{A}$:

$$
\begin{aligned}
n!\,\mathscr{A}\Phi_0(\mathbf{r})\Theta_i(\boldsymbol{\sigma}) &= \sum_Q \varepsilon_Q \mathscr{Q}_r \Phi_0(\mathbf{r}) \mathscr{Q}_\sigma \Theta_i(\boldsymbol{\sigma}) \\
&= \sum_{j=1}^{d} \sum_Q \varepsilon_Q V_{ji}(Q) \mathscr{Q}_r \Phi_0(\mathbf{r}) \Theta_j(\boldsymbol{\sigma}). \qquad (26)
\end{aligned}
$$

To get the last line of Eq. (26) we used Eq. (9) to replace $\mathscr{Q}_\sigma \Theta_i(\boldsymbol{\sigma})$. By comparison with Eq. (23), using Eq. (17), we see that $\Psi^i(\mathbf{r}, \boldsymbol{\sigma})$, as defined by Eq. (25), is the same as the wave function defined by Eq. (23). This is useful information because it is easier to see the relationship of the spatial and spin functions from Eq. (25).

Yet a third way of writing the function $\Psi^i(\mathbf{r}, \boldsymbol{\sigma})$ is

$$
\Psi^i(\mathbf{r}, \boldsymbol{\sigma}) = d\mathscr{A} \sum_Q U_{ji}^*(Q) \mathscr{Q}_r \Phi_0(\mathbf{r}) \Theta_j(\boldsymbol{\sigma}), \qquad j = 1, \ldots d. \qquad (27)
$$

Notice that Eq. (27) describes not one but a set of d formulations of $\Psi^i(\mathbf{r}, \boldsymbol{\sigma})$, all of which we plan to show are equivalent. To verify Eq. (27), we put $U_{ji}^*(Q) = \varepsilon_Q V_{ji}(Q) = \varepsilon_Q V_{ij}^*(Q^{-1})$, and we use Eq. (5) to replace $\mathscr{A}\varepsilon_Q \mathscr{Q}_r$ by $\mathscr{A}\mathscr{Q}_\sigma^{-1}$. We then have

$$
\Psi^i(\mathbf{r}, \boldsymbol{\sigma}) = d\mathscr{A}\Phi_0(\mathbf{r}) \sum_Q V_{ij}^*(Q^{-1}) \mathscr{Q}_\sigma^{-1} \Theta_j(\boldsymbol{\sigma}), \qquad j = 1, \ldots d. \qquad (28)
$$

With the aid of Eq. (9), this becomes

$$
\Psi^i(\mathbf{r}, \boldsymbol{\sigma}) = d\mathscr{A}\Phi_0(\mathbf{r}) \sum_Q \sum_{k=1}^{d} V_{ij}^*(Q^{-1}) V_{kj}(Q^{-1}) \Theta_k(\boldsymbol{\sigma}). \qquad (29)
$$

The group representation properties of $\mathbf{V}$ enable us to perform the sum over $\mathscr{Q}$. The theorem involved (see, for example, Hamermesh, 1962) is

$$
\sum_Q V_{ij}^*(Q) V_{kl}(Q) = \frac{n!}{d}\, \delta_{ik}\delta_{jl}. \qquad (30)
$$

Inserting this into Eq. (29), we have the same result for all j:

$$
\Psi^i(\mathbf{r}, \boldsymbol{\sigma}) = n!\mathscr{A}\Phi_0(\mathbf{r}) \sum_{k=1}^{d} \delta_{ik} \Theta_k(\boldsymbol{\sigma}). \qquad (31)
$$

This is clearly the same as Eq. (25). The significance of this result is based on the fact that Eq. (27) is itself of the form of Eq. (25), but with spatial function $(d/n!) \sum_Q U_{ji}^*(Q) \mathscr{Q}_r \Phi_0(\mathbf{r})$ in place of $\Phi_0(\mathbf{r})$, and with spin function $\Theta_j(\boldsymbol{\sigma})$ in place of $\Theta_i(\boldsymbol{\sigma})$. This gives us a means of exchanging one spin function for another, so that we may write the most general wave function based upon $\Phi_0(\mathbf{r})$ in terms of a single spin function.

We are now ready to discuss the most general wave function satisfying the spin and antisymmetry conditions. Such a function could be written in the form

$$\Psi(\mathbf{r}, \boldsymbol{\sigma}) = n!\,\mathscr{A} \sum_{i=1}^{d} \Xi_i(\mathbf{r})\Theta_i(\boldsymbol{\sigma}), \tag{32}$$

the antisymmetry being obvious and the generality clear if the $\Xi_i(\mathbf{r})$ are unrestricted. We have already seen that functions of this kind satisfy the spin requirements. But because of the analysis of the preceding paragaph, we also see that each term in the i summation of Eq. (32) can be reduced, according to Eq. (27), to some spatial function multiplied by *any* spin function. If we convert each term of Eq. (32) so that it involves, for example, $\Theta_1(\boldsymbol{\sigma})$, we can produce an expression for $\Psi(\mathbf{r}, \boldsymbol{\sigma})$ of the general form

$$\Psi(\mathbf{r}, \boldsymbol{\sigma}) = n!\,\mathscr{A}\Xi(\mathbf{r})\Theta_1(\boldsymbol{\sigma}), \tag{33}$$

where $\Xi(\mathbf{r})$ is the sum of the spatial functions produced from all the terms of Eq. (32). Our final result, then, is that the most general antisymmetric wave function of given S and M_s may be produced by antisymmetrizing the product of an arbitrary spatial function and *any* spin eigenfunction of the given S and M_s.

In actual practice it is often inefficient to use the general form given by Eq. (33), because we do not initially know $\Xi(\mathbf{r})$, and our approximations to $\Psi(\mathbf{r}, \boldsymbol{\sigma})$ may depend upon the permutational properties of $\Xi(\mathbf{r})$. For example, if we approximate $\Xi(\mathbf{r})$ by an orbital product, different orders of assigning electrons to the orbitals will result in different wave functions. It is frequently more convenient to use Eqs. (23) and (24) in place of Eq. (33). Permutational ordering in $\Phi_0(\mathbf{r})$ has no effect upon the wave function generated by Eq. (24), and a completely arbitrary $\Phi_0(\mathbf{r})$ specifies, and in fact overspecifies, a general wave function.

One method of approximating a general $\Phi_0(\mathbf{r})$ is as an expansion, of the form

$$\Phi_0(\mathbf{r}) = \sum_k a_k \Xi_k(\mathbf{r}). \tag{34}$$

Each spatial function in this series may be called a *configuration*, and the use of an expansion of this type is called a *configuration interaction* method. Using the expansion of Eq. (34) in Eqs. (23) and (24), we obtain results which may be expressed as follows:

$$\Psi_k{}^i(\mathbf{r}, \boldsymbol{\sigma}) = \sum_{j=1}^{d} \sum_{\mathscr{Q}} U_{ji}^*(Q)\mathscr{Q}_r \Xi_k(\mathbf{r})\Theta_j(\boldsymbol{\sigma}), \tag{35}$$

$$\Psi(\mathbf{r}, \boldsymbol{\sigma}) = \sum_k \sum_{i=1}^{d} a_{ik} \Psi_k{}^i(\mathbf{r}, \boldsymbol{\sigma}). \tag{36}$$

The coefficients a_{ik} may in principle be determined by use of the variation theorem.

We shall adopt Eqs. (35) and (36) as our standard form for an antisymmetric wave function which is an eigenfunction of $\mathcal{S}^2$ and $\mathcal{S}_z$.

D. Matrix Elements of Spin-Free Operators

We treat here the evaluation of the matrix elements of operators which are independent of the spin, using the general wave functions given in Eqs. (35) and (36). Since we contemplate application to observable quantities, we restrict the discussion to operators which are Hermitian and which are symmetric in the electronic coordinates. Letting $\mathscr{B}$ designate such an operator, the matrix elements we seek are of the form $\langle \Psi_k{}^i(\mathbf{r}, \boldsymbol{\sigma}) \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'}(\mathbf{r}, \boldsymbol{\sigma}) \rangle$.

We begin the evaluation by substitution from Eq. (35):

$$\langle \Psi_k{}^i(\mathbf{r}, \boldsymbol{\sigma}) \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'}(\mathbf{r}, \boldsymbol{\sigma}) \rangle$$

$$= \sum_{j=1}^{d} \sum_{j'=1}^{d} \sum_{Q,Q'} \langle U_{ji}^*(Q) \mathscr{Q}_r \Xi_k(\mathbf{r}) \Theta_j(\boldsymbol{\sigma}) \,|\, \mathscr{B} \,|\, U_{j'i'}^*(Q') \mathscr{Q}_r{}' \Xi_{k'}(\mathbf{r}) \Theta_{j'}(\boldsymbol{\sigma}) \rangle. \tag{37}$$

Because $\mathscr{B}$ does not depend upon the spin and because the $\Theta_j(\boldsymbol{\sigma})$ are orthonormal, the only nonzero terms on the right side of Eq. (37) are those for which $j' = j$. Taking the scalar product of the spin coordinates, and collecting the constant factors, we get

$$\langle \Psi_k{}^i \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'} \rangle = \sum_{j=1}^{d} \sum_{Q,Q'} U_{ji}(Q) U_{ji'}^*(Q') \langle \mathscr{Q}_r \Xi_k(\mathbf{r}) \,|\, \mathscr{B} \,|\, \mathscr{Q}_r{}' \Xi_{k'}(\mathbf{r}) \rangle. \tag{38}$$

We next make use of the properties of the operators $\mathscr{B}$ and $\mathscr{Q}$. First, $\mathscr{Q}$ is unitary, so $\mathscr{Q}^+ = \mathscr{Q}^{-1}$. This means that

$$\langle \mathscr{Q}_r \Xi_k(\mathbf{r}) \,|\, \mathscr{B} \,|\, \mathscr{Q}_r{}' \Xi_{k'}(\mathbf{r}) \rangle = \langle \Xi_k(\mathbf{r}) \,|\, \mathscr{Q}_r^{-1} \mathscr{B} \mathscr{Q}_r{}' \,|\, \Xi_{k'}(\mathbf{r}) \rangle.$$

Moreover, the symmetry of $\mathscr{B}$ causes $\mathscr{B}$ and $\mathscr{Q}$ to commute, so we may replace $\mathscr{Q}_r^{-1} \mathscr{B} \mathscr{Q}_r{}'$ by $\mathscr{B} \mathscr{Q}_r^{-1} \mathscr{Q}_r{}'$. The unitary of the matrices $\mathbf{U}$ also enables us to rewrite $U_{ji}(Q)$ as $U_{ij}^*(Q^{-1})$. We may then identify the sum over j as a matrix multiplication:

$$\sum_{j=1}^{d} U_{ij}^*(Q^{-1}) U_{ji'}^*(Q') = U_{ii'}^*(Q^{-1}Q').$$

All these changes lead to

$$\langle \Psi_k^i \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'} \rangle = \sum_{Q,Q'} U_{ii'}^*(Q^{-1}Q') \langle \Xi_k(\mathbf{r}) \,|\, \mathscr{B} \mathscr{Q}_r^{-1} \mathscr{Q}_r{}' \,|\, \Xi_{k'}(\mathbf{r}) \rangle. \tag{39}$$

Finally, we use the fact that the $\mathscr{Q}$ summation is over all elements of a group to replace $\mathscr{Q}^{-1}\mathscr{Q}'$, wherever it appears, by $\mathscr{Q}$. After doing so, the sum over $\mathscr{Q}'$ simply contributes $n!$ identical terms. We therefore get

$$\langle \Psi_k{}^i \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'} \rangle = n! \sum_{Q} U_{ii'}^*(Q) \langle \Xi_k(\mathbf{r}) \,|\, \mathscr{B} \mathscr{Q}_r \,|\, \Xi_{k'}(\mathbf{r}) \rangle. \tag{40}$$

An examination of Eq. (40) indicates that, although the presence of electron spin has a profound effect on the formulation of molecular calculations, spin-independent observables can be characterized without explicit use of the spin functions themselves. All that enters the theory is the transformation properties of the spin functions under permutation, as indicated by the matrices $\mathbf{U}(Q)$.

E. Matrix Elements of Spin-Dependent Operators

Some of the steps of the preceding section could only be carried out because of the spin independence of the operator $\mathscr{B}$. To discuss matrix elements of spin-dependent operators, it is more convenient to start from $\Psi_k{}^i(\mathbf{r}, \boldsymbol{\sigma})$ in the form derived from Eq. (25):

$$\Psi_k{}^i(\mathbf{r}, \boldsymbol{\sigma}) = n!\,\mathscr{A}\Xi_k(\mathbf{r})\Theta_i(\boldsymbol{\sigma}). \tag{41}$$

We now let $\mathscr{B}$ stand for a spin-dependent operator, and we use Eq. (41) to write its matrix elements in the form

$$\langle \Psi_k{}^i \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'} \rangle = (n!)^2 \langle \mathscr{A}\Xi_k(\mathbf{r})\Theta_i(\boldsymbol{\sigma}) \,|\, \mathscr{B} \,|\, \mathscr{A}\Xi_{k'}(\mathbf{r})\Theta_{i'}(\boldsymbol{\sigma}) \rangle. \tag{42}$$

We note that $\mathscr{A}$ is self-adjoint and that it commutes with $\mathscr{B}$. The commutation follows from the fact that $\mathscr{B}$ is symmetric in the electronic coordinates. Further, we recall that $\mathscr{A}$ is idempotent, so that $\mathscr{A}^2 = \mathscr{A}$. For these reasons, Eq. (42) is equivalent to

$$\langle \Psi_k{}^i \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'} \rangle = (n!)^2 \langle \Xi_k(\mathbf{r})\Theta_i(\boldsymbol{\sigma}) \,|\, \mathscr{B} \,|\, \mathscr{A}\Xi_{k'}(\mathbf{r})\Theta_{i'}(\boldsymbol{\sigma}) \rangle. \tag{43}$$

Now that we have gotten rid of the operator $\mathscr{A}$ in the left part of the scalar product, we replace the expression for $\Psi_k^{i'}(\mathbf{r}, \boldsymbol{\sigma})$ in the right half by the more explicit form given in Eq. (35). This gives

$$\langle \Psi_k{}^i \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'} \rangle = \sum_{j=1}^{d} \sum_{Q} n!\, U_{ji'}^{*}(Q) \langle \Xi_k(\mathbf{r})\Theta_i(\boldsymbol{\sigma}) \,|\, \mathscr{B} \,|\, \mathscr{Q}_r \Xi_k(\mathbf{r})\Theta_j(\boldsymbol{\sigma}) \rangle. \tag{44}$$

The result in Eq. (44) can be put in an alternative form which more explicitly illustrates the effect of the spin dependence of $\mathscr{B}$. Defining a matrix **B** whose elements are spatial operators,

$$\mathscr{B}_{ij} = \langle \Theta_i(\boldsymbol{\sigma}) \,|\, \mathscr{B} \,|\, \Theta_j(\boldsymbol{\sigma}) \rangle, \tag{45}$$

we may write

$$\langle \Psi_k{}^i \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'} \rangle = n! \sum_{Q} \langle \Xi_k(\mathbf{r}) \,|\, [\mathbf{B}\mathbf{U}^*(Q)]_{ii'} \mathscr{Q}_r \,|\, \Xi_{k'}(\mathbf{r}) \rangle. \tag{46}$$

If $\mathscr{B}$ were independent of spin, the matrix **B** would be simply $\mathscr{B}$ multiplied by the unit matrix, and $[\mathbf{B}\mathbf{U}^*(Q)]_{ii'}$ would be $\mathscr{B} U_{ii'}^{*}(Q)$. This would yield the result obtained in the previous section as Eq. (40).

Often $\mathscr{B}$ will have a spin dependence which causes it to fail to commute with $\mathscr{S}^2$ or $\mathscr{S}_z$. In such cases there will be matrix elements of $\mathscr{B}$ connecting states of different S or M_s. The formalism leading to Eq. (46) applies equally well to such matrix elements. All we need do is to interpret $\Theta_i(\boldsymbol{\sigma})$ and $\Theta_{i'}(\boldsymbol{\sigma})$ as referring to states which are no longer restricted to common values of S or M_s. Since $\mathbf{U}(Q)$ connects only states of common S and M_s, $[\mathbf{BU}^*(Q)]_{ii'}$ then is

$$[\mathbf{BU}^*(Q)]_{ii'} = \sum_{j=1}^{d} \mathscr{B}_{ij} U_{ji'}^*(Q), \tag{47}$$

with i' and j referring to wave functions of the same spin state, which need not be the same as the spin state referred to by i.

III. Orbital Theories

A. The Use of Orbitals

The expressions of the two preceding sections can be greatly simplified if we consider only spatial functions $\Xi_k(\mathbf{r})$ which can be written as products of one-electron functions, which we call *orbitals*. We denote such orbitals by $\chi_1(\mathbf{r}_i)$, $\chi_2(\mathbf{r}_i)$, ... , and we assume the existence of a complete set of orbitals $\chi_j(\mathbf{r}_i)$, $j = 1, 2, \ldots$, so that any spatial function $\Phi_0(\mathbf{r})$ can be expressed as an expansion

$$\Phi_0(\mathbf{r}) = \sum_k a_k \chi_{(k,1)}(\mathbf{r}_1)\chi_{(k,2)}(\mathbf{r}_2) \cdots \chi_{(k,n)}(\mathbf{r}_n), \tag{48}$$

where $(k, 1), (k, 2), \ldots (k, n)$ are a set of orbital numbers dependent upon the summation index k. Equation (48) is in the configuration interaction form of Eq. (34) if we identify each value of k with a configuration:

$$\Xi_k(\mathbf{r}) = \chi_{(k,1)}(\mathbf{r}_1)\chi_{(k,2)}(\mathbf{r}_2) \cdots \chi_{(k,n)}(\mathbf{r}_n). \tag{49}$$

Equations (48) and (49) are equivalent to the well-known observation that a configuration interaction remains completely general if each spatial function $\Xi_k(\mathbf{r})$ is assumed to be a product of orbitals. Since the most general wave function obtained from $\Xi_k(\mathbf{r})$ does not depend upon its permutational form, we shall assume each $\Xi_k(\mathbf{r})$ to have its orbitals arranged in ascending numerical order.

A second simplification of the two preceding sections may be obtained by making use of the fact that the observable quantities we discuss are almost invariably described by one- or two-electron operators, i.e., by operators of one of the following forms:

$$\mathscr{B} = \sum_{l=1}^{n} \mathcal{O}(\mathbf{r}_l, \boldsymbol{\sigma}_l), \tag{50}$$

$$\mathscr{B} = \sum_{m=2}^{n} \sum_{l=1}^{m-1} \mathcal{O}(\mathbf{r}_l, \mathbf{r}_m, \boldsymbol{\sigma}_l, \boldsymbol{\sigma}_m). \tag{51}$$

Before proceeding to the main discussion of this section, it is convenient to establish a few notational conventions. In scalar products, we shall show the orbital composition of the function $\Xi_k(\mathbf{r})$, not by the right side of Eq. (49), but by the more compact designation $(k, 1)(k, 2) \cdots (k, n)$. When $\Xi_k(\mathbf{r})$ has been operated on by the permutation $\mathscr{Q}_r$, we shall indicate its permuted orbital form by the notations (k, q_1), (k, q_2), ... (k, q_n), where (k, q_i) refers to the orbital which, in the permuted form, describes electron i. Thus, in a scalar product, $\mathscr{Q}_r\Xi_k(\mathbf{r})$ may be designated by $(k, q_1)(k, q_2) \cdots (k, q_n)$.

Let's consider first the matrix elements of a particularly simple operator. The overlap matrix elements, $\langle \Psi_k{}^i \,|\, \Psi_{k'}^{i'} \rangle$, may be regarded as of the form $\langle \Psi_k{}^i \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'} \rangle$, with $\mathscr{B}$ equal to the identity operator. Using Eq. (40) and our recently adopted notational conventions, we have

$$\langle \Psi_k{}^i \,|\, \Psi_{k'}^{i'} \rangle = n! \sum_{Q} U_{ii'}^{*}(Q) \langle (k, 1)(k, 2) \cdots (k, n) \,|\, (k', q_1)(k', q_2) \cdots (k', q_n) \rangle. \tag{52}$$

Separating the scalar product on the right of Eq. (52) into factors referring to individual electrons, we have

$$\langle \Psi_k{}^i \,|\, \Psi_{k'}^{i'} \rangle = n! \sum_{Q} U_{ii'}^{*}(Q) \sum_{j=1}^{n} \langle (k, j) \,|\, (k', q_j) \rangle. \tag{53}$$

The individual factors on the right side of Eq. (53) are just overlap integrals for orbitals:

$$\langle (k, j) \,|\, (k', {}_j q) \rangle = \int d\mathbf{r}_j \chi_{(k,j)}^{*}(\mathbf{r}_j) \chi_{(k',q_j})(\mathbf{r}_j). \tag{54}$$

The meaning of Eq. (53) may be illustrated with a simple example. We take a two-electron system (so $n = 2$) with a spatial configuration k which is $\chi_1(\mathbf{r}_1)\chi_2(\mathbf{r}_2)$ and another spatial configuration k' which is $\chi_3(\mathbf{r}_1)\chi_4(\mathbf{r}_2)$. In other words, $(k, 1) = 1$, $(k, 2) = 2$, $(k', 1) = 3$, $(k', 2) = 4$. Let's suppose we consider the singlet spin state, for which $d = 1$, so that the only possible values for i and i' are $i = i' = 1$. This just means that there is only one two-electron singlet state (the well-known form $\alpha\beta - \beta\alpha$). The two possible permutations $\mathscr{Q}$ are the identity and the interchange of (the two electrons. For both these permutations, in this spin state $U_{11}^{*}(Q) = 1$. Equation (53) is thus seen to state

$$\langle \Psi_k{}^1 \mid \Psi_{k'}^1 \rangle = 2!(\langle 1 \mid 3 \rangle \langle 2 \mid 4 \rangle + \langle 1 \mid 4 \rangle \langle 2 \mid 3 \rangle). \tag{55}$$

This is of course the result we could have gotten without such an elaborate formalism by recognizing that the two-electron singlet state for configuration k is $\frac{1}{2}[\chi_1(\mathbf{r}_1)\chi_2(\mathbf{r}_2) + \chi_2(\mathbf{r}_1)\chi_1(\mathbf{r}_2)](\alpha\beta - \beta\alpha)$, while that for k' is $\frac{1}{2}[\chi_3(\mathbf{r}_1)\chi_4(\mathbf{r}_2) + \chi_4(\mathbf{r}_1)\chi_3(\mathbf{r}_2)](\alpha\beta - \beta\alpha)$, and then evaluating the scalar product $\langle \Psi_k{}^1 \mid \Psi_{k'}^1 \rangle$.

On the other hand, if we had looked at a component of the triplet state, for which also $d = 1$, we would have $U_{11}^{*}(Q) = +1$ for the identity permutation, but -1 for the interchange, so that Eq. (53) would have given

$$\langle \Psi_k{}^1 \mid \Psi_{k'}^1 \rangle = 2!(\langle 1 \mid 3 \rangle \langle 2 \mid 4 \rangle - \langle 1 \mid 4 \rangle \langle 2 \mid 3 \rangle). \tag{56}$$

This result is also obtainable by more direct means, the minus sign appearing because the triplet-state spatial function is antisymmetric in the electronic coordinates. Results corresponding to those discussed above are considerably more difficult to obtain directly for larger systems, and it is for such systems that the formalism here presented is designed.

In order to adopt a notation which will be particularly convenient for more complicated operators, let us rewrite the results we have found for the overlap matrix. First we define

$$\Delta_{kk'}(Q) = \prod_{j=1}^{n} \langle (k, j) \mid (k', q_j) \rangle, \tag{57}$$

the n-dimensional overlap integral between the function $\Xi_k(\mathbf{r})$ and $\mathscr{Q}_r \Xi_{k'}(\mathbf{r})$. Then,

$$\langle \Psi_k{}^i \mid \Psi_{k'}^{i'} \rangle = n! \sum_{Q} U_{ii'}^{*}(Q) \Delta_{kk'}(Q). \tag{58}$$

We pass next to a discussion of one-electron operators of the form given in Eq. (50). For the present we consider operators which are independent of the spin. Introducing the orbital form for $\Xi_k(\mathbf{r})$ and $\mathscr{Q}_r \Xi_{k'}(\mathbf{r})$ and Eq. (50) for $\mathscr{B}$ into Eq. (40),

$$\langle \Psi_k{}^i \mid \mathscr{B} \mid \Psi_{k'}^{i'} \rangle$$

$$= n! \sum_{Q} U_{ii'}^{*}(Q) \sum_{l=1}^{n} \langle (k, 1)(k, 2) \cdots (k, n) \mid \mathscr{b}(\mathbf{r}_l) \mid (k', q_1)(k', q_2) \cdots (k', q_n) \rangle. \tag{59}$$

Separating the right side of Eq. (59) into factors describing individual electrons,

$$\langle \Psi_k{}^i | \mathcal{B} | \Psi_{k'}^{i'} \rangle = n! \sum_Q U_{ii'}^*(Q) \sum_{l=1}^{n} \langle (k, l) | \mathcal{O}(\mathbf{r}_l) | (k', q_l) \rangle \prod_{\substack{j=1 \\ j \neq l}}^{n} \langle (k, j) | (k', q_j) \rangle .$$

If the quantities $\langle (k, l) | (k', q_l) \rangle$ are nonzero for $l = 1, \ldots n$, Eq. (60) may be rewritten

$$\langle \Psi_k{}^i | \mathcal{B} | \Psi_{k'}^{i'} \rangle = n! \sum_Q U_{ii'}^*(Q) \Delta_{kk'}(Q) \sum_{l=1}^{n} \frac{\langle (k, l) | \mathcal{O}(\mathbf{r}_l) | (k', q_l) \rangle}{\langle (k, l) | (k', q_l) \rangle} . \tag{61}$$

Equation (61) may be used even when some of the factors $\langle (k, l) | (k', q_l) \rangle$ are zero if it is understood that cancellation of common factors between $\Delta_{kk'}(Q)$ and the summation over l is to be done before values are inserted for any zero factors.

Two-electron spin-free operators may be handled by methods which are entirely analogous to those just employed for one-electron operators. A two-electron operator $\mathcal{B}$, of the form given in Eq. (51), can be shown to have matrix elements

$$\langle \Psi_k{}^i | \mathcal{B} | \Psi_{k'}^{i'} \rangle$$
$$= n! \sum_Q U_{ii'}^*(Q) \Delta_{kk'}(Q) \sum_{m=2}^{n} \sum_{l=1}^{m-1} \frac{\langle (k, l)(k, m) | \mathcal{O}(\mathbf{r}_l, \mathbf{r}_m) | (k', q_l)(k', q_m) \rangle}{\langle (k, l) | (k', q_l) \rangle \langle (k, m) | (k', q_m) \rangle} . \tag{62}$$

In Eq. (62), as in Eq. (61), zero factors in the denominator are to be cancelled against $\Delta_{kk'}(Q)$ before numerical evaluation.

Next we look at the matrix elements of spin-dependent operators. Take first a one-electron operator as in Eq. (50). The operator space for a single electron spin is spanned by four operators (e.g., $\mathscr{s}_x$, $\mathscr{s}_y$, $\mathscr{s}_z$, and the identity), so that $\mathcal{O}(\mathbf{r}_l, \boldsymbol{\sigma}_l)$ can be written either as $\mathcal{O}_r(\mathbf{r}_l)\mathcal{O}_\sigma(\boldsymbol{\sigma}_l)$ or as a sum of up to four such terms. We assume that this expansion has already been made and we restrict our attention to one of its terms, so that

$$\mathcal{O}(\mathbf{r}_l, \boldsymbol{\sigma}_l) = \mathcal{O}_r(\mathbf{r}_l)\mathcal{O}_\sigma(\boldsymbol{\sigma}_l). \tag{63}$$

With the aid of Eq. (63), Eq. (46) becomes

$$\langle \Psi_k^i | \mathcal{B} | \Psi_{k'}^{i'} \rangle = n! \sum_Q \sum_{l=1}^{n} [\mathbf{b}(l)\mathbf{U}^*(Q)]_{ii'} \langle \Xi_k(\mathbf{r}) | \mathcal{O}_r(\mathbf{r}_l)\mathcal{Q}_r | \Xi_{k'}(\mathbf{r}) \rangle , \tag{64}$$

where $\mathbf{b}(l)$ is a matrix [cf. Eq. (45)] with elements

$$b_{ij}(l) = \langle \Theta_i(\boldsymbol{\sigma}) | \mathcal{O}_\sigma(\boldsymbol{\sigma}_l) | \Theta_j(\boldsymbol{\sigma}) \rangle . \tag{65}$$

Another way to characterize $\mathbf{b}(l)\mathbf{U}^*(Q)$ is to combine Eqs. (16), (17), (65), and the resolution of the identity $\sum_{j=1}^{d} |\Theta_j(\sigma)\rangle\langle\Theta_j(\sigma)|$ to yield

$$[\mathbf{b}(l)\mathbf{U}^*(Q)]_{ii'} = \langle \Theta_i(\sigma) \,|\, \mathscr{O}_\sigma(\sigma_l)\varepsilon_Q \mathscr{Q}_\sigma \,|\, \Theta_{i'}(\sigma)\rangle. \tag{66}$$

Equation (64) is like Eq. (59), except that elements of $\mathbf{b}(l)\mathbf{U}^*(Q)$ stand in place of $\mathbf{U}^*(Q)$. Equation (64) therefore leads to a result analogous to that obtained from Eq. (59):

$$\langle \Psi_k^{i} \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'}\rangle = n! \sum_Q \sum_{l=1}^{n} [\mathbf{b}(l)\mathbf{U}^*(Q)]_{ii'} \Delta_{kk'}(Q) \frac{\langle (k, l) \,|\, \mathscr{O}_r(\mathbf{r}_l) \,|\, (k', q_l)\rangle}{\langle (k, l) \,|\, (k', q_l)\rangle}. \tag{67}$$

A parallel analysis may be given for a two-electron spin-dependent operator whose terms factor to give

$$\mathscr{O}(\mathbf{r}_l, \mathbf{r}_m, \boldsymbol{\sigma}_l, \boldsymbol{\sigma}_m) = \mathscr{O}_r(\mathbf{r}_l, \mathbf{r}_m)\mathscr{O}_\sigma(\boldsymbol{\sigma}_l, \boldsymbol{\sigma}_m). \tag{68}$$

The matrix elements are

$$\langle \Psi_k^{i} \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'}\rangle = n! \sum_Q \sum_{m=2}^{n} \sum_{l=1}^{m-1} [\mathbf{b}(l, m)\mathbf{U}^*(Q)]_{ii'} \Delta_{kk'}(Q) \times \frac{\langle (k, l)(k, m) \,|\, \mathscr{O}_r(\mathbf{r}_l, \mathbf{r}_m) \,|\, (k', q_l)(k', q_m)\rangle}{\langle (k, l) \,|\, (k', q_l)\rangle\langle (k, m) \,|\, (k', q_m)\rangle}. \tag{69}$$

Here $\mathbf{b}(l, m)$ is a matrix with elements

$$b_{ij}(l, m) = \langle \Theta_i(\sigma) \,|\, \mathscr{O}_\sigma(\sigma_l, \sigma_m) \,|\, \Theta_j(\sigma)\rangle. \tag{70}$$

B. The Effect of Closed Shells

The matrix element expressions we have obtained can be greatly simplified if the various configurations contain doubly occupied orbitals. The simplifications are of three kinds. First, the presence of double occupied orbitals causes the vanishing of the $\Psi_k^{i}(\mathbf{r}, \boldsymbol{\sigma})$ for certain spin functions $\Theta_i(\boldsymbol{\sigma})$. This means we need not consider some elements of the matrices $\mathbf{U}(Q)$. Second, there will be permutations which are of identical effect upon $\Xi_k(\mathbf{r})$, and these can be grouped so that each need not be computed individually. Third, the presence of doubly occupied orbitals makes $\Psi_k^{i}(\mathbf{r}, \boldsymbol{\sigma})$ invariant under certain unitary transformations of the orbitals among themselves. Using such a transformation, orthogonalities may be created among the orbitals. These orthogonalities can cause certain permutations to fail to contribute to the matrix elements. Those permutations may then be omitted from the summations.

Before discussing these simplifications let us note that we may not have an arbitrary amount of double orbital occupancy for arbitrary S, because we must avoid functions $\Xi_k(\mathbf{r})\Theta_i(\boldsymbol{\sigma})$ which cannot be antisymmetrized.

Since a doubly occupied orbital is symmetric in its two electrons, it must appear in combination with a spin function which has an antisymmetric component in those two electrons. Since a pair of electrons with an antisymmetric spin function (i.e., $\alpha\beta - \beta\alpha$) constitute a subsystem with zero spin, a spin function of given S must have at least $2S$ electrons which are not in antisymmetric pairs. This, in turn, means that at least $2S$ orbitals must be singly occupied. We also note that there always exists a spin function with all but $2S$ electrons in antisymmetric pairs, so that it is always possible to place all but $2S$ electrons into doubly occupied orbitals. We need not consider triple or higher orbital occupancy because the spin space of an electron is only of order two, and consequently there exists no spin function with a component which is antisymmetric in the coordinates of more than two electrons.

We next inquire as to whether the generality of a configuration interaction is reduced by using only configurations with doubly occupied orbitals. We observe that an arbitrary pair of orbitals $\chi_1(\mathbf{r}_1)\chi_2(\mathbf{r}_2)$, when multiplied by spin function $\alpha\beta - \beta\alpha$, is equivalent to $(\chi_1\chi_2 + \chi_2\chi_1)(\alpha\beta - \beta\alpha)$ when both expressions are multiplied by spatial and spin functions of all other electrons and antisymmetrized. The combination $(\chi_1\chi_2 + \chi_2\chi_1)(\alpha\beta - \beta\alpha)$ can be reproduced by a configuration interaction involving three configurations containing, respectively, $\chi_1\chi_1(\alpha\beta - \beta\alpha)$, $\chi_2\chi_2(\alpha\beta - \beta\alpha)$, and $(\chi_1 + \chi_2)(\chi_1 + \chi_2)(\alpha\beta - \beta\alpha)$. Since the introduction of doubly occupied orbitals presupposes the existence of a spin function with the postulated pairwise antisymmetry, a complete configuration interaction loses no generality by a restriction to doubly occupied orbital configurations. However, it is important to notice that the number of configurations needed to obtain a given wave function may be increased if doubly occupied orbitals are used.

As we remarked previously, the use of doubly occupied orbitals must be accompanied by the use of spin functions with antisymmetric components in the corresponding electrons. It is possible to choose the set of spin functions $\Theta_i(\sigma)$, $i = 1, \ldots d$, in such a way that either $\Theta_i(\sigma)$ is antisymmetric in all pairs of electrons in doubly occupied orbitals or that $\Theta_i(\sigma)$ leads to a vanishing antisymmetrized wave function. Let's get more specific. We consider spatial configurations in which there are $2p$ electrons in p doubly occupied orbitals and u other electrons, so $2p + u = n$. The sufficiently antisymmetric spin functions $\Theta_i(\sigma)$ will all have the form

$$\Theta_i(\sigma) = \underbrace{(\alpha\beta - \beta\alpha) \cdots (\alpha\beta - \beta\alpha)}_{p \text{ factors}}(\text{spin function of } u \text{ electrons})_i. \tag{71}$$

Applying $\mathscr{S}^2$ and $\mathscr{S}_z$ to $\Theta_i(\sigma)$ as given in Eq. (71), we find that the $2p$ electrons in antisymmetric pairs have a resultant spin $S = 0$, so that the u electron function of the remaining spins determine the eigenvalues of $\mathscr{S}^2$ and $\mathscr{S}_z$. This means that the suitable u electron spin functions are those which are themselves eigenfunctions with the S and M_s values desired for the n electron system, and the number of such spin functions will be the value of d for the given S, M_s, but for u electrons.

We shall use the spin functions $\Theta_i(\sigma)$ in combination with doubly occupied orbitals to make wave functions of the form obtainable from Eq. (41):

$$\Psi_k^i(\mathbf{r}, \sigma) = n!\,\mathscr{A}\chi_{(k,2)}\chi_{(k,2)}\chi_{(k,4)}\chi_{(k,4)} \cdots \chi_{(k,2p)}\chi_{(k,2p)}\chi_{(k,2p+1)} \times \chi_{(k,2p+2)} \cdots \chi_{(k,n)}(\alpha\beta - \beta\alpha) \cdots (\alpha\beta - \beta\alpha)(u \text{ spin function}). \tag{72}$$

We note that the double occupancy and the operator $\mathscr{A}$ permit us to recast Eq. (72) in the form

$$\Psi_k^i(\mathbf{r}, \sigma) = n!\,\mathscr{A}\chi_{(k,2)}\chi_{(k,2)}\chi_{(k,4)}\chi_{(k,4)} \cdots \chi_{(k,2p)}\chi_{(k,2p)} \times \chi_{(k,2p+1)}\chi_{(k,2p+2)} \cdots \chi_{(k,n)}\alpha\beta\alpha\beta \cdots \alpha\beta(u \text{ spin function}). \tag{73}$$

Equation (73) is a convenient expression to use in discussing orbital transformations and orthogonalization procedures.

In Eq. (73), because of the presence of $\mathscr{A}$, any spatial orbital with an α spin function may have added to it any linear combination of other α spin spatial orbitals without changing the value of $\Psi_k^i(\mathbf{r}, \sigma)$. The same is true of the spatial orbitals having β spin functions. It is thus possible to make linear transformations among the doubly occupied orbitals. Since the α spin and β spin orbitals are identical, transformations may be made in a way which preserves the double occupancy. It is also possible to transform the singly occupied orbitals by adding arbitrary amounts of the doubly occupied orbitals to them. Such transformations clearly leave the wave function unaltered, since each added doubly occupied orbital term will, on expansion, yield a triply occupied orbital configuration which must vanish. Notice, however, that we may not transform the singly occupied orbitals among themselves unless we are willing to change the wave function.

The orbital transformation properties permit us to generate orthogonality in various ways, suggesting the obvious possibility that we could set up the entire configuration-interaction wave function in terms of a complete set of orthogonal orbitals. While this is indeed possible, it should be noted that the simultaneous use of double occupancy and a fixed set of orthogonal orbitals is *not* consistent with maintaining full generality of the wave function, even in a configuration interaction of infinite extent. The truth of this statement becomes apparent if we consider a two-electron system and a complete orthogonal set of orbitals $\chi_1, \chi_2, \ldots$. The spatial function $\chi_1\chi_2$ can only be created in a doubly occupied orbital formulation by using $\chi_1\chi_1$, $\chi_2\chi_2$, and $(\chi_1 + \chi_2)(\chi_1 + \chi_2)$, if we insist on retaining χ_1 and χ_2 as members of the orbital set. But $\chi_1 + \chi_2$ is not orthogonal to χ_1 or χ_2 and therefore cannot be in the orbital set. Notice, however, that, *after* we have decided we want a wave function of a particular form, we can choose an orbital set which yields it while excluding other forms not then of interest to us. In the example under discussion, $\chi_1\chi_2$ can be reached by a linear combination of $(\chi_1 + \chi_2)(\chi_1 + \chi_2)$ and $(\chi_1 - \chi_2)(\chi_1 - \chi_2)$, where $\chi_1 + \chi_2$ and $\chi_1 - \chi_2$ are orthogonal. But we have then given up the possibility of making $\chi_1\chi_1$. The point of this discussion is that the use of doubly occupied orthogonal orbitals leads to a loss of generality in the wave function unless the orthogonal orbitals themselves are regarded as subject to an arbitrary unitary transformation.

Even though we cannot hope to make a general wave function from a single set of previously chosen orthogonal orbitals, using double occupancy, we can nevertheless make effective use of orthogonality to simplify the calculation of matrix elements. For evaluating a matrix element $\langle \Psi_k{}^i | \mathscr{H} | \Psi_{k'}^{i'} \rangle$ the most useful orthogonality is between the orbitals of configurations k and k', rather than within either configuration individually. In particular, we may make orbital transformations to orthogonalize each doubly occupied orbital of configuration k to each doubly occupied orbital of configuration k', except that corresponding orbitals of the two configurations (i.e., those with the same electron numbers) need not be orthogonal. A proof of this and related statements is given in Appendix A. For closed-shell wave functions, i.e., wave functions consisting only of doubly occupied orbitals, this is sufficient orthogonality to permit an optimum simplification of the matrix elements. If the wave functions also contain singly occupied orbitals, they may be orthogonalized to the doubly occupied orbitals of the other configuration, with the exception of those doubly occupied orbitals which are orthogonal to the corresponding orbital of the other configuration. Unfortunately, it is not possible to orthogonalize the singly occupied orbitals with these remaining doubly occupied orbitals, nor with the singly occupied orbitals of the other configuration, without altering the wave function. Notice that the orthogonalization procedures for a configuration k are determined by its relationships to another configuration k', and each k' may require a different orthogonalization of the orbitals of configuration k. If two configurations k and k' have different numbers of doubly occupied orbitals, the analysis of this paragraph may be carried out with the noncorresponding doubly occupied orbitals regarded as degenerate singly occupied orbitals.

When the orthogonalization procedure of the foregoing paragraph is applied there result three well-defined cases. First, there is the *closed-shell* case, where configurations k and k' consist entirely of doubly occupied orbitals. In this case every orbital of k is orthogonal to every orbital, except possibly the corresponding orbital, of k'. Next we distinguish what may be called a *maximally overlapping open-shell* case, in which there are both singly and doubly occupied orbitals, but with each doubly occupied orbital of configuration k having a nonzero overlap with its corresponding orbital in configuration k'. In this case the orthogonalization procedure results in making every doubly occupied orbital of each configuration orthogonal to every orbital of the other configuration, whether singly or doubly occupied. Finally there is the *general open-shell* case, where one or more doubly occupied orbitals are orthogonal to the corresponding orbital of the other configuration. These orbitals cause complications because they cannot be orthogonalized to the singly occupied orbitals of the other configuration. It is therefore most convenient to treat this case as one of maximally overlapping open shells, by including the offending doubly occupied orbitals as degenerate singly occupied orbitals. Accordingly, we need study the matrix-element formulas only for closed-shell and maximally overlapping open-shell situations.

The present discussion can be facilitated by a more specialized notation than that used in the preceding sections. Since we deal here entirely with given values of k and k', we drop them from the orbital subscripts. To be more specific, we let configurations k and k' contain p doubly occupied orbitals and u singly occupied orbitals. For configuration k, we use $\chi_1, \chi_2, \ldots \chi_p$ for the doubly occupied orbitals, and $\varphi_1, \varphi_2, \ldots \varphi_u$ for the singly occupied orbitals. For configuration k', we use $\chi_1', \chi_2', \ldots \chi_n'$, and $\varphi_1', \varphi_2', \ldots \varphi_u'$. We assume $\Xi_k(\mathbf{r})$ or $\Xi_{k'}(\mathbf{r})$ are written with the orbitals in order, doubly occupied orbitals first. Thus,

$$\Xi_k(\mathbf{r}) = \chi_1(\mathbf{r}_1)\chi_1(\mathbf{r}_2) \cdots \chi_i(\mathbf{r}_{2i-1})\chi_i(\mathbf{r}_{2i}) \cdots$$
$$\chi_p(\mathbf{r}_{2p-1})\chi_p(\mathbf{r}_{2p})\varphi_1(\mathbf{r}_{2p+1}) \cdots \varphi_i(\mathbf{r}_{2p+i}) \cdots \varphi_u(\mathbf{r}_n). \quad (74)$$

We also need to make reference to specific permutations. We write $Q_{\mu,\nu}$ to indicate the permutation in which electrons μ and ν are interchanged. Notice that the way the doubly occupied orbitals are numbered, $Q_{\mu,\nu}$ does not permute orbitals μ and ν. The permutations which do this are $Q_{2\mu-1,2\nu-1}$, $Q_{2\mu-1,2\nu}$, $Q_{2\mu,2\nu-1}$, and $Q_{2\mu,2\nu}$.

C. Closed-Shell Matrix Elements

We are at last ready to work on the matrix elements. We take first the closed-shell case, and we start with the overlap matrix, as given in Eq. (58). Due to the orbital overlap conditions we have created, no permutation $\mathscr{Q}$ can contribute in Eq. (58) if that permutation causes an interchange of orbitals. This means that the permutations which do contribute in Eq. (58) are just those which cause only interchanges within doubly occupied orbital pairs. Since there are p orbital pairs, there will be a total of 2^p such permutations. Letting R stand for such a permutation, and $\mathfrak{R}$ for the group of all such permutations, the contributing permutations satisfy $R \in \mathfrak{R}$. Since $R_r \Xi_{k'}(\mathbf{r}) = \Xi_{k'}(\mathbf{r})$ for these permutations, Eq. (58) reduces to

$$\langle \Psi_k{}^i \,|\, \Psi_{k'}^{i'} \rangle = n! \sum_{R \in \mathfrak{R}} U_{ii'}^{*}(R)\, \Delta, \tag{75}$$

where

$$\Delta = \prod_{j=1}^{p} \langle \chi_j \,|\, \chi_j{}' \rangle^2. \tag{76}$$

In the closed-shell case there is only one spin function, namely, that proportional to $(\alpha\beta - \beta\alpha) \cdots (\alpha\beta - \beta\alpha)$, and application of Eqs. (16) and (17) show that $U_{11}^{*}(R) = 1$ for all $R \in \mathfrak{R}$. Thus,

$$\langle \Psi_k{}^1 \,|\, \Psi_{k'}^{1} \rangle = (2p)!\, 2^p \Delta \qquad \text{(closed shells).} \tag{77}$$

We next turn to one-electron spin-free operators, whose matrix elements are given in Eq. (61). We note that Eq. (61) contains the factor $\Delta_{kk'}(Q)$, which will certainly vanish if the permutation Q causes an interchange of orbitals. We also note that there is one overlap factor in the denominator which can be used to cancel a zero factor in $\Delta_{kk'}(Q)$, but an orbital exchange will result in two zero-overlap factors. The situation is therefore similar to that already discussed for the overlap matrix, and only permutations $R \in \mathfrak{R}$ contribute to the matrix elements. Equation (61) simplifies to

$$\langle \Psi_k{}^1 | \mathscr{B} \,|\, \Psi_{k'}^{1} \rangle = (2p)!\, 2^{p+1} \Delta \sum_{l=1}^{p} \frac{\langle \chi_l \,|\, \mathscr{b} \,|\, \chi_l{}' \rangle}{\langle \chi_l \,|\, \chi_l{}' \rangle} \tag{78}$$

(one-electron spin-free operator, closed shells).

In Eq. (78), the summation is over orbitals rather than electrons. The double occupancy of the orbitals has resulted in an additional factor of 2, which is included before the sum. The result is well-known, and has been extensively discussed recently by Karplus *et al.* (1958).

Take now a two-electron spin-free operator with matrix elements given in Eq. (62). Again the factor $\Delta_{kk'}(Q)$ appears, but this time there are two overlap factors in the denominator which can be used to eliminate zero factors. Permutations which produce no more than two zero-overlap factors therefore contribute to the matrix elements. Such permutations are those with at most a single orbital interchange. These permutations are of the form R, $Q_{2\mu-1,2\nu-1}R$, $Q_{2\mu-1,2\nu}R$, $Q_{2\mu,2\nu-1}R$, or $Q_{2\mu,2\nu}R$, where $1 \leq \mu < \nu \leq p$, and R is any permutation which does not interchange orbitals (i.e., $R \in \mathfrak{R}$).

The permutations of the form R make the following contribution to $\langle \Psi_k{}^1 | \mathscr{B} | \Psi^1{}_{k'} \rangle$:

$$R \text{ term} = n! \sum_{R \in \mathfrak{R}} U^*_{11}(R) \Delta \Bigg[4 \sum_{m=2}^{p} \sum_{l=1}^{m-1} \frac{\langle \chi_l \chi_m | \mathscr{b} | \chi_l{}' \chi_m{}' \rangle}{\langle \chi_l | \chi_l{}' \rangle \langle \chi_m | \chi_m{}' \rangle} + \sum_{l=1}^{p} \frac{\langle \chi_l \chi_l | \mathscr{b} | \chi_l{}' \chi_l{}' \rangle}{\langle \chi_l | \chi_l{}' \rangle^2} \Bigg]. \tag{79}$$

The summations appear different than in Eq. (62) because they are now over orbitals. The factor "4" in the first set of sums is due to the double occupancy of orbitals l and m. The second sum is the contribution from a pair of electrons occupying the same orbital. The other permutations make contributions to $\langle \Psi_k{}^1 | \mathscr{B} | \Psi^1_{k'} \rangle$ like this:

$$Q_{2\mu-1,2\nu-1}R \text{ term} = n! \sum_{R \in \mathfrak{R}} U^*_{11}(Q_{2\mu-1,2\nu-1}R) \Delta \frac{\langle \chi_\mu \chi_\nu | \mathscr{b} | \chi_\nu{}' \chi_\mu{}' \rangle}{\langle \chi_\mu | \chi_\mu{}' \rangle \langle \chi_\nu | \chi_\nu{}' \rangle}. \tag{80}$$

The sums over l and m in Eq. (62) are reduced to the single term $l = 2\mu - 1$, $m = 2\nu - 1$, as zero factors in $\Delta_{kk'}(Q_{2\nu-1,2\nu-1}R)$ make all other terms vanish. Differences in definition between $\Delta_{kk'}(Q)$ and Δ are accounted for by corresponding changes in the denominator on going from Eq. (62) to Eq. (80). Terms involving $Q_{2\mu-1,2\nu}R$, $Q_{2\mu,2\nu-1}R$, or $Q_{2\mu,2\nu}R$ give results analogous to Eq. (80).

We already saw that $U^*_{11}(R) = 1$ for all $R \in \mathfrak{R}$. Using Eqs. (16) and (17), we also have $U^*_{11}(Q_{2\mu-1,2\nu-1}R) = U^*_{11}(Q_{2\mu-1,2\nu}R) = U^*_{11}(Q_{2\mu,2\nu-1}R) = U^*_{11}(Q_{2\mu,2\nu}R) = -\frac{1}{2}$, for $1 \leq \mu < \nu \leq p$ and all $R \in \mathfrak{R}$. This means that the $Q_{2\mu-1,2\nu-1}R$, $Q_{2\mu-1,2\nu}R$, $Q_{2\mu,2\nu-1}R$, and $Q_{2\mu,2\nu}R$ terms are all equal.

We thus multiply Eq. (80) by 4 and sum over μ and ν such that $1 \leq \mu < \nu \leq p$ to get

$$\text{sum of all } QR \text{ terms} = -(2p)!\,2^{p+1}\Delta \sum_{\nu=2}^{p} \sum_{\mu=1}^{\nu-1} \frac{\langle \chi_\mu \chi_\nu | \mathscr{E} | \chi_\nu' \chi_\mu' \rangle}{\langle \chi_\mu | \chi_\mu' \rangle \langle \chi_\nu | \chi_\nu' \rangle}. \tag{81}$$

Combining Eq. (79) and (81), changing dummy indices in Eq. (81),

$$\langle \Psi_k{}^1 | \mathscr{B} | \Psi_{k'}^1 \rangle = (2p)!\,2^p\Delta \left[\sum_{m=2}^{p} \sum_{l=1}^{m-1} \left(\frac{4\langle \chi_l \chi_m | \mathscr{E} | \chi_l' \chi_m' \rangle - 2\langle \chi_l \chi_m | \mathscr{E} | \chi_m' \chi_l' \rangle}{\langle \chi_l | \chi_l' \rangle \langle \chi_m | \chi_m' \rangle} \right) + \sum_{l=1}^{p} \frac{\langle \chi_l \chi_l | \mathscr{E} | \chi_l' \chi_l' \rangle}{\langle \chi | \chi_l' \rangle^2} \right]. \tag{82}$$

Finally, we rearrange the sums to obtain

$$\langle \Psi_k{}^1 | \mathscr{B} | \Psi_{k'}^1 \rangle = (2p)!\,2^p\Delta \sum_{l=1}^{p} \sum_{m=1}^{p} \left(\frac{2\langle \chi_l \chi_m | \mathscr{E} | \chi_l' \chi_m' \rangle - \langle \chi_l \chi_m | \mathscr{E} | \chi_m' \chi_l' \rangle}{\langle \chi_l | \chi_l' \rangle \langle \chi_m | \chi_m' \rangle} \right) \tag{83}$$

(two-electron spin-free operator, closed shells).

Equations (77), (78), and (83) contain the essential relationships for studying spin-free operators in closed-shell systems. We may illustrate the use of these equations by forming the matrix elements for an operator of particular interest, namely the Hamiltonian, in the approximation of Eq. (2). The result is

$$\langle \Psi_k{}^1 | \mathscr{H} | \Psi_{k'}^1 \rangle = (2p)!\,2^p\,\Delta \left[2 \sum_{l=1}^{p} \frac{\langle \chi_l | h_1 | \chi_l' \rangle}{\langle \chi_l | \chi_l' \rangle} + \sum_{l=1}^{p} \sum_{m=1}^{p} \left(\frac{2\langle \chi_l \chi_m | \dfrac{e^2}{r_{12}} | \chi_l' \chi_m' \rangle - \langle \chi_l \chi_m | \dfrac{e_2}{r_{12}} | \chi_m' \chi_l' \rangle}{\langle \chi_l | \chi_l' \rangle \langle \chi_m | \chi_m' \rangle} \right) + \sum_{j=2}^{N} \sum_{i=1}^{j-1} \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|} \right] \quad \text{(closed shells).} \tag{84}$$

The operator h_1 appearing in Eq. (84) is

$$h_1 = -\frac{\hbar^2}{2m}\nabla^2 - \sum_{j=1}^{N} \frac{Z_j e^2}{|\mathbf{r} - \mathbf{R}_j|}. \tag{85}$$

It perhaps should be reiterated that the orbitals χ_i and χ_i' have been chosen in such a way that $\langle \chi_i' | \chi_{j'}' \rangle = 0$ unless $i = j$, and that, if the orbitals as originally supplied did not have this property, they can be transformed so as to acquire it without change in the wave function. If k and k' describe the same configuration, if the χ_i are orthonormal, and if we normalize $\Psi_k{}^1(\mathbf{r}, \boldsymbol{\sigma})$, Eq. (84) reduces to the well-known result

$$\langle \mathscr{H} \rangle = 2 \sum_{l=1}^{p} \langle \chi_l | h_1 | \chi_l \rangle + \sum_{l=1}^{p} \sum_{m=1}^{p} \left(2 \left\langle \chi_l \chi_m \left| \frac{e^2}{r_{12}} \right| \chi_l \chi_m \right\rangle - \left\langle \chi_l \chi_m \left| \frac{e^2}{r_{12}} \right| \chi_m \chi_l \right\rangle \right) + \sum_{j=2}^{N} \sum_{i=1}^{j-1} \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|} \text{ (closed shells).} \quad (86)$$

The results of this section can be extended to spin-dependent operators. We first notice that the permutations which contribute to the matrix elements are the same as in the spin-free case. Take first a one-electron operator, for which the contributing permutations R are those for which $R \in \mathfrak{R}$. We therefore need values of $[\mathbf{b}(l)\mathbf{U}^*(R)]_{11}$ for $R \in \mathfrak{R}$ and for all l [cf. Eq. (67)]. Because $R\Theta_1(\boldsymbol{\sigma}) = \varepsilon_r \Theta_1(\boldsymbol{\sigma})$, $[\mathbf{b}(l)\mathbf{U}^*(R)]_{11} = b_{11}(l)$. Looking at Eq. (65), we see that $b_{11}(l)$ is independent of l, so we simply write it as b_{11}. The matrix elements of Eq. (67) thus reduce to

$$\langle \Psi_k{}^1 | \mathscr{B} | \Psi_{k'}^1 \rangle = (2p)!\, 2^{p+1} b_{11} \Delta \sum_{l=1}^{p} \frac{\langle \chi_l | \mathscr{b}_r | \chi_l' \rangle}{\langle \chi_l | \chi_l' \rangle} \quad (87)$$

(one-electron spin-dependent operator, closed shells).

We may further characterize b_{11}. Starting from Eq. (65) for

$$\langle \Theta_1(\boldsymbol{\sigma}) | \mathscr{b}_\sigma(\boldsymbol{\sigma}_1) | \Theta_1(\boldsymbol{\sigma}) \rangle,$$

we form the scalar product of all but the first pair of spins to get

$$b_{11} = \tfrac{1}{2} \langle (\alpha\beta - \beta\alpha) | \mathscr{b}_\sigma(\boldsymbol{\sigma}_1) | (\alpha\beta - \beta\alpha) \rangle. \quad (88)$$

This may be further simplified to

$$b_{11} = \tfrac{1}{2} [\langle \alpha | \mathscr{b}_\sigma | \alpha \rangle + \langle \beta | \mathscr{b}_\sigma | \beta \rangle]. \quad (89)$$

For a closed-shell matrix element we see that b_{11} is the average of $\langle \mathscr{b}_\sigma \rangle$ over both spin states. Notice also that if $\mathscr{b}_\sigma = I$, the identity operator, Eq. (89) reduces to $b_{11} = 1$, which is the spin-free result we expect in that case.

Proceeding to two-electron operators, we need $[\mathbf{b}(l, m)\mathbf{U}^*(Q)]_{11}$ for all Q which cause at most a single orbital interchange, and for the values of l and m which contribute for each Q. For permutations $R \in \mathfrak{R}$ which do not interchange orbitals, $[\mathbf{b}(l, m)\mathbf{U}^*(R)]_{11} = b_{11}(l, m)$, and all l and m values are needed. Because of the form of $\Theta_1(\boldsymbol{\sigma})$, the various $b_{11}(l, m)$ have only two distinct values depending upon whether l and m refer to the same or to different orbitals. When l and m refer to the same orbital we have, using Eq. (70) and the form of $\Theta_1(\boldsymbol{\sigma})$,

$$b_{11}(\text{same}) = \langle\alpha\beta\,|\,\mathscr{e}_\sigma\,|\,\alpha\beta\rangle - \langle\alpha\beta\,|\,\mathscr{e}_\sigma\,|\,\beta\alpha\rangle. \tag{90}$$

When l and m refer to different orbitals,

$$b_{11}(\text{dir}) = \tfrac{1}{4}[\langle\alpha\alpha\,|\,\mathscr{e}_\sigma\,|\,\alpha\alpha\rangle + \langle\beta\beta\,|\,\mathscr{e}_\sigma\,|\,\beta\beta\rangle + 2\langle\alpha\beta\,|\,\mathscr{e}_\sigma\,|\,\alpha\beta\rangle]. \tag{91}$$

The contribution of the permutations $R \in \mathfrak{R}$ to Eq. (69) may therefore be written

$$\begin{aligned} R\text{ term} = (2p)!\,2^p\,\Delta\Bigg[&4b_{11}(\text{dir})\sum_{m=2}^{p}\sum_{l=1}^{m-1}\frac{\langle\chi_l\chi_m\,|\,\mathscr{e}_r\,|\,\chi_l{}'\chi_m{}'\rangle}{\langle\chi_l\,|\,\chi_l{}'\rangle\langle\chi_m\,|\,\chi_m{}'\rangle} \\ &+ \mathscr{e}_{11}(\text{same})\sum_{l=1}^{p}\frac{\langle\chi_l\chi_l\,|\,\mathscr{e}_r\,|\,\chi_l{}'\chi_l{}'\rangle}{\langle\chi_l\,|\,\chi_l{}'\rangle^2}\Bigg]. \end{aligned} \tag{92}$$

For the remaining permutations which contribute to Eq. (69), we need expressions such as $[\mathbf{b}(l, m)\mathbf{U}^*(Q_{2\mu-1,2\nu-1}R)]_{11}$, for all $R \in \mathfrak{R}$, and for the single l and m values $l = 2\mu - 1$, $m = 2\nu - 1$. This simplifies at once to $[\mathbf{b}(2\mu - 1, 2\nu - 1)\mathbf{U}^*(Q_{2\mu-1,2\nu-1})]_{11}$. Because of the form of $\Theta_1(\boldsymbol{\sigma})$, this expression is independent of μ and ν, and is also unaltered if 2μ replaces $2\mu - 1$, if 2ν replaces $2\nu - 1$, or if both replacements are made. Setting $[\mathbf{b}(2\mu - 1, 2\nu - 1)\mathbf{U}^*(Q_{2\mu-1,2\nu-1})]_{11} = b_{11}(\text{exch})$, we may use Eq. (70) to find

$$b_{11}(\text{exch}) = -\tfrac{1}{4}[\langle\alpha\alpha\,|\,\mathscr{e}_\sigma\,|\,\alpha\alpha\rangle + \langle\beta\beta\,|\,\mathscr{e}_\sigma\,|\,\beta\beta\rangle + 2\langle\alpha\beta\,|\,\mathscr{e}_\sigma\,|\,\beta\alpha\rangle]. \tag{93}$$

We now sum the interchanged-orbital contributions to Eq. (69):

$$\text{sum of all } QR \text{ terms} = (2p)!2^{p+2}\,\Delta b_{11}(\text{exch})\sum_{\nu=2}^{p}\sum_{\mu=1}^{\nu-1}\frac{\langle\chi_\mu\chi_\nu|\,\mathscr{e}_r|\,\chi_\nu{}'\chi_\mu{}'\rangle}{\langle\chi_\mu\,|\,\chi_\mu{}'\rangle\langle\chi_\nu{}'\,|\,\chi_\nu{}'\rangle}. \tag{94}$$

The final steps of producing the matrix element given by Eq. (69) are to combine Eqs. (92) and (94), rearranging the summations to produce a result analogous to the spin-free case given as Eq. (83). In order to do this, we need to make use of the fact that the three spin-dependent quantities $b_{11}(\text{same})$, $b_{11}(\text{dir})$, and $b_{11}(\text{exch})$ are not linearly independent, but are related by

$$b_{11}(\text{dir}) + b_{11}(\text{exch}) = \tfrac{1}{2}b_{11}(\text{same}). \tag{95}$$

Using Eq. (95) to simplify the sum of Eqs. (92) and (94),

$$\langle \Psi_k{}^1 | \mathscr{B} | \Psi_{k'}^1 \rangle$$

$$= (2p)!\, 2^p \Delta \sum_{l=1}^{p} \sum_{m=1}^{p} \left(\frac{2b_{11}(\text{dir}) \langle \chi_l \chi_m | \mathscr{b}_r | \chi_l{}' \chi_m{}' \rangle + 2b_{11}(\text{exch}) \langle \chi_l \chi_m | \mathscr{b}_r | \chi_m{}' \chi_l{}' \rangle}{\langle \chi_l | \chi_l{}' \rangle \langle \chi_m | \chi_m{}' \rangle} \right) \tag{96}$$

(two-electron spin-dependent operator, closed shells).

We note that $b_{11}(\text{dir})$ and $b_{11}(\text{exch})$ are averages over all the two-electron spin states of $\langle \mathscr{b}_\sigma \rangle$, and $-\langle \mathscr{b}_\sigma Q_{12} \rangle$, respectively. These have the character of direct and exchange contributions. We also check that Eq. (96) reduces to the spin-free result if $\mathscr{b}_\sigma = I$, because in that case $b_{11}(\text{dir}) = 1$, and $b_{11}(\text{exch}) = -\frac{1}{2}$.

D. Open-Shell Matrix Elements

In this section we examine matrix elements arising from a pair of maximally overlapping open-shell configurations, as defined in Section III, B. As we saw there, the maximally overlapping feature permits the doubly occupied orbitals of one configuration to be made orthogonal to all orbitals of the other configuration except the one orbital to which each corresponds. Accordingly, the permutations which do not produce zero overlap are those of the form RP, $R \in \mathfrak{R}$, and $P \in \mathfrak{P}$, where $\mathfrak{R}$ is the group of permutations totally within doubly occupied orbital pairs, and $\mathfrak{P}$ is the group of permutations involving only electrons initially in singly occupied orbitals. The permutations causing two zero-overlap factors are those of the form $Q_{\mu,\nu}RP$, where $R \in \mathfrak{R}$, $P \in \mathfrak{P}$, and μ is an electron in a doubly occupied orbital and ν is any electron not paired with μ. All more complicated permutations produce more than two zero-overlap factors and cannot contribute to any matrix element we shall study.

We shall need the $U_{ii'}^*(Q)$ for the various contributing permutations enumerated above, but only for spin functions i and i' which are consistent with the assumed double occupancy. These spin functions, of the form Eq. (70), all have $(\alpha\beta - \beta\alpha)$ factors for the electrons in doubly occupied orbitals. Let us first look at $\mathbf{U}^*(P)$ for permutations $P \in \mathfrak{P}$, which involve only the singly occupied orbitals. According to Eq. (16) and (17),

$$U_{ii'}^*(P) = \langle \Theta_i(\boldsymbol{\sigma}) | \varepsilon_p \mathscr{P}_\sigma | \Theta_{i'}(\boldsymbol{\sigma}) \rangle. \tag{97}$$

Because none of the P affect the $(\alpha\beta - \beta\alpha)$ pairs of the needed $\Theta_i(\boldsymbol{\sigma})$, these $\Theta_i(\boldsymbol{\sigma})$ will be transformed by P only into linear combinations within the needed set of $\Theta_i(\sigma)$. If we write the matrix for $U^*(P)$, it will therefore have the general form

$$U^*(P) = \left(\begin{array}{c|c} \bar{U}^*(P) & 0 \\ \hline 0 & \end{array}\right) \tag{98}$$

where the open area contains unspecified numbers, and the first blocks of rows and columns refer to the $\Theta_i(\sigma)$ consistent with the assumed double occupancy. The zero blocks show that P does not mix these spin functions with the other spin functions. In Eq. (98), $\bar{U}^*(P)$ is a matrix given by Eq. (97), but with $\Theta_i(\sigma)$ and $\Theta_{i'}(\sigma)$ referring only to the u unpaired spins rather than to the entire n-spin system.

Next we look at $U^*(R)$, $R \in \mathfrak{R}$. For the needed i and i' values, R permutes only within the $(\alpha\beta - \beta\alpha)$ factors, and for needed functions $\Theta_i(\sigma)$, $R\Theta_i(\sigma) = \varepsilon_{\mathrm{R}}\Theta_i(\sigma)$. This has the effect that $U^*(R)$ has the form

$$U^*(R) = \left(\begin{array}{c|c} \mathbf{1} & 0 \\ \hline 0 & \end{array}\right) \tag{99}$$

where $\mathbf{1}$ is a unit matrix.

Finally, we shall need $U^*(Q_{\mu,\nu})$, where μ is an electron in a doubly occupied orbital, and ν is any electron not paired with μ. Using Eq. (97), we may find

$$U^*(Q_{\mu,\nu}) = \left(\begin{array}{c|c} -\frac{1}{2}\mathbf{1} & \\ \hline & \end{array}\right). \tag{100}$$

We may now use matrix multiplication to obtain the results

$$U^*(RP) = \left(\begin{array}{c|c} \bar{U}^*(P) & 0 \\ \hline 0 & \end{array}\right) \tag{101}$$

$$U^*(Q_{\mu,\nu}RP) = \left(\begin{array}{c|c} -\frac{1}{2}\bar{U}^*(P) & \\ \hline & \end{array}\right). \tag{102}$$

These equations tell us that for the i and i' values consistent with the assumed double occupancy,

$$U^*_{ii'}(RP) = \overline{U}^*_{ii'}(P), \tag{103}$$

$$U^*_{ii'}(Q_{\mu,\nu}RP) = -\tfrac{1}{2}\overline{U}^*_{ii'}(P), \tag{104}$$

where, it may be recalled, the $\overline{\mathrm{U}}^*$ depend only upon the u unpaired electrons. More detail on these matrix elements is given by Kotani *et al.* (1955).

We are now ready to calculate matrix elements. The overlap matrix, Eq. (58), is obtained by summing over the permutations which do not generate zero overlap:

$$\langle \Psi_k{}^i \,|\, \Psi^{i'}_{k'} \rangle = n! \sum_{R \in \mathfrak{R}} \sum_{P \in \mathfrak{P}} U^*_{ii'}(RP)\, \Delta_{kk'}(RP). \tag{105}$$

Since R operates only on the doubly occupied orbitals and P operates only on the singly occupied orbitals, their effects are independent. As we saw previously, R has no effect on the doubly occupied spatial orbitals. We therefore make the following subdivision of $\Delta_{kk'}(RP)$:

$$\Delta_{kk'}(RP) = \Delta\Delta'(P), \tag{106}$$

where Δ describes the overlap of the doubly occupied orbitals,

$$\Delta = \prod_{j=1}^{p} \langle \chi_j \,|\, \chi_j{}' \rangle^2, \tag{76}$$

just as it did in the closed-shell case. The only difference is that there are now also singly occupied orbitals whose overlap is described by $\Delta'(P)$:

$$\Delta'(P) = \prod_{j=1}^{u} \langle \varphi_j \,|\, \varphi'_{p_j} \rangle. \tag{107}$$

With these notations, and Eq. (103) for $\overline{U}^*_{ii'}(RP)$,

$$\langle \Psi_k{}^i \,|\, \Psi^{i'}_{k'} \rangle = n!\, 2^p\, \Delta \sum_{P = \mathfrak{P}} \overline{U^*_{ii'}}(P)\Delta'(P) \quad \text{(open shells)}. \tag{108}$$

We can better exploit the parallelism between the closed-shell results we obtained previously and the open-shell results we are now obtaining if we introduce still further symbolism. We let $\langle \Psi_k{}^1 \,|\Psi^1_{k'} \rangle_p$ stand for the overlap matrix element of the $2p$ paired electrons, taken as a system by themselves, according to Eq. (77). We further let $\langle \Psi_k{}^i \,|\, \Psi^{i'}_{k'} \rangle_u$ stand for the overlap matrix element of the u unpaired electrons taken alone, according to Eq. (58). Then Eq. (108) is equivalent to

$$\langle \Psi_k{}^i \,|\, \Psi_{k'}^{i'} \rangle = \binom{n}{u} \langle \Psi_k{}^1 \,|\, \Psi_{k'}^1 \rangle_p \langle \Psi_k{}^i \,|\, \Psi_{k'}^{i'} \rangle_u. \tag{109}$$

Look now at one-electron spin-free operators. Again we need only permutations RP, with $R \in \mathfrak{R}$, $P \in \mathfrak{P}$. Summation of Eq. (61) over these permutations leads, after some simplification, to

$$\begin{aligned}\langle \Psi_k{}^i | \mathscr{B} \,|\, \Psi_{k'}^{i'} \rangle = n!\,2^p \Delta \sum_{P \in \mathfrak{P}} \overline{U_{ii'}^*}(P) \Delta'(P) \Bigg[2 \sum_{l=1}^{p} \frac{\langle \chi_l \,|\, \mathscr{b} \,|\, \chi_l{}' \rangle}{\langle \chi_l \,|\, \chi_l{}' \rangle} \\ + \sum_{l=1}^{u} \frac{\langle \varphi_l \,|\, \mathscr{b} \,|\, \varphi'{}_{p_l} \rangle}{\langle \varphi_l \,|\, \varphi'{}_{p_l} \rangle} \Bigg]\end{aligned} \tag{110}$$

(one-electron spin-free operator, open shells).

We introduce

$$\langle \Psi_k{}^1 \,|\, \mathscr{B} \,|\, \Psi_{k'}^1 \rangle_p \qquad \text{and} \qquad \langle \Psi_k{}^i | \, \mathscr{B} \,|\, \Psi_{k'}^{i'} \rangle_u$$

to refer to matrix elements of operators like $\mathscr{B}$, but restricted to the paired and unpaired electrons, respectively. These quantities may be calculated by use of Eqs. (78) and (61). Equation (110) then becomes

$$\begin{aligned}\langle \Psi_k{}^i \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'} \rangle = \binom{n}{u} [\langle \Psi_k{}^1 \,|\, \mathscr{B} \,|\, \Psi_{k'}^1 \rangle_p \langle \Psi_k{}^i \,|\, \Psi_k^{i'} \rangle_u \\ + \langle \Psi_k{}^1 \,|\, \Psi_k{}^1 \rangle_p \langle \Psi_k{}^i \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'} \rangle_u].\end{aligned} \tag{111}$$

Equation (111) is clearly a sum of separate closed-shell and open-shell contributions.

For two-electron spin-free operators we need permutations of the forms RP and $Q_{\mu,\nu}RP$. The RP permutations lead, on substitution into Eq. (62) for $\langle \Psi_k{}^i \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'} \rangle$, to

$$\begin{aligned} RP \text{ terms} = n!\,2^p \Delta \sum_{P \in \mathfrak{P}} \overline{U_{ii'}^*}(P) \Delta'(P) \Bigg[4 \sum_{m=2}^{p} \sum_{l=1}^{m-1} \frac{\langle \chi_l \chi_m \,|\, \mathscr{b} \,|\, \chi_l{}' \chi_m{}' \rangle}{\langle \chi_l \,|\, \chi_l{}' \rangle \langle \chi_m \,|\, \chi_m{}' \rangle} \\ + \sum_{l=1}^{p} \frac{\langle \chi_l \chi_l \,|\, \mathscr{b} \,|\, \chi_l{}' \chi_l{}' \rangle}{\langle \chi_l \,|\, \chi_l{}' \rangle^2} + 2 \sum_{l=1}^{p} \sum_{m=1}^{u} \frac{\langle \chi_l \varphi_m \,|\, \mathscr{b} \,|\, \chi_l{}' \varphi'_{p_m} \rangle}{\langle \chi_l \,|\, \chi_l{}' \rangle \langle \varphi_m \,|\, \varphi'_{p_m} \rangle} \\ + \sum_{m=2}^{u} \sum_{l=1}^{m-1} \frac{\langle \varphi_l \varphi_m \,|\, \mathscr{b} \,|\, \varphi'_{p_l} \varphi'_{p_m} \rangle}{\langle \varphi_l \,|\, \varphi_{p_l} \rangle \langle \varphi_m \,|\, \varphi_{p_m} \rangle} \Bigg]. \end{aligned} \tag{112}$$

The $Q_{\mu,\nu}RP$ permutations each contribute only for a single set of values of l and m in Eq. (62). Bearing in mind that μ refers to a paired electron and v to any electron not paired with μ,

$$\text{sum of all } QRP \text{ terms} = n!\,2^p\Delta \sum_{P\in\mathfrak{P}} [-\tfrac{1}{2}\overline{U^*_{ii'}}(P)]\Delta'(P)$$
$$\times \left[4\sum_{\nu=2}^{p}\sum_{\mu=1}^{\nu-1} \frac{\langle \chi_\mu\chi_\nu \,|\, \mathscr{b} \,|\, \chi_\nu'\chi_\mu' \rangle}{\langle \chi_\mu \,|\, \chi_\mu' \rangle\langle \chi_\nu \,|\, \chi_\nu' \rangle} + 2\sum_{\mu=1}^{p}\sum_{\nu=1}^{u} \frac{\langle \chi_\mu\varphi_\nu \,|\, \mathscr{b} \,|\, \varphi'_{p_\nu}\varphi'_\mu \rangle}{\langle \chi_\mu \,|\, \chi_\mu' \rangle\langle \varphi_\nu \,|\, \chi_{p_\nu} \rangle}\right]. \tag{113}$$

There is no totally singly occupied orbital term in Eq. (113) because such permutations are included in $\mathfrak{P}$ rather than in the set of $Q_{\mu,\nu}$.

Combining Eqs. (112) and (113),

$$\langle \Psi_k{}^i \,|\, \mathscr{B} \,|\, \Psi^{i'}_{k'} \rangle = n!\,2^p\Delta \sum_{P\in\mathfrak{P}} \overline{U^*_{ii'}}(P)\Delta'(P)$$
$$\times \left[\sum_{l=1}^{p}\sum_{m=1}^{p}\left(\frac{2\langle \chi_l\chi_m \,|\, \mathscr{b} \,|\, \chi_l'\chi_m' \rangle - \langle \chi_l\chi_m \,|\, \mathscr{b} \,|\, \chi_m'\chi_l' \rangle}{\langle \chi_l \,|\, \chi_l' \rangle\langle \chi_m \,|\, \chi_m' \rangle}\right) + \sum_{l=1}^{p}\sum_{m=1}^{u}\left(\frac{2\langle \chi_l\varphi_m \,|\, \mathscr{b} \,|\, \chi_l'\varphi'_{p_m} \rangle - \langle \chi_l\varphi_m \,|\, \mathscr{b} \,|\, \varphi'_{p_m}\chi_l' \rangle}{\langle \chi_l \,|\, \chi_l' \rangle\langle \varphi_m \,|\, \varphi'_{p_m} \rangle}\right) + \sum_{m=2}^{u}\sum_{l=1}^{m-1} \frac{\langle \varphi_l\varphi_m \,|\, \mathscr{b} \,|\, \varphi'_{p_l}\varphi'_{p_m} \rangle}{\langle \varphi_l \,|\, \varphi'_{p_l} \rangle\langle \varphi_m \,|\, \varphi'_{p_m} \rangle}\right] \tag{114}$$

(two-electron spin-free operator, open shells).

A review of the steps leading to Eq. (114) indicates that the last term should be omitted if there is only one unpaired electron (i.e., if $u = 1$).

Equation (114) may be written

$$\langle \Psi_k{}^i | \mathscr{B} \,|\, \Psi^{i'}_{k'} \rangle = \binom{n}{u}[\langle \Psi_k{}^1 \,|\, \mathscr{B} \,|\, \Psi_k{}^1 \rangle_p \langle \Psi_k{}^i \,|\, \Psi^{i'}_{k'} \rangle_u + \langle \Psi_k{}^1 \,|\, \Psi^1_{k'} \rangle_p \langle \Psi^{i'}_k \,|\, \mathscr{B} \,|\, \Psi^{i'}_{k'} \rangle_u + \langle \Psi_k{}^i \,|\, \mathscr{B} \,|\, \Psi^{i'}_{k'} \rangle_{pu}], \tag{115}$$

where $\langle \Psi_k{}^1 \,|\, \mathscr{B} \,|\, \Psi^1_{k'} \rangle_p$ and $\langle \Psi_k{}^i \,|\, \mathscr{B} \,|\, \Psi^{i'}_{k'} \rangle_u$ may be calculated from Eqs. (83) and (62). Equation (115) shows the matrix elements of $\mathscr{B}$ as a sum of closed-shell term, an open-shell term, and an open-shell–closed-shell interaction term:

$$\langle \Psi_k{}^i \,|\, \mathscr{B} \,|\, \Psi^{i'}_{k'} \rangle_{pu} = (2p)!\,u!\,\Delta \sum_{P\in\mathfrak{P}} \overline{U^*_{ii'}}(P)\Delta'(P) \times \sum_{l=1}^{p}\sum_{m=1}^{u}\left[\frac{2\langle \chi_l\varphi_m \,|\, \mathscr{b} \,|\, \chi_l'\varphi'_{p_m} \rangle - \langle \chi_l\varphi_m \,|\, \mathscr{b} \,|\, \varphi'_{p_m}\chi_l' \rangle}{\langle \chi_l \,|\, \chi_l' \rangle\langle \varphi_m \,|\, \varphi'_{p_m} \rangle}\right] \tag{116}$$

($\mathscr{B}$ spin free).

As in the closed-shell case, we illustrate the use of these formulas by writing matrix elements of the Hamiltonian operator. In general, we have

$$\begin{aligned}
&\langle \Psi_k{}^i | \mathscr{H} | \Psi_{k'}^{i'} \rangle \\
&= n!\,2^p \Delta \sum_{P \in \mathfrak{P}} \overline{U_{ii'}^*}(P) \Delta'(P) \left[2 \sum_{l=1}^{p} \frac{\langle \chi_l | \mathscr{h}_1 | \chi_l{}' \rangle}{\langle \chi_l | \chi_l{}' \rangle} + \sum_{l=1}^{u} \frac{\langle \varphi_l | \mathscr{h}_1 | \varphi'_{p_l} \rangle}{\langle \varphi_l | \varphi'_{p_l} \rangle} \right. \\
&\quad + \sum_{l=1}^{p} \sum_{m=1}^{p} \left(\frac{2 \left\langle \chi_l \chi_m \middle| \dfrac{e^2}{r_{12}} \middle| \chi_l{}' \chi_m{}' \right\rangle - \left\langle \chi_l \chi_m \middle| \dfrac{e^2}{r_{12}} \middle| \chi_m{}' \chi_l{}' \right\rangle}{\langle \chi_l | \chi_l{}' \rangle \langle \chi_m | \chi_m{}' \rangle} \right) \\
&\quad + \sum_{l=1}^{p} \sum_{m=1}^{u} \left(\frac{2 \left\langle \chi_l \varphi_m \middle| \dfrac{e^2}{r_{12}} \middle| \chi_l{}' \varphi'_{p_m} \right\rangle - \left\langle \chi_l \varphi_m \middle| \dfrac{e^2}{r_{12}} \middle| \varphi'_{p_m} \chi_l{}' \right\rangle}{\langle \chi_l | \chi_l{}' \rangle \langle \varphi_m | \varphi'_{p_m} \rangle} \right) \\
&\quad \left. + \sum_{m=2}^{u} \sum_{l=1}^{m-1} \frac{\left\langle \varphi_l \varphi_m \middle| \dfrac{e^2}{r_{12}} \middle| \varphi'_{p_l} \varphi'_{p_m} \right\rangle}{\langle \varphi_l | \varphi'_{p_l} \rangle \langle \varphi_m | \varphi'_{p_m} \rangle} \right] + \sum_{j=2}^{N} \sum_{i=1}^{j-1} \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|} \qquad (117)
\end{aligned}$$

(open shells).

Note that the orbitals to be used in Eq. (117) are assumed to have been transformed, if necessary, so that $\langle \chi_i | \chi_j{}' \rangle = 0$ unless $i = j$, and so that $\langle \chi_i | \varphi_j{}' \rangle = \langle \varphi_i | \chi_j{}' \rangle = 0$ for all i and j. Notice also that $\Psi_k{}^i$ of Eq. (117) is not normalized, and that overlap matrix elements among various $\Psi_k{}^i$ are as given in Eq. (108).

Next we look at one-electron spin-dependent operators. We need values of $[\mathbf{b}(l)\mathbf{U}^*(RP)]_{ii'}$ for both paired and unpaired electrons l. If l refers to a paired electron, we see that $\langle \Theta_i(\sigma) | \ell_\sigma(\sigma_l) | \Theta_{i'}(\sigma) \rangle$ will vanish if $i \neq i'$, and will also be independent of l. For all paired electrons, $\mathbf{b}(l)$ will therefore have the block form

$$\mathbf{b}(l) = \left(\begin{array}{c:c} b_{11}\mathbf{1} & \\ \hdashline & \end{array} \right) \qquad \text{(electron } l \text{ paired)}, \qquad (118)$$

where b_{11} is as given in Eq. (89). Referring to the form of $\mathbf{U}^*(RP)$, given in Eq. (101), we see that

$$[\mathbf{b}(l)\mathbf{U}^*(RP)]_{ii'} = b_{11} \overline{U_{ii'}^*}(P) \qquad \text{(electron } l \text{ paired)}. \qquad (119)$$

If l refers to an unpaired electron, we observe that $\mathscr{E}_\sigma(\boldsymbol{\sigma}_l)$ will not disturb the pairing structure, so $\mathbf{b}(l)$ will have the form

$$\mathbf{b}(l) = \left(\begin{array}{c|c} \bar{\mathbf{b}}(l) & 0 \\ \hline 0 & \end{array}\right) \qquad \text{(electron } l \text{ unpaired)}, \tag{120}$$

where $\bar{\mathbf{b}}(l)$ is as defined in Eq. (65) but using the u electron, rather than the n electron spin function. Using Eqs. (120) and (101),

$$[\mathbf{b}(l)\mathbf{U}^*(RP)]_{ii'} = [\bar{\mathbf{b}}(l)\overline{\mathbf{U}^*}(P)]_{ii'} \qquad \text{(electron } l \text{ unpaired)}, \tag{121}$$

which may be calculated as described in Section III, A.

Employing Eqs. (119) and (121), we may proceed much as in the spin-free case to obtain

$$\begin{aligned} \langle \Psi_k{}^i | \mathscr{B} | \Psi_{k'}^{i'} \rangle = n!\,2^p \Delta \sum_{P \in \mathfrak{P}} \Delta'(P) \Bigg[2\overline{U_{ii'}^*}(P) b_{11} \sum_{l=1}^{p} \frac{\langle \chi_l | \mathscr{E}_r | \chi_l{}' \rangle}{\langle \chi_l | \chi_l{}' \rangle} \\ + \sum_{l=1}^{u} [\bar{\mathbf{b}}(l)\overline{\mathbf{U}^*}(P)]_{ii'} \frac{\langle \varphi_l | \mathscr{E}_r | \varphi'_{p_l} \rangle}{\langle \varphi_l | \varphi'_{p_l} \rangle} \Bigg] \end{aligned} \tag{122}$$

(one-electron spin-dependent operator, open shells).

Just as in the spin-free case, Eq. (122) can be written as a sum of closed- and open-shell contributions according to Eq. (111).

Finally we treat two-electron spin-dependent operators. For the permutations of the form RP, we will require $[\mathbf{b}(l, m)\mathbf{U}^*(RP)]_{ii'}$ for all l and m. We distinguish three cases: l and m both paired electrons; l paired, m unpaired; and both unpaired. When both l and m are paired, $\mathbf{b}(l, m)$ has the general form

$$\mathbf{b}(l, m) = \left(\begin{array}{c|c} b_{11}(l, m)\mathbf{1} & \\ \hline & \end{array}\right) \qquad (l, m \text{ paired}), \tag{123}$$

so

$$\mathbf{b}(l, m)\mathbf{U}^*(RP) = \left(\begin{array}{c|c} b_{11}(l, m)\overline{\mathbf{U}^*}(P) & \\ \hline & \end{array}\right) \qquad (l, m \text{ paired}). \tag{124}$$

The value of $b_{11}(l, m)$ will depend only upon whether or not l and m refer to the same pair. Just as in the closed-shell case, we will have $b_{11}(\text{same})$ and $b_{11}(\text{dir})$, given by Eqs. (90) and (91). Thus,

$$[\mathbf{b}(l, m)\mathbf{U}^*(RP)]_{ii'} = b_{11}(\text{same})\overline{U^*_{ii'}}(P) \qquad (l, m \text{ in same pair}), \quad (125)$$

$$[\mathbf{b}(l, m)\mathbf{U}^*(RP)]_{ii'} = b_{11}(\text{dir})\overline{U}^*_{ii'}(P) \qquad (l, m \text{ in different pairs}). \quad (126)$$

If neither l nor m are paired, $\mathbf{b}(l, m)$ has the block structure

$$\mathbf{b}(l, m) = \left(\begin{array}{c:c} \bar{\mathbf{b}}(l, m) & 0 \\ \hdashline 0 & \end{array}\right) \qquad (l, m \text{ unpaired}), \qquad (127)$$

where $\bar{\mathbf{b}}(l, m)$ is given by Eq. (70), using the u electron spin functions. Then

$$[\mathbf{b}(l, m)\mathbf{U}^*(RP)]_{ii'} = [\bar{\mathbf{b}}(l, m)\overline{\mathbf{U}}^*(P)]_{ii'} \qquad (l, m \text{ unpaired}). \quad (128)$$

If l is paired and m is unpaired, $\mathbf{b}(l, m)$ does not depend upon l. By direct application of Eq. (70), we find, writing $b_{ij}(\text{dir}; m)$ for $b_{ij}(l, m)$:

$$\begin{aligned} b_{ij}(\text{dir}; m) = \tfrac{1}{2}[&\langle\overline{\Theta}_i(\boldsymbol{\sigma})\alpha(\boldsymbol{\sigma}_l)\,|\,\ell_\sigma(m, l)\,|\,\overline{\Theta}_j(\boldsymbol{\sigma})\alpha(\boldsymbol{\sigma}_l)\rangle \\ &+ \langle\overline{\Theta}_i(\boldsymbol{\sigma})\beta(\boldsymbol{\sigma}_l)\,|\,\ell_\sigma(m, l)\,|\,\overline{\Theta}_j(\boldsymbol{\sigma})\beta(\boldsymbol{\sigma}_l)\rangle] \end{aligned}$$

$$(l \text{ paired}, m \text{ unpaired}), \quad (129)$$

where $\overline{\Theta}_i(\boldsymbol{\sigma})$ and $\overline{\Theta}_j(\boldsymbol{\sigma})$ refer to the system of u unpaired spins. Equation (129) only describes the elements of $\mathbf{b}(l, m)$ for spin functions of the assumed amount of spin pairing, but the block structure of $\mathbf{U}^*(RP)$ makes this the only part of $\mathbf{b}(l, m)$ which is needed to evaluate $[\mathbf{b}(l, m)\mathbf{U}^*(RP)]_{ii'}$.

When we consider permutations $Q_{\mu,\nu}RP$ we need to use $\mathbf{b}(l, m)$ only for $l = \mu$, $m = \nu$. Accordingly, we consider $[\mathbf{b}(l, m)\mathbf{U}^*(Q_{l,m}RP)]_{ii'}$, which we require for two cases: l and m in different pairs, or l paired, m unpaired. Using the representation property of $\mathbf{U}^*$, we begin the evaluation by writing

$$[\mathbf{b}(l, m)\mathbf{U}^*(Q_{l,m}RP)]_{ii'} = [\{\mathbf{b}(l, m)\mathbf{U}^*(Q_{l,m})\}\mathbf{U}^*(RP)]_{ii'}. \quad (130)$$

Because of the block structure of $\mathbf{U}^*(RP)$, we need $[\mathbf{b}(l, m)\mathbf{U}^*(Q_{l,m})]_{ij}$ only for spin functions i and j with the assumed amount of pairing.

Taking first the case l, m in different pairs, $[\mathbf{b}(l, m)\mathbf{U}^*(Q_{l,m})]_{ij}$ has, independently of l and m, the value $b_{11}(\text{exch})\delta_{ij}$, with $b_{11}(\text{exch})$ given in Eq. (93). This leads to

$$[\mathbf{b}(l, m)\mathbf{U}^*(Q_{l,m}RP)]_{ii'} = b_{11}(\text{exch})\overline{U}^*_{ii'}(P) \qquad (l, m \text{ in different pairs}). \quad (131)$$

If l is paired and m is unpaired, $[\mathbf{b}(l, m)\mathbf{U}^*(Q_{l,m})]_{ij}$ is independent of l. Writing $b_{ij}(\text{exch}; m)$ for $[\mathbf{b}(l, m)\mathbf{U}^*(Q_{l,m})]_{ij}$, direct evaluation leads to

$$\begin{aligned} b_{ij}(\text{exch}; m) = -\tfrac{1}{2}[&\langle \overline{\Theta}_i(\boldsymbol{\sigma})\alpha(\boldsymbol{\sigma}_l) \,|\, \mathscr{O}_\sigma(m, l)Q_{m,l} \,|\, \overline{\Theta}_j(\boldsymbol{\sigma})\alpha(\boldsymbol{\sigma}_l)\rangle \\ &+ \langle \overline{\Theta}_i(\boldsymbol{\sigma})\beta(\boldsymbol{\sigma}_l) \,|\, \mathscr{O}_\sigma(m, l)Q_{m,l} \,|\, \overline{\Theta}_j(\boldsymbol{\sigma})\beta(\boldsymbol{\sigma}_l)\rangle] \\ &\qquad (l \text{ paired, } m \text{ unpaired}). \end{aligned} \tag{132}$$

Starting from Eq. (69), we may use the techniques of the preceding section and the formulas just developed to obtain

$$\begin{aligned} \langle \Psi_k{}^i \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'}\rangle = n!\,2^p\Delta \sum_{P\in\mathfrak{P}} \Delta'(P) & \\ \times \Bigg[\sum_{l=1}^{p}\sum_{m=1}^{p} \overline{U_{ii'}^*}(P) & \left(\frac{2b_{11}(\text{dir})\langle \chi_l\chi_m \,|\, \mathscr{O}_r \,|\, \chi_l'\chi_m'\rangle + 2b_{11}(\text{exch})\langle \chi_l\chi_m \,|\, \mathscr{O}_r \,|\, \chi_m'\chi_l'\rangle}{\langle \chi_l \,|\, \chi_l'\rangle\langle \chi_m \,|\, \chi_m'\rangle} \right) \\ + \sum_{l=1}^{p}\sum_{m=1}^{u}\sum_{j=1}^{\bar{d}} \overline{U_{ji'}^*}(P) & \left(\frac{2b_{ij}(\text{dir}; m)\langle \chi_l\varphi_m \,|\, \mathscr{O}_r \,|\, \chi_l'\varphi'_{Pm}\rangle + 2b_{ij}(\text{exch}; m)\langle \chi_l\varphi_m \,|\, \mathscr{O}_r \,|\, \varphi'_{Pm}\chi_l'\rangle}{\langle \chi_l \,|\, \chi_l'\rangle\langle \varphi_m \,|\, \varphi'_{Pm}\rangle} \right) \\ + \sum_{m=2}^{u}\sum_{l=1}^{m-1} [\bar{\mathbf{b}}(l, m)\overline{\mathbf{U}}^*(P)]_{ii'} & \frac{\langle \varphi_l\varphi_m \,|\, \mathscr{O}_r \,|\, \varphi'_{Pl}\varphi'_{Pm}\rangle}{\langle \varphi_l \,|\, \varphi'_{Pl}\rangle\langle \varphi_m \,|\, \varphi'_{Pm}\rangle} \Bigg] \end{aligned} \tag{133}$$

(two-electron spin-dependent operator, open shells).

The upper limit of the j sum, $\bar{d}$, is the number of u electron spin functions $\overline{\Theta}_i(\boldsymbol{\sigma})$. The last term of Eq. (133) is to be omitted if $u = 1$. Equation (133) may be regarded as a sum of closed-shell, open-shell, and interaction contributions, according to Eq. (115). The spin-dependent open-shell–closed-shell interaction, $\langle \Psi_k{}^i \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'}\rangle_{pu}$, is computed from

$$\begin{aligned} \langle \Psi_k{}^i \,|\, \mathscr{B} \,|\, \Psi_{k'}^{i'}\rangle_{pu} = (2p)!\,u!\,\Delta \sum_{P\in\mathfrak{P}} \Delta'(P) \sum_{l=1}^{p}\sum_{m=1}^{u}\sum_{j=1}^{\bar{d}} \overline{U_{ji'}^*}(P) & \\ \times \left[\frac{2b_{ij}(\text{dir}; m)\langle \chi_l\varphi_m \,|\, \mathscr{O}_r \,|\, \chi_l'\varphi'_{Pm}\rangle + 2b_{ij}(\text{exch}; m)\langle \chi_l\varphi_m \,|\, \mathscr{O}_r \,|\, \varphi_{Pm}\chi_l\rangle}{\langle \chi_l \,|\, \chi_l'\rangle\langle \varphi_m \,|\, \varphi_{pm}\rangle} \right] & \end{aligned} \tag{134}$$

($\mathscr{B}$ spin-dependent).

E. Examples of Spin-Dependent Operators

The current interest in quantities such as the spin density has prompted many calculations of spin-dependent properties. Let us look at some examples which show that the methods we have described can be applied to spin-dependent operators without undue difficulties.

First, let's take the operator for the spin density $\boldsymbol{\rho}$, the z component of which at the point $\mathbf{r}_0$ is essentially

$$\rho_z = \sum_l \delta(\mathbf{r}_l - \mathbf{r}_0)\mathscr{s}_z(\boldsymbol{\sigma}_l),$$

where $\delta(\mathbf{r}_l)$ is the Dirac delta function. This is clearly a one-electron operator with

$$\mathscr{O}(\mathbf{r}_l, \boldsymbol{\sigma}_l) = \delta(\mathbf{r}_l - \mathbf{r}_0)\mathscr{s}_z(\boldsymbol{\sigma}_l), \tag{135}$$

or

$$\mathscr{O}_r(\mathbf{r}_l) = \delta(\mathbf{r}_l - \mathbf{r}_0), \tag{136}$$

$$\mathscr{O}_\sigma(\boldsymbol{\sigma}_l) = \mathscr{s}_z(\boldsymbol{\sigma}_l). \tag{137}$$

A discussion of spin density calculations has recently been given by McLachlan (1960).

If we apply the operator ρ_z to a closed-shell system, according to Eq. (87), we get zero because the spin-dependent coefficient b_{11} given by Eq. (89) vanishes. A similar result obtains for the spin density components ρ_x and ρ_z. This is of course the behavior we expect for a closed-shell system.

Suppose now that we consider an open-shell case with the aid of Eq. (122). Dropping the vanishing closed-shell term, and using Eq. (136) for $\mathscr{O}_r$, we have

$$\langle \Psi_k{}^i | \boldsymbol{\rho} | \Psi_{k'}^{i'} \rangle = n!\, 2^p\, \Delta \sum_{P \in \mathfrak{P}} \Delta'(P) \sum_{l=1}^{u} [\bar{\mathfrak{b}}(l)\bar{\mathrm{U}}^*(P)]_{ii'} \frac{\varphi_l{}^*(\mathbf{r}_0)\varphi_{Pl}(\mathbf{r}_0)}{\langle \varphi_l | \varphi_{Pl} \rangle}. \tag{138}$$

Further simplification depends upon the particular spin state. For a radical described by a single-configuration wave function with a single unpaired electron of spin α, $u = 1$, $\mathfrak{P}$ contains only the identity permutation, and there is only one spin state, so $i = i' = 1$. For the z component of the spin density, $[\bar{\mathfrak{b}}(l)\bar{\mathrm{U}}^*(P)]_{11} = \hbar/2$. This leads to the obvious result

$$\langle \Psi_k{}' | \rho_z | \Psi_k{}' \rangle = n!\, 2^p \Delta \frac{\hbar}{2} |\varphi_1(\mathbf{r}_0)|^2. \tag{139}$$

Since $[\bar{\mathfrak{b}}(l)\bar{\mathrm{U}}^*(P)]_{11}$ vanishes for ρ_x and ρ_y, these components do not contribute to the spin density.

Take next a triplet state with two unpaired electrons and $M_s = 1$. There is again one spin function. For ρ_z, $[\mathfrak{b}(l)\mathbf{U}^*(I)]_{11} = \hbar/2$, $[\mathfrak{b}(l)\mathbf{U}^*(P_{1,2})]_{11} = -\hbar/2$, for either electron ($l = 1$ or 2). Thus

$$\langle \Psi_k^1 | \rho_z | \Psi_k^1 \rangle = n!\,2^p \Delta \frac{\hbar}{2} [\langle \varphi_2 | \varphi_2 \rangle |\varphi_1(\mathbf{r}_0)|^2 + \langle \varphi_1 | \varphi_1 \rangle |\varphi_2(\mathbf{r}_0)|^2 - \langle \varphi_2 | \varphi_1 \rangle \varphi_1^*(\mathbf{r}_0)\varphi_2(\mathbf{r}_0) - \langle \varphi_1 | \varphi_2 \rangle \varphi_2^*(\mathbf{r}_0)\varphi_1(\mathbf{r}_0)]. \tag{140}$$

On the other hand, if $M_s = 0$, for ρ_z, $[\mathfrak{b}(l)\mathbf{U}^*(P)]_{11} = 0$ for all l and P, so that $\langle \Psi_k^1 | \rho_z | \Psi_k^1 \rangle$ vanishes.

A less trivial example is provided by a doublet state with three unpaired electrons, as would arise in an open-shell study of the Li atom. Using spin functions

$$\Theta_1(\boldsymbol{\sigma}) = \frac{1}{\sqrt{2}} (\alpha\beta\alpha - \beta\alpha\alpha), \tag{141}$$

$$\Theta_2(\boldsymbol{\sigma}) = \frac{1}{\sqrt{6}} (2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha), \tag{142}$$

the matrices $\mathfrak{b}(l)$ for ρ_z are

$$\mathfrak{b}(1) = \frac{\hbar}{2} \begin{pmatrix} 0 & -\dfrac{1}{\sqrt{3}} \\ -\dfrac{1}{\sqrt{3}} & \dfrac{2}{3} \end{pmatrix}, \quad \mathfrak{b}(2) = \frac{\hbar}{2} \begin{pmatrix} 0 & \dfrac{1}{\sqrt{3}} \\ \dfrac{1}{\sqrt{3}} & \dfrac{2}{3} \end{pmatrix}, \quad \mathfrak{b}(3) = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -\dfrac{1}{3} \end{pmatrix}. \tag{143}$$

These matrices may be multiplied by the $\mathbf{U}^*(P)$, available for example in Kotani *et al.* (1955). Then the use of Eq. (138) requires only the values of wave functions and overlap integrals.

A second spin-dependent operator of some importance is that arising in the Fermi contact contribution to nuclear spin coupling. Some calculations of this operator have been presented by Karplus and Anderson (1959). Here we have essentially the two-electron operator

$$\mathscr{O}(\mathbf{r}_l, \mathbf{r}_m, \boldsymbol{\sigma}_l, \boldsymbol{\sigma}_m) = \tfrac{1}{2}[\delta(\mathbf{r}_l - \mathbf{R}_1)\delta(\mathbf{r}_m - \mathbf{R}_2) + \delta(\mathbf{r}_l - \mathbf{R}_2)\delta(\mathbf{r}_m - \mathbf{R}_1)]\mathscr{s}_l \cdot \mathscr{s}_m, \tag{144}$$

with $\mathbf{R}_1$ and $\mathbf{R}_2$ being the positions of the nuclei whose spin coupling is under discussion. The spin-dependent part of this operator can be written in terms of permutations, with

$$\mathscr{O}_\sigma(\boldsymbol{\sigma}_l, \boldsymbol{\sigma}_m) = \mathscr{s}_l \cdot \mathscr{s}_m = \frac{\hbar^2}{4} (2Q_{l,m} - 1). \tag{145}$$

Using Eq. (70) to define $\mathbf{b}(l, m)$, we note that the permutation $Q_{l,m}$ operates on the same functions as were used to define the matrices **V** and **U**. With the aid of this observation, we find

$$\mathbf{b}(l, m) = -\frac{\hbar^2}{4}\,[2\mathbf{U}^*(Q_{l,m}) + \mathbf{1}]. \tag{146}$$

Then, using matrix multiplication and group properties,

$$\mathbf{b}(l, m)\mathbf{U}^*(P) = -\frac{\hbar^2}{4}\,[2\mathbf{U}^*(Q_{l,m}P) + \mathbf{U}^*(P)]. \tag{147}$$

The closed-shell contributions to the spin coupling operator may also be obtained from Eq. (145). Evaluating the expressions in Eqs. (91) and (93),

$$b_{11}(\text{dir}) = 0, \tag{148}$$

$$b_{11}(\text{exch}) = -3\hbar^2/8. \tag{149}$$

These values indicate that a closed-shell state has no direct contribution to the contact interaction, but there may be a nonvanishing exchange contribution.

For open-shell–closed-shell contact interactions we need $b_{ij}(\text{dir}; m)$ and $b_{ij}(\text{exch}; m)$, given in Eqs. (129) and (132). Our first step in obtaining these quantities is to note that

$$\langle\bar{\Theta}_i(\boldsymbol{\sigma})\alpha(\sigma_l)|\,Q_{m,l}\,|\,\bar{\Theta}_j(\boldsymbol{\sigma})\alpha(\sigma_l)\rangle + \langle\bar{\Theta}_i(\boldsymbol{\sigma})\beta(\sigma_l)|\,Q_{m,l}\,|\bar{\Theta}_j(\boldsymbol{\sigma})\beta(\sigma_l)\rangle = \delta_{ij}, \tag{150}$$

where $\bar{\Theta}_i(\boldsymbol{\sigma})$ and $\bar{\Theta}_j(\boldsymbol{\sigma})$ are spin functions for the unpaired spins, m refers to one of the unpaired spins, and l refers to a paired spin, so that $\boldsymbol{\sigma}_l$ is not one of the spins included in the argument of $\bar{\Theta}_i(\boldsymbol{\sigma})$. To verify Eq. (150), regard $\bar{\Theta}_j(\boldsymbol{\sigma})$ as expanded into terms each of which is a string of α and β spin functions. If a term contains $\alpha(\boldsymbol{\sigma}_m)$, it contributes only to the first scalar product in Eq. (150); if a term contains $\beta(\boldsymbol{\sigma}_m)$, it contributes only to the second scalar product. The sum of all these contributions is just $\langle\bar{\Theta}_i(\boldsymbol{\sigma})\,|\,\bar{\Theta}_j(\boldsymbol{\sigma})\rangle$, which is δ_{ij}, as claimed.

Now we use Eq. (145) to aid in evaluating Eqs. (129) and (132). Noting that $Q_{l,m}Q_{l,m} = I$, we obtain the result

$$b_{ij}(\text{dir}; m) = 0, \tag{151}$$

$$b_{ij}(\text{exch}; m) = -(3\hbar^2/8)\delta_{ij}. \tag{152}$$

The results are independent of the unpaired spin functions for electron m.

Using Eqs. (147), (148), (149), (151), and (152), Eq. (133) yields

$$\begin{aligned}\langle\Psi_k{}^i|\mathscr{B}|\Psi_{k'}^{i'}\rangle = -\frac{\hbar^2}{8}\,n!\,2^P\,\Delta\sum_{P\in\mathfrak{P}}\Delta'(P)\\ \times\Bigg[3\overline{U_{ii'}^{*}}(P)\Bigg(\sum_{l=1}^{P}\sum_{m=1}^{P}\frac{[\chi_l{}^*(\mathbf{R}_1)\chi_m{}^*(\mathbf{R}_2)\chi_m{}'(\mathbf{R}_1)\chi_l{}'(\mathbf{R}_2) + \chi_l{}^*(\mathbf{R}_2)\chi_m{}^*(\mathbf{R}_1)\chi_m{}'(\mathbf{R}_2)\chi_l{}'(\mathbf{R}_1)]}{\langle\chi_l|\chi_l{}'\rangle\langle\chi_m|\chi_m{}'\rangle}\\ +\sum_{l=1}^{P}\sum_{m=1}^{u}\frac{[\chi_l{}^*(\mathbf{R}_1)\varphi_m{}^*(\mathbf{R}_2)\varphi'_{Pm}(\mathbf{R}_1)\chi_l{}'(\mathbf{R}_2) + \chi_l{}^*(\mathbf{R}_2)\varphi_m{}^*(\mathbf{R}_1)\varphi'_{Pm}(\mathbf{R}_2)\chi_l{}'(\mathbf{R}_1)]}{\langle\chi_l|\chi_l{}'\rangle\langle\varphi_m|\varphi'_{Pm}\rangle}\Bigg)\\ +\sum_{m=2}^{u}\sum_{l=1}^{m-1}[2\overline{U_{ii'}^{*}}(Q_{l,m}P)+\overline{U_{ii'}^{*}}(P)]\\ \times\left(\frac{\varphi_l{}^*(\mathbf{R}_1)\varphi_m{}^*(\mathbf{R}_2)\varphi'_{Pl}(\mathbf{R}_1)\varphi'_{Pm}(R_2) + \varphi_l{}^*(\mathbf{R}_2)\varphi_m{}^*(\mathbf{R}_1)\varphi'_{Pl}(\mathbf{R}_2)\varphi'_{Pm}(\mathbf{R}_1)}{\langle\varphi_l|\varphi'_{Pl}\rangle\langle\varphi_m|\varphi'_{Pm}\rangle}\right)\Bigg].\qquad(153)\end{aligned}$$

Equation (153) can be greatly simplified if certain conditions are met. Taking k and k' as the same configuration, assuming no doubly occupied orbital is appreciable at both $\mathbf{R}_1$ and $\mathbf{R}_2$, and assuming that, among the singly occupied orbitals, only orbital l is appreciable at $\mathbf{R}_1$ and only orbital m is appreciable at $\mathbf{R}_2$, we get

$$\begin{aligned}\langle\Psi_k{}^i|\mathscr{B}|\Psi_k^{i'}\rangle = -\frac{\hbar^2}{8}\,n!\,2^P\Delta\sum_{P\in\mathfrak{P}_{lm}}\Delta'(P)\\ \times[2\overline{U_{ii'}^{*}}(Q_{l,m}P)+\overline{U_{ii'}^{*}}(P)]\,\frac{|\varphi_l(\mathbf{R}_1)|^2|\varphi_m(\mathbf{R}_2)|^2}{\langle\varphi_l|\varphi_l\rangle\langle\varphi_m|\varphi_m\rangle}.\qquad(154)\end{aligned}$$

In Eq. (154), $\mathfrak{P}_{lm}$ refers to the set of permutations in which l and m are kept fixed. The conditions leading to Eq. (154) are often approximately met in valence bond calculations.

The spin-dependent factor in Eq. (154) predicts a nonzero contact interaction even if spin functions i and i' do not pair electrons l and m. Notice, however, that, if P is the identity permutation, the factor in Eq. (154) becomes $2\overline{U_{ii'}^{*}}(Q_{l,m}) + \delta_{ii'}$. If either electron l or electron m is paired to some other electron, this factor vanishes [cf. Eq. (100)]. Thus, spin functions which pair electrons l or m, but not to each other, only have contact interactions of exchange type. Such interactions will often be small.

IV. Single-Configuration Methods

A. Spin-Projected Determinants

Because of the relative ease of interpretation of functions which are based on a single product of one-electron orbitals, considerable development has been given to methods which result in the determination of a more or less optimum set of such orbitals. The better known of these methods employ wave functions which are made by antisymmetrizing a product of spin orbitals each of which consists of an ordinary spatial orbital and either an α or a β spin function. Letting $\Xi_0(\mathbf{r})$ stand for a product of spatial orbitals and $\Theta_0(\boldsymbol{\sigma})$ stand for a product of α and β spin functions, such a spin orbital product is of the form $\Xi_0(\mathbf{r})\Theta_0(\boldsymbol{\sigma})$, and the antisymmetrized wave function is of the form

$$\Psi(\mathbf{r}, \boldsymbol{\sigma}) = \mathscr{A}\Xi_0(\mathbf{r})\Theta_0(\boldsymbol{\sigma}). \tag{155}$$

Since a wave function of the type given in Eq. (155) can be written as a determinant, it is frequently called a *determinantal* wave function. Unless a determinantal wave function is of as nearly as possible completely closed-shell type, it will not be an eigenfunction of $\mathscr{S}^2$. Since an eigenfunction of $\mathscr{S}^2$ is to be preferred from many points of view, it is natural to consider how one might, starting from a form such as Eq. (155), generate its components with particular values of S. Formally, this may be done using an operator $\mathscr{O}_s$ which projects the function Ψ onto the function space of given S. Projection operator techniques have been extensively developed, particularly by Löwdin (1955a), who has supplied an explicit expression for $\mathscr{O}_s$ and has pioneered in its use in practical problems. One of the aims of this section will be to relate the work of Löwdin and his colleagues to the approach followed in the earlier sections of this chapter. That there is a connection is apparent, because the techniques already developed permit the description of the most general wave function based on an orbital product.

A second motivation for studying the projector $\mathscr{O}_s$ is that its use will permit us to employ orthogonalization of orbitals to a far greater extent than was possible in the context of the most general set of wave functions derivable from a given spatial orbital product. We gain the orthogonalization at a price, however, because in order to get it we must use, in place of a complete set of spin functions $\Theta_i(\boldsymbol{\sigma})$, $i = 1, \ldots d$, the single spin function generated by the projector $\mathscr{O}_s$. To see that this is so, notice that any orthogonalization of orbitals which we might obtain in $\Xi_0(\mathbf{r})$ is of no use to us unless the projector $\mathscr{O}_s$ commutes with $\mathscr{A}$ and depends upon the spin coordinates only. Otherwise application of $\mathcal{O}_s$ will destroy the orthogonality. But the only projector $\mathcal{O}_s$ with enough permutational symmetry to commute with $\mathcal{A}$ is that which projects onto the whole subspace of given S and M_s. The irreducibility of the representation $\mathrm{V}(P)$ guarantees the nonexistence of smaller subspaces of the necessary symmetry.

We construct the projector $\mathcal{O}_s$ with the aid of the representation matrices $\mathrm{V}(P)$ for the desired values of S and M_s. We first observe that a basis function for this representation may be made from $\Theta_0(\sigma)$ by forming $\sum_P V_{ij}^*(P)\mathcal{P}_\sigma\Theta_0(\sigma)$, using any values of i and j such that the summation does not vanish. However, a formulation of this sort will not have sufficient symmetry to yield the projector onto the entire subspace of given S and M_s unless the coefficients possess invariance with respect to the basis used to make the matrices $\mathrm{V}(P)$. The only applicable linear invariant is the *trace* of the matrix $\mathrm{V}(P)$, which we accordingly use to define a projector

$$\mathcal{O}_s = \frac{d}{n!}\sum_P \sum_{i=1}^{d} V_{ii}^*(P)\mathcal{P}_\sigma. \tag{156}$$

This approach has similarities to that of Percus and Rotenberg (1962). The operator adjoint to $\mathcal{O}_s$ may be obtained by replacing $\mathcal{P}_\sigma$ by $\mathcal{P}_\sigma^{-1}$ and by taking the complex coefficient of its coefficient. Since $V_{ii}(P) = V_{ii}(P^{-1})$, we find that $\mathcal{O}_s$ is self-adjoint:

$$\mathcal{O}_s^{\dagger} = \mathcal{O}_s. \tag{157}$$

To verify that $\mathcal{O}_s$ is a projector, compute $\mathcal{O}_s^2 = \mathcal{O}_s^{\dagger}\mathcal{O}_s$. This is

$$\mathcal{O}_s^2 = \left(\frac{d}{n!}\right)^2 \sum_{P,Q} \sum_{i=1}^{d} \sum_{j=1}^{d} V_{ii}(P)V_{jj}^*(Q)\mathcal{P}_\sigma^{-1}\mathcal{Q}_\sigma. \tag{158}$$

Replacing Q by PQ, and expanding $V_{jj}^*(PQ) = \sum_k V_{jk}^*(P)V_{kj}^*(Q)$,

$$\mathcal{O}_s^2 = \left(\frac{d}{n!}\right)^2 \sum_{P,Q} \sum_{i',j,k=1}^{d} V_{ii}(P)V_{jk}^*(P)V_{kj}^*(Q)\mathcal{Q}_\sigma. \tag{159}$$

Applying the group representation orthogonality theorem, Eq. (30), the P summation yields

$$\mathcal{O}_s^2 = \frac{d}{n!}\sum_Q \sum_{i=1}^{d} V_{ii}^*(Q)\mathcal{Q}_\sigma = \mathcal{O}_s. \tag{160}$$

Equation (160) shows that $\mathcal{O}_s$ is idempotent, the key property of a projector.

Next we verify that $\mathcal{O}_s$ commutes with $\mathcal{A}$. We write

$$\mathcal{O}_s\mathcal{A} = \frac{d}{(n!)^2}\sum_{P,Q} \sum_{i=1}^{d} \varepsilon_Q V_{ii}^*(P)\mathcal{P}_\sigma\mathcal{Q}_\sigma\mathcal{Q}_r. \tag{161}$$

Then rewrite $\mathcal{P}_\sigma \mathcal{Q}_\sigma$ as $\mathcal{Q}_\sigma(\mathcal{Q}_\sigma^{-1}\mathcal{P}_\sigma\mathcal{Q}_\sigma)$, after which replace P by QPQ^{-1}. This leads to

$$\mathcal{O}_s\mathcal{A} = \frac{d}{(n!)^2}\sum_{P,Q}\sum_{i=1}^{d}\varepsilon_Q V_{ii}^*(QPQ^{-1})\mathcal{Q}_\sigma\mathcal{Q}_r\mathcal{P}_\sigma. \tag{162}$$

But the trace of QPQ^{-1} is the same as the trace of P, so that the right side of Eq. (162) may be identified as $\mathcal{A}\mathcal{O}_s$, proving that $\mathcal{O}_s$ and $\mathcal{A}$ commute. Note that the argument just given shows that $\mathcal{O}_s$ commutes with each individual permutation $\mathcal{Q}$ as well as with $\mathcal{A}$:

$$\mathcal{O}_s\mathcal{Q} = \mathcal{Q}\mathcal{O}_s. \tag{163}$$

Now let us show that $\mathcal{O}_s$ projects an eigenfunction of $\mathcal{S}^2$ and $\mathcal{S}_z$ corresponding to the representation $\mathbf{V}(P)$. Let $\Theta(\boldsymbol{\sigma})$ stand for an arbitrary spin function and let $\overline{\Theta}_k(\boldsymbol{\sigma})$ stand for an eigenfunction corresponding to some value of S and M_s not necessarily the same as that corresponding to $\mathbf{V}(P)$. We consider the component of $\mathcal{O}_s\Theta(\boldsymbol{\sigma})$ along the function $\overline{\Theta}_k(\boldsymbol{\sigma})$. If this component is nonzero only for functions $\overline{\Theta}_k(\boldsymbol{\sigma})$ with a single S and a single M_s, $\mathcal{O}_s$ will have projected a pure spin state. Accordingly, look at

$$\langle\overline{\Theta}_k\,|\,\mathcal{O}_s\Theta\rangle = \langle\mathcal{O}_s\overline{\Theta}_k\,|\,\Theta\rangle = \frac{d}{n!}\sum_P\sum_{i=1}^{d}V_{ii}(P)\langle\mathcal{P}_\sigma\overline{\Theta}_k\,|\,\Theta\rangle. \tag{164}$$

Now $\mathcal{P}_\sigma\overline{\Theta}_k(\boldsymbol{\sigma})$ will be given by an expression of the form appearing in Eq. (9),

$$\mathcal{P}_\sigma\overline{\Theta}_k(\boldsymbol{\sigma}) = \sum_{j=1}^{\bar{d}}\overline{V}_{jk}(P)\overline{\Theta}_j(\boldsymbol{\sigma}), \tag{165}$$

where $\overline{\Theta}_j(\boldsymbol{\sigma})$ is of the same S and M_s as $\overline{\Theta}_k(\boldsymbol{\sigma})$, and $\overline{\mathbf{V}}(P)$ describes coefficients belonging to the same irreducible representation as $\mathbf{V}(P)$ if and only if both $\mathbf{V}(P)$ and $\overline{\mathbf{V}}(P)$ refer to the same S and M_s. Substituting Eq. (165) into Eq. (164),

$$\langle\overline{\Theta}_k\,|\,\mathcal{O}_s\Theta\rangle = \frac{d}{n!}\sum_p\sum_{i=1}^{d}\sum_{j=1}^{\bar{d}}\overline{V}_{jk}^*(P)V_{ii}(P)\langle\overline{\Theta}_j\,|\,\Theta\rangle. \tag{166}$$

Summing over P, the group representation orthogonality theorem indicates a zero result unless $\overline{V}_{jk}^*(P)$ and $V_{ii}(P)$ refer to the same representation, thereby proving that $\mathcal{O}_s$ projects the S and M_s values corresponding to $\mathbf{V}$.

If $\overline{\Theta}_k(\boldsymbol{\sigma})$ has the S and M_s values corresponding to $\mathbf{V}$, it is the function we have called $\Theta_k(\boldsymbol{\sigma})$. The P summation in Eq. (166) then gives, using Eq. (30),

$$\langle\Theta_k\,|\,\mathcal{O}_s\Theta\rangle = \langle\Theta_k\,|\,\Theta\rangle, \qquad k = 1, \ldots d. \tag{167}$$

Equation (167) shows that $\mathcal{O}_s$ projects onto the entire subspace of chosen S and M_s.

Now that the essential properties of $\mathcal{O}_s$ are established, let us see how we can take advantage of them. Applying $\mathcal{O}_s$ to both sides of Eq. (155), we find that the commutation of $\mathcal{O}_s$ and $\mathscr{A}$ makes $\mathcal{O}_s\Psi(\mathbf{r}, \boldsymbol{\sigma})$ an eigenfunction of $\mathscr{S}^2$ and $\mathscr{S}_z$, provided that $\Theta_0(\boldsymbol{\sigma})$ has a component of the chosen S and M_s. But, keeping $\mathcal{O}_s$ to the left of $\mathscr{A}$, we may alternatively make linear transformations among the orbitals of $\Xi_0(\mathbf{r})$ to achieve some orthogonality. If we only mix in this way orbitals with the same spin functions, we may make all the α spin orbitals mutually orthogonal, all the β spin orbitals mutually orthogonal, and each α spin orbital orthogonal to all except at most one β spin orbital. These transformations have been discussed, for example, by Amos and Hall (1961) and by Löwdin (1962), and are described in detail in Appendix A to this chapter. If we use i and i' to refer to α spin and β spin orbitals, respectively, the orthogonalization procedures yield, after normalizing the resulting functions,

$$\langle i \,|\, j\rangle = \langle i' \,|\, j'\rangle = \delta_{ij}, \tag{168}$$

$$\langle i \,|\, j'\rangle = \lambda_i \delta_{ij}. \tag{169}$$

Here $|\lambda_i| \leq 1$, and the orbitals can be chosen so as to make $0 \leq \lambda_i \leq 1$.

It is of course possible to use $\mathcal{O}_s$ in conjunction with spin functions more complicated than products of α and β functions. But in such a case it is not easy to introduce an optimum orbital orthogonalization.

B. Matrix Elements for Spin-Projected Determinants

To use spin-projected determinantal functions it is necessary to be able to calculate matrix elements of relevant operators. Discussions of the overlap matrix and spin-free operators were obtained by the projection-operator methods of Löwdin by Pauncz *et al.* (1962) in their studies of the alternant molecular orbital method. The results were generalized further by Pauncz (1962). Spin-dependent coefficients appearing in the development were worked out by those authors, by Harris (1962), by Sasaki and Ohno (1963), and by Smith (1964). For certain applications, particularly to spin-dependent operators, it is convenient to form an explicitly spin-dependent density matrix. The first-order density matrix of a spin-projected determinant has been found and discussed in detail by Harriman (1964).

We take a spin-projected n-electron determinantal function

$$\Psi(\mathbf{r}, \boldsymbol{\sigma}) = \mathcal{O}_s \mathscr{A} \Xi_0(\mathbf{r})\Theta_0(\boldsymbol{\sigma}), \tag{170}$$

where $\Theta_0(\boldsymbol{\sigma})$ consists of n_α α factors followed by n_β β factors, with $n_\alpha + n_\beta = n$. Starting with Eq. (170), we form the matrix element of an operator $\mathscr{B}$. Using the self-adjointness and commutation properties of $\mathscr{O}_s$ and $\mathscr{A}$:

$$\langle \Psi(\mathbf{r}, \boldsymbol{\sigma}) \,|\, \mathscr{B} \,|\, \Psi(\mathbf{r}, \boldsymbol{\sigma}) \rangle = \langle \Xi_0(\mathbf{r})\Theta_0(\boldsymbol{\sigma}) \,|\, \mathscr{O}_s \mathscr{B} \mathscr{O}_s \mathscr{A} \,|\, \Xi_0(\mathbf{r})\Theta_0(\boldsymbol{\sigma}) \rangle. \tag{171}$$

Considering first spin-free operators, we separate the spatial and spin coordinates of Eq. (171), obtaining

$$\langle \Psi(\mathbf{r}, \boldsymbol{\sigma}) \,|\, \mathscr{B} \,|\, \Psi(\mathbf{r}, \boldsymbol{\sigma}) \rangle = (n!)^{-1} \sum_{Q} C(Q) \langle \Xi_0(\mathbf{r}) \,|\, \mathscr{B} \mathscr{Q} \,|\, \Xi_0(\mathbf{r}) \rangle. \tag{172}$$

The coefficients $C(Q)$ depend upon $\Theta_0(\boldsymbol{\sigma})$ and the chosen S and M_s, and are given by

$$C(Q) = \varepsilon_Q \langle \Theta_0(\boldsymbol{\sigma}) \,|\, \mathscr{Q} \mathscr{O}_s \,|\, \Theta_0(\boldsymbol{\sigma}) \rangle. \tag{173}$$

In obtaining Eq. (173) we used the fact that $\mathscr{O}_s$ and $\mathscr{Q}$ commute.

Certain properties of the $C(Q)$ may be verified by inserting the definition of $\mathscr{O}_s$. Doing so, replacing P by $Q^{-1}P$, we have

$$C(Q) = \frac{d}{n!} \varepsilon_Q \sum_P \sum_{i=1}^{d} V_{ii}^*(Q^{-1}P) \langle \Theta_0 \,|\, \mathscr{P}_\sigma \Theta_0 \rangle. \tag{174}$$

Since $\Theta_0(\boldsymbol{\sigma})$ is a simple product of α and β spin functions, $\langle \Theta_0 \,|\, \mathscr{P}_\sigma \Theta_0 \rangle$ is zero or unity, depending upon whether or not $\mathscr{P}$ exchanges any α and β functions. We therefore write

$$C(Q) = \frac{d}{n!} \varepsilon_Q \sum_{P \in \mathfrak{P}} \sum_{i=1}^{d} V_{ii}^*(Q^{-1}P), \tag{175}$$

where $\mathfrak{P}$ is the set of all permutations which leave $\Theta_0(\boldsymbol{\sigma})$ invariant. Now notice that if two permutations $\mathscr{Q}$ and $\mathscr{Q}'$ are related by $\mathscr{Q}' = \mathscr{P}'\mathscr{Q}$, with $P' \in \mathfrak{P}$, then $\sum_P V_{ii}([Q']^{-1}P) = \sum_P V_{ii}^*(Q^{-1}P)$, so $\varepsilon_{Q'} C(Q') = \varepsilon_Q C(Q)$. Since the permutations in $\mathfrak{P}$ do not interchange α and β functions in Θ_0, permutations $\mathscr{Q}$ and $\mathscr{Q}'$ must interchange equal numbers of α-β pairs. This means we can divide the group of all permutations $\mathscr{Q}$ into subsets (which in fact are cosets defined by $\mathfrak{P}$) according to the number of α and β spin functions which they interchange. Permutations $\mathscr{Q}$ interchanging k α-β pairs will all have $C(Q)$ values which can be written

$$C(Q) = \varepsilon_Q C_k \tag{176}$$

(Q interchanges k α-β pairs in $\Theta_0(\boldsymbol{\sigma})$).

The C_k have the values (Smith, 1964)

$$C_k = \frac{4S+2}{2S+n+2} \sum_{j=0}^{S-M_s} (-1)^{S-M_s+k-j} \binom{S-M_s}{j} \binom{S+M_s}{S-M_s-j} \binom{\frac{n}{2}+S}{n_\alpha + j - k}^{-1}$$

$$(n_\alpha \geq n_\beta). \quad (177)$$

We shall occasionally have a need to refer simultaneously to coefficients C_k for various values of S, M_s, and n. When it is necessary to identify these variables, we write $C_k(S, M_s, n)$. Coefficients C_k for contiguous values of S, M_s, and n are related by recurrence formulas, some of which are given in Appendix B. We note here that Eq. (177) may be used to obtain values when $n_\alpha < n_\beta$ through the relation

$$C_k(S, M_s, n) = C_k(S, -M_s, n). \quad (178)$$

We are now ready to proceed further with the matrix element expression of Eq. (172). Consider first the case that $\mathscr{B}$ is the identity operator. Then Eq. (172) describes the overlap matrix:

$$\langle \Psi | \Psi \rangle = (n!)^{-1} \sum_Q C(Q) \Delta(Q), \quad (179)$$

where

$$\Delta(Q) = \prod_{i=1}^{n} \langle i | q_i \rangle. \quad (180)$$

For a one-electron operator, Eq. (172) becomes

$$\langle \Psi | \mathscr{B} | \Psi \rangle = (n!)^{-1} \sum_{l=1}^{n} \sum_Q C(Q) \Delta(Q) \frac{\langle l | \mathscr{E} | q_l \rangle}{\langle l | q_l \rangle}, \quad (181)$$

while for a two-electron operator,

$$\langle \Psi | \mathscr{B} | \Psi \rangle = (n!)^{-1} \sum_{m=2}^{n} \sum_{l=1}^{m-1} \sum_Q C(Q) \Delta(Q) \frac{\langle lm | \mathscr{E} | q_l q_m \rangle}{\langle l | q_l \rangle \langle m | q_m \rangle}, \quad (182)$$

Equations (179)–(182) simplify considerably if we make use of the orbital orthogonality described in Section A. To start, notice that the only permutations Q for which $\Delta(Q)$ does not vanish are those which interchange only corresponding α spin and β spin orbitals. Letting $\mathfrak{R}$ be the set of all such permutations, we see that in Eqs. (179) and (181) we may restrict Q to $R \in \mathfrak{R}$, while in Eq. (182) the contributing permutations are R and $Q_{\mu,\nu} R$, where $Q_{\mu,\nu}$ is any single interchange not included in $\mathfrak{R}$.

If a permutation $R \in \mathfrak{R}$ interchanges electrons i and i', $\Delta(Q)$ will contain from these two electrons the quantity $|\lambda_i|^2$; all electrons which are not interchanged contribute a unit factor to $\Delta(R)$. Thus, characterizing R by a set of i to be interchanged, which we denote $\{i\}_R$, we have

$$\Delta(R) = \prod_{\{i\}_R} |\lambda_i|^2. \tag{183}$$

If we now sum $\Delta(R)$ for all permutations R in which the same number, k, of α-β spin pairs are interchanged, we get

$$\Delta^k = \sum_{\{i\}} \prod_{i} |\lambda_i|^2 \tag{184}$$

(sum over $\{i\}$ with k interchanges).

The value of ε_Q for k interchanges is $(-1)^k$. Therefore, combining Eqs. (176), (179), and (184), the overlap matrix element becomes

$$\langle\Psi\,|\,\Psi\rangle = (n!)^{-1} \sum_{k=0}^{n_\beta} (-1)^k C_k \Delta^k \qquad (n_\alpha \geq n_\beta). \tag{185}$$

We proceed next to the integrals for one-electron spin-free operators. It is convenient to adopt some further notational conventions. First, the α spin orbitals will be denoted by unprimed numbers or symbols running from 1 to n_α, while β spin orbitals will be denoted either by primed symbols running from 1 to n_β or by unprimed symbols running from $n_\alpha + 1$ to n. This allows us to write sums over all n orbitals compactly without giving up an easy identification of corresponding orbitals with opposite spins. Second, we shall continue to use $\mathfrak{R}$ to refer to the set of permutations which make interchanges only within corresponding pairs of orbitals, but we shall use $\mathfrak{R}_l$ or $\mathfrak{R}_{lm}$ to refer to the members of $\mathfrak{R}$ which do not permute the electrons referred to by subscripts. Similarly, we shall use Δ_l^k or Δ_{lm}^k to identify overlap products defined as in Eq. (184), but with the summation carried out only over interchanges not involving the electrons referred to by the subscripts. Third, we shall not explicitly show the range of summations over k, the number of interchanged α-β pairs, but shall understand that the range of these summations includes all k values for which Δ^k, Δ_l^k, or Δ_{lm}^k factors appearing in the sum are meaningful.

We now use the conventions of the foregoing paragraph to simplify Eq. (181), writing separately the permutations not involving l (these permutations are in $\mathfrak{R}_l$), and those involving l (these are in $Q_{l,l'}\mathfrak{R}_l$):

$$\begin{aligned}\langle\Psi\,|\,\mathscr{B}\,|\,\Psi\rangle = {} & (n!)^{-1} \sum_{l=1}^{n} \sum_{R\in\mathfrak{R}_l} C(R)\,\Delta(R)\,\frac{\langle l\,|\,\mathscr{b}\,|\,l\rangle}{\langle l\,|\,l\rangle} \\ & + (n!)^{-1} \sum_{l=1}^{n_\beta} \sum_{R\in\mathfrak{R}_l} C(Q_{l,l'}R)\Delta(R) \\ & \times \left[\frac{\langle l'\,|\,l\rangle\langle l\,|\,\mathscr{b}\,|\,l'\rangle + \langle l\,|\,l'\rangle\langle l'\,|\,\mathscr{b}\,|\,l\rangle}{\langle l\,|\,l\rangle\langle l'\,|\,l'\rangle}\right] \qquad (n_\alpha \geq n_\beta).\end{aligned} \tag{186}$$

We apply Eqs. (168), (169), and (176):

$$\langle\Psi|\mathscr{B}|\Psi\rangle = (n!)^{-1}\sum_{l=1}^{n}\sum_{k}(-1)^k C_k \Delta_l^k \langle l|\mathscr{b}|l\rangle$$
$$+ (n!)^{-1}\sum_{l=1}^{n_\beta}\sum_{k}(-1)^{k+1} C_{k+1}\,\Delta_l^k[\lambda_l{}^*\langle l|\mathscr{b}|l'\rangle + \lambda_l\langle l'|\mathscr{b}|l\rangle]$$
$$(n_\alpha \geq n_\beta) \quad (187)$$

(one-electron spin-free operator).

Next consider two-electron spin-free operators. We proceed as in the one-electron operator discussion, separating the contributing permutations into the following sets: $\mathfrak{R}_{lm}$, $Q_{l,l'}\mathfrak{R}_{lm}$, $Q_{m,m'}\mathfrak{R}_{lm}$, $Q_{l,l'}Q_{m,m'}\mathfrak{R}_{lm}$, $Q_{l,m}\mathfrak{R}_{lm}$, $Q_{l,m}Q_{l,l'}\mathfrak{R}_{lm}$, $Q_{l,m}Q_{m,m'}\mathfrak{R}_{lm}$, $Q_{l,m}Q_{l,l'}Q_{m,m'}\mathfrak{R}_{lm}$. Being careful to choose summation limits for l and m so as to enumerate each operator contribution and each permutation exactly once, we find after some tedious but not difficult manipulation

$$\langle\Psi|\mathscr{B}|\Psi\rangle = \sum_{m=2}^{n_\alpha}\sum_{l=1}^{m-1} D_{lm}^0[\langle lm|\mathscr{b}|lm\rangle - \langle lm|\mathscr{b}|ml\rangle]$$
$$+ \sum_{m=2}^{n_\beta}\sum_{l=1}^{m-1} D_{lm}^0[\langle l'm'|\mathscr{b}|l'm'\rangle - \langle l'm'|\mathscr{b}|m'l'\rangle]$$
$$+ \sum_{l=1}^{n_\alpha}\sum_{m=1}^{n_\beta}[D_{lm}^0\langle lm'|\mathscr{b}|lm'\rangle + D_{lm}^1\langle lm'|\mathscr{b}|m'l\rangle]$$
$$+ \sum_{l=1}^{n}\sum_{m=1}^{n_\beta} D_{lm}^1[\lambda_m{}^*(\langle lm|\mathscr{b}|lm'\rangle - \langle lm|\mathscr{b}|m'l\rangle) + \text{c.c.}]$$
$$+ \sum_{m=2}^{n_\beta}\sum_{l=1}^{m-1}[D_{lm}^2\lambda_l{}^*\lambda_m{}^*(\langle lm|\mathscr{b}|l'm'\rangle - \langle lm|\mathscr{b}|m'l'\rangle)$$
$$+ \lambda_l\lambda_m{}^*(D_{lm}^2\langle l'm|\mathscr{b}|lm'\rangle + D_{lm}^1\langle l'm|\mathscr{b}|m'l\rangle) + \text{c.c.}]$$
$$(n_\alpha \geq n_\beta) \quad (188)$$

(two-electron spin-free operator).

In Eq. (188), "c.c." stands for "complex conjugate," and the coefficients D_{lm}^0, D_{lm}^1, and D_{lm}^2 are defined as follows:

$$D_{lm}^0 = (n!)^{-1}\sum_k(-1)^k C_k \Delta_{lm}^k, \quad (189)$$

$$D_{lm}^1 = (n!)^{-1}\sum_k(-1)^{k+1} C_{k+1} \Delta_{lm}^k, \quad (190)$$

$$D_{lm}^2 = (n!)^{-1}\sum_k(-1)^{k+2} C_{k+2} \Delta_{lm}^k. \quad (191)$$

In the special case $n_\alpha = n_\beta$ and all λ_i equal, Eqs. (187)–(191) reduce to much more compact expressions. These expressions, and further detail on the processes involved in generating equations like Eqs. (187) and (188), are to be found in the work of Pauncz *et al.* (1962) and Pauncz (1962). The functions Δ^k, $\Delta_l^{\,k}$, and Δ_{lm}^k may be conveniently evaluated by a method described by Harriman (1964).

We pass now to spin-dependent operators. Starting from Eq. (171), we see that the separation into spatial and spin coordinates will depend on the form assumed for the operator $\mathscr{B}$. Taking first a one-electron operator, we have

$$\langle \Psi(\mathbf{r}, \boldsymbol{\sigma}) \,|\, \mathscr{B} \,|\, \Psi(\mathbf{r}, \boldsymbol{\sigma}) \rangle = (n!)^{-1} \sum_l \sum_Q C(l, Q) \langle \Xi_0(\mathbf{r}) \,|\, \mathscr{b}_r(l)\mathscr{Q} \,|\, \Xi_0(\mathbf{r}) \rangle, \tag{192}$$

where

$$C(l, Q) = \varepsilon_Q \langle \Theta_0(\boldsymbol{\sigma}) \,|\, \mathscr{O}_s \mathscr{b}_\sigma(l) \mathscr{Q} \mathscr{O}_s \,|\, \Theta_0(\boldsymbol{\sigma}) \rangle. \tag{193}$$

The assumed orbital orthogonality allows us to restrict the permutations $\mathscr{Q}$ in Eq. (192) to interchanges of corresponding orbitals. We distinguish two types of $\mathscr{Q}$: those which include an interchange involving the argument of $\mathscr{b}_\sigma$, and those which do not. In our previous notation, these types of $\mathscr{Q}$ are of the form $Q_{l,l'}\mathfrak{R}_l$ and $\mathfrak{R}_l$. Just as for the spin-free case, within permutations of the same type the value of $C(l, Q)$ depends only upon the *number* of interchanges. This may be seen by noticing that all permutations commute with $\mathscr{O}_s$, that interchanges not involving l commute with $\mathscr{b}_\sigma(l)$, and that any interchange not involving l can be converted into any other by permutations under which $\Theta_0(\boldsymbol{\sigma})$ remains invariant. Further, we note that $C(l, Q)$ depends upon l only to the extent that l refers to an α or a β spin in $\Theta_0(\boldsymbol{\sigma})$. Combining these arguments we write, for the case that l refers to an α spin in $\Theta_0(\boldsymbol{\sigma})$:

$$C(l, Q) = \varepsilon_Q C_k(\alpha\alpha) \tag{194}$$

(Q interchanges k α-β pairs in $\Theta_0(\boldsymbol{\sigma})$ and does not involve l);

$$C(l, Q) = \varepsilon_Q C_k(\alpha\beta) \tag{195}$$

(Q interchanges k α-β pairs in $\Theta_0(\boldsymbol{\sigma})$ plus that involving l).

When l refers to a β spin in $\Theta_0(\boldsymbol{\sigma})$, Eqs. (194) and (195) can be replaced by corresponding equations involving coefficients we denote by $C_k(\beta\beta)$ and $C_k(\beta\alpha)$. However, these coefficients are not all independent, because $\mathscr{b}_\sigma(l)Q_{l,l'} = Q_{l,l'}\mathscr{b}_\sigma(l')$, and therefore

$$C_k(\beta\alpha) = C_k(\alpha\beta). \tag{196}$$

Introducing Eqs. (194)–(196), we proceed to the evaluation of Eq. (192). Straightforward manipulation leads to

$$\begin{aligned}\langle\Psi|\mathcal{B}|\Psi\rangle &= (n!)^{-1}\sum_{l=1}^{n_\alpha}\sum_k(-1)^k C_k(\alpha\alpha)\Delta_l{}^k\langle l|\mathcal{O}_r|l\rangle\\ &+(n!)^{-1}\sum_{l=1}^{n_\beta}\sum_k(-1)^k C_k(\beta\beta)\Delta_l{}^k\langle l'|\mathcal{O}_r|l'\rangle\\ &+(n!)^{-1}\sum_{l=1}^{n_\beta}\sum_k(-1)^{k+1}C_k(\alpha\beta)\Delta_l{}^k[\lambda_l{}^*\langle l|\mathcal{O}_r|l'\rangle\\ &\qquad\qquad+\lambda_l\langle l'|\mathcal{O}_r|l\rangle](n_\alpha\geq n_\beta)\end{aligned}\tag{197}$$

(one-electron spin-dependent operator).

Evaluation of the coefficients $C_k(\alpha\alpha)$, $C_k(\beta\beta)$, and $C_k(\alpha\beta)$ is described in Appendix B. These coefficients are expressible in terms of the spin projection coefficients introduced in Eqs. (176) and (177), and also depend upon matrix elements of the one-electron spin operator $\mathcal{O}_\sigma$. As shown in the appendix, the coefficients have the values

$$\begin{aligned}C_k(\alpha\alpha) = C_k(S, M_s, n)b_+ - \frac{M_s}{S+1}\biggl[C_k(S, M_s, n) - \frac{(2S+1)(S+M_s)}{2S^2}\\ \times C_k(S-\tfrac{1}{2}, M_s-\tfrac{1}{2}, n-1)\biggr]b_-,\end{aligned}\tag{198}$$

$$\begin{aligned}C_k(\beta\beta) = C_k(S, M_s, n)b_+ - \frac{M_s}{S+1}\biggl[C_k(S, M_s, n) - \frac{(2S+1)(S-M_s)}{2S^2}\\ \times C_k(S-\tfrac{1}{2}, M_s+\tfrac{1}{2}, n-1)\biggr]b_-,\end{aligned}\tag{199}$$

$$C_k(\alpha\beta) = \tfrac{1}{2}[C_k(\alpha\alpha) + C_k(\beta\beta)] - C_k(S, M_s, n-2)\mathcal{O}_+,\tag{200}$$

with b_+ defined as $(\langle\alpha|\mathcal{O}_\sigma|\alpha\rangle+\langle\beta|\mathcal{O}_\sigma|\beta\rangle)/2$ and b_- as $(\langle\alpha|\mathcal{O}_\sigma|\alpha\rangle-\langle\beta|\mathcal{O}_\sigma|\beta\rangle)/2$. In Eqs. (198)–(200), any C_k coefficients involving impossible combinations of arguments are to be taken as vanishing sufficiently strongly that the terms in which they appear may be set to zero.

As an example of the application of Eqs. (197)–(200), take $\mathcal{B}$ to be the spin density operator, so that $\mathcal{O}_r = \delta(\mathbf{r}-\mathbf{r}_0)$, and $\mathcal{O}_\sigma = s_z$. Then, for the important special case $M_s = S$, Eqs. (198)–(200) reduce to the simpler expressions

$$C_k(\alpha\alpha) = \hbar\binom{n_\alpha}{k}^{-1}\frac{(-1)^k S(2S+1)(2S+n+2k+4)}{(S+1)(2S+n-2k)(2S+n+2)}, \tag{201}$$

$$C_k(\beta\beta) = -\hbar\binom{n_\alpha}{k}^{-1}\frac{(-1)^k S(2S+1)}{(S+1)(2S+n+2)}, \tag{202}$$

$$C_k(\alpha\beta) = 2\hbar\binom{n_\alpha}{k}^{-1}\frac{(-1)^k S(2S+1)(k+1)}{(S+1)(2S+n-2k)(2S+n+2)}. \tag{203}$$

Equation (197) can then be written

$$\begin{aligned}\langle\Psi|\mathscr{B}|\Psi\rangle = \frac{\hbar S(2S+1)}{2(S+1)(n_\alpha+1)n!}\sum_{l=1}^{n_\alpha}\sum_{k}\binom{n_\alpha}{k}^{-1}\Delta_l{}^k\Bigg[|\varphi_l|^2 - |\varphi_{l'}|^2 \\ + \left(\frac{k+1}{n_\alpha-k}\right)(2|\varphi_l|^2 - \lambda_l{}^*\varphi_l{}^*\varphi_{l'} - \lambda_l\varphi_{l'}^*\varphi_l)\Bigg],\end{aligned} \tag{204}$$

where it is to be understood that $\varphi_{l'}$ is to be taken as zero if $l > n_\beta$. Equation (204) shows that electrons in closed shells do not contribute to the spin density, because for such electrons $\varphi_{l'} = \varphi_l$ and $\lambda_l = \lambda_l{}^* = 1$, and the terms on the right side of Eq. (204) then vanish. If $S = \frac{1}{2}$, describing a doublet state, and all but one of the electrons are in closed shells, Eq. (204) reduces to the well-known result given in Eq. (139) (note that the result there given is unnormalized). This reduction is easily verified after dropping all terms of the l summation except $l = n_\alpha$, and noting that $\Delta^k_{n_\alpha} = \binom{n_\alpha - 1}{k}$. On the other hand, if there are several electrons outside of closed shells, Eq. (204) shows that the correct spin density is not obtained simply by taking the sum of individually computed spin densities of the various orbitals.

We next proceed to examine two-electron spin-dependent operators. The expectation values are given by

$$\langle\Psi(\mathbf{r},\boldsymbol{\sigma})|\mathscr{B}|\Psi(\mathbf{r},\boldsymbol{\sigma})\rangle$$

$$= (n!)^{-1}\sum_{m=2}^{n}\sum_{l=1}^{m-1}\sum_{Q} C(l,m,Q)\langle\Xi_0(\mathbf{r})|\mathscr{E}_r(l,m)\mathscr{Q}|\Xi_0(\mathbf{r})\rangle, \tag{205}$$

with

$$C(l,m,Q) = \varepsilon_Q\langle\Theta_0(\boldsymbol{\sigma})|\mathscr{O}_s\mathscr{E}_\sigma(l,m)\mathscr{Q}\mathscr{O}_s|\Theta_0(\boldsymbol{\sigma})\rangle. \tag{206}$$

Just as for the two-electron spin-free operators, the permutations contributing to Eq. (205) are restricted to those which cause at most a single interchange of noncorresponding spatial functions.

By the arguments already given when discussing one-electron spin-dependent operators, we reduce the various $C(l, m, Q)$ to expressions which depend upon the number k of α-β interchanges not involving l or m, and upon the details of Q only insofar as they apply to the spin pairs involving l and m. The various types of permutations Q and spins referred to by l and m [in $\Theta_0(\boldsymbol{\sigma})$] result in seven sets of coefficients, which occur according to the scheme indicated in Table I. Letting 1 and 2 stand for the spins appearing in ℓ_σ, and 3 and 4 for the spins paired with 1 and 2, respectively, and letting Q_k be the permutation interchanging k α-β pairs not involving the electrons 1, 2, 3, 4, the coefficients in Table I have the following meaning:

TABLE I

COEFFICIENTS $C(l, m, Q)/\varepsilon_Q$, AS DEFINED IN EQ. (206), FOR PERMUTATIONS OF THE TYPES INDICATED IN WHICH k α-β PAIRS ARE INTERCHANGED, NOT INCLUDING l OR m[a]

Permutation	l is α m is α	l is α m is β	l is β m is β
$\mathfrak{R}_{lm}$	$C_k(\alpha\alpha\alpha\alpha)$	$C_k(\alpha\beta\alpha\beta)$	$C_k(\beta\beta\beta\beta)$
$Q_{l,l'}\mathfrak{R}_{lm}$	$C_k(\alpha\alpha\alpha\beta)$	$C_k(\beta\beta\beta\alpha)$	$C_k(\beta\beta\beta\alpha)$
$Q_{m,m'}\mathfrak{R}_{lm}$	$C_k(\alpha\alpha\alpha\beta)$	$C_k(\alpha\alpha\alpha\beta)$	$C_k(\beta\beta\beta\alpha)$
$Q_{l,l'}Q_{m,m'}\mathfrak{R}_{lm}$	$C_k(\alpha\alpha\beta\beta)$	$C_{k+1}(\alpha\beta\beta\alpha)$	$C_k(\alpha\alpha\beta\beta)$
$Q_{l,m}\mathfrak{R}_{lm}$	$C_k(\alpha\alpha\alpha\alpha)$	$C_k(\alpha\beta\beta\alpha)$	$C_k(\beta\beta\beta\beta)$
$Q_{l,m}Q_{l,l'}\mathfrak{R}_{lm}$	$C_k(\alpha\alpha\alpha\beta)$	$C_k(\beta\beta\beta\alpha)$	$C_k(\beta\beta\beta\alpha)$
$Q_{l,m}Q_{m,m'}\mathfrak{R}_{lm}$	$C_k(\alpha\alpha\alpha\beta)$	$C_k(\alpha\alpha\alpha\beta)$	$C_k(\beta\beta\beta\alpha)$
$Q_{l,m}Q_{l,l'}Q_{m,m'}\mathfrak{R}_{lm}$	$C_k(\alpha\alpha\beta\beta)$	$C_{k+1}(\alpha\beta\alpha\beta)$	$C_k(\alpha\alpha\beta\beta)$

[a] Columns indicate whether l and m refer to α or β spins in $\Theta_0(\boldsymbol{\sigma})$.

$$C_k(\alpha\alpha\alpha\alpha) = \langle\alpha(1)\alpha(2)\beta(3)\beta(4)\cdots|\mathcal{O}_s\ell_\sigma(1,2)Q_k\mathcal{O}_s\,|\,\alpha(1)\alpha(2)\beta(3)\beta(4)\cdots\rangle, \tag{207}$$

$$C_k(\alpha\alpha\alpha\beta) = \langle\alpha(1)\alpha(2)\beta(3)\beta(4)\cdots|\mathcal{O}_s\ell_\sigma(1,2)Q_k\mathcal{O}_s\,|\,\alpha(1)\beta(2)\alpha(3)\beta(4)\cdots\rangle, \tag{208}$$

$$C_k(\alpha\alpha\beta\beta) = \langle\alpha(1)\alpha(2)\beta(3)\beta(4)\cdots|\mathcal{O}_s\ell_\sigma(1,2)Q_k\mathcal{O}_s\,|\,\beta(1)\beta(2)\alpha(3)\alpha(4)\cdots\rangle, \tag{209}$$

$$C_k(\alpha\beta\alpha\beta) = \langle \alpha(1)\beta(2)\alpha(3)\beta(4)\cdots | \mathcal{O}_s \mathcal{E}_\sigma(1, 2) Q_k \mathcal{O}_s | \alpha(1)\beta(2)\alpha(3)\beta(4)\cdots\rangle, \tag{210}$$

$$C_k(\alpha\beta\beta\alpha) = \langle \alpha(1)\beta(2)\beta(3)\alpha(4)\cdots | \mathcal{O}_s \mathcal{E}_\sigma(1,2) Q_k \mathcal{O}_s | \beta(1)\alpha(2)\beta(3)\alpha(4)\cdots\rangle, \tag{211}$$

$$C_k(\beta\beta\beta\alpha) = \langle \beta(1)\beta(2)\alpha(3)\alpha(4)\cdots | \mathcal{O}_s \mathcal{E}_\sigma(1,2) Q_k \mathcal{O}_s | \alpha(1)\beta(2)\beta(3)\alpha(4)\cdots\rangle, \tag{212}$$

$$C_k(\beta\beta\beta\beta) = \langle \beta(1)\beta(2)\alpha(3)\alpha(4)\cdots | \mathcal{O}_s \mathcal{E}_\sigma(1,2) Q_k \mathcal{O}_s | \beta(1)\beta(2)\alpha(3)\alpha(4)\cdots\rangle. \tag{213}$$

In Eqs. (207)–(213), the dots indicate the remainder of $\Theta_0(\boldsymbol{\sigma})$, taken in unpermuted order.

We now reduce the general expression given in Eq. (205), making use of Table I. The result is

$$\begin{aligned}
\langle \Psi | \mathscr{B} | \Psi \rangle = {} & \sum_{m=2}^{n_\alpha} \sum_{l=1}^{m-1} D_{lm}^0(\alpha\alpha)[\langle lm | \mathcal{E}_r | lm\rangle - \langle lm | \mathcal{E}_r | ml\rangle] \\
& + \sum_{m=2}^{n_\beta} \sum_{l=1}^{m-1} D_{lm}^0(\beta\beta)[\langle l'm' | \mathcal{E}_r | l'm'\rangle - \langle l'm' | \mathcal{E}_r | m'l'\rangle] \\
& + \sum_{l=1}^{n_\alpha} \sum_{m=1}^{n_\beta} [D_{lm}^0(\alpha\beta)\langle lm' | \mathcal{E}_r | lm'\rangle + D_{lm}^1(-)\langle lm' | \mathcal{E}_r | m'l\rangle] \\
& + \sum_{l=1}^{n_\alpha} \sum_{m=1}^{n_\beta} D_{lm}^1(\alpha\alpha)[\lambda_m{}^*(\langle lm | \mathcal{E}_r | lm'\rangle - \langle lm | \mathcal{E}_r | m'l\rangle) + \text{c.c.}] \\
& + \sum_{l=1}^{n_\beta} \sum_{m=1}^{n_\beta} D_{lm}^1(\beta\beta)[\lambda_m{}^*(\langle l'm | \mathcal{E}_r | l'm'\rangle \\
& \qquad - \langle l'm | \mathcal{E}_r | m'l'\rangle) + \text{c.c.}] \\
& + \sum_{m=2}^{n_\beta} \sum_{l=1}^{m-1} D_{lm}^2(+)[\lambda_l{}^*\lambda_m{}^*(\langle lm | \mathcal{E}_r | l'm'\rangle \\
& \qquad - \langle lm | \mathcal{E}_r | m'l'\rangle) + \text{c.c.}] \\
& + \sum_{m=2}^{n_\beta} \sum_{l=1}^{m-1} [\lambda_l \lambda_m{}^*(D_{lm}^2(-)\langle l'm | \mathcal{E}_r | lm'\rangle \\
& \qquad + D_{lm}^1(+)\langle l'm | \mathcal{E}_r | m'l\rangle) + \text{c.c.}] \qquad (n_\alpha \geq n_\beta)
\end{aligned} \tag{214}$$

(two-electron spin-dependent operator).

The coefficients appearing in Eq. (214) have the values:

$$D_{lm}^0(\alpha\alpha) = (n!)^{-1} \sum_k (-1)^k \Delta_{lm}^k C_k(\alpha\alpha\alpha\alpha), \tag{215}$$

$$D^0_{lm}(\beta\beta) = (n!)^{-1} \sum_k (-1)^k \Delta^k_{lm} C_k(\beta\beta\beta\beta), \tag{216}$$

$$D^0_{lm}(\alpha\beta) = (n!)^{-1} \sum_k (-1)^k \Delta^k_{lm} C_k(\alpha\beta\alpha\beta), \tag{217}$$

$$D^1_{lm}(-) = (n!)^{-1} \sum_k (-1)^{k+1} \Delta^k_{lm} C_k(\alpha\beta\beta\alpha), \tag{218}$$

$$D^1_{lm}(\alpha\alpha) = (n!)^{-1} \sum_k (-1)^{k+1} \Delta^k_{lm} C_k(\alpha\alpha\alpha\beta), \tag{219}$$

$$D^1_{lm}(\beta\beta) = (n!)^{-1} \sum_k (-1)^{k+1} \Delta^k_{lm} C_k(\beta\beta\beta\alpha), \tag{220}$$

$$D^2_{lm}(+) = (n!)^{-1} \sum_k (-1)^{k+2} \Delta^k_{lm} C_k(\alpha\alpha\beta\beta), \tag{221}$$

$$D^2_{lm}(-) = (n!)^{-1} \sum_k (-1)^{k+2} \Delta^k_{lm} C_{k+1}(\alpha\beta\beta\alpha), \tag{222}$$

$$D^1_{lm}(+) = (n!)^{-1} \sum_k (-1)^{k+1} \Delta^k_{lm} C_{k+1}(\alpha\beta\alpha\beta). \tag{223}$$

The C_k coefficients defined in Eqs. (207)–(213) are evaluated as described in Appendix B. They have the values

$$\begin{aligned} C_k(\alpha\alpha\alpha\alpha) = C_k(\alpha\alpha) - \frac{b_x}{2}\Bigg[& \frac{(S+M_s)(S-M_s+1){M_s}^2}{S^2(S+1)^2}\, C_k(S, M_s-1, n-2) \\ & + \frac{(S+M_s)^2(S-M_s)(S+M_s-1)}{S^2(2S-1)^2}\, C_k(S-1, M_s-1, n-2) \\ & + \frac{(S-M_s+1)^2(S-M_s+2)(S+M_s+1)}{(S+1)^2(2S+3)^2} \\ & \times C_k(S+1, M_s-1, n-2)\Bigg], \end{aligned} \tag{224}$$

$$\begin{aligned} C_k(\alpha\alpha\alpha\beta) = \tfrac{1}{2}[C_{k+1}(\alpha\alpha) + C_k(\alpha\beta)] + \frac{b_x}{2}\Bigg[& M_s\left(\frac{M_s}{S(S+1)}\right)^2 C_k'(S, M_s, n-2) \\ & - (S-M_s)\left(\frac{S+M_s}{S(2S-1)}\right)^2 C_k'(S-1, M_s, n-2) \\ & + (S+M_s+1)\left(\frac{S-M_s+1}{(S+1)(2S+3)}\right)^2 C_k'(S+1, M_s, n-2)\Bigg], \end{aligned} \tag{225}$$

$$\begin{aligned} C_k(\alpha\alpha\beta\beta) = {} & C_{k+1}(\alpha\beta) + \frac{b_x}{2}\left[\left(\frac{M_s}{S(S+1)}\right)^2 C''_k(S, M_s, n-2)\right. \\ & - \frac{(S\ - M_s^{\,2})}{S^2(2S-1)^2} C''_k(S-1, M_s, n-2) \\ & \left. + \left(\frac{(S+1)^2 - M_s^{\,2}}{(s+1)^2(2S+3)^2}\right) C''_k(S+1, M_s, n-2)\right], \end{aligned} \tag{226}$$

$$\begin{aligned} C_k(\alpha\beta\alpha\beta) = {} & \tfrac{1}{2}[C_k(\alpha\alpha) + C_k(\beta\beta) + b_y C_k(S, M_s, n-2)] \\ & - \frac{b_x}{2}\left[\left(\frac{M_s^{\,2}}{S(S+1)}\right)^2 C_k(S, M_s, n-2)\right. \\ & + \left(\frac{S^2 - M_s^{\,2}}{S(2S-1)}\right)^2 C_k(S-1, M_s, n-2) \\ & \left. + \left(\frac{(S+1)^2\ - M_s^{\,2}}{(S+1)(2S+3)}\right)^2 C_k(S+1, M_s, n-2)\right], \end{aligned} \tag{227}$$

$$C_k(\alpha\beta\beta\alpha) = C_k(\alpha\beta\alpha\beta) - (b_+ + b_y)C_k(S, M_s, n-2), \tag{228}$$

$$\begin{aligned} C_k(\beta\beta\beta\alpha) = {} & \tfrac{1}{2}[C_{k+1}(\beta\beta) + C_k(\alpha\beta)] - \frac{b_x}{2}\left[M_s\left(\frac{M_s}{S(S+1)}\right)^2 C_k'(S, -M_s, n-2)\right. \\ & + (S + M_s)\left(\frac{S - M_s}{S(2S-1)}\right)^2 C_k'(S-1, -M_s, n-2) \\ & \left. - (S - M_s + 1)\left(\frac{S + M_s + 1}{(S+1)(2S+3)}\right)^2 C_k'(S+1, -M_s, n-2)\right], \end{aligned} \tag{229}$$

$$\begin{aligned} C_k(\beta\beta\beta\beta) = {} & C_k(\beta\beta) - \frac{b_x}{2}\left[\frac{(S - M_s)(S + M_s + 1)M_s^{\,2}}{S^2(S+1)^2} C_k(S, M_s + 1, n-2)\right. \\ & + \frac{(S - M_s)^2(S + M_s)(S - M_s - 1)}{S^2(2S-1)^2} C_k(S-1, M_s + 1, n-2) \\ & + \frac{(S + M_s + 1)^2(S + M_s + 2)(S - M_s + 1)}{(S+1)^2(2S+3)^2} \\ & \left. \times C_k(S+1, M_s + 1, n-2)\right]. \end{aligned} \tag{230}$$

In Eqs. (224)–(230),

$$b_+ \equiv (\langle \alpha\alpha | \mathscr{E}_\sigma | \alpha\alpha \rangle + \langle \beta\beta | \mathscr{E}_\sigma | \beta\beta \rangle)/2,$$

$$b_- \equiv (\langle \alpha\alpha | \mathscr{E}_\sigma | \alpha\alpha \rangle - \langle \beta\beta | \mathscr{E}_\sigma | \beta\beta \rangle)/2,$$

$$b_x \equiv b_+ - \langle \alpha\beta | \mathscr{E}_\sigma | \alpha\beta \rangle - \langle \alpha\beta | \mathscr{E}_\sigma | \beta\alpha \rangle,$$

and

$$b_y \equiv \langle \alpha\beta | \mathscr{E}_\sigma | \alpha\beta \rangle - \langle \alpha\beta | \mathscr{E}_\sigma | \beta\alpha \rangle - b_+.$$

When $C_k(\alpha\alpha)$, $C_k(\beta\beta)$, and $C_k(\alpha\beta)$ appear in these equations, they are to be evaluated using the present meaning of b_+ and b_-. Finally, the new symbols C_k' and C_k'' are defined as

$$\begin{aligned} C_k'(S, M_s, n-2) = {} & (k+1)C_k(S, M_s - 1, n-2) \\ & + \left(\frac{n}{2} + M_s - k - 2\right) C_{k+1}(S, M_s - 1, n-2), \end{aligned}$$

$$\begin{aligned} C_k''(S, M_s, n-2) = {} & (k+1)(k+2)C_k(S, M_s - 1, n-2) \\ & + 2(k+2)\left(\frac{n}{2} + M_s - k - 2\right) C_{k+1}(S, M_s - 1, n-2) \\ & + \left(\frac{n}{2} + M_s - k - 2\right)\left(\frac{n}{2} + M_s - k - 3\right) \\ & \times C_{k+2}(S, M_s - 1, n-2). \end{aligned}$$

Appendix A. Orthogonalization Procedures

As indicated in the main text, it is possible to partially orthogonalize open-shell orbitals without altering the over-all wave function. Let us assume we start from two spatial configurations $\Xi_k(\mathbf{r})$ and $\Xi_{k'}(\mathbf{r})$, defined as in Eq. (74), but with bars over the orbital symbols, e.g., $\bar{\chi}_i$, $\bar{\chi}_i'$, $\bar{\varphi}_i$, $\bar{\varphi}_i'$, to indicate orbitals prior to orthogonalization. We outline a series of steps whereby

(1) the doubly occupied orbitals of $\Xi_k(\mathbf{r})$ are orthogonalized to those of $\Xi_{k'}(\mathbf{r})$, except possibly for corresponding orbitals;

(2) the singly occupied orbitals of $\Xi_k(\mathbf{r})$ are orthogonalized as much as possible to the doubly occupied orbitals of $\Xi_{k'}(\mathbf{r})$;

(3) the singly occupied orbitals of $\Xi_{k'}(\mathbf{r})$ are orthogonalized as much as possible to the doubly occupied orbitals of $\Xi_k(\mathbf{r})$.

As we shall see, we cannot orthogonalize the singly occupied orbitals of $\Xi_k(\mathbf{r})$ to a doubly occupied orbital of $\Xi_{k'}(\mathbf{r})$ unless the doubly occupied orbital has a nonvanishing overlap with the corresponding orbital of $\Xi_k(\mathbf{r})$. The same remark of course applies to the singly occupied orbitals of $\Xi_{k'}(\mathbf{r})$.

To start, take any doubly occupied orbital of Ξ_k. If it is orthogonal to *all* doubly occupied orbitals of $\Xi_{k'}$, set it aside. If not, select any doubly occupied orbital of $\Xi_{k'}$ to which it is not orthogonal, and designate these orbitals χ_1 and χ_1'. Then orthogonalize all the remaining orbitals of $\Xi_{k'}$ to χ_1 by adding to them suitable multiples of χ_1', and orthogonalize all the remaining orbitals of Ξ_k to χ_1' by adding to them suitable multiples of χ_1. Since the contributions added are all from doubly occupied orbitals, the operations described here do not alter the wave function.

Next look among the (modified) doubly occupied orbitals of Ξ_k (excluding χ_1) for another doubly occupied orbital which overlaps a (modified) doubly occupied orbital of $\Xi_{k'}$. If such orbitals exist, designate them χ_2 and χ_2', orthogonalize all orbitals of $\Xi_{k'}$ (except χ_1' and χ_2') to χ_2 by addition of a suitable multiple of χ_2', and orthogonalize all orbitals of Ξ_k (except χ_1 and χ_2) to χ_2' by addition of a suitable multiple of χ_2. These orthogonalizations do not alter the wave function, nor do they destroy the previously achieved orthogonalities to χ_1 or χ_1'.

Proceeding with further (modified) doubly occupied orbitals in this way, we finally arrive at a situation where every doubly occupied orbital of Ξ_k is either orthogonal to all doubly occupied orbitals of $\Xi_{k'}$ or has been orthogonalized to all but one doubly occupied orbital of $\Xi_{k'}$ and in addition to all singly occupied orbitals of $\Xi_{k'}$. A corresponding statement applies to each doubly occupied orbital of $\Xi_{k'}$. Note that we have no mechanism for orthogonalizing the singly occupied orbitals of $\Xi_{k'}$ to a doubly occupied orbital of Ξ_k unless there is a doubly occupied orbital of $\Xi_{k'}$ which can be used to bring about the orthogonalization. If the doubly occupied orbital of Ξ_k is orthogonal to all doubly occupied orbitals of $\Xi_{k'}$, no such doubly occupied orbital of $\Xi_{k'}$ exists.

Another orthogonalization problem arises in connection with spin-projected single-determinantal wave functions. Here there are n_α α spin orbitals and n_β β spin orbitals, originally with arbitrary overlap integrals between them. Linear transformations among the α spin orbitals alone, or among the β spin orbitals alone, leave the wave function invariant, but we may not make linear combinations mixing orbitals of α and β spin. We require a procedure which will yield the partial orthogonalization indicated by Eqs. (168) and (169). The method we describe here is that set forth by Löwdin (1962).

Let us start by orthogonalizing the α spin orbitals among themselves by any convenient method. We do likewise for the β spin orbitals. We denote these orthogonalized sets $\bar{\varphi}_1, \bar{\varphi}_2, \ldots$, and $\bar{\varphi}_{1'}, \bar{\varphi}_{2'}, \ldots$, with primes indicating orbitals of β spin. These orthogonalized sets are to some extent arbitrary, as the orthogonalization is preserved under unitary transformations. We let $\mathbf{C} \equiv (c_{ij})$ and $\mathbf{C}' \equiv (c'_{ij})$ stand for such transformations to orbitals $\varphi_1, \varphi_2, \ldots$, and $\varphi_{1'}, \varphi_{2'}, \ldots$, with

$$\varphi_i = \sum_j c_{ji}\bar{\varphi}_j, \tag{231}$$

$$\varphi_{i'} = \sum_j c'_{ji}\bar{\varphi}_{j'}. \tag{232}$$

Our remaining problem is to find unitary transformations $\mathbf{C}$ and $\mathbf{C}'$ to orbitals satisfying Eq. (169), which in the present notation is

$$\langle \varphi_i \,|\, \varphi_{j'} \rangle = \lambda_i \delta_{ij}. \tag{233}$$

Equation (168) is satisfied by virtue of the earlier orthogonalization of α spin and β spin orbitals separately.

We let $S_{ij} = \langle \bar{\varphi}_i \,|\, \bar{\varphi}_{j'} \rangle$ be the $n_\alpha \times n_\beta$ rectangular matrix describing the overlap of the arbitrarily orthogonalized $\bar{\varphi}_i$ and $\bar{\varphi}_{j'}$. Then, using Eqs. (231) and (232), the condition given in Eq. (233) can be written

$$\mathbf{C}^{-1}\mathbf{S}\mathbf{C}' = \mathbf{\Lambda}, \tag{234}$$

where $\mathbf{\Lambda}$ is a diagonal matrix with (unknown) elements λ_i. Because $\mathbf{C}$ and $\mathbf{C}'$ are both unitary, the Hermitean adjoint of Eq. (234) is

$$\mathbf{C}'^{-1}\mathbf{S}^\dagger\mathbf{C} = \mathbf{\Lambda}^*. \tag{235}$$

Multiplying each side of Eq. (234) on the right by the corresponding side of Eq. (235),

$$\mathbf{C}^{-1}\mathbf{S}\mathbf{S}^\dagger\mathbf{C} = \mathbf{\Lambda}\mathbf{\Lambda}^* \tag{236}$$

or

$$(\mathbf{S}\mathbf{S}^\dagger)\mathbf{C} = \mathbf{C}(\mathbf{\Lambda}\mathbf{\Lambda}^*), \tag{237}$$

which is an eigenvalue equation in standard form, with eigenvalues $|\lambda_i|^2$ and eigenvectors which are columns of $\mathbf{C}$. Once we have $\mathbf{C}$ we may get $\mathbf{C}'$

from Eq. (234). If any λ_i vanish, $\mathbf{C}'$ will not be determined unambiguously and there will be a manifold of satisfactory choices.

Appendix B. Coefficients for Spin Projections

Using the explicit formula of Eq. (177), the integral formulation given by Smith (1964), relations involving hypergeometric functions, or techniques similar to those described below, a number of recurrence relations among the coefficients $C_k(S, M_s, n)$ may be derived. For compactness in notation we shall in this appendix write M for M_s. Some of the recurrence relations needed in connection with the present discussion are the following:

$$C_{k+1}(S, M, n) = C_k(S, M, n) - C_k(S, M, n-2), \tag{238}$$

$$\left(\frac{S-M+1}{2S+2}\right)C_k(S+\tfrac{1}{2}, M-\tfrac{1}{2}, n-1) + \left(\frac{S+M}{2S}\right)C_k(S-\tfrac{1}{2}, M-\tfrac{1}{2}, n-1) = C_k(S, M, n), \tag{239}$$

$$\left(\frac{S+M+1}{2S+2}\right)C_k(S+\tfrac{1}{2}, M+\tfrac{1}{2}, n-1) + \left(\frac{S-M}{2S}\right)C_k(S-\tfrac{1}{2}, M+\tfrac{1}{2}, n-1) = C_k(S, M, n), \tag{240}$$

$$\left(\frac{S+M}{2S}\right)C_k(S-\tfrac{1}{2}, M-\tfrac{1}{2}, n-1) - \left(\frac{S-M}{2S}\right)C_k(S-\tfrac{1}{2}, M+\tfrac{1}{2}, n-1) = \left(\frac{2M}{2S+1}\right)C_k(S, M, n-2), \tag{241}$$

$$-\left(\frac{2M-1}{2S+2}\right)C_k(S+\tfrac{1}{2}, M-\tfrac{1}{2}, n-1) + \left(\frac{2M-1}{2S}\right)C_k(S-\tfrac{1}{2}, M-\tfrac{1}{2}, n-1) = C_k(S, M, n) - C_k(S, M-1, n), \tag{242}$$

$$\left(\frac{2S+1}{2S+2}\right)C_k(S+\tfrac{1}{2}, M-\tfrac{1}{2}, n-1) + \left(\frac{2S+1}{2S}\right)C_k(S-\tfrac{1}{2}, M-\tfrac{1}{2}, n-1) = C_k(S, M, n) + C_k(S, M-1, n), \tag{243}$$

$$C_{k-1}(S, M, n) + \left(\frac{n-2M-2k+2}{2k}\right)C_k(S, M, n) = C_{k-1}(S, M-1, n) + \left(\frac{n+2M-2k}{2k}\right)C_k(S, M-1, n), \tag{244}$$

$$\left(\frac{S+M-k}{2S+1}\right)C_k(S, M, n) - \left(\frac{n+2M-2k}{4S+2}\right)C_{k+1}(S, M, n)$$
$$= \left(\frac{S+M+1}{2S+2}\right)C_k(S+\tfrac{1}{2}, M+\tfrac{1}{2}, n-1). \qquad (245)$$

Equation (238) has been previously given by Harriman (1964).

We first consider the coefficients $C_k(\alpha\alpha)$, $C_k(\beta\beta)$, and $C_k(\alpha\beta)$ introduced in Eqs. (194) and (195). Letting 1 and 1′ refer to an α-β spin pair, these coefficients may be written explicitly as

$$C_k(\alpha\alpha) = \langle \alpha(1)\beta(1')\cdots \,|\, \mathcal{O}_S{}^n \mathcal{E}_\sigma(1) Q_k \mathcal{O}_S{}^n \,|\, \alpha(1)\beta(1')\cdots \rangle, \qquad (246)$$

$$C_k(\beta\beta) = \langle \beta(1)\alpha(1')\cdots \,|\, \mathcal{O}_S{}^n \mathcal{E}_\sigma(1) Q_k \mathcal{O}_S{}^n \,|\, \beta(1)\alpha(1')\cdots \rangle, \qquad (247)$$

$$C_k(\alpha\beta) = \langle \alpha(1)\beta(1')\cdots \,|\, \mathcal{O}_S{}^n \mathcal{E}_\sigma(1) Q_k \mathcal{O}_S{}^n \,|\, \beta(1)\alpha(1')\cdots \rangle. \qquad (248)$$

Here Q_k is an interchange of k α-β pairs not involving 1 or 1′, and the dots indicate the remainder of $\Theta_0(\boldsymbol{\sigma})$ in unpermuted order. We write $\mathcal{O}_S{}^n$ to focus attention on the fact that it is a projector for an n-spin system producing a state of total spin S.

We proceed by recognizing that $\mathcal{O}_S{}^n$ is the projection onto the *entire* n-spin subspace of total spin S. Introducing a basis of spin eigenfunctions for the complete n-spin space, we may accordingly write $\mathcal{O}_S{}^n$ as a partial resolution of the identity:

$$\mathcal{O}_S{}^n = \sum_i |\Theta^n_{S,i}\rangle\langle\Theta^n_{S,i}|, \qquad (249)$$

where in $\Theta^n_{S,i}$ i numbers the basis functions, while S and n identify the total spin and number of electrons. Because $\Theta_0(\boldsymbol{\sigma})$, and its permutations appearing in Eq. (248), have the definite eigenvalue M for $\mathcal{S}_z$, only the $\Theta^n_{S,i}$ with $\mathcal{S}_z$ eigenvalue M need be included in Eq. (249) if it is to be used in Eqs. (246)–(248). With this observation, Eqs. (246)–(248) may be written

$$C_k(\alpha\alpha) = \sum_{i,i'} \langle \alpha(1)\beta(1')\cdots \,|\, \Theta^n_{S,M,i}\rangle\langle\Theta^n_{S,M,i} \,|\, \mathcal{E}_\sigma(1) Q_k \,|\, \Theta^n_{S,M,i'}\rangle$$
$$\times \langle \Theta^n_{S,M,i'} \,|\, \alpha(1)\beta(1')\cdots\rangle, \qquad (250)$$

$$C_k(\beta\beta) = \sum_{i,i'} \langle \beta(1)\alpha(1')\cdots \,|\, \Theta^n_{S,M,i}\rangle\langle\Theta^n_{S,M,i} \,|\, \mathcal{E}_\sigma(1) Q_k \,|\, \Theta^n_{S,M,i'}\rangle$$
$$\times \langle \Theta^n_{S,M,i'} \,|\, \beta(1)\alpha(1')\cdots\rangle, \qquad (251)$$

$$C_k(\alpha\beta) = \sum_{i,i'} \langle \alpha(1)\beta(1')\cdots \mid \Theta^n_{S,M,i}\rangle\langle\Theta^n_{S,M,i} \mid \mathscr{E}_\sigma(1)Q_k \mid \Theta^n_{S,M,i'}\rangle \times \langle\Theta^n_{S,M,i'} \mid \beta(1)\alpha(1')\cdots\rangle. \tag{252}$$

While Eqs. (250)–(252) are valid with any choice of basis characterized by S and M, they are more easily simplified by a judicious choice. Our choice is to use the geneological construction in which $\Theta^n_{S,M,i}$ is related to basis functions for $(n-1)$-spin systems. A complete basis for the set of $\Theta^n_{S,M,i}$ may be chosen to consist of the functions

$$\Theta^{n,+}_{S,M,i} = -\sqrt{\frac{S-M+1}{2S+2}}\,\alpha(1)\Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i} + \sqrt{\frac{S+M+1}{2S+2}}\,\beta(1)\Theta^{n-1}_{S+\frac{1}{2},M+\frac{1}{2},i} \tag{253}$$

together with (if $S \neq 0$) the functions

$$\Theta^{n,-}_{S,M,i} = \sqrt{\frac{S+M}{2S}}\,\alpha(1)\Theta^{n-1}_{S-\frac{1}{2},M-\frac{1}{2},i} + \sqrt{\frac{S-M}{2S}}\,\beta(1)\Theta^{n-1}_{S-\frac{1}{2},M+\frac{1}{2},i}. \tag{254}$$

Here the $(n-1)$-spin functions have as arguments all the n spins except 1, and it is assumed that the labeling i is internally consistent, so that spin raising or lowering operators connect functions of the same i. The range of i in Eqs. (253) and (254) is determined by the dimensionality of the subspaces for the $(n-1)$-spin functions.

Consider now what happens when Eqs. (253) or (254) are inserted into Eqs. (250)–(252). Where we have $\langle\alpha(1)\beta(1')\cdots \mid \Theta^N_{S,M,i}\rangle$, only the term of Eq. (253) or (254) involving $\alpha(1)$ will give a nonzero contribution, so that, for Eq. (253), we get

$$-\sqrt{\frac{S-M+1}{2S+2}}\,\langle\beta(1')\cdots \mid \Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i}\rangle.$$

In $\langle\beta(1)\alpha(1')\cdots \mid \Theta^N_{S,M,i}\rangle$, on the other hand, the only nonzero contribution from Eq. (253) or (254) is from the term with $\beta(1)$.

In the middle scalar product of Eqs. (250)–(252), of the form $\langle\Theta^N_{S,M,i} \mid \mathscr{E}_\sigma(1)Q_k \mid \Theta^N_{S,M,i'}\rangle$, similar simplifications are possible. Here we can factor out the contributions involving spin 1, which appears separately in Eqs. (253) and (254). This leaves us with an $(n-1)$-spin expression of the general form $\langle\Theta^{n-1}_{S',M',i} \mid Q_k \mid \Theta^{n-1}_{S'',M'',i'}\rangle$. Expressions of this type will vanish unless both spin functions have the same S and M values, due to the fact that permutations commute with $\mathscr{S}^2$ and $\mathscr{S}_z$.

The considerations of the two preceding paragraphs enable us to bring Eq. (250) to the form

$$
\begin{aligned}
C_k(\alpha\alpha) = {} & \left(\frac{S-M+1}{2S+2}\right) \sum_{i,i'} \langle \beta(1')\cdots \mid \Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i}\rangle \\
& \times \left[\left(\frac{S-M+1}{2S+2}\right)\langle\alpha\mid \ell_\sigma \mid\alpha\rangle\langle\Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i}\mid Q_k \mid \Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i'}\rangle \right.\\
& \left. + \left(\frac{S+M+1}{2S+2}\right)\langle\beta\mid \ell_\sigma \mid\beta\rangle\langle\Theta^{n-1}_{S+\frac{1}{2},M+\frac{1}{2},i}\mid Q_k \mid \Theta^{n-1}_{S+\frac{1}{2},M+\frac{1}{2},i'}\rangle\right] \\
& \times \langle\Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i'}\mid \beta(1')\cdots\rangle + \left(\frac{S+M}{2S}\right)\sum_{i,i'}\langle \beta(1')\cdots \mid \Theta^{n-1}_{S-\frac{1}{2},M-\frac{1}{2},i}\rangle \\
& \times \left[\left(\frac{S+M}{2S}\right)\langle\alpha\mid \ell_\sigma \mid\alpha\rangle\langle\Theta^{n-1}_{S-\frac{1}{2},M-\frac{1}{2},i}\mid Q_k \mid \Theta^{n-1}_{S-\frac{1}{2},M-\frac{1}{2},i'}\rangle \right.\\
& \left. + \left(\frac{S-M}{2S}\right)\langle\beta\mid \ell_\sigma \mid\beta\rangle\langle\Theta^{n-1}_{S-\frac{1}{2},M+\frac{1}{2},i}\mid Q_k \mid \Theta^{n-1}_{S-\frac{1}{2},M+\frac{1}{2},i'}\rangle\right] \\
& \times \langle\Theta^{n-1}_{S-\frac{1}{2},M-\frac{1}{2},i'}\mid \beta(1')\cdots\rangle. \qquad (255)
\end{aligned}
$$

Corresponding expressions obtain for $C_k(\beta\beta)$ and $C_k(\alpha\beta)$.

Next we note that because $\Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i}$ and $\Theta^{n-1}_{S+\frac{1}{2},M+\frac{1}{2},i}$ are corresponding functions under $\mathscr{S}_+$ and $\mathscr{S}_-$, the matrix elements

$$\langle\Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i}\mid Q_k \mid \Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i'}\rangle \quad \text{and} \quad \langle\Theta^{n-1}_{S+\frac{1}{2},M+\frac{1}{2},i}\mid Q_k \mid \Theta^{n-1}_{S+\frac{1}{2},M+\frac{1}{2},i}\rangle$$

are equal. We thereupon rewrite Eq. (255) as

$$
\begin{aligned}
C_k(\alpha\alpha) = {} & \left(\frac{S-M+1}{2S+2}\right) \sum_{i,i'} \langle \beta(1')\cdots \mid \Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i}\rangle \\
& \times \langle\Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i}\mid Q_k \mid \Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i'}\rangle\langle\Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i'}\mid \beta(1')\cdots\rangle \\
& \times \left[\left(\frac{S-M+1}{2S+2}\right)\langle\alpha\mid \ell_\sigma \mid\alpha\rangle + \left(\frac{S+M+1}{2S+2}\right)\langle\beta\mid \ell_\sigma \mid\beta\rangle\right] \\
& + \left(\frac{S+M}{2S}\right)\sum_{i,i'}\langle \beta(1')\cdots \mid \Theta^{n-1}_{S-\frac{1}{2},M-\frac{1}{2},i}\rangle \\
& \times \langle\Theta^{n-1}_{S-\frac{1}{2},M-\frac{1}{2},i}\mid Q_k \mid \Theta^{n-1}_{S-\frac{1}{2},M-\frac{1}{2},i'}\rangle\langle\Theta^{n-1}_{S-\frac{1}{2},M-\frac{1}{2},i'}\mid \beta(1')\cdots\rangle \\
& \times \left[\left(\frac{S+M}{2S}\right)\langle\alpha\mid \ell_\sigma \mid\alpha\rangle + \left(\frac{S-M}{2S}\right)\langle\beta\mid \ell_\sigma \mid\beta\rangle\right]. \qquad (256)
\end{aligned}
$$

At this point the process of introducing the expansion of Eq. (249) may be reversed, whereupon the first double summation in Eq. (256) will be recognized as $\langle \beta(1')\cdots | \mathcal{O}^{n-1}_{S+\frac{1}{2}} Q_k \mathcal{O}^{n-1}_{S+\frac{1}{2}} | \beta(1')\cdots\rangle$ which is $C_k(S+\frac{1}{2}, M-\frac{1}{2}, n-1)$, while the second double summation is $C_k(S-\frac{1}{2}, M-\frac{1}{2}, n-1)$. Thus,

$$\begin{aligned} C_k(\alpha\alpha) = {}& \left(\frac{S-M+1}{2S+2}\right) C_k(S+\tfrac{1}{2}, M-\tfrac{1}{2}, n-1)\left[\left(\frac{S-M+1}{2S+2}\right)\langle\alpha|\ell_\sigma|\alpha)\rangle\right. \\ & \left. + \left(\frac{S+M+1}{2S+2}\right)\langle\beta|\ell_\sigma|\beta\rangle\right] + \left(\frac{S+M}{2S}\right) C_k(S-\tfrac{1}{2}, M-\tfrac{1}{2}, n-1) \\ & \times \left[\left(\frac{S+M}{2S}\right)\langle\alpha|\ell_\sigma|\alpha\rangle + \left(\frac{S-M}{2S}\right)\langle\beta|\ell_\sigma|\beta\rangle\right]. \end{aligned} \tag{257}$$

With the aid of the recurrence formulas already given, Eq. (257) can be rearranged to the form given at Eq. (198). A similar approach gives $C_k(\beta\beta)$ as the expression appearing at Eq. (199).

To obtain Eq. (200) for $C_k(\alpha\beta)$ is a bit more interesting. At the stage corresponding to Eq. (256), we have

$$\begin{aligned} C_k(\alpha\beta) = {}& -\sqrt{\left(\frac{S-M+1}{2S+2}\right)\left(\frac{S+M+1}{2S+2}\right)} \sum_{i,i'} \langle\beta(1')\cdots|\Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i}\rangle \\ & \times \langle\Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i}|Q_k|\Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i'}\rangle\langle\Theta^{n-1}_{S+\frac{1}{2},M+\frac{1}{2},i'}|\alpha(1')\cdots\rangle \\ & \times \left[\left(\frac{S-M+1}{2S+2}\right)\langle\alpha|\ell_\sigma|\alpha\rangle + \left(\frac{S+M+1}{2S+2}\right)\langle\beta|\ell_\sigma|\beta\rangle\right] \\ & + \sqrt{\left(\frac{S+M}{2S}\right)\left(\frac{S-M}{2S}\right)} \sum_{i,i'} \langle\beta(1')\cdots|\Theta^{n-1}_{S-\frac{1}{2},M-\frac{1}{2},i}\rangle \\ & \times \langle\Theta^{n-1}_{S-\frac{1}{2},M-\frac{1}{2},i}|Q_k|\Theta^{n-1}_{S-\frac{1}{2},M-\frac{1}{2},i'}\rangle\langle\Theta^{n-1}_{S-\frac{1}{2},M+\frac{1}{2},i'}|\alpha(1')\cdots\rangle \\ & \times \left[\left(\frac{S+M}{2S}\right)\langle\alpha|\ell_\sigma|\alpha\rangle + \left(\frac{S-M}{2S}\right)\langle\beta|\ell_\sigma|\beta\rangle\right]. \end{aligned} \tag{258}$$

Notice that the M values are not right for identifying the double summations as for $C_k(\alpha\alpha)$. But if we write

$$\Theta^{n-1}_{S+\frac{1}{2},M+\frac{1}{2},i'} = \frac{1}{\hbar\sqrt{(S-M+1)(S+M+1)}}\,\mathscr{S}_+\Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i'} \tag{259}$$

and then write

$$\langle\Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i'}|\mathscr{S}_-|\alpha(1')\cdots\rangle \quad \text{for} \quad \langle\mathscr{S}_+\Theta^{n-1}_{S+\frac{1}{2},M-\frac{1}{2},i'}|\alpha\,(1')\cdots\rangle,$$

we may perform the sums over i and i' in Eq. (258) to get (after some rearrangement, noting that Q_k and $\mathcal{O}^{n-1}_{S\pm\frac{1}{2}}$ commute and that $\mathcal{O}^{n-1}_{S\pm\frac{1}{2}}$ is idempotent):

$$C_k(\alpha\beta) = -\frac{1}{\hbar}\left(\frac{1}{2S+2}\right)\langle\beta(1')\cdots|\,\mathcal{O}^{n-1}_{S+\frac{1}{2}}Q_k\mathscr{S}_-\,|\alpha(1')\cdots\rangle\left[b_+ - \left(\frac{M}{S+1}\right)b_-\right]$$
$$+\frac{1}{2\hbar S}\langle\beta(1')\cdots|\,\mathcal{O}^{n-1}_{S-\frac{1}{2}}Q_k\mathscr{S}_-\,|\alpha(1')\cdots\rangle\left[b_+ + \frac{M}{S}\,b_-\right]. \tag{260}$$

Further reduction of Eq. (260) is afforded by considering the effect of $\mathscr{S}_-$. Since $\mathscr{S}_-$ is a sum of $\mathscr{s}_-$ operators for the individual spins, $\mathscr{S}_-|\alpha(1')\cdots\rangle$ will result in a sum of n_α terms in each of which a different single α spin has been changed to β and a factor $\hbar$ appended. If we now apply Q_k to each of these n_α terms, we find that in $k+1$ cases the net effect is to produce a spin product differing by k α-β interchanges from $\langle\beta(1')\cdots|$, while the remaining $(n_\alpha - k - 1)$ terms result in a spin product differing from $\langle\beta(1')\cdots|$ by $k+1$ interchanges. Thus, for example,

$$\langle\beta(1')\cdots|\,\mathcal{O}^{n-1}_{S+\frac{1}{2}}Q_k\mathscr{S}_-\,|\alpha(1')\cdots\rangle$$
$$= \hbar(k+1)\langle\beta(1')\cdots|\,\mathcal{O}^{n-1}_{S+\frac{1}{2}}Q_k\,|\beta(1')\cdots\rangle + \hbar(n_\alpha - k - 1)$$
$$\times\langle\beta(1')\cdots|\,\mathcal{O}^{n-1}_{S+\frac{1}{2}}Q_{k+1}\,|\beta(1')\cdots\rangle. \tag{261}$$

The terms on the right side of Eq. (261) are now C_k coefficients for $n-1$ spins and an $\mathscr{S}_z$ eigenvalue $M-\frac{1}{2}$, so

$$\langle\beta(1')\cdots\,|\mathcal{O}^{n-1}_{S+\frac{1}{2}}Q_k|\,\mathscr{S}_-\alpha(1')\cdots\rangle$$
$$= \hbar(k+1)C_k(S+\tfrac{1}{2}, M-\tfrac{1}{2}, n-1) + \hbar(n_\alpha - k - 1)$$
$$\times C_{k+1}(S+\tfrac{1}{2}, M-\tfrac{1}{2}, n-1). \tag{262}$$

Inserting expressions such as Eq. (262) into Eq. (260), we get

$$C_k(\alpha\beta) = -\left(\frac{1}{2S+2}\right)[(k+1)C_k(S+\tfrac{1}{2}, M-\tfrac{1}{2}, n-1)$$
$$+(n_\alpha - k - 1)C_{k+1}(S+\tfrac{1}{2}, M-\tfrac{1}{2}, n-1)]\left[b_+ - \left(\frac{M}{S+1}\right)b_-\right]$$
$$+\left(\frac{1}{2S}\right)[(k+1)C_k(S-\tfrac{1}{2}, M-\tfrac{1}{2}, n-1)$$
$$+(n_\alpha - k - 1)C_{k+1}(S-\tfrac{1}{2}, M-\tfrac{1}{2}, n-1)]\left[b_+ + \frac{M}{S}\,b_-\right]. \tag{263}$$

Equation (263) can be reduced to the form appearing as Eq. (200).

Procedures similar to those already outlined in this appendix serve to treat the coefficients arising for two-electron spin-dependent operators, listed in Eq. (207)–(213). However, because $\mathcal{O}_\sigma$ now depends upon two spins, it is convenient to relate the n-spin basis functions to those for $n - 2$ spins. There are four different sets of such basis functions (three if $S < 1$) together spanning the n-spin subspace of given S and M. They are

$$\begin{aligned}\Theta^{n,1}_{S,M,i} = {} & -\sqrt{\frac{(S+M)(S-M+1)}{2S(S+1)}}\,\alpha(1)\alpha(2)\Theta^{n-2}_{S,M-1}, \\ & + \frac{M}{\sqrt{2S(S+1)}}\,(\alpha(1)\beta(2)+\beta(1)\alpha(2))\Theta^{n-2}_{S,M,i} \\ & + \sqrt{\frac{(S-M)(S+M+1)}{2S(S+1)}}\,\beta(1)\beta(2)\Theta^{n-2}_{S,M+1,i}, \end{aligned} \tag{264}$$

$$\Theta^{n,2}_{S,M,i} = \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))\Theta^{n-2}_{S,M,i}, \tag{265}$$

$$\begin{aligned}\Theta^{n,3}_{S,M,i} = {} & \sqrt{\frac{(S-M+1)(S-M+2)}{(2S+2)(2S+3)}}\,\alpha(1)\alpha(2)\Theta^{n-2}_{S+1,M-1,i} \\ & - \sqrt{\frac{(S-M+1)(S+M+1)}{(2S+2)(2S+3)}}\,(\alpha(1)\beta(2)+\beta(1)\alpha(2))\Theta^{n-2}_{S+1,M,i} \\ & + \sqrt{\frac{(S+M+1)(S+M+2)}{(2S+2)(2S+3)}}\,\beta(1)\beta(2)\Theta^{n-2}_{S+1,M+1,i}, \end{aligned} \tag{266}$$

$$\begin{aligned}\Theta^{n,4}_{S,M,i} = {} & \sqrt{\frac{(S+M)(S+M-1)}{2S(2S-1)}}\,\alpha(1)\alpha(2)\Theta^{n-2}_{S-1,M-1,i} \\ & + \sqrt{\frac{(S+M)(S-M)}{2S(2S-1)}}\,(\alpha(1)\beta(2)+\beta(1)\alpha(2))\Theta^{n-2}_{S-1,M,i} \\ & + \sqrt{\frac{(S-M)(S-M-1)}{2S(2S-1)}}\,\beta(1)\beta(2)\Theta^{n-2}_{S-1,M+1,i}. \end{aligned} \tag{267}$$

Use of Eqs. (264)–(267), with the techniques already described, suffices to yield all the coefficient formulas in Eq. (224)–(230), excepting Eq. (226) for $C_k(\alpha\alpha\beta\beta)$. In obtaining $C_k(\alpha\alpha\beta\beta)$, the equations parallel to Eq. (260) involve terms such as $\hbar^{-2}\langle\beta(3)\beta(4)\cdots|\mathcal{O}^{n-2}_S Q_k \mathcal{S}_-{}^2|\alpha(3)\alpha(4)\cdots\rangle$, where the notation is as described at Eqs. (207)–(213). The application of $\mathcal{S}_{-2}$

to $|\alpha(3)\alpha(4)\cdots\rangle$ produces a factor $2\hbar^2$ and $\frac{1}{2}n_\alpha(n_\alpha - 1)$ terms, each containing a different combination of two β spins in place of α spins. After applying Q_k, we find that $\frac{1}{2}(k+1)(k+2)$ of these terms have spin orderings differing by k α-β interchanges from $\langle\beta(3)\beta(4)\cdots|$, $(k+2)(n_\alpha - k - 2)$ terms differ by $k+1$ interchanges, and $\frac{1}{2}(n_\alpha - k - 2)(n_\alpha - k - 3)$ terms differ by $k+2$ interchanges. Hence,

$$\begin{aligned}\frac{1}{\hbar^2}\langle\beta(3)\beta(4)\cdots|\mathcal{O}_S^{n-2}Q_k\mathcal{S}_-^{\,2}|\alpha(3)\alpha(4)\cdots\rangle \\ = (k+1)(k+2)C_k(S, M-1, n-2) \\ + 2(k+2)(n_\alpha - k - 2)C_{k+1}(S, M-1, n-2) \\ + (n_\alpha - k - 2)(n_\alpha - k - 3)C_{k+2}(S, M-1, n-2). \quad (268)\end{aligned}$$

With the aid of expressions such as Eq. (268), we obtain Eq. (226).

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Nonadditivity of Intermolecular Forces*

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I. Introduction

This paper presents a critical review of certain features of the nonadditivity problem which have recently become of interest. It faces the question whether the multibody series [Eq. (35)] has convenient properties of convergence. Four-body forces are calculated with the use of an oscillator model for two particular configurations: a regular tetrahedron and a square. Their sign is in both cases opposite to that of the three-body forces calculated by Jansen and collaborators. For the tetrahedron they are small; for the square, at distances equal to the lattice spacing of crystals, they are of the same order of magnitude as the three-body forces. The calculations are carried out in the first order of perturbation theory.

II. Long-Range Forces

The elementary Coulomb interactions from which molecular forces are compounded have two important properties: they are central and they are additive. The first implies the absence of torques; the second means this: When many particles interact, the total force on one is the vector sum of the forces exerted upon it by all other particles, considered one at

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a time. A consequence of this characteristic with respect to the potential energy V of a system is its *pairwise* additivity,

$$V = \sum_{i>j} V_{ij} \tag{1}$$

where V_{ij} is the potential energy of particle i relative to j. It follows from these facts that every classical Hamiltonian from which intermolecular forces are derived has the property of (pairwise) additivity.

When two *sets* of elementary charges interact it is in general not possible to find a point within each set about which the other will not produce a torque; hence the central property is lost for a collection of charges, except for sets of spherical symmetry. Multipoles, for instance, do not exhibit central forces.

But the additive property persists as long as all individual charges are rigidly held in position. Thus the potential energy of three rigid dipoles, fixed in their orientations, can be computed as the sum of intersystem pair potentials. However, if only the centers of the dipoles are fixed and the orientations allowed to adjust themselves for minimum potential energy, additivity is lost. The relative orientation of two will be altered when a third is introduced, and the potential energy of the first two will therefore depend on the position of the third.

In quantum mechanics, the change from additivity of the classical Hamiltonian to nonadditivity of intermolecular potentials occurs in the same way: the charges within each molecule readjust their motions in response to every new molecule entering its force range. The question of additivity therefore arises naturally; yet it cannot be dealt with in a uniform way since its aspects are different for the different types of intermolecular forces.

Some features are apparent from the manner in which these forces are calculated. Interactions which appear in first-order perturbation theory are clearly not additive, for they are mean values over functions having complicated symmetries with respect to intermolecular exchanges, or else the roots of secular equations. In the second order of perturbation theory, however, certain notable regularities occur, and these will first be summarized.

The long-range forces between unexcited molecules, i.e., the dispersion forces and those arising from all higher multiples, are additive in second order of perturbation theory (Margenau, 1939). This statement has been questioned by Wojtala (1964), and we shall show below in what sense his assertions are correct.

Let there be n molecules, their separations being such that it is proper to write their state as a product of individual molecule states:

$$|k\rangle = |k_1\rangle|k_2\rangle\cdots|k_n\rangle.$$

They are subject to the perturbation $V=\sum_{i<j}V(ij)$, (ij) denoting all coordinates pertaining to the ith and jth molecules. We now assume for $V(ij)$ its multipole expansion (cf. last reference). This obeys the relation

$$\langle k_ik_j|V(ij)|\kappa_i\kappa_j\rangle = f(R)[1-\delta(k_i\kappa_i)][1-\delta(k_j\kappa_j)]. \tag{2}$$

The complete second-order perturbation energy is

$$E_2 = \sum_{\{\kappa\}} \frac{|\langle k|V|\kappa\rangle|^2}{\sum_{i=1}^{n}[E(k_i)-E(\kappa_i)]} \tag{3}$$

where $\{\kappa\}$ denotes the set of quantum numbers $\kappa_1, \kappa_2, \ldots \kappa_n$ and the E's are unperturbed energies. Now

$$\langle k|V|\kappa\rangle = \sum_{i>j}\langle k_ik_j|V(i,j)|\kappa_i\kappa_j\rangle \prod_{s\neq ij}\delta(k_s\kappa_s) \tag{4}$$

When this is squared *and use is made of Eq. (2)*, only the squares of individual matrix elements remain and we find

$$E_2 = \sum_{i>j}\left[\sum_{\kappa_i\kappa_j}{}' \frac{|\langle k_ik_j|V(ij)|\kappa_i\kappa_j\rangle|^2}{E(k_i)-E(\kappa_i)+E(k_j)-E(\kappa_j)}\right]. \tag{5}$$

The bracketed expression, however, represents the second-order interaction between molecules i and j; hence additivity is established.

Wojtala did not expand V in a multipole series; hence his V does not satisfy Eq. (2). As a result he obtains cross terms which are not present in the asymptotic expansion. Their meaning will be discussed later in connection with Fig. 1.

Nonadditive contributions from the multipole series first occur in the third order of perturbation theory. In the literature attention has been confined for the most part to the dipole-dipole term in a configuration of three molecules. A qualitative formula for the triple-dipole interaction was first given by Axilrod and Teller (1943); it was established in detail by Muto (1943); Axilrod (1951) as well as Midzuno and Kihara (1956) later published fuller derivations. In developing it here we employ a useful technique devised by Sinanoğlu and applied to this problem by Kestner and Sinanoğlu (1963).

Three atoms, a, b, and c, are represented by state functions $\varphi_a(1)$, $\varphi_b(2)$, and $\varphi_c(3)$. They are far enough apart so that their charge clouds do not overlap. Interatomic exchanges will therefore be neglected. Each set of electrons (denoted by a numeral) is fixed to its atom, and summations over 1, 2, 3 are equivalent to summations over a, b, c. The complete function is the product

$$\phi_0 = \varphi_a \varphi_b \varphi_c \tag{6}$$

$$H_0 \varphi_0 = [H_0(a) + H_0(b) + H_0(c)]\phi_0 = E_0 \phi_0 = [E_0(a) + E_0(b) + E_0(c)]\phi_0 \tag{7}$$

and we define $H_0(a) - E_0(a) \equiv e_a$, so that

$$H_0 - E_0 = e_a + e_b + e_c. \tag{8}$$

We note that each e acts only on the electron coordinates of the atom whose subscript it carries.

The first-order perturbation is

$$H_1 = V_{ab} + V_{ac} + V_{bc} \tag{9}$$

and we mean by V_{ab} the dipole-dipole energy which has the form

$$V_{ab} = \frac{e^2}{R^3}\left(\mathbf{r}_a \cdot \mathbf{r}_b - 3\,\frac{\mathbf{r}_a \cdot \mathbf{R}\mathbf{r}_b \cdot \mathbf{R}}{R^2}\right) \tag{9a}$$

provided $e\mathbf{r}_a$ and $e\mathbf{r}_b$ are the dipole moments of the electrons in a and b, and $\mathbf{R}$ is the intermolecular vector between a and b.

The third-order perturbation energy (Dalgarno, 1961) may be written

$$E_3 = \langle \phi_1 \,|\, H_1 - E_1 \,|\, \phi_1 \rangle. \tag{10}$$

Since the first-order energy $E_1 = \langle \phi_0 \,|\, H_1 \,|\, \phi_0 \rangle = 0$, E_3 is simply the perturbation H_1 averaged over the first-order state function ϕ_1. We compute the latter as follows.

It is well-known (cf. last reference) that ϕ_1 satisfies in general the equation

$$(H_0 - E_0)\phi_1 = -H_1 \phi_0 + E_1 \phi_0. \tag{11}$$

In our case the last term is absent. Hence in view of Eqs. (6), (8), and (9):

$$\phi_1 = -(e_a + e_b + e_c)^{-1}(V_{ab} + V_{ac} + V_{bc})\varphi_a \varphi_b \varphi_c. \tag{12}$$

It is understood that the reciprocals of the e operators, undefined as they stand, take on meaning when inverted or expanded. We consider first the contribution to ϕ_1 which comes from V_{ab}, and we define the new operator

$$M_c = (e_a + e_b)^{-1} e_c. \tag{13}$$

In terms of it,

$$\phi_1^{ab} = -(e_a + e_b + e_c)^{-1} V_{ab}\varphi_a\varphi_b\varphi_c = -(1 + M_c)^{-1}(e_a + e_b)^{-1} V_{ab}\varphi_a\varphi_b\varphi_c$$
$$= -(1 - M_c + M_c^2 \cdots)(e_a + e_b)^{-1} V_{ab}\varphi_a\varphi_b\varphi_c.$$

At this point we observe that, because $e_c\varphi_c = 0$,

$$M_c\phi_c = 0. \tag{14}$$

Furthermore, φ_c commutes with $(e_a + e_b)^{-1} V_{ab}\varphi_a\varphi_b$ and may therefore be written after the first parenthesis in the expression for ϕ_1^{ab}, where it causes every power of M_c to disappear. Hence

$$\phi_1^{ab} = \varphi_c u_{ab} \tag{15}$$

provided

$$-u_{ab} = (e_a + e_b)^{-1} V_{ab}\varphi_a\varphi_b. \tag{16}$$

The usefulness of Eq. (15) arises from the manner in which ϕ_1^{ab} factors into a function of the coordinates of atom c alone (φ_c) and a pair function involving a and b.

In dealing with the contributions of V_{ac} and V_{bc} we introduce operators

$$M_b = (e_a + e_c)^{-1} e_b$$
$$M_a = (e_b + e_c)^{-1} e_a$$

and proceed similarly. Two other pair functions, u_{ac} and u_{bc}, appear, and they are constructed in analogy with (16). Thus one obtains

$$\phi_1 = u_{bc}\varphi_a + u_{ac}\varphi_b + u_{ab}\varphi_c \tag{17}$$

and the u functions satisfy the inhomogeneous differential equations

$$(e_a + e_b)u_{ab} = -V_{ab}\varphi_a\varphi_b, \tag{18}$$

etc.

Next, (17) is to be inserted in Eq. (10),

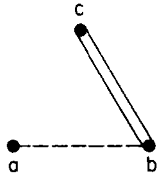
$$E_3 = \langle \phi_1 | (V_{ab} + V_{bc} + V_{ac})\phi_1 \rangle. \tag{19}$$

There are twenty-seven terms when E_3 is expanded. Each contains, aside from atomic state functions φ, two u factors and one V factor. The first, for instance, is

$$\langle u_{bc}\varphi_a | V_{ab} u_{bc}\varphi_a \rangle. \tag{20}$$

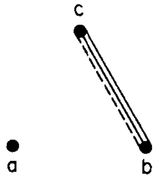
It vanishes when the integration over atom a is carried out [cf. Eq. (2)].

If, following Sinanoğlu, we represent individual brackets by graphs, using solid lines for u links and dotted lines for V links between the atoms, element (20) corresponds to



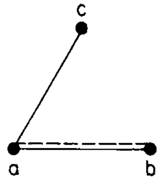
All elements of this type, i.e., with diagrams having two solid lines between one pair of atoms and a dotted line extending to the third atom, vanish for the reason just given.

Another bracket has the form $\langle u_{bc}\varphi_a \mid V_{bc}u_{bc}\varphi_a\rangle$. It corresponds to



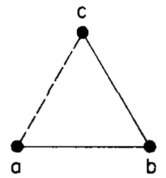
and vanishes upon integration over b or c. So do all elements of this type.

A third type is exemplified by $\langle u_{ab}\varphi_c \mid V_{ab}u_{ac}\varphi_b\rangle$. Its diagram is



It is zero because φ_c and u_{ac} are orthogonal with respect to integration over the coordinates of c.

We are thus left with six matrix elements of the form



They are

$$E_3 = 2\langle u_{ab}\varphi_c \mid V_{ac}u_{bc}\varphi_a\rangle + 2\langle u_{ab}\varphi_c \mid V_{bc}u_{ac}\varphi_b\rangle + 2\langle u_{ac}\varphi_b \mid V_{ab}u_{bc}\varphi_a\rangle. \quad (21)$$

The u functions, which must be obtained as solutions of (18), are most simply constructed as expansions involving φ_a, φ_b, and their excited states. If, writing $\varphi_a{}^\lambda$, $\varphi_b{}^\mu$ for the latter, we put

$$u_{ab} = \varphi_a\varphi_b + \sum_{\lambda\mu} a_{\lambda\mu}\varphi_a{}^\lambda\varphi_b{}^\mu$$

and substitute in (18), we find after the usual integrations

$$a_{\lambda\mu} = -\langle\lambda\mu\,|\,V_{ab}\,|\,00\rangle/(\Delta_a{}^\lambda + \Delta_b{}^\mu)$$

with the excited-state energies $\Delta_a{}^\lambda = E_a{}^\lambda - E_a{}^0$, $\Delta_b{}^\mu = E_b{}^\mu - E_b{}^0$.

The first integral in (21), which we now evaluate, involves the factor

$$\int u_{ab}^* u_{bc}\,d\tau_b = \varphi_a{}^*\varphi_c{}^* + \sum_{\lambda\mu\nu} \frac{\langle 00\,|\,V_{ab}\,|\,\lambda\mu\rangle}{\Delta_a{}^\lambda + \Delta_b{}^\mu}\,\frac{\langle\mu\nu\,|\,V_{bc}\,|\,00\rangle}{\Delta_b{}^\mu + \Delta_c{}^\nu}$$

and

$$\langle u_{ac}\varphi_c\,|\,V_{ac}u_{bc}\varphi_a\rangle = \sum_{\lambda\mu\nu} \frac{\langle 00\,|\,V_{ab}\,|\,\lambda\mu\rangle\langle\lambda 0\,|\,V_{ac}\,|\,0\nu\rangle\langle\mu\nu\,|\,V_{bc}\,|\,00\rangle}{(\Delta_a{}^\lambda + \Delta_b{}^\mu)(\Delta_b{}^\mu + \Delta_c{}^\nu)}. \tag{22}$$

With suitable permutations of subscripts we obtain the other terms in Eq. (21). In evaluating the summations we follow Kihara (1958). V_{ab} is expressed in the form

$$V_{ab} = \mathbf{p}_a\cdot T_{ab}\cdot\mathbf{p}_b \tag{23}$$

which is equivalent to (9a) provided $\mathbf{p}$ denotes the dipole moment operator of an atom and T_{ab} the *dyadic* $(1 - 3\mathbf{e}_{ab}\mathbf{e}_{ab})/R_{ab}^3$. The dots signify ordinary dot products between vectors, 1 is the unit dyadic, and $\mathbf{e}_{ab}$ the unit vector pointing from a to b.

Note the following rules for dyadics, A, B. In writing them we employ dyadic notation on the left and tensor notation on the right of the equations:

$$(A\cdot B)_{ij} = \sum_\lambda A_{i\lambda}B_{\lambda j}$$

$$A{:}B = \sum_{\lambda\mu} A_{\lambda\mu}B_{\lambda\mu}$$

$$1\cdot A = A$$

$$1{:}A = \operatorname{Tr} A.$$

If $\mathbf{x}$ and $\mathbf{y}$ are vectors, we have $\mathbf{x}\cdot A\cdot\mathbf{y} = \mathbf{x}\mathbf{y}{:}A$.

Now the summations in Eq. (22) include those over "magnetic" quantum numbers, which are equivalent to rotations in space (correspond to an irreducible representation of the rotation group). Hence a dyadic like

$$\sum \langle 0 | \mathbf{p}_a | \lambda \rangle \langle \lambda | \mathbf{p}_a | 0 \rangle,$$

the sum extending over the space quantum numbers, can at once be replaced by $\sum \langle 0 | p_{ax} | \lambda \rangle \langle \lambda | p_{ax} | 0 \rangle \mathbf{1}$.

Thus we find

$$\langle u_{ac} \varphi_c | V_{ac} u_{bc} \varphi_a \rangle = \sum_{\lambda \mu \nu} \frac{|\langle 0 | p_{ax} | \lambda \rangle|^2 |\langle 0 | p_{bx} | \mu \rangle|^2 |\langle 0 | p_{cx} | \nu \rangle|^2}{(\Delta_a{}^\lambda + \Delta_b{}^\mu)(\Delta_b{}^\mu + \Delta_c{}^\nu)} \times \text{Trace}\,(T_{ab} \cdot T_{bc} \cdot T_{ca}). \qquad (24)$$

For the trace one obtains

$$\begin{aligned} \text{Tr}(T_{ab} \cdot T_{bc} \cdot T_{ca}) = 3(R_{ab} R_{bc} R_{ac})^{-3} \{ 1 - 3 + 3[(\mathbf{e}_{ab} \cdot \mathbf{e}_{ac})^2 + (\mathbf{e}_{ab} \cdot \mathbf{e}_{bc})^2 \\ + (\mathbf{e}_{bc} \cdot \mathbf{e}_{ac})^2] - 9(\mathbf{e}_{ab} \cdot \mathbf{e}_{ac})(\mathbf{e}_{ab} \cdot \mathbf{e}_{bc})(\mathbf{e}_{bc} \cdot \mathbf{e}_{ac}) \}. \end{aligned}$$

The dot products can be expressed in terms of the inner angles of the triangle *abc*:

$$\cos \theta_a = -\mathbf{e}_{ab} \cdot \mathbf{e}_{ac}, \text{ etc.,}$$

and

$$\cos^2 \theta_a + \cos^2 \theta_b + \cos^2 \theta_c = 1 - 2 \cos \theta_a \cos \theta_b \cos \theta_c.$$

On using these relations we find

$$\text{Tr}(T_{ab} \cdot T_{bc} \cdot T_{ca}) = 3(R_{ab} R_{bc} R_{ac})^{-3} (3 \cos \theta_a \cos \theta_b \cos \theta_c + 1).$$

There now remains the calculation of the two last terms of Eq. (21). This merely duplicates the foregoing procedure and leads again to (24), but with properly modified denominators. The final result is therefore:

$$\begin{aligned} E_3 = {} & \frac{6(3 \cos \theta_a \cos \theta_b \cos \theta_c + 1)}{R_{ab}^3 R_{ac}^3 R_{bc}^3} \\ & \times \sum_{\lambda \mu \nu} |\langle 0 | p_{ax} | \lambda \rangle|^2 |\langle 0 | p_{bx} | \mu \rangle|^2 |\langle 0 | p_{cx} | \nu \rangle|^2 \\ & \times \{ [(\Delta_a{}^\lambda + \Delta_b{}^\mu)(\Delta_b{}^\mu + \Delta_c{}^\nu)]^{-1} + [(\Delta_a{}^\lambda + \Delta_b{}^\mu)(\Delta_a{}^\lambda + \Delta_c{}^\nu)]^{-1} \\ & + [(\Delta_a{}^\lambda + \Delta_c{}^\nu)(\Delta_b{}^\mu + \Delta_c{}^\nu)]^{-1} \}. \end{aligned} \qquad (25)$$

The first factor, containing the θ's, determines the sign of the nonadditive contribution to the triple-dipole effect; it is positive when every $\theta < 117°$, negative if one $\theta > 126°$.

A simple result holds for isotropic oscillators, where $\Delta_a^{\lambda} = h\nu_a\delta_{\lambda 1}$ (since **p** connects the ground state with the first excited state only) and the polarizability $P_a = \frac{2}{3}\langle 0 | p_a^2 | 0 \rangle / h\nu_a$. In this case Eq. (25) reduces to

$$E_3 = \tfrac{3}{2}h \frac{(\nu_a + \nu_b + \nu_c)\nu_a\nu_b\nu_c}{(\nu_a + \nu_b)(\nu_a + \nu_c)(\nu_b + \nu_c)} P_a P_b P_c \frac{3\cos\theta_a \cos\theta_b \cos\theta_c + 1}{R_{ab}^3 R_{ac}^3 R_{bc}^3}. \tag{26}$$

In Fig. 1 we have plotted the two three-body effects, E_3 and the complicated result of Wojtala, for three hydrogen atoms in an equilateral triangle configuration. Ordinates represent the ratio of three-body to two-body energies, abscissas are lengths of the triangle sides. The third curve is the overlap integral, $\Delta^2 = e^{-2\rho}(1 + \rho + \rho^2/3)^2$, $\rho = R/a_0$. It was included to show that the nonadditive second-order effect is confined to the region where Δ is appreciable. Here, however, neglect of intermolecular

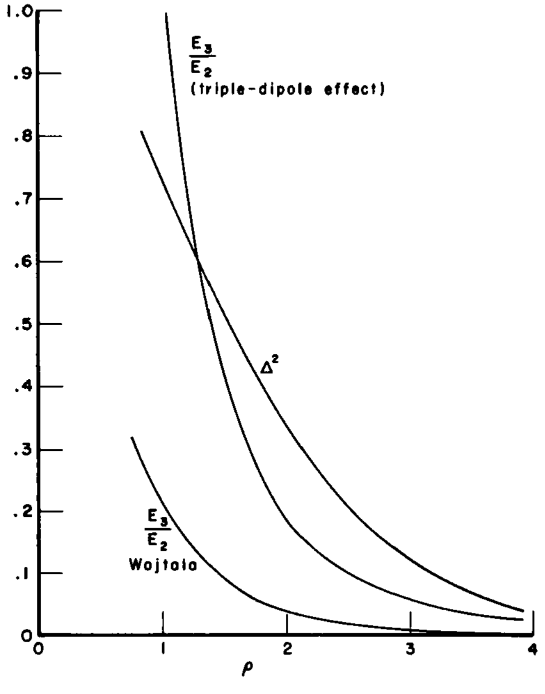


Fig. 1 Long-range, three-body effects in hydrogen.

electron exchange, i.e., the exclusion principle, is no longer legitimate. Hence the results of Wojtala are physically not very meaningful, and their lesson is to remind us that large nonadditive effects occur at small distances of separation where states of the separable form employed so far are inadequate.

The triple-dipole effect, too, is of no interest at intermolecular distances where Δ is large; it may be seen, however, that its range is longer. At intermediate distances, therefore, it is worth consideration. Indeed Graben and Present (1962) have applied Axilrod's formulas in a calculation of the third virial coefficient for Ne, Ar, Kr, and Xe, obtaining better agreement with experimental values than is afforded by additive van der Waals forces alone. In another study Kestner and Sinanoğlu (1963) have calculated "effective" dispersion forces between two molecules embedded in a nonpolar medium. They show, using the triple-dipole interaction between two molecules and their nearer solvent neighbors, that pair potentials are reduced by three-body effects as much as 32% (in carbon tetrachloride). Dispersion forces between (lateral base) pairs of atoms in a DNA double helix decrease by about 28% when the four adjacent bases of each pair, which have large polarizabilities, are included as third bodies in the calculation. How these forces are further modified by solvents is discussed by Sinanoğlu *et al.* (1964). Higher orders of perturbation theory beyond the third, based on the dipole-dipole interaction alone, have been computed with the use of the oscillator model by Bade (1957) and applied to a linear lattice by Bade and Kirkwood (1957) and by Zwanzig (1963). An extension of this work to include the effects of distant perturbers was made by Doniach (1963). Finally we record a publication by Ayres and Tredgold (1956) in which the three-body asymptotic interaction up to the dipole-dipole-quadrupole term is examined.

These three-body effects contribute strongly to physical adsorption, where the third body is the solid. Sinanoğlu and Pitzer (1960), McLachlan (1964), and Mavroyannis (1963) have considered various aspects of this problem. Experimental evidence here is in accord with a large three-body contribution (Johnson and Klein, 1964; Barker and Everett, 1962; Sams *et al.*, 1962; Steele and Kebbekus, 1965). The application of all these results involves regions of intermolecular distances in which overlap cannot be neglected with confidence. Thus, while quantitative conclusions represent important indications of the nonadditivity of even long-range effects, they do not tell the entire story and must not be trusted in detail. Hence we turn now to the calculation of first-order effects at small separations, using properly antisymmetrized electron wave functions.

III. Short-Range, Three-Body Forces

In dealing with multiple interactions it becomes essential to use a convenient and nonredundant notation. No confusion will arise if we use the letters a, b, and c in two senses: as the points at which the nuclei of the three atoms are situated and as atomic orbitals constructed about these points. When signifying the latter they will usually carry arguments specifying the electron occupying the orbital, e.g., $a(1)$. Furthermore, to simplify writing the Hamiltonian, we abbreviate

$$\frac{e^2}{r_{ai}} \equiv \alpha_i, \qquad \frac{e^2}{r_{bj}} \equiv \beta_j, \quad \text{etc.,} \qquad \text{and} \qquad \frac{e^2}{r_{ij}} \equiv \rho_{ij}. \tag{27}$$

Here r_{ai} is the distance between a and electron i, r_{ij} that between electrons i and j.

In the following we shall encounter a variety of elementary exchange integrals, which can be classified into two-center and three-center integrals, with a possible subdivision into one-electron and two-electron classes. These can be labeled perspicuously in a manner proposed for the more complicated four-center problem (Margenau, 1943), viz.,

$$(a\beta c) \equiv \int a^*(1)\frac{e^2}{r_{b1}}\, c(1)\, d\tau_1$$

$$(ab\rho bc) \equiv \int a^*(1)b^*(2)\frac{e^2}{r_{12}}\, b(1)c(2)\, d\tau_1\, d\tau_2, \qquad \text{etc.}$$

As usual, the overlap integral is denoted by

$$\Delta_{ab} \equiv (ab) = \int a^*(1)b(1)\, d\tau_1.$$

As to symmetry, we note that

$$(a\beta c) = (c\beta a)$$

$$(a\alpha b) = (a\beta b)$$

$$(ab\rho bc) = (bb\rho ac) = (ac\rho bb) = (bc\rho ab) = (ba\rho cb)$$

provided the orbitals are real.

All one-center integrals, like $(a\alpha a)$ and $(b\beta b)$, are of course equal and independent of the position of the nuclei. All two-center integrals,

$$(a\beta a), \quad (a\beta b), \quad (ab\rho ab), \quad \text{and} \quad (ab\rho ba)$$

occur in the pair interaction; they are well-known from the Heitler–London theory of H_2. Three-center integrals fall into three classes, characterized by

$$(a\beta c), \quad (ac\rho bc), \quad (ac\rho cb).$$

Our knowledge concerning these integrals is still incomplete. They are discussed by Slater (1963) and in greater detail elsewhere (Alder *et al.*, 1962).

The Hamiltonian for three interacting, *one-electron atoms* is

$$H = H_0 + V.$$

We suppose that $H_0 = H_a + H_b + H_c$, $H_a a(1) = E_a a(1)$, etc. Then, as before,

$$\begin{aligned} V &= V_{ab} + V_{ac} + V_{bc} \\ V_{ab} &= e^2 R_{ab}^{-1} + \rho_{12} - \alpha_2 - \beta_1 \\ V_{ac} &= e^2 R_{ac}^{-1} + \rho_{13} - \alpha_3 - \gamma_1 \\ V_{bc} &= e^2 R_{bc}^{-1} + \rho_{23} - \beta_3 - \gamma_2. \end{aligned} \tag{28}$$

The normalized, unperturbed state of the triplet is

$$\Psi_0 = \sqrt{\tfrac{1}{6}}(1 - \delta_{abc})^{-1/2} \mathscr{A} a(1) b(2) c(3) \tag{29}$$

where $\mathscr{A}$ is the antisymmetrizing operator and

$$\delta_{abc} = \Delta_{ab}^2 + \Delta_{ac}^2 + \Delta_{bc}^2 - 2\Delta_{ab}\Delta_{ac}\Delta_{bc}. \tag{30}$$

Straightforward substitution of (28) and (29) and use of our symmetry rules leads to

$$\begin{aligned} \langle 0 | H | 0 \rangle - 3E_H = e^2 R_{ab}^{-1} + (1 - \delta_{abc})^{-1} \{ & (\Delta_{ac}^2 + \Delta_{bc}^2 - 2)(a\beta a) \\ & + 2(\Delta_{ab} - \Delta_{ac}\Delta_{bc})(a\beta b) \\ & + (\Delta_{ac} - \Delta_{ab}\Delta_{bc})(a\beta c) + (\Delta_{bc} - \Delta_{ab}\Delta_{ac})(b\alpha c) \\ & + (ab\rho ab) - (aa\rho bb) + \Delta_{ac}[(ab\rho bc) - (ab\rho cb)] \\ & + \Delta_{bc}[(aa\rho bc) - (ab\rho ac)] \} + \cdots + \cdots. \end{aligned} \tag{31}$$

The two sets of terms not written are constructed from those displayed by interchanging a with c and α with γ, then b with c and β with γ. Here $E_H = E_a = E_b = E_c$ represents the energy of a hydrogen atom. If atom c is removed to infinity, every term involving c in this expression drops out and we find

$$E_{ab} = \frac{e^2}{R_{ab}} + (1 - \Delta_{ab}^2)^{-1} \{ -2(a\beta a) + 2\Delta_{ab}(a\beta b) + (ab\rho ab) - (aa\rho bb) \} \tag{32}$$

which is the repulsive Heitler–London energy between the two atoms.

The specific three-body contribution over and above the energy of pairs is

$$\langle 0 | H | 0 \rangle - E_a - E_b - E_c - E_{ab} - E_{ac} - E_{bc} \equiv E_{abc}. \tag{33}$$

Thus the total energy is

$$\langle 0 | H | 0 \rangle \equiv E = E_a + E_b + E_c + E_{ab} + E_{ac} + E_{bc} + E_{abc}. \tag{34}$$

It is clearly of interest to know whether this series can be extended and, if so, whether it converges. For instance, one might suppose that the total energy of n interacting atoms can be written as a series

$$E = \sum_r E_r + \sum_{r<s} E_{rs} + \sum_{r<s<t} E_{rst} + \cdots + E_{rst\ldots n} \tag{35}$$

in which the sums have progressively smaller values. Very little is known about this at the present time, but we shall return to this problem below.

The evaluation of Eq. (31) for specific configurations of H atoms, though not difficult, has not been carried out to our knowledge.[1] While it represents a possible mode of interaction of three H atoms, namely, that in which all electron spins are parallel, experimental data are lacking. The effect is interesting for He, however, and Rosen was the first to perform a calculation analogous to the above for six electrons attached to three He nuclei (Rosen, 1953). His result can be written in fairly simple form, as follows.

Let ψ_a, ψ_b, and ψ_c be antisymmetric functions for atomic helium, each composed of two atomic orbitals. Write $\mathscr{A}^{ab}$ for the interatomic antisymmetrizer, $\sum_\lambda (-1)^{\lambda_{ab}} P_{\lambda_{ab}}$, between atoms a and b. (The $P_{\lambda_{ab}}$ are all permutations of electrons *between* a and b.) Similarly, $\mathscr{A}^{abc}$ is the triatomic antisymmetrizing operator. Further, introduce

$$\begin{aligned}
S_{ab} &= \langle \psi_a \psi_b | \mathscr{A}^{ab} \psi_a \psi_b \rangle, \qquad \psi_a \psi_b \psi_c \equiv \Psi \\
S_{abc} &= \langle \Psi | \mathscr{A}^{abc} \Psi \rangle, \qquad S = 1 + S_{ab} + S_{ac} + S_{bc} + S_{abc} \\
\bar{H} &= \langle \Psi | H \mathscr{A}^{abc} \Psi \rangle \\
Q_a &= \langle \Psi | (V_{ab} + V_{ac}) \Psi \rangle \\
Q_b &= \langle \Psi | (V_{ab} + V_{bc}) \Psi \rangle \\
Q_c &= \langle \Psi | (V_{ac} + V_{bc}) \Psi \rangle.
\end{aligned}$$

---

[1] McGinnies and Jansen (1956, p. 1301) examine a simplified version of (33) in which atoms a and b are close together, but c is far enough away to permit a multipole expansion.

Then

$$E_{abc}S = \bar{H} + Q_a + Q_b + Q_c - \delta_{abc}(E_a + E_b + E_c + E_{ab} + E_{ac} + E_{bc})$$
$$-(S_{ac} + S_{bc})E_{ab} - (S_{ab} + S_{bc})E_{ac} - (S_{ab} + S_{ac})E_{bc}. \qquad (36)$$

The quantities $\bar{H}$ and Q break up into elementary exchange integrals of the type discussed, most but not all of which have been tabulated.

Rosen evaluated Eq. (36) for two configurations, an equilateral triangle and three atoms equally spaced on a line. For the ratio of triple to pairwise interactions he finds (for $ZR > 3a_0$)

$$\frac{E_{abc}}{E_{ab} + E_{ac} + E_{bc}} = -1.15e^{-0.33(R_{ab}+R_{ac}+R_{bc})/a_0} \quad \text{(equilateral triangle)} \qquad (37)$$

$$= +9.8e^{-0.66(R_{ab}+R_{ac}+R_{bc})/a_0} \quad \text{(linear array).} \qquad (38)$$

The triangular configuration has maximum overlap, and it is therefore not surprising that (37) is larger than (38) for interatomic distances where nonadditivity matters. Unexpected is the change of sign. It looks as if in the triangular disposition the electrons enjoyed enough freedom to weaken the demands of the Pauli principle, which causes repulsion in the forces between pairs. The linear arrangement, on the contrary, offers no such freedom, in fact increases the repulsion to a small extent. It is also noteworthy that the sign of the nonadditive component coming from the present, first-order interactions agrees with that of the triple-dipole effect: it, too, is negative for $\theta = 60°$, positive for $\theta = 180°$.

The problem of three He atoms was also investigated by Shostak (1955) who employed molecular orbitals (linear combination of atomic orbitals) in his calculation. He evaluated results only for Rosen's linear configuration, where molecular orbitals are likely to yield better precision. While in general agreement with Rosen's conclusions, his method gives larger nonadditive effects—at the shortest distances considered—by almost a factor 2.

Three-body interactions were studied in connection with crystal properties in a well-known publication by Löwdin (1948),[1a] who found in them the cause of departures from Cauchy's relations (between the elastic constants of crystals). Starting from a complete many-body Hamiltonian he arrives at terms corresponding to nonadditive, three-body interactions which account for his interesting findings. His results, though obtained by an approach that is somewhat foreign to the methods employed in

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[1a] Later work suggested by these investigations, but using a macroscopic model (polarizabilities) may be found in Linderberg (1964), Linderberg and Bystrand (1964).

this article, are analogous to the three-body interactions discussed in the sequel. A careful comparison, which would be illuminating, has apparently not been made.

More recently McGinnies and Jansen (1956) seized upon many-body interactions to explain a renowned paradox in crystal structure theory. An illuminating account of it is given in a recent review (Jansen, 1965). The facts to be explained are these.[2]

Among the rare gas elements only He crystallizes in a hexagonal lattice; all other form face-centered cubic crystals. Pair potentials, computed in the usual way or derived semiempirically, always favor the hexagonal lattice. That is to say, the hexagonal configuration invariably produces the lowest value for the Gibbs free energy at 0°K. Thus the behavior of He seems regular, but that of the heavier rare gases anomalous. The effect computed by Rosen for He *in*creases the stability of the hexagonal lattice and therefore provides little hope of accounting for the crystal forms of Ne, Ar, Kr, and Xe. To certify this expectation Jansen (1965) and Zimering (1965) performed a first-order calculation of the kind outlined above for three H atoms, but with the following modifications for the sake of feasibility and application to heavier (spherical) atoms. Instead of the full shell of electrons in each atom they assume one to be effective in bringing about the interaction. This leads to Eqs. (31) and (32). In evaluating the integrals which appear there Jansen uses not hydrogen functions but Gaussian exponentials, i.e., simple harmonic oscillator functions of the form

$$a(1) = \beta^{3/2}\pi^{-3/4}e^{-B^2r_{a1}^2/2} \tag{39}$$

for they permit all integrals to be expressed in a simple form. The parameter B is obtained by fitting a formula for the dispersion forces, computed with function (39), to the empirical van der Waals potential. Since this model is useful in this and other respects we list Jansen's expressions for the integrals that appear:

$$\Delta_{ab} = e^{-B^2R_{ab}^2/4}.$$

Introducing $F(x^2) \equiv 2e^2/\sqrt{\pi}\,x\int_0^x e^{-u^2}du \equiv e^2\,\mathrm{erf}(x)/x$ one finds for the other integrals

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[2] The actual situation may be more complex than is suggested below. See an important note by Meyer *et al.* (1965).

$$
\begin{aligned}
(a\beta a) &= BF(B^2R^2_{ab}) \\
(a\alpha b) &= \Delta_{ab}BF(B^2R^2_{ab/4}) \\
(b\alpha c) &= \Delta_{bc}BF(B^2R^2_{a\overline{bc}}) \\
(a\beta c) &= \Delta_{ac}BF(B^2R^2_{b\overline{ac}}) \\
\sqrt{2}(ab\rho ab) &= BF(B^2R^2_{ab/2}) \\
\sqrt{2}(aa\rho bb) &= \frac{2e^2}{\sqrt{\pi}}Be^{-B^2R^2_{ab}/2} \qquad (40) \\
\sqrt{2}(ab\rho ac) &= \Delta_{bc}BF(B^2R^2_{a\overline{bc}/2}) \\
\sqrt{2}(ab\rho cb) &= \Delta_{ac}BF(B^2R^2_{b\overline{ac}/2}) \\
\sqrt{2}(aa\rho bc) &= \Delta_{ab}\Delta_{ac}BF(B^2R^2_{bc/8}) \\
\sqrt{2}(ab\rho bc) &= \Delta_{ab}\Delta_{bc}BF(B^2R^2_{ac/8}).
\end{aligned}
$$

Here $R_{a\overline{bc}}$ denotes the distance from a to the midpoint of the line joining b and c.

Our account of Jansen's calculation differs from his version in these respects. Instead of computing $\langle 0|H|0\rangle - 3E_H$ he claims to calculate $\langle 0|V|0\rangle$, which he obtains by adding $\langle 0|V_{ab}|0\rangle$ to the two permuted expressions. The form of V_{ab} is given in Eq. (28). Now, as shown in a forthcoming publication (Margenau, 1966), $\langle 0|V_{ab}|0\rangle$ when properly computed is without meaning, for it does not go to zero when R_{ab} becomes large. Neither do $\langle 0|V_{ac}|0\rangle$ nor $\langle 0|V_{bc}|0\rangle$. Evidently, therefore, the meaning of these terms must have been changed somewhere in the calculation (e.g., use of $\mathscr{A}V$ instead of V in computing $\langle 0|V|0\rangle$ would have removed the finite part at $R\to\infty$). At any rate, the result given by Jansen is indeed $\langle 0|H|0\rangle - 3E_H$, and is correct. The use of oscillator functions, whose eigenvalues are not E_H, introduces further complications from the point of view of perturbation theory. But the procedure discussed seems very difficult to improve.

We have also noted elsewhere (Margenau and Rosen, 1953) that questions as to the meaning of intermolecular potentials arise when $H_0\varphi_0 \neq E_0\varphi_0$. They emerge here. The quantity calculated with the use of oscillator functions is the one denoted by $\tilde{V}$ in the reference above.

Figure 2 illustrates magnitude and angular dependence of the three-body effect under study. The curves are drawn for the isosceles triangle, the distances being those appropriate for solid argon and xenon, and fractional energies are plotted as functions of the opening, θ, of the triangle. Between $\theta \approx 60°$ and $\theta \approx 110°$ the nonadditive contribution is negative, at larger angles it is positive; the situation found by Rosen is reproduced.

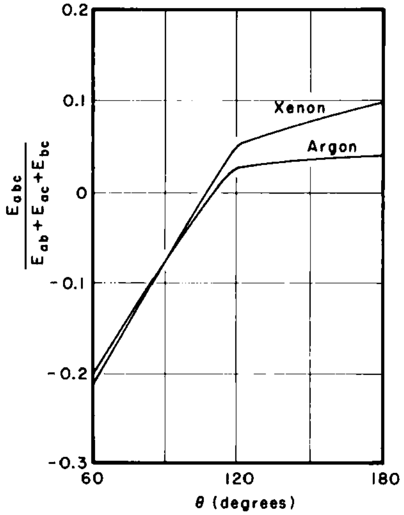

Fig. 2 First-order, three-body effects in argon and neon crystals.

When applying this theory to the crystal problem it is evidently necessary to accept Eq. (35), supposing that terms beyond the third on the right can be neglected. Thus, in examining the stability of different lattices, Jansen selects a central atom and first, computes all pairwise interactions with its nearest neighbors ($\sum_{r<s} E_{rs}$); then he constructs all possible triangles involving the central atom and two nearest neighbors and calculates $\sum E_{rst}$. When this is done it becomes quite clear that the hexagonal close-packed configuration is the stable one.[3]

[3] The reasoning is this. The Gibbs free energy is $G = U - TS + PV$, U being the crystal energy. The comparison involves no volume changes; hence PV drops out. T can be put equal to zero if the crystal structure examined is the same as it is at absolute zero. Indications are that this is true. Thus G becomes U. But U consists of two parts: the static crystal energy and the zero point energy of its constituents. On this last, careful calculations, mentioned in Jansen (1965), exist suggesting that it cannot cause the difference between the two structures. Hence Jansen holds that part of U which comes from all static interactions responsible for the lattice type.

Hence the paradox remains. Let us recall, however, that the main forces which hold a rare gas crystal together are those calculated in second order. Indeed at interatomic distances prevailing in a lattice the attractive second-order energies are greater, in absolute value, than the first-order exchange forces. Jansen and Zimering (1963; Jansen, 1963, 1964) therefore investigate the second-order exchange effect arising in the interaction of three model atoms whose charges are distributed in accordance with (39).

They apply perturbation theory in the usual way, writing

$$= -(\bar{E})^{-1}[\langle 0 | V_{abc}^2 | 0 \rangle - \langle 0 | V_{abc} | 0 \rangle^2],$$

$$E_{2,abc} = \sum_{\lambda}{}' \frac{\langle 0 | V_{abc} | \lambda \rangle \langle \lambda | V_{abc} | 0 \rangle}{E_0 - E_\lambda}$$

replacing $(E_0 - E_\lambda)^{-1}$ by some undefined average $\bar{E}^{-1}$. This suffers from lack of meaning, as before. It appears that what Jansen and Zimering actually calculate is

$$-(\bar{E})^{-1}[\langle 0 | (H - E_\infty)^2 | 0 \rangle - \langle 0 | H - E_\infty | 0 \rangle^2] \tag{41}$$

where $E_\infty = \lim_{R \to \infty} E = E_a + E_b + E_c$. This formula can be justified as follows.

Perturbation theory depends on the availability of a ϕ_0 which is an eigenfunction of some Hamiltonian H_0, preferably, in this case, of $H_a + H_b + H_c$. An antisymmetrized set of atomic orbitals like (29) is far from satisfying these requirements, nor does it yield $\langle 0 | H_a + H_b + H_c | 0 \rangle = E_a + E_b + E_c$. Hence the best one can do is to employ the method of linear variation functions, assuming the trial function to be

$$\phi = \phi_0 + c\phi_1. \tag{42}$$

Concerning ϕ_1 we suppose (a) that it is orthogonal to ϕ_0, and (b) that ϕ_0 and ϕ_1 together form a complete set. This, of course, is never true, but is equivalent to the Unsöld approximation, i.e., to replacing every $(E_0 - E_\lambda)^{-1}$ by $\bar{E}^{-1}$.

Choice of (42) leads to the condition for E:

$$\begin{vmatrix} H_{00} - E & H_{01} \\ H_{10} & H_{11} - E \end{vmatrix} = 0.$$

We may neglect the dependence of $H_{11} - E$ upon the R and write $H_{11} - E \equiv \bar{E}$. Then $E = H_{00} - \bar{E}^{-1} |H_{01}|^2 = H_{00} - \bar{E}^{-1}[(H^2)_{00} - H_{00}^2]$, since $|H_{00}|^2 + |H_{10}|^2 = (H^2)_{00}$. Therefore the van der Waals energy

$$E - E_\infty = \langle 0 | H - E_\infty | 0 \rangle - \frac{(H^2)_{00} - H_{00}^2}{\bar{E}}.$$

We recognize the first expression on the right as the first-order energy, Eq. (31). Hence the "second-order" term is

$$E_{2,abc} = -\frac{(H^2)_{00} - H_{00}^2}{\bar{E}}$$

and this is identical with Eq. [41].

The calculation of $(H^2)_{00}$ is lengthy and requires electronic computation. Details are found in the work of Jansen (1964), Lombardi and Jansen (1964), and Zimering (1965). They remove the uncertainty with respect to the value of $\bar{E}$ by forming the ratio $E_{2,abc}/E_{2,abc}^0$, the denominator being the long-range, additive van der Waals energy, $E_{2,ab} + E_{2,ac} + E_{2,bc}$, as given by London's formula. The latter also contains an unknown energy difference; it is taken to be equal to the present $\bar{E}$ and therefore both drop out of the calculation. The result for $E_{2,abc}/E_{2,abc}^0$ is amazingly similar to the curves of Fig. 2. In Fig. 3 we plot this ratio together with $E_{1,abc}/E_{1,abc}^0$ (which is the ordinate of Fig. 2) for argon. The triangle is again an isosceles, and the value of BR has been chosen as 2.4, which corresponds to the lattice spacing of solid argon.

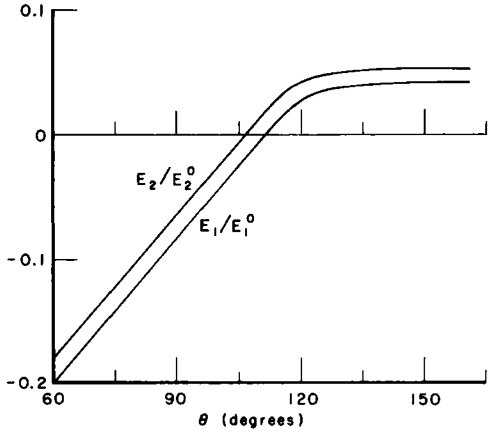

Fig. 3 First- and second-order, three-body effects in argon crystals.

Jansen and his collaborators perform extensive calculations of this type for all the triangles involving nearest neighbors which are encountered in rare gas crystals, both for the hexagonal and for the face-centered cubic configuration. Upon their results, which are typified by Fig. 3, they base the following remarkable conclusions.

First-order and second-order ratios (Fig. 3) are practically the same when plotted as functions of θ. Since $E^0_{2,abc}$ is negative while $E_1{}^0$ is positive, first-order nonadditive effects increase repulsion and second-order effects reduce it where both ratios are positive. While the precise manner of compounding the two effects is subject to ambiguities, it is nevertheless clear that in the region of the van der Waals minimum $E_2{}^0$ is numerically about twice as large as $E_1{}^0$; hence the second-order correction, which introduces predominantly attraction, carries twice the weight of the first. The consequences flowing from the analysis of $E_{1,abc}$ must therefore be reversed, and the net result is that, because of the second-order three-body interactions, rare gas crystals favor the face-centered cubic configuration.

This leaves He as the sole offender. In this case, however, one can see from Rosen's and Shostak's calculation that third-order effects are minimal, for the spacing of atoms is wide and the atoms are small. Jansen shows that for large BR the ratio of $(E_{1,abc}+E_{2,abc})/E^0_{abc}$ becomes small. Hence the three-body correction seems insufficient to make the fcc configuration the stabler one for He.

Having thus regularized the anomalies[4] of the rare gas crystals he turns his attention to the alkali halides and indicates how similar considerations produce gratifying agreement with observations. Their detailed presentation is beyond the scope of this article.

In view of these successes, a closer scrutiny of the basis on which the many-body theory rests becomes essential. In the next section, therefore, we present some new calculations designed to throw light on the convergence of the expansion of E as a series of multiparticle terms, Eq. (35). We shall extend previous treatments to include four-atom interactions In a manner similar to Jansen's, a determination of the nonadditive four-body components will be made to see if, perchance, it remains smaller than the three-body component. For obvious practical reasons the calculation of four-body forces will be restricted to one order of perturbation theory, the first. The fact that the "second-order contribution" to three-body forces is, as we have seen, even greater than the first at distances near the lattice parameter may seem disturbing. Nevertheless it is interesting to know what happens within one consistent scheme of computation, and our results do become physically meaningful at small values of R, where first-order exchange forces always predominate.

---

[4] It might be noted, however, that the observations on which the foregoing reasoning is based require further scrutiny in view of the findings of Meyer *et al.* (1965).

IV. Short-Range, Four-Body Forces

To the three atoms considered in the previous section we add a fourth, locate it at d and describe it by the orbital $d(4)$. The total Hamiltonian is

$$H = H_a(1) + H_b(2) + H_c(3) + H_d(4) + V_{ab}(2, 1) + V_{ac}(3, 1) + V_{ad}(4, 1)$$
$$+ V_{bc}(3, 2) + V_{bd}(4, 2) + V_{cd}(4, 3) \tag{43}$$

where the V are defined in a manner analogous to Eq. (28) and $H_d(i)d(i) = E_d d(i)$. The normalized state function is, in the notation of Eq. (29),

$$\Psi_0 = \sqrt{\frac{1}{4!}}(1 - \delta_{abcd})^{-1/2}\mathscr{A}a(1)b(2)c(3)d(4) \tag{44}$$

where

$$\delta_{abcd} = 1 - \int a(1)b(2)c(3)d(4)\mathscr{A}a(1)b(2)c(3)d(4)\,d\tau$$
$$= (\Delta_{ab}^2 + \Delta_{ac}^2 + \Delta_{ad}^2 + \Delta_{bc}^2 + \Delta_{bd}^2 + \Delta_{cd}^2) - (\Delta_{ab}^2\Delta_{cd}^2 + \Delta_{ac}^2\Delta_{bd}^2 + \Delta_{ad}^2\Delta_{bc}^2)$$
$$-2(\Delta_{ab}\Delta_{ac}\Delta_{bc} + \Delta_{ab}\Delta_{ad}\Delta_{bd} + \Delta_{ac}\Delta_{ad}\Delta_{cd} + \Delta_{bc}\Delta_{bd}\Delta_{cd})$$
$$+ 2(\Delta_{ab}\Delta_{ac}\Delta_{bd}\Delta_{cd} + \Delta_{ab}\Delta_{ad}\Delta_{bc}\Delta_{cd} + \Delta_{ac}\Delta_{ad}\Delta_{bc}\Delta_{bd}). \tag{45}$$

A clear understanding of the meaning of the terms in Eq. (35) is necessary; hence we insert a few further comments. Let the total energy of n interacting bodies of the same kind be $E(n)$; we shall denote by $E^{(\alpha)}(n)$ the α-body component of $E(n)$. $E^{(n)}(n)$ derives its meaning only from $E(n)$ and cannot be separately defined. We label the bodies a, b, c, ... n and understand that indices like i, j, k take on values from a to n. One may then write

$$E^{(1)}(1) = E_a = E_b = \cdots E_n,$$

where E_a, etc., are the energies of the isolated bodies,

$$E^{(1)}(n) = nE^{(1)}(1) = nE_a$$

$$E^{(2)}(2) = E_{ab}, \qquad E^{(2)}(n) = \frac{1}{2!}\sum_{i \neq j} E_{ij}$$

$$E^{(3)}(3) = E_{abc}, \qquad E^{(3)}(n) = \frac{1}{3!}\sum_{i \neq j \neq k} E_{ijk}, \text{ etc.}$$

Then

$$E(n) = \sum_{\alpha=1}^{n} E^{(\alpha)}(n). \tag{46}$$

In the four-body case

$$E(4) = 4E_a + \tfrac{1}{2}\sum_{i \neq j} E_{ij} + \tfrac{1}{6}\sum_{i \neq j \neq k} E_{ijk} + E_{abcd}. \tag{47}$$

The total interaction energy may be written as

$$E(4) - 4E_a = \langle 0 | H | 0 \rangle - 4E_a.$$

Use of (43) leads to

$$\begin{aligned} E(4) - 4E_a = (1 - \delta_{abcd})^{-1} \int & a(1)b(2)c(3)d(4)\mathscr{A}\{[V_{ab}(2, 1) + V_{ac}(3, 1) \\ & + V_{ad}(4, 1) + V_{bc}(3, 2) + V_{bd}(4, 2) + V_{cd}(4, 3)] \\ & \times a(1)b(2)c(3)d(4)\}\, d\tau. \end{aligned} \tag{48}$$

We now abbreviate

$$(1 - \delta_{abcd})^{-1} \int a(1)b(2)c(3)d(4)\mathscr{A}[V_{ab}(2,1)a(1)b(2)c(3)d(4)]\, d\tau \equiv v_{ab,cd}. \tag{49}$$

This expression remains unchanged by an interchange of the variables of integration 3 and 4, which has the same effect as an interchange of c and d. Hence $v_{ab,cd}$ is independent of the order of c and d and is sufficiently characterized as v_{ab}. Nevertheless, to indicate that $v_{ab,cd}$ is the interaction between a and b in the presence of two other atoms we will retain the full notation. From $v_{ab,cd}$ the other five terms in (48) are obtained by permutations of a, b, c, and d, together with α, β, γ, and δ. We write

$$E(4) - 4E_a = (v_{ab,cd} + v_{ac,bd} + v_{ad,bc} + v_{bc,ad} + v_{bd,ac} + v_{cd,ab}). \tag{50}$$

Direct evaluation yields

$$\begin{aligned} v_{ab,cd} = \frac{e^2}{R_{ab}} + (1 - \delta_{abcd})^{-1}\{ & -2[1 - \tfrac{1}{2}(\Delta_{ac}^2 + \Delta_{ad}^2 + \Delta_{bc}^2 + \Delta_{bd}^2 + 2\Delta_{cd} \\ & \qquad \times [\Delta_{cd} - \Delta_{bc}\Delta_{bd} - \Delta_{ac}\Delta_{ad}])](a\beta a) \\ & + 2[\Delta_{ab} - \Delta_{bc}\Delta_{ac} - \Delta_{bd}\Delta_{ad} + \Delta_{cd}(\Delta_{ac}\Delta_{bd} + \Delta_{bc}\Delta_{ad} - \Delta_{cd}\Delta_{ab})](a\alpha b) \\ & + [\Delta_{ac} - \Delta_{ab}\Delta_{bc} - \Delta_{ad}\Delta_{cd} + \Delta_{bd}(\Delta_{ab}\Delta_{cd} + \Delta_{ad}\Delta_{bc} - \Delta_{ac}\Delta_{bd})](a\beta c) \\ & + [\Delta_{bc} - \Delta_{ab}\Delta_{ac} - \Delta_{bd}\Delta_{cd} + \Delta_{ad}(\Delta_{ab}\Delta_{cd} + \Delta_{ac}\Delta_{bd} - \Delta_{ad}\Delta_{bc})](b\alpha c) \\ & + [\Delta_{bd} - \Delta_{ab}\Delta_{ad} - \Delta_{bc}\Delta_{cd} + \Delta_{ac}(\Delta_{ab}\Delta_{cd} + \Delta_{ad}\Delta_{bc} - \Delta_{ac}\Delta_{bd})](b\alpha d) \\ & + [\Delta_{ad} - \Delta_{ab}\Delta_{bd} - \Delta_{ac}\Delta_{cd} + \Delta_{bc}(\Delta_{ab}\Delta_{cd} + \Delta_{ac}\Delta_{bd} - \Delta_{ad}\Delta_{bc})](a\beta d) \\ & + (1 - \Delta_{cd}^2)[(ab\rho ab) - (aa\rho bb)] + (\Delta_{ac} - \Delta_{ad}\Delta_{cd})[(ab\rho bc) - (ab\rho cb)] \\ & + (\Delta_{bc} - \Delta_{bd}\Delta_{cd})[(aa\rho bc) - (ab\rho ac)] \\ & \qquad + (\Delta_{bd} - \Delta_{bc}\Delta_{cd})\ [(aa\rho bd) - (ab\rho ad)] \\ & + (\Delta_{ad} - \Delta_{ac}\Delta_{cd})[(ab\rho bd) - (ab\rho db)] \\ & \qquad + (\Delta_{ac}\Delta_{bd} - \Delta_{ad}\Delta_{bc})[(ab\rho cd) - (ab\rho dc)]\}. \end{aligned} \tag{51}$$

Three-body effects have already been computed; they are given by Eq. (31). The one term written there on the right [with δ_{abc} given by Eq. (30)] is $v_{ab,c}$. The two-body interaction is represented by Eq. (32), which in the present notation would read v_{ab}.

Clearly, $E^{(2)}(4)$ is

$$E^{(2)}(4) = E_{ab} + E_{ac} + E_{ad} + E_{bc} + E_{bd} + E_{cd}. \tag{52}$$

Since $E_{ab} = v_{ab}$, etc., we find from (50) and (52) that

$$\begin{aligned} E^{(3)}(4) + E^{(4)}(4) &= E(4) - 4E_a - E^{(2)}(4) \\ &= (v_{ab,cd} - v_{ab}) + (v_{ac,bd} - v_{ac}) + (v_{ad,bc} - v_{ad}) \\ &\quad + (v_{bc,ad} - v_{bc}) + (v_{bd,ac} - v_{bd}) + (v_{cd,ab} - v_{cd}) \end{aligned} \tag{53}$$

while

$$\begin{aligned} E^{(3)}(4) &= E_{abc} + E_{abd} + E_{acd} + E_{bcd} \\ E_{abc} &= (v_{ab,c} - v_{ab}) + (v_{ac,b} - v_{ac}) + (v_{bc,a} - v_{bc}), \quad \text{etc.} \end{aligned} \tag{54}$$

We consider two specific configurations, (*a*) the regular tetrahedron and (*b*) the square.

A. The Regular Tetrahedron

From symmetry, all parenthetical expressions of Eq. (53) are equal and have the value

$$\begin{aligned} v_{ab,cd} - v_{ab} = \frac{4\Delta}{(1-\Delta^2)(1+3\Delta)} \biggl\{ &-\Delta(a\beta a) - \Delta(a\alpha b) + (1+\Delta)\,(a\beta c) \\ &+ \frac{\Delta}{1-\Delta}[(ab\rho ab) - (aa\rho bb)] + \frac{1+\Delta}{1-\Delta}\,[(ab\rho bc) - (ab\rho cb)]\biggr\}. \end{aligned} \tag{55}$$

In writing Eq. (55) use has been made of the following equalities, each deriving from symmetry considerations:

$$\begin{gathered} \Delta_{ab} = \Delta_{ac} = \Delta_{ad} = \Delta_{bc} = \Delta_{bd} = \Delta_{cd} \equiv \Delta \\ (a\beta c) = (b\alpha c) = (b\alpha d) = (a\beta d) \\ (ab\rho bc) = (aa\rho bc) = (aa\rho bd) = (ab\rho bd) \\ (ab\rho cb) = (ab\rho ac) = (ab\rho ad) = (ab\rho db). \end{gathered}$$

Similarly, all E_{ijk} are equal, as are the three parentheses in each. In particular

$$v_{ab,c} - v_{ab} = \frac{2\Delta}{(1-\Delta^2)(1+2\Delta)}\left\{-\Delta(a\beta a) - \Delta(a\alpha b) + (1+\Delta)\,(a\beta c) + \frac{\Delta}{1-\Delta}\,[(abpab) - (aapbb)] + \frac{1+\Delta}{1-\Delta}\,[(abpbc) - (abpcb)]\right\}. \tag{56}$$

Comparison shows that the contents of the curly brackets in (55) and (56) are the same. If we call them A we arrive at the simple formulas

$$E^{(3)}(4) + E^{(4)}(4) = \frac{24\Delta A}{(1-\Delta^2)(1+3\Delta)} \tag{57}$$

and

$$E^{(3)}(4) = \frac{24\Delta A}{(1-\Delta^2)(1+2\Delta)}\,. \tag{58}$$

Hence

$$\frac{E^{(4)}(4)}{E^{(3)}(4)} = -\frac{\Delta}{1+3\Delta}. \tag{59}$$

Several conclusions can be drawn from Eq. (59).

(1) Since $E^{(3)}$ is negative, $E^{(4)}$ must be positive, like $E^{(2)}$, and increase the repulsive exchange forces.

(2) The magnitude of $E^{(4)}/E^{(3)}$ is $\frac{1}{4}$ at $R = 0$ and decreases monotonically as the atoms are separated. This is in accord with physical intuition: the importance on n-body effects relative to $(n-1)$-body effects should diminish as each atom becomes less effective in influencing the $(n-1)$-atom interaction.

(3) The ratio $E^{(4)}/E^{(3)}$ depends only on the overlap of the atomic wave function. This, of course, is a fortunate peculiarity of the regular tetrahedron and cannot be expected for other configurations.

(4) We have calculated four-body interactions using antisymmetrized state functions; Wojtala (1964) has shown that they also exist when exclusion is not respected. He calculated $E^{(3)}(3)$ and $E^{(2)}(3)$, as already noted, but also $[E^{(3)}(4) + E^{(4)}(4)]/E^{(2)}(4)$ for a regular tetrahedron, and has presented these in the form of graphs. This permits us to make the following comparisons. Let

$$\frac{E^{(3)}(3)}{E^{(2)}(3)} \equiv C(R), \qquad \frac{E^{(3)}(4) + E^{(4)}(4)}{E^{(2)}(4)} \equiv D(R).$$

Since $E^{(3)}(4) = 4E^{(3)}(3)$ and $E^{(2)}(4) = 2E^{(2)}(3)$, we find

$$D(R) = 2C(R)\left[1 + \frac{E^{(4)}(4)}{E^{(3)}(4)}\right]$$

whence

$$\frac{E^{(4)}(4)}{E^{(3)}(4)} = \frac{D(R)}{2C(R)} - 1.$$

Now, study of Wojtala's curves shows that, while D and C reach appreciable magnitudes (in regions, to be sure, where exchange cannot be neglected!), D is always near $2C$, so that in view of our last equation the ratio of four-body to three-body interactions in the case of a regular tetrahedron *without exchange* is practically zero. Hence we conclude that exchange forces are responsible for four-body effects.

It is tempting to examine what bearing our results have upon Jansen's work. Clearly, they do not affect it directly because his crucial conclusions are based upon second-order effects, which we shrink from attacking. But it is easy to make comparisons within the first order provided we adopt Gaussian wave functions. This leads to the integrals tabulated in Eqs. (40) plus one four-center integral,

$$\sqrt{2}\,(abpcd) = B\Delta_{ac}\Delta_{bd}F\left(\frac{B^2R^2_{\overline{ac}\,\overline{bd}}}{2}\right), \tag{60}$$

$R_{\overline{ac}\,\overline{bd}}$ meaning the distance between the midpoints of $\overline{ac}$ and $\overline{bd}$. For our tetrahedron, of course, we do not need this result and rely on formula (59) with $\Delta = \exp -(\frac{1}{4}B^2R^2)$. Choosing the proper values of BR for argon, krypton, and xenon we obtain Table I.

TABLE I

Rare gas crystal	BR	$\left.\dfrac{E^{(3)}(3)}{E^{(2)}(3)}\right\|_{\theta=60°}$	$\dfrac{E^{(4)}(4)}{E^{(3)}(4)}$
Argon	2.40	−0.200	−0.1385
Krypton	2.10	−0.21	−0.1663
Xenon	1.99	−0.214	−0.1757

The second column contains values read from the curves given by Jansen and Zimering. When the total interaction energy of the regular tetrahedron is computed, and written in the form of (47),

$$\begin{aligned} E(4) - 4E_a &= E^{(2)}(4) + E^{(3)}(4) + E^{(4)}(4) \\ &= E^2(4)[1 + \varepsilon_3 + \varepsilon_4], \end{aligned}$$

we obtain for the three crystals the values given in Table II.

TABLE II

Rare gas crystal	ε_3	ε_4
Argon	-0.40	$+0.055$
Krypton	-0.42	$+0.070$
Xenon	-0.43	$+0.075$

The appearance of rapid convergence here may be deceptive. Four-body forces are, in this instance, computed for a single tetrahedron, which contains four triangles (and therefore four terms contributing to ε_3) but only one E_{abcd}. In a crystal, where a domain of interacting atoms comprises something like one atom plus its nearest neighbors, ε_3 has $\binom{n}{3}$ and ε_4 $\binom{n}{4}$ terms, and these numbers are comparable for $n \approx 12$. It is very likely, therefore, that Table II overestimates the rate of convergence for a large aggregate of atoms. It will also be seen that the story is quite different for the square, to which we now turn.

B. The Square

The atoms comprising the square are labeled as shown in Fig. 4. Symbols have the same meaning as before but the distances are different.

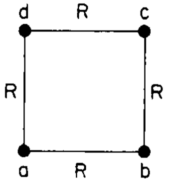

Fig. 4.

The departure from pairwise additivity is once again given by Eq. (53), which, in view of the symmetry properties inherent in Fig. 4, takes the form

$$E^{(3)}(4) + E^{(4)}(4) = 4(v_{ab,cd} - v_{ab}) + 2(v_{ac,bd} - v_{ac}). \qquad (61)$$

In the evaluation of $(v_{ab,cd} - v_{ab})$ use is made of the following equalities:

$$
\begin{aligned}
\Delta_{ab} = \Delta_{bc} = \Delta_{cd} = \Delta_{ad} &\equiv \Delta \\
\Delta_{ac} = \Delta_{bd} &= \Delta^2 \\
(a\beta c) &= (b\alpha d) \\
(b\alpha c) &= (a\beta d) \\
(ab\rho bc) &= (ab\rho cb) \\
(aa\rho bc) - (ab\rho ac) &= (ab\rho bd) - (ab\rho db) \\
(ab\rho cd) - (ab\rho dc) &= -\Delta^2[(ab\rho ab) - (aa\rho bb)].
\end{aligned}
\tag{62}
$$

Here, specific appeal is made to the Gaussian character of the atomic orbitals. Thus, our treatment of the square represents a straightforward extension of the three-atom formalism, but lacks exact applicability to hydrogen. From Eq. (62) we find that

$$
\begin{aligned}
v_{ab,cd} - v_{ab} = \frac{2\Delta}{(1-\Delta^2)^2} \Bigg\{ & -\Delta(a\beta a) + \Delta^2(a\alpha b) - \Delta(a\beta c) + (b\alpha c) \\
& + \frac{\Delta}{1-\Delta^2}[(ab\rho ab) - (aa\rho bb)] + \frac{1}{1-\Delta^2}[(aa\rho bc) - (ab\rho ac)]\Bigg\}.
\end{aligned}
\tag{63}
$$

Obtaining the proper expression for $v_{ac,bd}$ requires an interchange of b and β with c and γ, respectively. Specifically,

$$
\begin{aligned}
v_{ac,bd} = \frac{e^2}{R_{ac}} + (1-\delta_{abcd})^{-1}\{ & -2[1 - \tfrac{1}{2}(\Delta_{ab}^2 + \Delta_{ad}^2 + \Delta_{bc}^2 + \Delta_{cd}^2 + 2\Delta_{bd} \\
& \qquad \times [\Delta_{bd} - \Delta_{bc}\Delta_{cd} - \Delta_{ab}\Delta_{ad}])](a\gamma a) \\
& + 2[\Delta_{ac} - \Delta_{bc}\Delta_{ab} - \Delta_{cd}\Delta_{ad} + \Delta_{bd}(\Delta_{ab}\Delta_{cd} + \Delta_{bc}\Delta_{ad} - \Delta_{bd}\Delta_{ac})](a\alpha c) \\
& + [\Delta_{ab} - \Delta_{ac}\Delta_{bc} - \Delta_{ad}\Delta_{bd} + \Delta_{cd}(\Delta_{ac}\Delta_{bd} + \Delta_{ad}\Delta_{bc} - \Delta_{ab}\Delta_{cd})](a\gamma b) \\
& + [\Delta_{bc} - \Delta_{ac}\Delta_{ab} - \Delta_{cd}\Delta_{bd} + \Delta_{ad}(\Delta_{ac}\Delta_{bd} + \Delta_{ab}\Delta_{cd} - \Delta_{ad}\Delta_{bc})](b\alpha c) \\
& + [\Delta_{cd} - \Delta_{ac}\Delta_{ad} - \Delta_{bc}\Delta_{bd} + \Delta_{ab}(\Delta_{ac}\Delta_{bd} + \Delta_{ad}\Delta_{bc} - \Delta_{ab}\Delta_{cd})](c\alpha d) \\
& + [\Delta_{ad} - \Delta_{ac}\Delta_{cd} - \Delta_{ab}\Delta_{bd} + \Delta_{bc}(\Delta_{ac}\Delta_{bd} + \Delta_{ab}\Delta_{cd} - \Delta_{ad}\Delta_{bc})](a\gamma d) \\
& + (1-\Delta_{bd}^2)[(ac\rho ac) - (aa\rho cc)] + (\Delta_{ab} - \Delta_{ad}\Delta_{bd})[(ac\rho cb) - (ac\rho bc)] \\
& + (\Delta_{bc} - \Delta_{cd}\Delta_{bd})[(aa\rho cb) - (ac\rho ab)] \\
& \qquad + (\Delta_{cd} - \Delta_{bc}\Delta_{bd})[(aa\rho cd) - (ac\rho ad)] \\
& + (\Delta_{ad} - \Delta_{ab}\Delta_{bd})[(ac\rho cd) - (ac\rho dc)] \\
& \qquad + (\Delta_{ab}\Delta_{cd} - \Delta_{ad}\Delta_{bc})[(ac\rho bd) - (ac\rho db)]\}.
\end{aligned}
\tag{64}
$$

Similarly,

$$v_{ac,b} = \frac{e^2}{R_{ac}} + (1 - \delta_{abc})^{-1}\{[-2 + \Delta_{ab}^2 + \Delta_{bc}^2](a\gamma a) + 2[\Delta_{ac} - \Delta_{ab}\Delta_{bc}](a\alpha c)$$
$$+ [\Delta_{ab} - \Delta_{ac}\Delta_{bc}](a\gamma b) + [\Delta_{bc} - \Delta_{ac}\Delta_{ab}](b\alpha c) + [(ac\rho ac) - (aa\rho cc)]$$
$$+ \Delta_{ab}[(ac\rho cb) - (ac\rho bc)] + \Delta_{bc}[(aa\rho cb) - (ac\rho ab)]\}. \tag{65}$$

and

$$v_{ac} = \frac{e^2}{R_{ac}} + (1 - \Delta_{ac}^2)^{-1}\{-2(a\gamma a) + 2\Delta_{ac}(a\alpha c) + [(ac\rho ac) - (aa\rho cc)]\}. \tag{66}$$

From the relations

$$(a\gamma b) = (b\alpha c) = (c\alpha d) = (a\gamma d)$$
$$(ac\rho cb) - (ac\rho bc) = (aa\rho cd) - (ac\rho ad)$$
$$= (ac\rho cd) - (ac\rho dc) = (aa\rho cb) - (ac\rho ab)$$
$$\equiv (aa\rho bc) - (ab\rho ac) \tag{67}$$

one finds that

$$v_{ac,bd} - v_{ac} = \frac{4\Delta}{(1 - \Delta^2)^2}\left\{-\frac{\Delta}{1 + \Delta^2}(a\gamma a) - \frac{\Delta}{1 + \Delta^2}(a\alpha c) + (b\alpha c)\right.$$
$$\left. + \frac{\Delta}{1 - \Delta^4}[(ac\rho ac) - (aa\rho cc)] + \frac{1}{1 - \Delta^2}[(aa\rho bc) - (ab\rho ac)]\right\}. \tag{68}$$

Hence, in view of (63) and (68), (61) reads

$$E^{(3)}(4) + E^{(4)}(4) = \frac{8\Delta}{(1 - \Delta^2)^2}\left\{-\Delta(a\beta a) - \frac{\Delta}{1 + \Delta^2}(a\gamma a) + \Delta^2(a\alpha b)\right.$$
$$- \frac{\Delta}{1 + \Delta^2}(a\alpha c) - \Delta(a\beta c) + 2(b\alpha c)$$
$$+ \frac{\Delta}{1 - \Delta^2}[(ab\rho ab) - (aa\rho bb)]$$
$$+ \frac{2}{1 - \Delta^2}[(aa\rho bc) - (ab\rho ac)]$$
$$\left. + \frac{\Delta}{1 - \Delta^4}[ac\rho ac) - (aa\rho cc)]\right\}. \tag{69}$$

Clearly, all E_{ijk} are equal, so that

$$E^{(3)}(4) = 4E_{abc} \tag{70}$$

$$= 8(v_{ab,c} - v_{ab}) + 4(v_{ac,b} - v_{ac}). \tag{71}$$

Equations (31) and (32), together with Eqs. (62), provide that

$$v_{ab,c} - v_{ab} = \frac{\Delta}{1-\Delta^2}\{-\Delta(a\beta a) + (b\alpha c) + \frac{\Delta}{1-\Delta^2}[(ab\rho ab) - (aa\rho bb)] + \frac{1}{1-\Delta^2}[(aa\rho bc) - (ab\rho ac)]\}. \tag{72}$$

while Eqs. (65–67) yield

$$v_{ac,b} - v_{ac} = \frac{2\Delta}{1-\Delta^2}\left\{-\frac{\Delta}{1+\Delta^2}(a\gamma a) - \frac{\Delta}{1+\Delta^2}(a\alpha c) + (b\alpha c) + \frac{\Delta}{1-\Delta^4}[(ac\rho ac) - (aa\rho cc)] + \frac{1}{1-\Delta^2}[(aa\rho bc) - (ab\rho ac)]\right\}. \tag{73}$$

Hence, (71) becomes

$$E^{(3)}(4) = \frac{8\Delta}{1-\Delta^2}\left\{-\Delta(a\beta a) - \frac{\Delta}{1+\Delta^2}(a\gamma a) - \frac{\Delta}{1+\Delta^2}(a\alpha c) + 2(b\alpha c) + \frac{\Delta}{1-\Delta^2}[(ab\rho ab) - (aa\rho bb)] + \frac{2}{1-\Delta^2}[(aa\rho bc) - (ab\rho ac)] + \frac{\Delta}{1-\Delta^4}[(ac\rho ac) - (aa\rho cc)]\right\}. \tag{74}$$

In view of (74), it is apparent that (69) can be written as follows:

$$E^{(3)}(4) + E^{(4)}(4) = \frac{1}{1-\Delta^2}E^{(3)}(4) + \frac{8\Delta}{(1-\Delta^2)^2}[\Delta^2(a\alpha b) - \Delta(a\beta c)]$$

or

$$E^{(4)}(4) = \frac{\Delta^2}{1-\Delta^2}E^{(3)}(4) + \frac{8\Delta^2}{(1-\Delta^2)^2}[\Delta(a\alpha b) - (a\beta c)]. \tag{75}$$

We have

$$(a\alpha b) \fallingdotseq \Delta BF\left(\frac{B^2R^2}{4}\right) = \frac{2\Delta e^2}{R}\operatorname{erf}\left(\frac{BR}{2}\right)$$

$$(a\beta c) \fallingdotseq \Delta^2 BF\left(\frac{B^2R^2}{2}\right) = \frac{\sqrt{2}\Delta^2 e^2}{R}\operatorname{erf}\left(\frac{BR}{\sqrt{2}}\right).$$

Thus,

$$\frac{E^{(4)}(4)}{E^{(3)}(4)} = \frac{\Delta^2}{1-\Delta^2}\left\{1+\frac{\dfrac{8e^2}{R}\dfrac{\Delta^2}{1-\Delta^2}\left[\operatorname{erf}\left(\dfrac{BR}{2}\right)-\dfrac{1}{\sqrt{2}}\operatorname{erf}\left(\dfrac{BR}{\sqrt{2}}\right)\right]}{\left[\dfrac{E^{(3)}(3)}{E^{(2)}(3)}\right]E^{(2)}(4)}\right\} \tag{76}$$

where on the right we have replaced $E^{(3)}(4)$ by $2[E^{(3)}(3)/E^{(2)}(3)]E^{(2)}(4)$.

It is not difficult to calculate $E^{(2)}(4)$ for each of the heavy rare gases and, once again, Jansen's results for $E^{(3)}(3)/E^{(2)}(3)$ may be utilized. The results are presented in Table III.

TABLE III

Rare gas crystal	BR	$\left.\frac{E^{(3)}(3)}{E^{(2)}(3)}\right\|_{\theta=90^\circ}$	$\frac{E^{(4)}(4)}{E^{(3)}(4)}$
Argon	2.40	−0.075	−0.9438
Krypton	2.10	−0.075	−1.031
Xenon	1.99	−0.075	−1.198

If, as before, we put $E(4) - 4E_a = E^{(2)}(4)(1 + \varepsilon_3 + \varepsilon_4)$, Table IV results.

TABLE IV

Rare gas crystal	ε_3	ε_4
Argon	−0.150	+0.142
Krypton	−0.150	+0.155
Xenon	−0.150	+0.180

The outcome is somewhat unexpected and disturbing, for it shows that for a square configuration four-body forces may outweigh three-body forces. How this affects applications, such as those reviewed in this article, is at present difficult to foresee, chiefly because our calculation was performed only in first order of perturbation theory. Extension in two directions is needed to resolve these issues: other configurations must be included, and second-order effects require investigation. Unfortunately, both of these tasks are time consuming. But it is worth knowing that thoughtless use of the multibody series, Eq. (46), is fraught with risks.

Our first-order results are not wholly without physical meaning. For as R decreases, first-order effects predominate. Hence the failure of the multibody series for very closely packed atoms is already clear.

The total departure from additivity, $(E^{(3)} - E^{(4)})/E^{(2)}$, is about 2% for the square configuration, but 35% for the regular tetrahedron, where the arrangement is more compact. The sign of $E^{(4)}$ remains positive for both configurations, opposing the three-body effects.

V. Conclusions

In conclusion the following points may well be recalled concerning the role of many-body forces.

(1) For dense states of matter they are quite important, may even be crucial in determining structure.

(2) There is no conclusive evidence to show that the multibody series, Eq. (35), has convenient features of rapid convergence.

(3) Relevant calculations are at present based for the most part on simple state functions, i.e., on one-electron oscillator functions. This introduces errors which have not been estimated.

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Quantum Theory of Chemical Reactivity*

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I. General Introduction

In principle two main methods can be used to predict the chemical reactivity of molecules, the collision theory and the transition state theory.

The theoretical basis of the collision theory is certainly much more satisfactory than the basis of the transition state theory. But the collision theory leads to very tedious calculations, and for this reason its practical

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* This paper is based on my courses of lectures delivered during the last International Summer Institute in Menton (July, 1965) and during the International Summer Institute organized in August, 1965, by Professor Löwdin in Uppsala.

interest is presently limited to the field of small molecules. An interesting survey of this topic which also contains very significant original contributions has been written by D. A. Micha [Acta Universitatis Upsaliensis, Abstracts of Uppsala Dissertations in Science, No. 63 (1965)]. On the contrary, the transition theory has been used extensively to predict the chemical reactivity of both small and large molecules. This is why we shall use only this theory in the present paper.

The basis of the transition state theory is described in Section II, for the case of small molecules. It is known that following this way the constant rate of a chemical reaction appears to be the product of an equilibrium constant and of the rate of decomposition of the intermediate complex. Section III is devoted to the calculation of equilibrium constants. Many examples are given including conformational equilibria, oxydo-reduction potential, and base strength. The role of the various factors involved (delocalized bond energy, steric hindrance, solvent effect, etc.) is analyzed. In the last section various examples of calculation of rate constants are outlined. These discussions are concerned with Walden inversion, substitutions on a carbon atom belonging to an aromatic ring, and photochemical reactions.

II. Basis of the Theory

A. Introduction

It is usual to distinguish between three kinds of chemical reactions:

(*a*) those which are obtained under the effect of simple heating; we can call these *thermochemical reactions* (by heating, we understand an increase of the temperature above 0°K);
(*b*) the reactions which are produced by the effect of an electric field (*electrochemical reaction*); and
(*c*) those which result from the effect of radiations (*radiochemical reactions*) as in the case of photochemical processes.

We shall be only concerned with the first and the last group of reactions. In any case the medium can be homogeneous or heterogeneous. We shall not discuss the case of heterogeneous medium because the application of the wave mechanical methods to such a case remains extremely difficult.

For this reason we shall take examples of reactions taking place in the liquid or gaseous phase. But, even in this case, the phenomenon can be partially heterogeneous. The walls of the vessel which contains the reagents can play a very important role. The role of the *vessel walls* can be detected by studying the effect of the change of the nature of the walls on the rate of the reaction and the variation of this rate as a function of the ratio between the surface and the volume of the apparatus.

The thermal decomposition of methyl ether (Pease, 1937) is an example of a reaction which has a rate which depends on the ratio:

$$\frac{\text{vessel surface}}{\text{vessel volume}}.$$

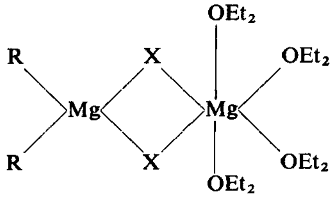
On the other hand, the rate of oxidation of hydrocarbons (E. R. Bell *et al.* 1949) in the presence of hydrogen bromide depends on the nature of the vessel walls.

Such phenomena prove that a part of the reactions considered take place on the wall.[1] It is only when the two tests are negative that the reaction can be really considered to be homogeneous.

But even in this case we must recall that a chemical reaction is an extremely complex phenomenon. Even if the purification of the reagent has been carefully performed small amounts of impurities remain and these *impurities* can play an important role in the observed reactions.

It has been noticed, for example, that very small amounts of copper or iron have a very strong effect on the oxidation of ascorbic acid (Weissberg *et al.*, 1943).

Furthermore, the "*inert*" *gas* may contribute significantly to some chemical reactions. It is known that an addition of argon, for example, can modify the kinetic mechanism of a reaction in giving the necessary third body for the recombination of two free radicals. *The solvents* are in some cases of such importance that they must be considered as real reagents. It is believed, for example, that the Grignard reagent, which is symbolized by the formula R—Mg—X, contains, in fact, molecules as:



where the solvent OEt_2 is included (Rochow *et al.*, 1957).

Finally, the real kinetic mechanism is usually much more complex than suggested by the usual chemical equation.

The photochemical combination of hydrogen and chlorine:

$$H_2 + Cl_2 \rightarrow 2ClH,$$

---

[1] The wall effect is analyzed in Semenov (1958).

results from a set of *elementary processes* such as (Rollefson and Burton, 1939):

$$Cl_2 + h\nu \rightarrow Cl + Cl$$

$$Cl + H_2 \rightarrow ClH + H$$

$$H + Cl_2 \rightarrow ClH + Cl$$

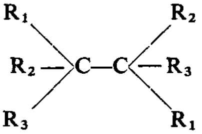
$$Cl + Cl + \text{third body} \rightarrow Cl_2 + \text{third body}$$

$$H + H + \text{third body} \rightarrow H_2 + \text{third body}$$

$$Cl + O_2 \text{ (impurity)} \rightarrow ClO_2$$

...

The main purpose of quantum chemistry is the a priori calculation of the rate constant of such elementary processes. This problem remains a difficult one because even an "elementary" process of a chemical reaction is a complex phenomenon. We must recall that very often a given molecule has various *conformations*. This is, for example, due to the fact that along a given simple bond the rotation is not completely free. Various stable positions exist and this leads to various rotation isomers. The introduction in a chemical medium of a molecule such as



corresponds, in fact, to the introduction of a large number of conformational isomers. A chemical species symbolized by a classical formula is in fact a population of various isomers. Furthermore, each conformation possesses various vibration, rotation, or libration and translation energies, and the percentage of molecules at a given energy level depends on the temperature.

Therefore, at a given temperature the same chemical species is represented by various conformations and each conformation by molecules having different energies. Finally, a chemical species corresponds to a *double population of molecules* (population of conformations, population of energy levels) and an elementary process of a chemical reaction results from collisions between various chemical species.

B. Rate Constant of a Bimolecular Process

1. *The Transition State Theory*

In gas phase the elementary processes are mainly bimolecular processes:

$$A + B \rightarrow C + D + E + \cdots .$$

Therefore the discussion will be focused on this kind of phenomenon. Two alternative approaches can be used: the collision theory and the transition state theory. The transition state theory is more convenient if wave mechanical calculations have to be performed. Therefore we shall be concerned only with this theory.

Let k be the rate constant of a bimolecular process:

$$\mathrm{A} + \mathrm{B} \xrightarrow{k} \mathrm{C} + \mathrm{D} + \mathrm{E} + \cdots. \tag{1}$$

Following the transition state theory (Glasstone *et al.*, 1941) it is supposed that during the collision between a molecule A and a molecule B a certain complex M is formed. This complex M is called the *intermediate complex.* Furthermore it is assumed that a particular conformation of the complex, *the transition state* $\mathrm{M}^{\ddagger}$, is in thermodynamical equilibrium with the reagents:

$$\mathrm{A} + \mathrm{B} \overset{K^{\ddagger}}{\rightleftharpoons} M^{\ddagger} \xrightarrow{k^{\ddagger}} \mathrm{C} + \mathrm{D} + \cdots. \tag{2}$$

We must add that if the reaction is reversible it would be necessary to take account of the process:

$$M^{\ddagger} \leftarrow \mathrm{C} + \mathrm{D}. \tag{3}$$

In such a case the following discussion will only be valid at the beginning of the reaction, that is to say when the concentrations of the final products are negligible. We can write

$$\frac{d[\mathrm{C}]}{dt} = v = k[\mathrm{A}][\mathrm{B}] \tag{4}$$

and also

$$v = k^{\ddagger}[\mathrm{M}^{\ddagger}]. \tag{5}$$

Therefore,

$$k = k^{\ddagger}\frac{[\mathrm{M}^{\ddagger}]}{[\mathrm{A}][\mathrm{B}]}. \tag{6}$$

The ratio $[\mathrm{M}^{\ddagger}]/[\mathrm{A}][\mathrm{B}]$ can be considered to be a measure of the equilibrium constant between $\mathrm{M}^{\ddagger}$, A, and B if the process

$$\mathrm{M}^{\ddagger} \rightarrow \mathrm{C} + \mathrm{D}$$

is not too fast. The limitation of this assumption has been discussed by various authors (Fowler and Guggenheim, 1939; Zwolinski and Eyring, 1947). If this is true we can write

$$k = k^{\ddagger}K^{\ddagger}. \tag{7}$$

2. *The Calculation of* $K^{\ddagger}$

The knowledge of k is obtained by the calculation of the two terms $k^{\ddagger}$ and $K^{\ddagger}$. We shall discuss first the calculation of $K^{\ddagger}$.

Let us consider the equilibrium:

$$A \overset{K}{\rightleftharpoons} B. \tag{8}$$

The Boltzmann law tells us that the number N_{iA} of molecules possessing a certain given energy ε_{iA} is proportional to:

$$p_{iA}\, e^{-\varepsilon_i A/\chi T}$$

if χ denotes the Boltzmann constant and p_{iA} the "a priori" probability of the corresponding state. Therefore the concentration [A] can be written as:

$$[A] = \frac{\sum_i N_{iA}}{V} = \frac{\sum_i a p_{iA}\, e^{-\varepsilon_i A/\chi T}}{V}, \tag{9}$$

V being the volume containing the molecules A.

Therefore with obvious notations:

$$K = \frac{\sum_j p_{jB}\, e^{-\varepsilon_{jB}/\chi T}}{\sum_i p_{iA}\, e^{-\varepsilon_{iA}/\chi T}}. \tag{10}$$

Usually this expression is transformed in order to introduce the ground state energies ε_{0A} and ε_{0B} of the molecules. It is written:

$$K = \frac{\sum_j p_{jB}\, e^{-(\varepsilon_{jB}-\varepsilon_{0B})/\chi T}}{\sum_i p_{iA}\, e^{-(\varepsilon_{iA}-\varepsilon_{0A})/\chi T}}\, e^{-(\varepsilon_{0B}-\varepsilon_{0A})/\chi T}. \tag{11}$$

If we use the notations:

$$f_A = \sum_i p_{iA}\, e^{-(\varepsilon_{iA}-\varepsilon_{0A})/\chi T} \tag{12}$$

$$f_B = \sum_j p_{jB}\, e^{-(\varepsilon_{jB}-\varepsilon_{0B})/\chi T} \tag{13}$$

$$\Delta\varepsilon = \varepsilon_{0B} - \varepsilon_{0A}$$

the final expression of K is:

$$K = \frac{f_B}{f_A}\, e^{-\Delta\varepsilon/\chi T}. \tag{14}$$

By extension it is readily seen that:

$$K^{\ddagger} = \frac{f_{M^{\ddagger}}}{f_A f_B}\, e^{-\Delta\varepsilon^{\ddagger}/\chi T} \tag{15}$$

where

$$\Delta\varepsilon^{\ddagger} = \varepsilon_{0M^{\ddagger}} - (\varepsilon_{0A} + \varepsilon_{0B}). \qquad (16)$$

$\Delta\varepsilon^{\ddagger}$ is called the *potential barrier* and the f's are the partition functions.

3. *The Calculation of* $k^{\ddagger}$

The calculation of the constant rate of decomposition of the intermediate complex is much more delicate.

The calculation has been done assuming that during the collision the electronic energy of the complex can be represented by a curve like those of Fig. 1 and that the transition state corresponds to a maximum of the electronic energy. This assumption seems reasonable because when the electronic energy becomes higher the other kinds of energy (for example, the kinetic energy of the nuclei) must become smaller in such a way that the lifetime of the corresponding conformation becomes higher; a thermodynamical equilibrium becomes possible.

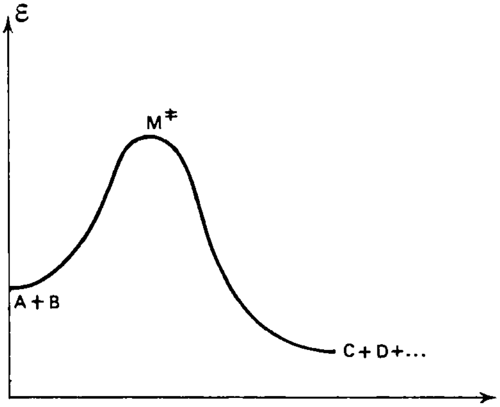


Fig. 1

If now we assume that every complex reaching the top of the barrier proceeds to decomposition we are led to the expression (Eyring, 1935a,b, 1938):

$$k^{\ddagger} = \frac{\chi T}{h}. \qquad (17)$$

But in fact there is a possibility that some of the complexes will be turned back to the initial state after having passed through the transition state. To take account of this possibility the second member of Eq. (17) has to be multiplied by a factor η called the *transmission coefficient*. Furthermore we must not forget the *tunneling effect* which allows a certain leakage through the potential barrier. For this reason a factor $(1 + t)$ must be introduced. Finally Eq. (17) becomes

$$k^{\ddagger} = \eta(1 + t)\frac{\chi T}{h}, \tag{18}$$

and, taking account of Eq. (15), Eq. (7) can be written as:

$$k = \eta(1 + t)\frac{\chi T}{h}\frac{f_{M^{\ddagger}}}{f_{A}f_{B}}e^{-\Delta\varepsilon^{\ddagger}/\chi T}. \tag{19}$$

This is a very important expression which shows that the constant rate of a bimolecular process in a gas phase at a given temperature depends on four factors:

(*a*) the transmission coefficient,
(*b*) the tunnel effect $(1 + t)$,
(*c*) the ratio of the partition functions $f = f_{M^{\ddagger}}/f_{A}f_{B}$,
(*d*) the potential barrier $\Delta\varepsilon^{\ddagger}$.

4. *The Case of the Reaction:* $H + H_2 \rightarrow H_2 + H$

Let us consider a reaction like the *para-ortho* hydrogen conversion:

$$H + H_{2(\text{para})} \rightarrow H_{2(\text{ortho})} + H \tag{20}$$

or similar exchange reactions as:

$$\begin{aligned} &H + D_2 \rightarrow DH + D\\ &D + H_2 \rightarrow DH + H\\ &H + DH \rightarrow H_2 + D. \end{aligned} \tag{21}$$

The most difficult step in the theory is the calculation of the potential barrier $\Delta\varepsilon^{\ddagger}$.

Following the Born–Oppenheimer approximation we must calculate the electronic energy of a system made of three electrons in the field of the three nuclei H_1, H_2, H_3 as a function $U(r_1, r_2, \theta)$ of the angle θ and of the interatomic distances r_1 and r_2 (Fig. 2). To obtain accurate energies it is necessary to use very elaborate wave functions and the calculations become very tedious. For this reason various semiempirical methods have been introduced. Eyring and Polanyi (1930; Eyring, 1931, 1932a,b) take as a starting point the London (1929) equation:

$$U(r_1, r_2, \theta) = Q - \sqrt{\tfrac{1}{2}[(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\alpha - \gamma)^2]} \tag{22}$$

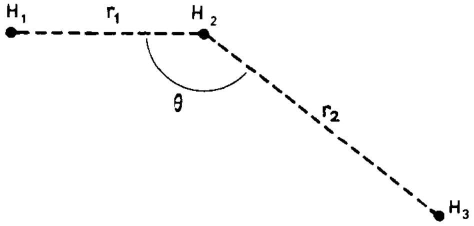


Fig. 2

which derived from the valence bond treatment and gives an approximate electronic energy of the intermediate complex H_3. In this equation Q denotes the coulombic integral and α, β, and γ the various exchange integrals. The coulombic integral is approximated by using the equation:

$$Q = Q_1 + Q_2 + Q_3 \tag{23}$$

where Q_1, Q_2, and Q_3 denote, respectively, the coulombic integrals associated with H_1H_2, H_2H_3, and H_1H_3.

It is readily seen from Eq. (22) that for given values of r_1 and r_2 the most stable configuration of H_3 is the linear one. As we are interested in the transition state of H_3 which is a relatively stable state, the discussion will be focused on the linear configurations of the complex.

Now the electronic energy of an hydrogen molecule is given by:

$$U_{HH} = Q_1 + \alpha \tag{24}$$

in the same approximation and the variation of U_{HH} as a function of r_1 is known from experimental data. Furthermore it is assumed that the ratio ρ between a coulombic integral and the total binding energy is a constant. For a given value of this constant ρ it becomes easy to evaluate Q_1 and α, and, therefore, Q_2, Q_3, β, and γ. Figure 3 shows the result of the corresponding calculation based on a assumed 14% coulombic energy:

$$(\rho = 0.14).$$

Two valleys representing $H + H_{2(\text{para})}$ and $H_{2(\text{ortho})} + H$, respectively, are clearly seen. They are separated by a shallow basin at the top of the energy pass. The height of the gap at the top of barrier through which the system has to pass before classical reaction can occur is at about 14 kcal per mole. Therefore the contribution to $\Delta\varepsilon^{\ddagger}$ of the electronic energy is of 14 kcal.

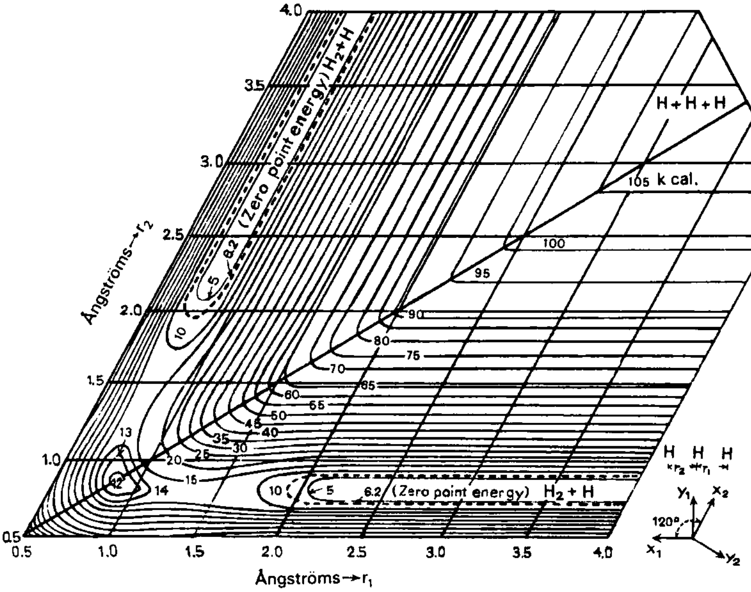


Fig. 3

Unhappily this value very much depends on the constant ρ. It becomes of 7 kcal/mole if $\rho = 0.20$.

Another semiempirical approach has been proposed by Sato (1955a,b) which leads to similar results.

Various nonempirical calculations also have been made (Snow and Eyring, 1957; Kimball and Trulio, 1958; Lippincott and Leifer, 1958; Shavitt, 1959). Shavitt calculated a wave function built on a basis made of six 1*s* orbitals (two for each hydrogen atom possessing two different exponents). The configuration interaction treatment is used and all possible configurations are introduced (i.e. thirty-four configurations when $r_1 = r_2$ and sixty when $r_1 \neq r_2$). The contribution $\Delta\varepsilon_e{}^{\ddagger}$ of the electronic energy to the potential barrier is found to be of 15.4 kcal/mole.

To obtain the potential barrier itself we must add a term $\Delta\varepsilon_v{}^{\ddagger}$ representing the difference in the vibrational energy between the transition state $H_3{}^{\ddagger}$ and the initial products. Table I gives an estimation of $\Delta\varepsilon_v{}^{\ddagger}$. Small variations appear in passing from one reaction to another; therefore this term contributes to the *isotopic effect*.

Taking account of the symmetry of the electronic energy surface (Fig. 3) it is reasonable to take the value $\frac{1}{2}$ for the *transmission coefficient*.

TABLE I

Reagents	$\Delta\varepsilon_v^{\ddagger}$ (kcal/mole)
$H + H_2$	0.87
$D + D_2$	0.61
$H + DH$	0.89
$D + HD$	0.72

TABLE II

T(°K)	$1 + t$
295	52
500	2.5
1000	1.2

The tunnel effect has been computed by Weston (1959) on the basis of the Sato (1955a,b) method with the Bell approximation (R. P. Bell, 1959). Table II contains some results.

Shavitt (1959) has used the Wigner (1932) and Eckart (1930) theory of the tunnel effect. Table III contains the corresponding results. The result depends on the way used to calculate $1 + t$. However, one conclusion does appear. The tunnel effect is certainly not negligible at low temperature and does contribute to the isotopic effect.

TABLE III

Reagents	T(°K)	$1 + t$ (Wigner)	$1 + t$ (Eckart)
$H + H_2$	200	5	180
	1000	1.1	1.2
$D + D_2$	200	3	13
	1000	1.1	1.1

To obtain a complete expression of the rate constant k we need to calculate the partition functions ratio $f = f_{M\ddagger}/f_A f_B$. This calculation is described in detail in Glasstone *et al.* (1941). As usual it is assumed that a partition function for a given molecule can be approximated by a product of factors: translational partition function, vibrational partition function, and rotational partition function:

$$f_M = f_{Mt} f_{Mv} f_{Mr}. \tag{25}$$

A translational function for a molecule in a volume v is:

$$f_{Mt} = \frac{(2\pi m \chi T)^{3/2}}{h^3}\, v. \tag{26}$$

For one mode of vibration we can introduce a vibrational partition function such as:

$$f_{Mv} = \frac{1}{1 - e^{-h\nu/\chi T}} \cdot \tag{27}$$

For a linear molecule a convenient expression of a rotational partition function is:

$$f_{Mr} = \frac{g}{\sigma} \frac{8\pi^2 I \chi T}{h^2}, \tag{28}$$

I being the moment of inertia, g the degeneracy due to the nuclear spin and the electronic angular momentum, and σ the symmetry number, i.e., the number of indistinguishable orientations of the molecule as a result of rotation.

The final expression of the rate constant of the reaction

$$H + H_2 \xrightarrow{k} H_2 + H \tag{29}$$

is:

$$k = (1 + t)\eta \frac{\sigma_H \sigma_{H_2}}{\sigma_{H_3‡}} \frac{g_{H_3‡}}{g_H g_{H_2}} \frac{I_{H_3‡}}{I_{H_2}} \frac{(m_{H_3‡})^{3/2}}{m_H m_{H_2}} \frac{h^2}{(2\pi)^{3/2}(\chi T)^{1/2}} \times \frac{(1 - e^{-(h\nu_{H_2}/\chi T)})e^{-\Delta\varepsilon‡\chi T}}{(1 - e^{-h\nu_s/\chi T})(1 - e^{-h\nu_\phi/\chi T})^2} \cdot \tag{30}$$

In this equation ν_s and ν_ϕ are the vibration frequencies associated with the transition state $H_3{}^‡$.

Table IV makes it possible to compare the values of k computed with the help of Eq. (30) (Eyring approximation: $\rho = 0.2$) and the experimental data (Greib and Harteck, 1931).

TABLE IV

k(cm^3 mole^{-1} sec^{-1})

Reagents	300°K	1000°K
$H + H_2$, calc.	7.3×10^7	1.5×10^{12}
obs.	9×10^7	2×10^{12}
$D + D_2$, calc.	3×10^7	0.76×10^{12}
obs.	—	1.2×10^{12}
$H + HD$, calc.	2.2×10^7	0.52×10^{12}
obs.	—	0.68×10^{12}

The striking agreement between the theory and the experiment is certainly fortuitous but it shows that it is possible to select a reasonable value for the constant ρ which allows a good representation of the variation of the rate constant as a function of the temperature and a convenient explanation of the isotopic effect. The basis of the theory seems to be satisfactory.

5. *The Case of the Reaction:* $H + H \rightarrow H_2$

The simple combination of two hydrogen atoms, a priori, appears as a very strange case. If we plot the electronic energy ε_e as a function of a parameter x representing the advance of the reaction a curve like that represented by an unbroken line on Fig. 4 is obtained. There is no maximum on this curve and it seems very difficult to define a transition state. But, in fact, the line on Fig. 4 corresponds to a "central collision." There are also other possibilities, for which the complex possesses a certain rotational energy ε_K related with a certain rotational quantum number K as in Eq. (31):

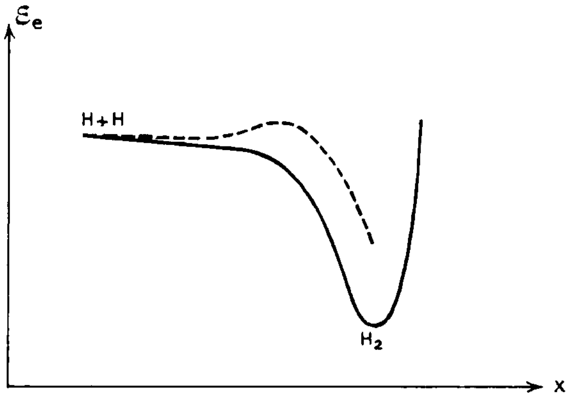


Fig. 4

$$\varepsilon_K = K(K+1)\frac{h^2}{8\pi^2 I} \tag{31}$$

where:

$$I = \mu r^2,$$

μ being the reduced mass and r the interatomic distance. This energy must be taken into account and if it is added to ε_e the dotted line of Fig. 4 is obtained and a maximum appears which permits us to define a transition state and therefore a certain potential barrier which depends on K and remains usually very small.

It is easy to see that to take account of all possible values of K we must replace the usual term $e^{-\Delta\varepsilon^{\ddagger}/\chi T}$ by the summation:

$$\sum_{K=0}^{K=\infty} (2K+1)\, e^{-\Delta\varepsilon_K{}^{\ddagger}/\chi T}.$$

We are led to:

$$k = (1+t)\eta \frac{\chi T}{h} \frac{f_{\mathrm{M}^{\ddagger}}}{f_{\mathrm{A}} f_{\mathrm{B}}} \sum_{K=0}^{K=\infty} (2K+1)\, e^{-\Delta\varepsilon_K{}^{\ddagger}/\chi T} \tag{32}$$

and finally to (Eyring *et al.*, 1935):

$$k = (1+t)\eta \frac{\chi T}{h} \frac{(2\pi m_{\mathrm{H}_2{}^{\ddagger}} \chi T)^{3/2}}{(2\pi m_{\mathrm{H}} \chi T)^3} \frac{h^3 g_{\mathrm{H}_2{}^{\ddagger}}}{g_{\mathrm{H}} g_{\mathrm{H}} \sigma_{\mathrm{H}_2{}^{\ddagger}}} \sum_{K=0}^{K=\infty} (2K+1) e^{-\Delta\varepsilon_K{}^{\ddagger}/\chi T}. \tag{33}$$

At normal temperature this equation leads to

$$k = 3(1+t)\eta\, 10^{14}\ \mathrm{cm}^3\ \mathrm{mole}^{-1}\ \mathrm{sec}^{-1}. \tag{34}$$

Furthermore as the potential barriers are small k does not depend very much on the temperature. On the other hand, as these barriers are thick the tunnel effect will be small and can be neglected.

Therefore the value of k in Eq. (34) appears to be great in comparison with the values obtained for the first reaction studied (Table IV). But, before giving such a conclusion, we must estimate the transmission coefficient η. The difference in the ground state energy between H + H and H_2 is of about 100 kcal/mole. During the collision this energy becomes vibrational energy and the reaction cannot take place before the loss of this energy by radiation. The lifetime for this radiative process has been estimated to be of the order of magnitude of 1 second. The time of a vibration has been estimated to 10^{-14} second. Therefore the transmission coefficient will satisfy the equation:

$$\eta \# 10^{-14}. \tag{35}$$

η has a very small value and Eq. (34) becomes:

$$k = 3\ \mathrm{cm}^3\ \mathrm{mole}^{-1}\ \mathrm{sec}^{-1} \tag{36}$$

which corresponds finally *to a very slow rate.*

Contrary to what happens in the case of a reaction such as

$$\mathrm{H} + \mathrm{H}_2 \rightarrow \mathrm{H}_2 + \mathrm{H}$$

where the role of *the potential barrier is important* and the role of the *transmission coefficient negligible*, the role of the *potential barrier is negligible* for a reaction such as

$$H + H \rightarrow H_2$$

but the role of the *transmission coefficient is essential.*

C. Rate Constant of a Trimolecular Process

The *transmission coefficient* is small in many bimolecular processes between free radicals. This is one of the reasons why some trimolecular processes become important in spite of the low probability of three-body collisions.

As an example of the trimolecular process we shall briefly discuss the case of the reaction between the nitric oxide, NO, and a halogen, hydrogen, or oxygen, X_2:

$$2NO + X_2 \rightarrow 2NOX. \tag{37}$$

The transition state theory can be applied to the study of such a process. We can write:

$$A + B + C \leftrightharpoons M^{\ddagger} \rightarrow D + E + \cdots \tag{38}$$

and the expression of the rate constant becomes:

$$k = \eta(1 + t)\frac{\chi T}{h}\frac{f_{M^{\ddagger}}}{f_A f_B f_C}\, e^{-\Delta\varepsilon^{\ddagger}/\chi T}. \tag{39}$$

In the special case of the reaction (Gershinowitz and Eyring, 1935)[2]:

$$2NO + O_2 \xrightarrow{k} 2NO_2$$

we are easily led to the equation:

$$k = \eta(1 + t)\frac{g^{\ddagger}\dfrac{(2\pi m^{\ddagger}\chi T)^{3/2}}{h^3}}{g_i\prod^{3}\dfrac{(2\pi m_i\chi T)^{3/2}}{h_3}}\;\frac{\dfrac{8\pi^2(8\pi^3 ABC)^{1/2}(\chi T)^{3/2}}{h^3\sigma^{\ddagger}}}{\prod^{3}\left(\dfrac{8\pi^2 I_i\chi T}{h^2\sigma_i}\right)}$$

$$\times\frac{\prod^{11}(1 - e^{-h\nu^{\ddagger}/\chi T})^{-1}}{\prod^{3}(1 - e^{-h\nu^{i}/\chi T})^{-1}}\, e^{-\Delta\varepsilon^{\ddagger}/\chi T}. \tag{40}$$

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[2] As another mechanism has been proposed now for this reaction the following discussion can be considered as a formal example.

The notations become obvious if we define *i* to denote the reagents, ‡ the transition state, and $\prod$ the products of the various partition functions involved. Equation (40) can be written as:

$$\frac{d}{d(1/T)} L\left[k\, \frac{\prod^{3}(1-e^{-h\nu_i/\chi T})^{-1}}{\prod^{11}(1-e^{-h\nu\ddagger/\chi T})^{-1}}\, T^{7/2}\right] = -\frac{\Delta\varepsilon^{\ddagger}}{\chi}. \tag{41}$$

The slope of the straight line which must be obtained in plotting the log of the bracket as a function of $1/T$ is a direct measurement of $\Delta\varepsilon^{\ddagger}$. The experimental results show that the *potential barrier is negligible* in such a way that Eq. (41) becomes

$$k = \frac{g\ddagger}{g_i} \prod^{7} (1 - e^{-h\nu\ddagger/\chi T}) \frac{3.2 \times 10^7}{T^3} (\text{cm}^3)^2\ \text{mole}^{-2}\ \text{sec}^{-1} \tag{42}$$

because the tunnel effect appears to be negligible and the transmission coefficient approaches unity.

The partition functions are the more important factor in this case and the theory indicates that *the rate constant must be a decreasing function of the temperature*. This surprising behavior has been observed by Briner *et al.* (1924).

D. Rate Constant of a Monomolecular Process

The monomolecular processes are not very common. Their treatment using the transition state theory is rather delicate. The step:

$$NO_2Cl \rightarrow NO_2 + Cl \tag{43}$$

of the decomposition of the nitryl chloride will be taken as an example. In fact a monomolecular process usually follows a bimolecular one. A molecule like NO_2Cl does not dissociate spontaneously if it is in its ground state. The dissociation will occur after a collision. Symbolically we can write:

$$A + A \xrightarrow{k_1} A^* + A \tag{44}$$

(where the asterisk denotes a vibrational excited state of the molecule), and

$$A^* \xrightarrow{k_2} B + C. \tag{45}$$

Step (44) is called the activation process. Usually a deactivation process:

$$A^* + A \xrightarrow[k_1']{} A + A \tag{46}$$

must also be considered.

When the activated molecule is in equilibrium with the reagents we can write:

$$k_1[A]^2 = k_2[A^*] + k_1'[A^*][A]. \tag{47}$$

Therefore the rate of the reaction becomes:

$$\frac{d[B]}{dt} = k_2[A^*] = \frac{k_1 k_2 [A]^2}{k_2 + k_1'[A]}. \tag{48}$$

Equation (48) permits us to conclude that the *apparent order of the reaction will depend on* [A], *that is to say on the pressure of the gas.* If we want to study such a reaction using the transition state theory we can consider A* as the transition state, the reaction being the breaking of the bond under the effect of the vibrations. Let us take as an example the case where

$$k_1'[A] \gg k_2. \tag{49}$$

Equation (48) becomes:

$$\frac{d[B]}{dt} = \frac{k_1 k_2 [A]}{k_1'} \tag{50}$$

and Eq. (47) can be written:

$$k_1[A]^2 = k_1'[A^*][A]. \tag{51}$$

Furthermore, if the total reaction is written as:

$$A \xrightarrow{k} B + C, \tag{52}$$

the rate constant k is given by

$$\frac{d[B]}{dt} = k[A]. \tag{53}$$

Taking account of Eqs. (50) and (51) it is readily obtained that:

$$\begin{aligned} k = \frac{k_1 k_2}{k_1'} &= \frac{[A^*]}{[A]} k_2 \\ &= \eta(1 + t)\frac{\chi T}{h}\frac{f_{A^*}}{f_A} e^{-\Delta\varepsilon^\ddagger/\chi T}. \end{aligned} \tag{54}$$

Other theories have been proposed to study the monomolecular processes [see, for example, Slater (1959) and Hall and Levine (1966)].

III. Equilibrium Constants

A. Introduction

We saw [Eq. (7)] that a rate constant is a product of two equilibrium constants. Before studying the calculation of the rate constants of some reactions involving large molecules it is therefore normal to study some equilibria between such molecules. Let us consider an equilibrium like:

$$\mathrm{A} + \mathrm{B} \underset{K}{\rightleftharpoons} \mathrm{C} + \mathrm{D} + \cdots . \tag{55}$$

We have already established that:

$$K = \frac{f_{\mathrm{A}} f_{\mathrm{B}}}{f_{\mathrm{C}} f_{\mathrm{D}} \cdots} e^{-\Delta\varepsilon/\chi T} \tag{56}$$

where:

$$\Delta\varepsilon = \varepsilon_{0\mathrm{C}} + \varepsilon_{0\mathrm{D}} + \cdots - \varepsilon_{0\mathrm{A}} - \varepsilon_{0\mathrm{B}}. \tag{57}$$

Now for a large molecule a ground state energy ε_{0i} may be divided into various parts:

(*a*) the vibrational energy ε_v corresponding to the zero point energy;
(*b*) the energy ε_l associated with the localized bonds and the atomic cores;
(*c*) the energy ε_d associated with the delocalized bonds taking account of the interaction of these bonds with the cores and the localized bonds;
(*d*) the energy ε_{nb} corresponding to the interaction between nonbonded atoms including the steric effect.

With the obvious notation we can write:

$$\Delta\varepsilon = \Delta\varepsilon_v + \Delta\varepsilon_l + \Delta\varepsilon_d + \Delta\varepsilon_{nb}, \tag{58}$$

which leads to

$$K = \frac{f_{\mathrm{A}} f_{\mathrm{B}}}{f_{\mathrm{C}} f_{\mathrm{D}} \cdots} \exp\left(-\frac{\Delta\varepsilon_v + \Delta\varepsilon_l + \Delta\varepsilon_d + \Delta\varepsilon_{nb}}{\chi T}\right). \tag{59}$$

Very often the reaction takes place in a solvent and we must introduce a solvent effect. We shall describe an approximate manner to take account of this phenomenon. We shall add a term $\Delta\varepsilon_s$ to the second member of Eq. (58) representing the difference in the solvation energies between the final and the initial products of the equilibrated reaction. But, as the solvation energy of a molecule depends on the temperature, we shall write this term as:

$$\Delta\varepsilon_s(T).$$

Furthermore, an index *s* will be put on each partition function to recall that this function can be considerably affected by the solvent. Finally Eq. (59) becomes:

$$K = \frac{f_{\mathrm{A}}{}^{s} f_{\mathrm{B}}{}^{s}}{f_{\mathrm{B}}{}^{s} f_{\mathrm{D}}{}^{s} \cdots} \exp\left(-\frac{\Delta\varepsilon_v + \Delta\varepsilon_l + \Delta\varepsilon_d + \Delta\varepsilon_{nb} + \Delta\varepsilon_s(T)}{\chi T}\right). \tag{60}$$

It turns out that an equilibrium constant *usually* depends on six terms:

(*a*) the ratio of the partition function

$$f_s = \frac{f_{\mathrm{A}}{}^{s} f_{\mathrm{B}}{}^{s}}{f_{\mathrm{C}}{}^{s} f_{\mathrm{D}}{}^{s}};$$

(*b*) the vibrational energy change $\Delta\varepsilon_v$;
(*c*) the localized bond energy change $\Delta\varepsilon_l$;
(*d*) the delocalized bond energy change $\Delta\varepsilon_d$;
(*e*) the nonbonded atoms energy change $\Delta\varepsilon_{nb}$;
(*f*) the solvation energy change $\Delta\varepsilon_s(T)$.

Furthermore we must recall that we have implicitly admitted that each chemical species was represented by only one conformation. To underline the possible importance of the conformations in a problem of chemical equilibrium we shall first of all study an example of conformational equilibrium.

B. An Example of Conformational Equilibrium; Role of $\Delta\varepsilon_{nb}$: Sign of the Cotton Effect[3]

It is well-known that many media transmit the two circularly polarized components of plane polarized light with unequal velocity. In addition there occurs unequal absorption of left and right circularly polarized light. The combined phenomenon is known as the Cotton effect. The measurement of the rotatory dispersion is the most common way to study the Cotton effect. Figure 5 represents a typical result of such a measurement. It is seen that the molecular rotation which is negative for the short wavelengths becomes positive for the large ones. In that case it is said that the Cotton effect is positive. But the reverse can happen; then the Cotton effect is said to be negative.

The Cotton effect of a given chemical species depends on its conformation. Therefore the study of the Cotton effect of a chemical gives important

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[3] For a more complete analysis of this phenomenon see Djerassi (1960).

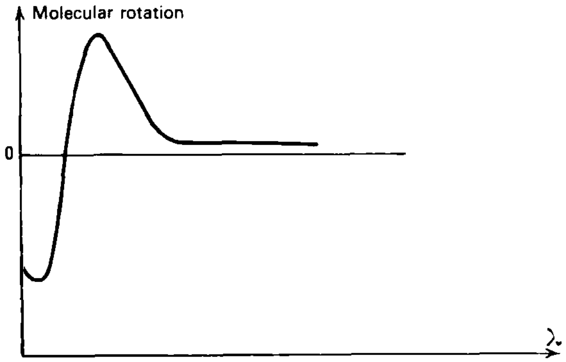


Fig. 5

information about the nature of the main conformations it contains. As an example of this point we shall discuss the case of some cyclanones.

In this family of compounds the sign of the Cotton effect is given by a semiempirical rule: the octant rule. As seen in Fig. 6, the molecule is divided into eight octants by means of three planes, the carbonyl group being the reference point. In fact Fig. 6 only shows explicitly four octants, but there are of course four other octants symmetric to the former, with respect to the plane P_3.

The octant rule states that: (*a*) substituents lying in the planes P_1 and P_2

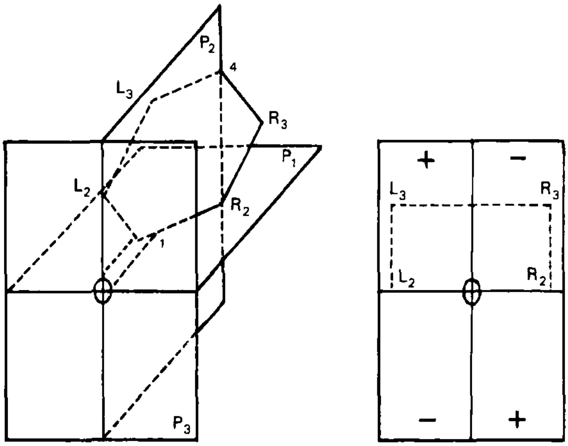


Fig. 6

make substantially no contribution to the Cotton effect; (*b*) atoms that are situated in the lower right and upper left octants of Fig. 6 make a positive contribution; (*c*) atoms that are situated in the lower left and upper right octants of the same figure make a negative contribution.

As a specific example let us take the case of 3-methylcyclopentanone:

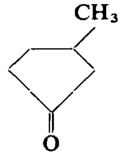


Figure 7 shows some of the possible conformations of this molecule and for each conformation the sign of its contribution to the Cotton effect following the octant rule. As some conformations contribute a negative sign and others a positive sign it is impossible to predict the sign of the resulting Cotton effect without a more refined analysis based on the study of the equilibrium which occurs between the various conformations. The equilibrium constant K corresponding to two of them, let us say A and B, is given by Eq. (60) which here becomes:

$$K = \frac{f_A}{f_B}\exp\left(-\frac{+\Delta\varepsilon_v + \Delta\varepsilon_l + \Delta\varepsilon_d + \Delta\varepsilon_{nb} + \Delta\varepsilon_s(T)}{\chi T}\right). \qquad (61)$$

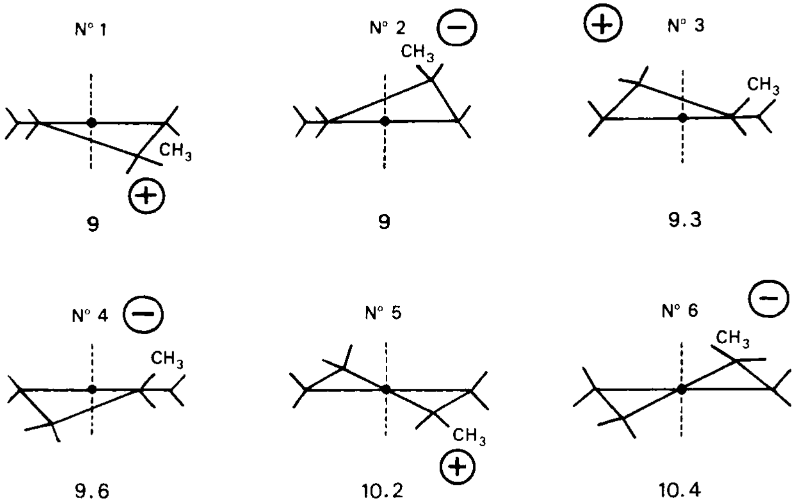


Fig. 7

In the molecule under consideration there are no delocalized bonds:

$$\Delta\varepsilon_d = 0, \tag{62}$$

and, as the various conformations contain the same localized bonds, it is normal to assume that:

$$\Delta\varepsilon_l = 0. \tag{63}$$

Of the four factors remaining in Eq. (61) it is reasonable to think that $\Delta\varepsilon_{nb}$ will be the most important because the distances between nonbonded atoms vary in passing from one given conformation to another. This is why Ouannès (1964) has proposed that an equilibrium constant like K could be represented by the approximate equation:

$$K = e^{-\Delta\varepsilon_{nb}/\chi T}. \tag{64}$$

Therefore, to know the concentrations of the various conformations involved at a given temperature we are led to the calculation of the various ε_{nb}.

Ouannès has calculated these energies in considering:

(*a*) the Baeyer strain energy;
(*b*) the twisting energy;
(*c*) the other interactions between nonbonded atoms.

The Baeyer strain energy ε_B can be estimated by the equation:

$$\varepsilon_B = k_0(\theta - \theta_0)^2 \tag{65}$$

where θ is the actual angle between two CC bonds and θ_0 the "normal" angle which is believed to be 109°.47 for a tetrahedral carbon atom and 116°.3 for a trigonal one. Ouannès has taken for k_0 the empirical value of 0.0175 kcal/mole.

The energy of twisting a single CC bond is obtained in considering each bond of the pentagon as a substituted derivative of ethane and in introducing the usual function which describes the energy of twisting as a function of φ, the angle of twist in the theory of the internal rotation potential barrier.

The other interactions between nonbonded atoms are introduced by using the Hill (1948) equation:

$$\varepsilon_{nb} = 8.2810^5 \varepsilon e^{-r/0.0736r^*} - \frac{2{\cdot}25r^{*6}}{r^6}. \tag{66}$$

It is obvious that in this equation the first term represents the effect of Pauli exclusion forces and the second is associated with the dispersion forces. ε is a coefficient which depends on the pair of atoms studied and r^* denotes the sum of the Van der Waals radii of the corresponding atoms.

The energies computed in this manner are seen in Fig. 7 below each conformation. They are given in kilocalories per mole. The conformations are classified in order of decreasing stability. It turns out that at the equilibrium the concentrations of the conformations contributing a positive sign will be greater than the concentrations of the conformations contributing a negative sign. We can anticipate that the resulting Cotton effect will be positive. This is, in fact, true.

To reach a more convincing conclusion it would be necessary to know the quantitative contribution of a given conformation to the Cotton effect. But this cannot be easily done and Ouannès' paper contains other examples showing that the above semiquantitative treatment is yet still useful.

C. An Example of the Role of $\Delta\varepsilon_d$: the Biradicaloid Character of Conjugated Molecules

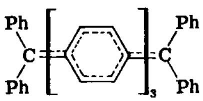
Many molecules which have a singlet ground state possess a triplet state not far away. At ordinary temperature the ground state is in equilibrium with the excited states but generally the population of the triplet state remains small and the molecules appear to be diamagnetic. But in certain cases, the first triplet is so close to the ground state that the population of the triplet state becomes significant and the substance becomes paramagnetic. In that case the molecule is said to be a biradicaloid. Then, we are led to the study of the equilibrium:

$$A_S \overset{K}{\rightleftharpoons} A_T \tag{67}$$

if A_S denotes the ground state and A_T the first triplet state. Again, the equilibrium constant K can be written as:

$$K = \frac{f_{A_T}}{f_{A_S}} \exp\left(-\frac{\Delta\varepsilon_v + \Delta\varepsilon_l + \Delta\varepsilon_d + \Delta\varepsilon_{nb} + \Delta\varepsilon_s(T)}{\chi T}\right). \tag{68}$$

Let us consider the family of the paraquinodimethanes which contain many biradicaloids such as:



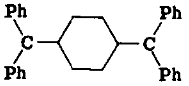
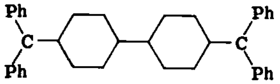
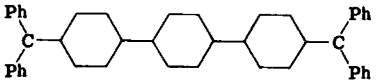
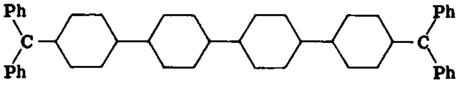
For such a molecule the geometry of the skeleton of the first triplet state probably does not greatly differ from the geometry of the ground state. Therefore it is normal to neglect $\Delta\varepsilon_v$, $\Delta\varepsilon_l$, and $\Delta\varepsilon_{nb}$ in comparison with $\Delta\varepsilon_d$ which is expected to be the main part of the energy difference between the two electronic states under consideration. As no important distribution of charge appears in this alternant hydrocarbon we can assume that the solvation energy change $\Delta\varepsilon_s(T)$ is small. A convenient approximation for K will be:

$$K = \frac{f_{A_T}}{f_{A_S}} e^{-\Delta\varepsilon_d/\chi T}. \tag{69}$$

If now we consider a set of analogous compounds for which the ratio of the partition functions is expected to be of about the same order of magnitude we can anticipate a relation between K and $\Delta\varepsilon_d$.

Table V shows such a relation, the equilibrium constant K increasing as

TABLE V

Quinodimethanes	$\Delta\varepsilon_d$ (in β units)	Magnetic susceptibility (in 2% benzene solution)
	0.31	Very small and negative[a]
	0.15	Very small and negative[a]
	0.08	26 ± 4 at 293°C[b] 82 ± 2 at 353°C
	0.04	44 ± 4 at 293°C[b] 95 ± 10 at 353°C

[a] E. Muller and Muller Rodloff (1935) and E. Muller and Hertel (1943, 1944).
[b] E. Muller and Pfanz (1941).

$\Delta\varepsilon_d$ decreases. For the quinodimethane derivatives considered in this table the values of $\Delta\varepsilon_d$ have been computed using the simple Hückel approximation. In this approximation $\Delta\varepsilon_d$ is simply twice the absolute value of the energy of the highest bonding orbital.

D. An Example of the Role of $\Delta\varepsilon_s(T)$: the Half Wave Potential of Polarographic Reduction of Alternant Hydrocarbons

Oxidation-reduction potentials are often closely related to equilibrium constants. It is, for example, supposed that the electrolytic reduction of alternant hydrocarbons can be represented as follows:

$$\begin{gathered} R + e^- \rightleftharpoons R^- \\ R^- + e^- \rightarrow R^{2-} \\ R^{2-} + H_2O \rightarrow RH_2 + O^{2-} \end{gathered} \tag{70}$$

if R represents the hydrocarbon and e^- an electron.

Based on this hypothesis a delicate discussion permits us to establish a precise theoretical relation between the polarographic half wave potential obtained for these hydrocarbons in using the dropping mercury electrode method and the various properties of the hydrocarbons considered.

There is no room here for a complete analysis of the question. The reader is referred to a recent survey of this topic written by Jano (1965) which contains various improvements. Key references are given in this paper.

We shall restrict ourselves to saying that it is possible to conclude that, taking account of an equation like (60), the half wave potential $E^{1/2}$ can be written as:

$$E^{1/2} = A - \Delta\varepsilon_s(T) + \cdots \tag{71}$$

if A denotes the electron affinity of the hydrocarbon. Many authors (Maccoll, 1949; Pullman *et al.*, 1950; Watson and Matsen, 1950; Lyons, 1950) have discussed the relations between $E^{1/2}$ and A. The most recent and sophisticated treatment is probably due to Chalvet and Jano (1964). As very few electron affinities are experimentally known, Chalvet and Jano have computed these properties in using the Pariser–Parr–Pople approximation in a way similar to the one followed by Hoyland and Goodman (1962).

Figure 8 shows the result of these studies. Various straight lines are obtained, one for each set of compounds possessing the same geometrical shape. For example, the first curve (Nos. 1 to 4) corresponds to the acenes (naphthalene, anthracene, tetracene, pentacene), and the second curve (Nos. 5 to 8) corresponds to the phenes (phenanthrene, 1,2-benzonaphthacene, 1,2-benzopentacene).

The effect of $\Delta\varepsilon_s(T)$ on $E^{1/2}$ has been underlined by Matsen (1956) and Hedges and Matsen (1958). Unfortunately the calculation of ΔE_s is not easy. The solvation energy of a molecule can be divided into at least three parts: the cavitation energy ε_{sc} associated with the hole that the molecule creates in the solvent, the orientation term ε_{so} due to the fact the molecule changes the average orientations of the molecules of the solvent, and the interaction term ε_{si} due to the average intermolecular forces which appear between the soluted molecule and the partially oriented molecules of the solvent. Therefore we can write:

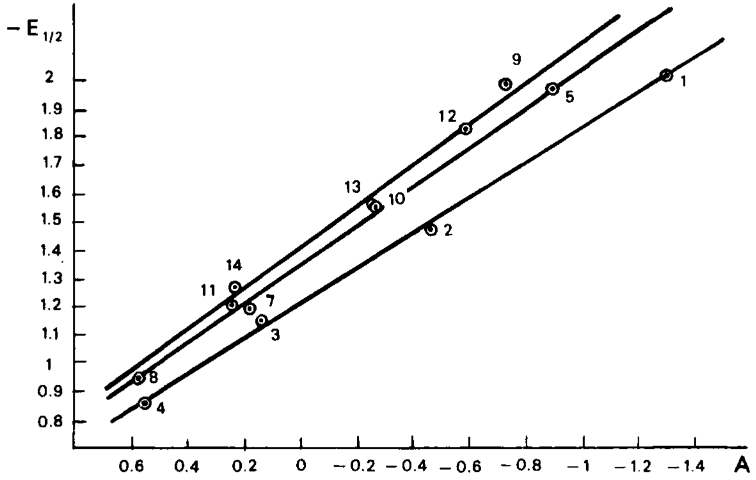


Fig. 8

$$\Delta\varepsilon_s = \Delta\varepsilon_{sc} + \Delta\varepsilon_{so} + \Delta\varepsilon_{si}. \qquad (72)$$

In the present case, since the hole due to a hydrocarbon is probably very similar to the hole corresponding to its negative ion, we can neglect $\Delta\varepsilon_{sc}$. Furthermore we shall assume that in going from a given aromatic hydrocarbon to another the variation of $\Delta\varepsilon_{si}$ is larger than the variation of $\Delta\varepsilon_{so}$. Therefore the discussion will be focused on the estimation of $\Delta\varepsilon_{si}$. This interaction itself appears to be the sum of various contributions. We usually have to consider:

the part ε_{sid} due to the dispersion forces;

the term ε_{sii} associated with the isotropic interaction between electric charges and dipole moments; and

the part ε_{sia} due to the anisotropic interactions like those created by hydrogen bonds.

It is obvious that in the present case $\Delta\varepsilon_{sii}$ will be the more important term because the distribution of the electronic charges changes very much during the ionization of the hydrocarbon, the other interactions being less altered. The term $\Delta\varepsilon_{sii}$ can be estimated from the formula (Born, 1920; Hoijtink *et al.*, 1956):

$$\Delta\varepsilon_{sii} = -\Delta\Sigma\frac{Q_iQ_j}{2r_{ij}}(1 - 1/D) \tag{73}$$

where the Q_i's are the apparent charge of each atom, and where r_{ij} denotes the distance between the atom i and the atom j except when i and j are identical. In this later case r_i represents a certain empirical effective radius. Furthermore D is an effective dielectric constant of the solvent. The application of this simple formula shows that $\Delta\varepsilon_{sii}$ is of the order of magnitude of an electron volt and that, furthermore, $\Delta\varepsilon_{sii}$ depends on the size of hydrocarbon studied. For example it is found that $\Delta\varepsilon_{sii}$ is of about 2 eV in the case of benzene and of only about 1 eV for anthracene.

Equation (71) can be written as:

$$E^{1/2} - A = \Delta\varepsilon_s(T) + \cdots \tag{74}$$

or:

$$E^{1/2} - A = \Delta\varepsilon_{sii} + \cdots \tag{75}$$

if $\Delta\varepsilon_{sii}$ is considered to be the most important part of $\Delta\varepsilon_s$. To test this relation Chalvet and Jano (1964) have plotted $E^{1/2} - A$ as a function of $\Delta\varepsilon_{sii}$ estimated from Eq. (74). Figure 9 shows that an excellent straight line is obtained. Therefore $\Delta\varepsilon_{sii}$ effectively appears to be the most important term in the second member of Eq. (75).

E. A More Complex Problem: Base Strength

The acid-base equilibrium can be written as:

$$\mathrm{BH^+} \overset{K}{\rightleftharpoons} \mathrm{B + H^+}. \tag{76}$$

The antilogarithm of K is called p_{K_a}. The larger the value of p_{K_a} the less the ion is dissociated and the greater is the strength of the base. Let us concentrate our attention on the particular case of some aza derivatives of alternant hydrocarbon such as pyridine, quinoline, acridine, etc., and their amino derivatives.

From Eq. (60) it is concluded that the p_{K_a} must obey the equation

$$p_{K_a} = \log\frac{f_{\mathrm{B}}^s f_{\mathrm{H^+}}^s}{f_{\mathrm{BH^+}}^s} + \frac{\Delta\varepsilon_v + \Delta\varepsilon_l + \Delta\varepsilon_d + \Delta\varepsilon_{nb} + \Delta\varepsilon_s(T)}{\chi T}. \tag{77}$$

Of the six factors which determine the p_K, the change in the delocalized bond energy $\Delta\varepsilon_d$ has been considered to be the most important because the

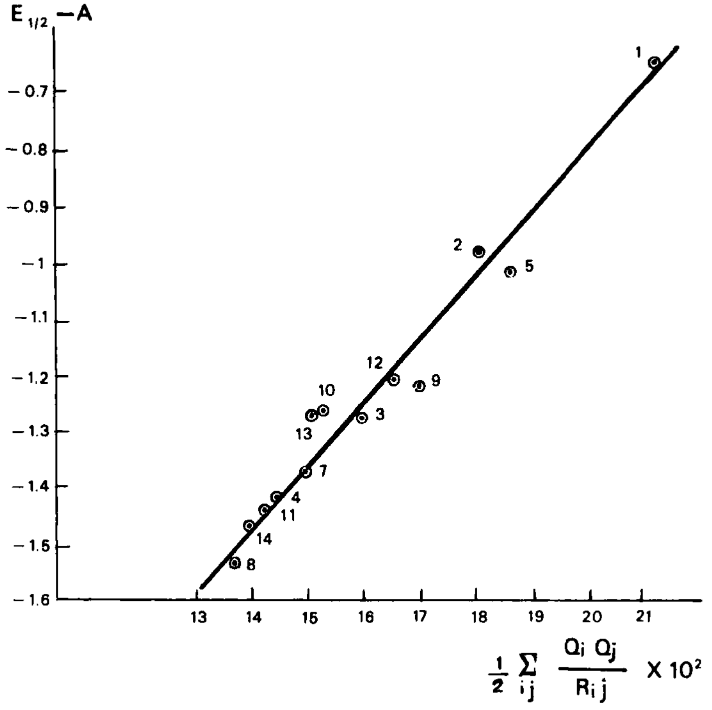


Fig. 9

geometry of the delocalized bond varies to a large extent from a molecule like pyridine to another like acridine (Ploquin, 1948; Daudel, 1948; Daudel and Chalvet, 1949; Chalvet *et al.*, 1954; Longuet-Higgins, 1950; Elliot and Mason, 1959).

When the p_{K_a} is plotted as a function of $\Delta\varepsilon_d$ as in Elliott and Mason's paper (1959), for example, a rough relation is observed, in such a way that the knowledge of $\Delta\varepsilon_d$ permits the prediction of the p_K with a precision of only ± 1. In some particular cases the precision is even worse. In order to see if this lack of precision is due to the nature of the approximation used in the calculation of $\Delta\varepsilon_d$ this term has been evaluated for the same molecules using five different approximations of the LCAO-MO method (Bunel *et al.*, 1961; Chalvet *et al.*, 1962; Peradejordi, 1963).

It turns out that the precision of the prediction of the p_K is not improved in passing from rough π electronic wave functions to more elaborate ones. Figure 10 corresponds to the best calculation, the self-consistent field method being used in the Pariser–Parr–Pople approximation to calculate separately the π energy of molecules and positive ions.

It is seen that the points corresponding to the set of compounds derived from a given skeleton (pyridine, isoquinoline, quinoline, or acridine) lie along a given straight line.

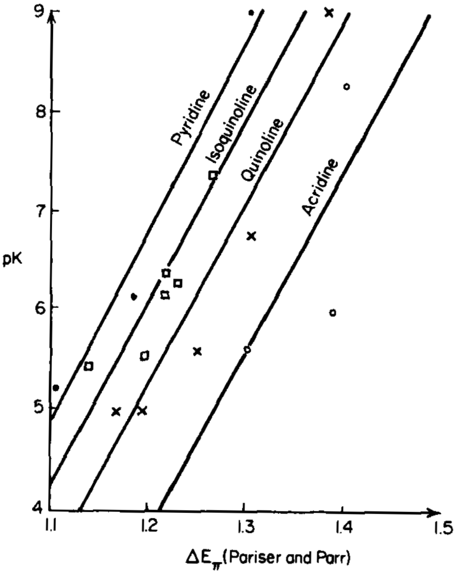


Fig. 10

As in the case of the oxidation-reduction potentials we can anticipate that at least another important factor must be considered.

The role of the solvent effect has been discussed in detail by Chalvet *et al.* (1962). The situation is rather similar to that in the case of the oxidation-reduction potentials and it appears that the main term in $\Delta\varepsilon_s$ is $\Delta\varepsilon_{sii}$.

Figure 11 shows what happens when the p_{K_a} is plotted as a function of $\Delta\varepsilon_d + \Delta\varepsilon_{sii}$, $\Delta\varepsilon_{sii}$ being derived from Eq. (73).

Twelve points are found at no more than 0.3 units of p_K from a straight line. They correspond to compounds belonging to all the families. As expected, the introduction of $\Delta\varepsilon_{sii}$ destroys the segregation of various families. This precision is very satisfactory. For this set of compounds, for which there is a factor of 10,000 between the highest values of K and the lowest, the theory predicts the constant with an uncertainty of a factor of only 2.

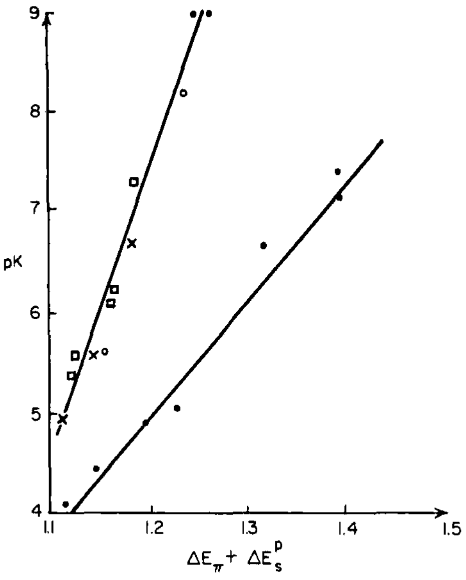


Fig. 11

There are also, on Fig. 11, various points which lie near another straight line. They correspond to molecules containing an amino group NH_2 in an *ortho* or *peri* position to the nitrogen hetero atom.

Therefore it appears that a special $\Delta\varepsilon_{nb}$ term mainly due to the interaction between the NH_2 group and the lone pair of the nitrogen hetero atom is necessary.

In conclusion, we see that $\Delta\varepsilon_d$, $\Delta\varepsilon_s$, and $\Delta\varepsilon_{nb}$ play important roles in the determination of the p_K of the molecules under consideration.

F. The Base Strength of Conjugated Molecules in Their Electronic Excited States

Förster (1950) has observed that, if a base such as 3-aminopyrene is irradiated by normal light, the excited molecules have acidic properties. More precisely, Förster studied absorption and fluorescence spectra as a function of the pH of the solution containing the amino compounds.

Obviously the absorption spectrum gives information about the ground state of the molecule. The fluorescence spectrum is related to the electronic excited states. Up to pH 2 the absorption spectra are essentially those of the $ArNH_3^+$ ions, whereas the fluorescence spectra correspond to $ArNH_2$.

This shows that the molecules in their excited states have less tendency to add a proton than the ground state molecules. Furthermore, near pH 12 some new bands appear in the fluorescence spectra which can be assigned to the $ArNH^-$ ions. These ions are probably the result of a reaction such as:

$$ArNH_2 \rightleftharpoons ArNH^- + H^+,$$

the amino compound acting as an acid. No such bands appear in the absorption spectra.

To interpret this result, Sandorfy (1951) has calculated the distribution of the electronic charges in an aromatic amine by the molecular orbital method, taking account of both the π and the σ orbitals. He found that the nitrogen which is negative in the ground state, becomes positive in the first electronic excited state, which explains why the molecule becomes an acid. Other cases have been discussed in the same way (Jaffé *et al.*, 1964).

IV. Rate Constants

A. Introduction

It is now easy to extend Eq. (19) for the study of an elementary process of a reaction, between large molecules, taking place in a solvent. Equation (78) is readily obtained:

$$k = \eta^s(1 + t^s)\frac{\chi T}{h}\frac{f^s{}_{M^\ddagger}}{f_A{}^s f_B{}^s}\exp\left(-\frac{\Delta\varepsilon_v{}^\ddagger + \Delta\varepsilon_l{}^\ddagger + \Delta\varepsilon_d^\ddagger + \Delta\varepsilon_{nb}^\ddagger + \Delta\varepsilon_s{}^\ddagger(T)}{\chi T}\right). \tag{78}$$

This is a very important equation which shows that the rate constant in the liquid phase at a given temperature depends on eight factors:

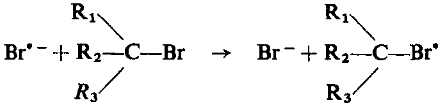
(*a*) the transmission coefficient η^s;
(*b*) the tunnel effect $(1 + t^s)$;
(*c*) the ratio of the partition function $f^s = f^s{}_{M^\ddagger}/f_A{}^s f_B{}^s$;
(*d*) the contribution of vibrational energy $\Delta\varepsilon_v{}^\ddagger$ to the potential barrier;
(*e*) the corresponding contribution of the localized bonds $\Delta\varepsilon_l{}^\ddagger$;
(*f*) the corresponding contribution of the delocalized bonds $\Delta\varepsilon_d{}^\ddagger$;
(*g*) the contribution of nonbonded atom interaction $\Delta\varepsilon_{nb}^\ddagger$ to the potential barrier;
(*h*) and the corresponding contribution $\Delta\varepsilon_s{}^\ddagger(T)$ due to the solvent.

As in the case of the equilibrium constants it is usually impossible to estimate all these factors. We must restrict ourselves to the calculation of relative rates. In this case it happens that for a certain family of molecules and for similar reactions some factors remain approximately constant. Therefore the relative rates mainly depend on the others and when we are able to estimate these factors we can have a clear understanding of the variation of the chemical reactivity in the family of molecules considered. In some particularly favorable cases it also becomes possible to predict the chemical reactivity of molecules for which experimental data are lacking.

The remaining part of this chapter will be concerned with the discussion of some examples of this kind.

B. The Walden Inversion; Importance of the Steric Term $\Delta\varepsilon^{\ddagger}_{nb}$

The main problem which arises in calculating a rate constant is to know the structure of the transition state of the intermediate complex. From this point of view the Walden inversion is a convenient reaction because we possess some rather precise information about this transition state. For an isotopic exchange reaction such as:



it has been possible to follow simultaneously the rate of the exchange and the variation of the rotatory power. From this comparison it appeared that in many cases each exchange corresponds to one inversion. Therefore it is assumed that the transition state corresponds to a structure in which the three bonds CR_1, CR_2, and CR_3 are in the same plane, the electric charge being shared between the two bromine atoms, the two bonds C—Br possessing the same length (Fig. 12).

Ingold *et al.* (1948) have measured the relative rates and the activation energies (following the Arrhenius formula) of a set of reactions of this kind in acetone or ethyl alcohol. Table VI summarizes some results.

TABLE VI

Nature of the bromide	Methyl	Ethyl	Propyl	Isobutyl	Neopentyl
Relative rate (at 55°C)	17.6	1	0.28	0.030	0.0000042
Activation energy (kcal/mole)	20	21		22.8	26.5

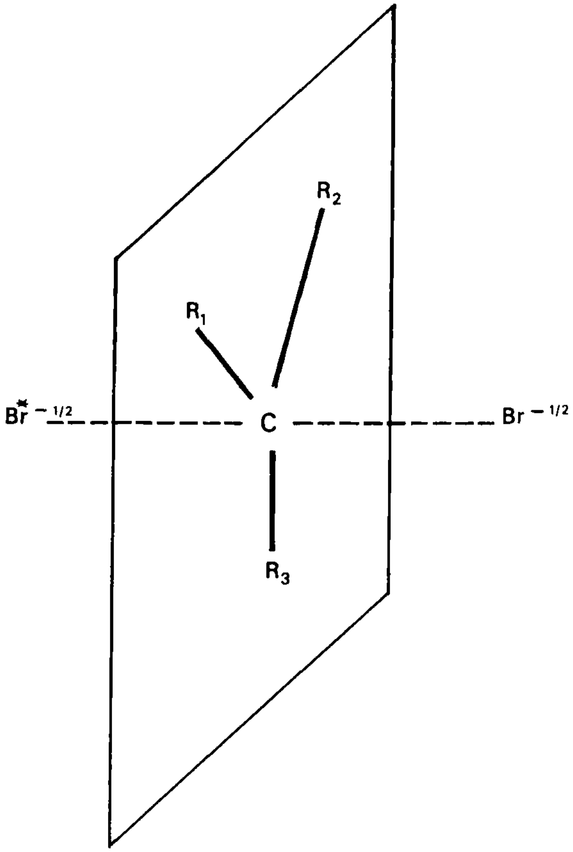


Fig. 12

We know that the activation energy cannot be identified with the potential barrier, but in the present case where the rate decreases to a large extent as the activation energy increases we can expect that the variation of the activation energy is in part due to the variation of the potential barrier.

Now if models are built it is seen that in the transition state some steric hindrance appears. Thus we are led to the estimation of the term $\Delta\varepsilon^{\ddagger}_{nb}$. A first step in the estimation of such a term is to make the length of the bond C···Br$^{-1/2}$ in the transition state precise. As the transition state corresponds to a point of the reaction path of lower energy on the potential energy surface, we must calculate the value of the interatomic distance r between Br and C which corresponds to a relative minimum of the energy.

Therefore we must express the energy of the intermediate complex as a function of r. In building this function we can neglect the terms which do not significantly depend on r.

In passing from the initial state to the transition state the various bonds CR_1, CR_2, and CR_3 must be pushed into the same plane. The corresponding deformation energy does not depend very much on r and can be neglected. On the other hand, we have to take into consideration:

(*a*) the repulsion between $Br^{*-1/2}$ and the various atoms of CR_1, CR_2, and CR_3;
(*b*) the extension energy of the bond $C\cdots Br^{-1/2}$.

The last energy can be estimated by a Morse equation such as:

$$\varepsilon_{ext} = D\{e^{-2\beta(r-r_0)} - 2e^{-\beta(r-r_0)}\}. \tag{79}$$

In this equation D denotes the dissociation energy, r_0 denotes the C—Br bond length in the initial molecule, and β is given by the equation:

$$\beta = 0.1227\omega\sqrt{\mu/D}, \tag{80}$$

ω being the stretching frequency of the C—Br bond and μ the reduced mass.

The repulsion energy between $Br^{-1/2}$ and another atom can be obtained from the sum of

(*a*) the polarization energy:

$$-\frac{\alpha(e/2)^2}{2r^4};$$

(*b*) the dispersion energy:

$$-\frac{3\alpha\alpha' II'}{2(I+I')r^6};$$

(*c*) the term related to the exclusion forces:

$$be^{-r/0.345}.$$

α and α' are the polarizabilities of the atoms involved, I and I' are the ionization energies, and b is chosen in such a way that the energy minimum of the sum of the energies (*a*), (*b*), and (*c*) corresponds to the sum of the van der Waals radii of the atoms considered.

The final expression giving the repulsion energy is:

$$\varepsilon_{rep} = -\frac{\alpha\left(\frac{e}{2}\right)^2}{r^4} - \frac{3\alpha\alpha' II'}{2(I+I')r^6} + be^{-r/0.345}. \tag{81}$$

Ingold *et al.* have calculated the sum:

$$\varepsilon(r) = \varepsilon_{\text{ext}} + \varepsilon_{\text{rep}}$$

for various values of *r*. Figure 13 shows their results. It is seen that the energy minimum is obtained for $2.2 < r < 2.3$ and that the corresponding value of *r* does not significantly depend on the alkyl bromide considered.

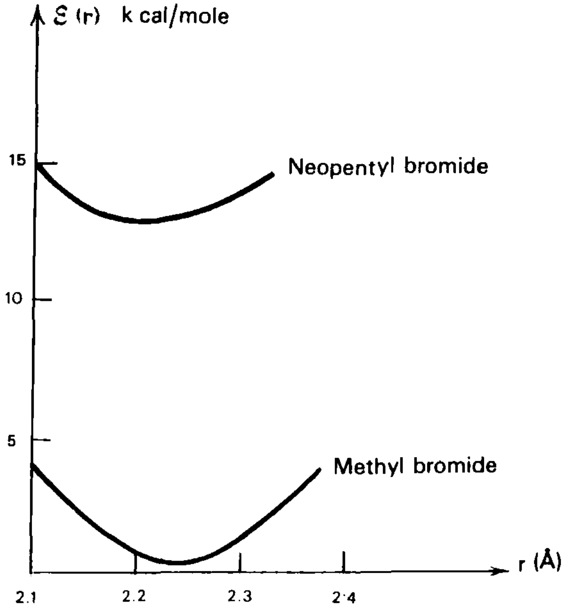


Fig. 13

Now it is easy to compute $\Delta\varepsilon^{\ddagger}_{nb}$ from the equation giving $\varepsilon_{\text{rep}}(r)$. Table VII summarizes the results. It appears that as expected $\Delta\varepsilon^{\ddagger}_{nb}$ increases as the activation energy. The steric factor seems to be the main reason for the slowing down of the rate in passing from the methyl to the neopentyl bromide.

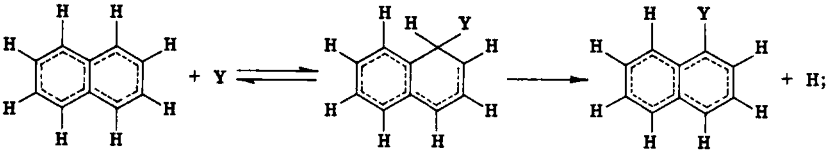
TABLE VII

Nature of the bromide	Methyl	Ethyl	Propyl	Isopropyl	Neopentyl
$\Delta\varepsilon^{\ddagger}_{nb}$ (kcal/mole)	0	0.9	0.9	2.3	12

C. Substitution on a Carbon Atom Belonging to an Aromatic Ring; Importance of $\Delta\varepsilon_d^{\ddagger}$

1. *Estimation of* $\Delta\varepsilon_d^{\ddagger}$ *Following the Wheland Hypothesis*

It is now believed that under various experimental conditions the important reagent of nitration is NO_2^+, and the important reagent of methylation is the free radical CH_3. Let us denote by Y the important reagent of a substitution taking place on naphthalene, for example; the Wheland hypothesis (1942) consists of assuming that the rate-determining step of the reaction can be represented as:



that is to say that in the transition state the perturbed carbon atom becomes a saturated one which is excluded from the delocalized bond.

If we have to compare the relative rates of a given kind of substitution on various carbon atoms belonging to the same conjugated hydrocarbon it is easy to see that $\Delta\varepsilon_d^{\ddagger}$ will be one of the most important factors because this term depends on the complete geometry of the transition state. On the other hand, for example, $\Delta\varepsilon_l^{\ddagger}$ which only depends on the neighborhood of the perturbed carbon is expected not to change very much from a given carbon to a similar one because the environments of the various carbon atoms are similar.

Therefore the discussion will be focused on $\Delta\varepsilon_d^{\ddagger}$. Following the Wheland hypothesis it is easy to calculate $\Delta\varepsilon_d^{\ddagger}$ using the Hückel approximation, for example. This energy can be expressed in β units (β being the standard resonance integral between two adjacent carbon atoms) and is called the localization energy of the perturbed carbon atom:

$$\Delta\varepsilon_d^{\ddagger} = m\beta. \tag{82}$$

N. Muller *et al.* (1954) have suggested calculating this localization energy by taking account of the phenomenon of hyperconjugation. Chalvet and Daudel (1955) have shown that the localization energy calculated when taking account of the hyperconjugation is roughly proportional to the localization energy obtained without the introduction of this phenomenon. We are therefore led to write:

$$\Delta\varepsilon_d^{\ddagger} = \eta m\beta, \tag{83}$$

η being a certain proportionality coefficient.

The localization energy obtained in this way is rather similar to the super delocalizability introduced by K. Fukui *et al.* (1957b).

Obviously $\Delta\varepsilon_d^{\ddagger}$ can be calculated using much more elaborate methods than the simple Hückel approximation. F. Fukui *et al.* (1958) have introduced the Hückel orbitals in the self-consistent field method with Pariser and Parr approximation. They found a linear relationship between the $\Delta\varepsilon_d^{\ddagger}$ calculated in this way and the $\Delta\varepsilon_d^{\ddagger}$ calculated in using the simple Hückel treatment in the case of alternant hydrocarbons. Some discrepancies appeared for nonalternant hydrocarbons. Nesbet (1962) has made an analogous study, doing all the necessary iterations to obtain the correct self-consistent field orbitals. He confirmed Fukui's results for alternant hydrocarbons. A more complete study of the same problem has been done by Chalvet *et al.* (1964) which leads to the same kind of conclusion and also confirms the Fukui result concerning nonalternant hydrocarbons.

On the other hand, Chalvet and Daudel (1952) have calculated various delocalization energies with the help of the configuration interaction method. They also found a rather good relation between their values and the data obtained in using the Hückel approximation in the case of alternant hydrocarbon.

We must also indicate that Dewar has introduced a reactivity number (1952) which is a certain approximation of the localization energy.

In conclusion we can say that in the case of alternant hydrocarbons all the usual ways of calculating $\Delta\varepsilon_d^{\ddagger}$ lead to analogous results. The situation for nonalternant hydrocarbons is not so satisfactory.

As an example of the use of the concept of localization energy $\Delta\varepsilon_l^{\ddagger}$ we shall study the nitration of phenanthrene. Table VIII makes it possible to compare the reactivity numbers of the various carbon atoms of phenanthrene and the percentage of corresponding mononitro compounds obtained by Schmidt and Heinle (1911). As in simultaneous reactions the

TABLE VIII

		Percentage of isomer	
Position of the carbon atom	Reactivity number	Schmidt and Heinle	Dewar and Warford
10	1.80	60	34
1	1.96	—	27
3	2.04	2	25
2	2.18	20	4

percentages of isomers obtained are directly proportional to the rate constants of the reactions; the percentages should be decreasing functions of the reactivity number (which is a measure of $\Delta\varepsilon_d^\ddagger$ if $\Delta\varepsilon_d^\ddagger$ was the only important term). As no such a relation appears it could be thought that $\Delta\varepsilon_d^\ddagger$ is not the only important term. Dewar was led to another conclusion. He believed that the Schmidt and Heinle experiment was unreliable.

For this reason, with Warford (Dewar and Warford, 1956) he performed a new careful experiment. The results also appear in Table VIII. *It is now seen that, as expected, a good decreasing relationship exists between the reactivity numbers and the percentages of mononitro isomers.*

2. *Relation between Static and Dynamic Indexes*

In order to establish when a relationship between the structure of a molecule and its chemical reactivity is possible some static indexes depending only on the initial molecule have been introduced.

For example, Daudel and Pullman (1945) have given (using the valence bond method) the first precise definition of the *free valence number* starting from an idea of Svartholm (1941). The concept of free valence number has been extended by Coulson to the molecular orbital method (Coulson, 1946).

The free valence F_i of a carbon atom belonging to an aromatic ring is simply the difference between an arbitrary constant C and the sum of the bond orders p_{ij} of the various CC bonds starting from this carbon atom:

$$F_i = C - \sum_j p_{ij}. \tag{84}$$

A good linear relationship has been observed by Daudel *et al.* (1950) and Roux (1950) between the free valence number of a carbon atom of an alternant hydrocarbon and its localization energy $\Delta\varepsilon_d^\ddagger$ (Fig. 14). This finding has been confirmed by Burkitt *et al.* (1951).

Assuming that the free valence determines the relative rates of methylation of the alternant hydrocarbon in some particular experimental conditions, it has been possible to calculate these relative rates. Figure 15 makes it possible to compare the theoretical results with the experimental data (Daudel and Chalvet, 1956). *The agreement is surprisingly good.*

Another concept which can be useful to establish a bridge between the structure of a molecule and its chemical reactivity is the autopolarizability. When the Hückel method is used the autopolarizability of a given atom belonging to a conjugated system is (Coulson and Longuet-Higgins, 1947):

$$\Pi = \frac{\partial q}{\partial \alpha} \tag{85}$$

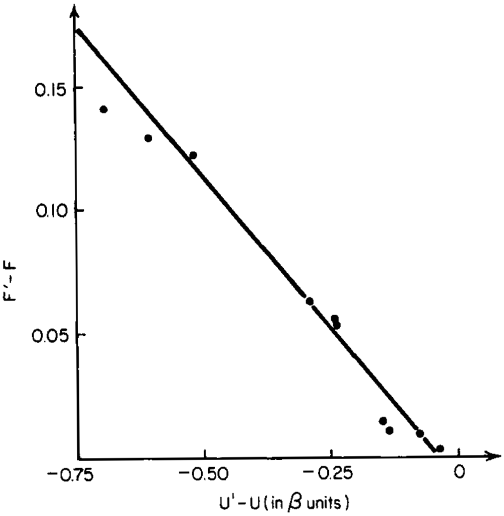

0.15
0.10
0.05
F'-F
−0.75
−0.50
−0.25
0
U' − U (in β units)

Fig. 14

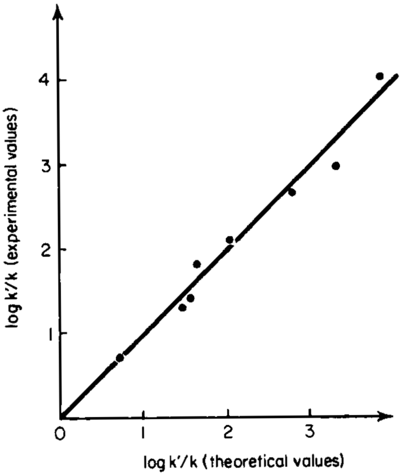

4
3
2
1
log k'/k (experimental values)
0
1
2
3
log k'/k (theoretical values)

Fig. 15

where q is the π electronic charge of the atom and α the corresponding coulombic integral.

It has been shown that for alternant hydrocarbons there is a good relationship between the free valence of a given carbon atom and its autopolarizability. Therefore there is also a satisfactory relationship between the localization energies and the autopolarizabilities (Daudel *et al.*, 1950, 1951; Busso *et al.*, 1950).

In conclusion we can say that to introduce the $\Delta\varepsilon_d^\ddagger$ associated with a substitution reaction on an alternant hydrocarbon we have the choice between various dynamic indexes such as localization energy, superdelocalizability, and reactivity number, and various static indexes such as free valence and autopolarizability. Sung *et al.* (1960) tried to see which are the best from the practical point of view. They found that it seems better to use the localization energies (Sung *et al.*, 1960) than the superdelocalizability or the static indexes.

Various attempts have been made to establish a relationship between dynamic and static indexes of nonalternant hydrocarbons and hetero molecules. The problem is more involved than in the case of alternant hydrocarbons.

For example, in the case of alternant hydrocarbons it has not been necessary to distinguish between the nature of the reagents because if the Wheland model is used the differences between two $\Delta\varepsilon_d^\ddagger$ which determine the relative rates do not depend on the nature of the reagent. This is not so when we are concerned with nonalternant hydrocarbons or hetero molecules and we must distinguish between radical, nucleophilic, or electrophilic reagents. For example, if we are concerned with an electrophilic reagent it is natural to search for a relation between $\Delta\varepsilon_d^\ddagger$ and the electronic charge q of the carbon atom perturbed. In fact only a rough relationship is observed (Sandorfy *et al.*, 1950; K. Fukui *et al.*, 1957a).

3. *The Accuracy of the Wheland Model*

As $\Delta\varepsilon_d^\ddagger$ is obtained in β units when the Hückel method is used, comparison between the calculated values of the relative rates and the experimental ones makes it possible to obtain empirical values of $\eta\beta$. Mason (1958) has obtained:

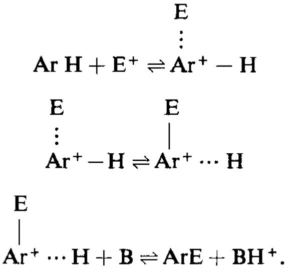
$\eta\beta = -7$ kcal in the case of methylation,
$\eta\beta = -16$ kcal in the case of nitration.

He was led to the conclusion that the transition state is more similar to the Wheland model in the case of nitration than in the case of methylation. In studying the role of $\Delta\varepsilon_s^{\ddagger}(T)$ and particularly its effect on the activation entropy, Mason (1959) concluded that for a given reaction the lower the localization energy the more the transition state looks like the Wheland model.

4. *Other Possible Mechanisms*

Brown (1959) had observed that if the Wheland model is used it is not easy to understand why there is no isotopic effect in the case of nitration but a striking isotopic effect in the case of sulfonation when tritiated compounds are used.

To explain this fact Brown has suggested the following mechanism for electrophilic substitution:



$$\mathrm{Ar\,H} + \mathrm{E}^+ \rightleftharpoons \overset{\overset{\mathrm{E}}{\vdots}}{\mathrm{Ar}^+} - \mathrm{H} \tag{I}$$

$$\overset{\overset{\mathrm{E}}{\vdots}}{\mathrm{Ar}^+} - \mathrm{H} \rightleftharpoons \overset{\overset{\mathrm{E}}{|}}{\mathrm{Ar}^+} \cdots \mathrm{H} \tag{II}$$

$$\overset{\overset{\mathrm{E}}{|}}{\mathrm{Ar}^+} \cdots \mathrm{H} + \mathrm{B} \rightleftharpoons \mathrm{ArE} + \mathrm{BH}^+. \tag{III}$$

It is obvious that if such a mechanism is convenient no isotopic effect will be observed when step (I) is rate determining, but an isotopic effect will appear when step (II) is the rate-determining process.

Therefore Brown has assumed that for nitration step (I) is the rate-determining process. This step corresponds to a charge transfer between ArH and E^+, and Brown has calculated $\Delta\varepsilon_d^{\ddagger}$ using the Mulliken theory of charge transfer complexes. He obtained a fair relationship between the relative rates of nitration of some alternant hydrocarbons and the $\Delta\varepsilon_d^{\ddagger}$ calculated in this way.

Nagakura and Tanaka (1959) have suggested another mechanism. They assume that the first step of the reaction is an ionization of the molecule:

$$\mathrm{ArH} + \mathrm{E}^+ \rightarrow \mathrm{E} + \mathrm{ArH}^+.$$

Then the free radical E reacts on the positive ion ArH^+. They have observed that the atom on which the substitution appears is really the one which has the highest free valence in the ArH^+ ion. If the Nagakura and Tanaka mechanism is convenient it can be anticipated that an electrophilic substitution will be easier the higher the last occupied orbital of the hydrocarbon and the lower the first unoccupied orbital of the reagent. This is so. Let us compare, for example, benzene and methane. The last occupied orbital of the first molecule is at -3.74 eV and the corresponding orbital of the second is at -13 eV. It is much easier to nitrate benzene than methane. Furthermore in Ag^+ the first unoccupied orbital is at -7.6 eV and in $NO_2{}^+$ it is at -11 eV. $NO_2{}^+$ leads to real substitutions; Ag^+ gives only charge transfer complexes.

5. *Relation between Substitution Rate and* p_K

It is well-known that when an alternant hydrocarbon is put in a very acid medium, such as $BF_3 + HF$, it can add a proton:

$$\mathrm{ArH} + \mathrm{H}^+ \overset{K}{\rightleftharpoons} \mathrm{ArH_2}^+.$$

The structure of the positive ion $ArH_2{}^+$ has been carefully studied (MacLean *et al.*, 1958). Figure 16 shows, for example, the structure of the

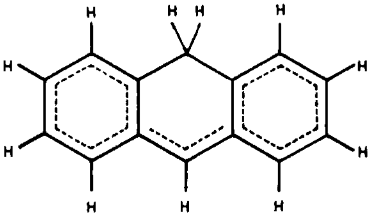


Fig. 16

ion which corresponds to anthracene. It is obvious that the $\Delta\varepsilon_d$ which determines the p_K of a given hydrocarbon is equal to the $\Delta\varepsilon_d{}^{\ddagger}$ which determines the rate of substitution when the Wheland model is used. Therefore, we can anticipate a linear relationship between, let us say, the logarithm of the rate of methylation of alternant hydrocarbons and their p_K. This relationship has been found by Mackor *et al.* (1958).

D. Rate of Photochemical Reactions

1. *Introduction*

We have previously said that one of the most difficult problems in studying a chemical reaction is to know the path of the reaction. Obviously this problem, which is a difficult one in the field of classical chemistry, is still more difficult when we are concerned with a photochemical reaction. Furthermore, some authors believe that it is not very convenient to use the transition state theory to discuss the reactivity of an excited state (Laidler, 1955).

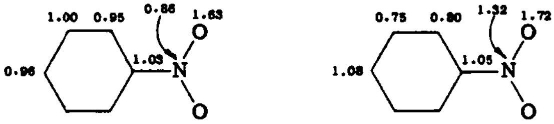
However, the simple use of static indexes has given useful results even for substituted or hetero molecules. A priori, it is not easy to understand why. We saw that even in the case of hetero molecules in their ground state there is not a fair relationship between, let us say, the electronic charges and the electrophilic localization energies. We do not know a systematic study of the same relationship for the excited states of the same molecules but, a priori, it could be anticipated that the situation is worse. However the static indexes appear to be useful. The reason for this result lies perhaps in the fact that for an excited state the potential barrier is usually smaller than for the ground state. Therefore the transition state seems to be more similar to the initial state than for a molecule reacting in its ground state. This could be an explanation why "tout se passe comme si" in the case of an excited state the static indexes, which only depend on the initial state, are a fair representation of the localization energies which, however, also depend on the transition state. It seems that the first proposal to use the static indexes in studying a photochemical problem is due to Pullman and Daudel (1946). They observed that the distribution of the bond orders and free valences of cyclopentadiene in its first excited state is completely different from the same distribution for its ground state. In the same way Crawford and Coulson (1948) studied the photodimerization of acenaphthylene. Later on it was observed (Sandorfy, 1950; Buu Hoi *et al.*, 1951) that all the free valences of molecules such as anthracene and naphthacene in their first electronic excited states are greater than those of the corresponding ground states, the greatest free valences remaining are those of the *meso* carbon atoms. This increase of the free valences could play a role during the photodimerization and during the photooxidation of the molecule considered.

On the contrary the bond order of the central bond of stilbene in its first excited state is smaller than those of the ground state (Buu Hoi *et al.*, 1951). This phenomenon could be an explanation of the *trans* → *cis* photoisomerization of stilbene. In the same way Masse (1954) and Bloch-Chaude and Masse (1955) try to explain the photochromic properties of some derivatives of pyranospirane.

2. *Photochemistry of Nitrobenzene Derivatives*

To end this chapter we shall now discuss with more details the photochemistry of some nitrobenzene derivatives.

The distribution of the electronic charges for various electronic states of nitrobenzene has been calculated by Fernandez-Alonso (1951). Figure 17 compares these distributions for the ground state and one of the excited states. A striking difference appears between the two states. In the ground state the nitro group withdraws electrons from the *ortho* and *para* positions and does not alter the electronic charge of the *meta* position. In the excited state, on the contrary, the nitro group withdraws electrons mainly from the *meta* position, the *para* position being not significantly perturbed. Five years later, Havinga *et al.* (1956) studied the photochemical hydrolysis of the isomeric nitrophenyl dihydrogen phosphate and also the bisulfate esters. They observed that the process is most efficient for the *meta* isomers suggesting that in excited states of these molecules the nitro group is able to withdraw electrons from the phenolic phosphate oxygen atom, thus facilitating heterolytic fission. More recently, Zimmerman (1963) studied the photochemical behavior of the trityl esters of *m*-nitrophenol and *p*-nitrophenol in aqueous dioxane. They observed that in the dark at 25°C the *meta* compound is stable and the *para* compound is slowly hydrolyzed. Under the effect of light, on the contrary, the quantum efficiency is much greater for the *meta* compound (0.062) than for the *para* derivative (0.006). Again an interpretation is given if we follow the suggestion of the Fernandez-Alonso calculation: in some excited states of these molecules the nitro group withdraws electrons from the *meta* position.



Ground state Excited state

Fig. 17

Zimmerman and Somasekhara (1963) have calculated the distribution of the electronic charges for the ground states and the first excited states of the considered trityl esters. Table IX contains the electronic charges

TABLE IX

OXYGEN ELECTRONIC CHARGES

	Ground state	Excited state
Meta derivative	1.764	1.279
Para derivative	1.703	1.307

obtained for the oxygen of the $OC\varphi_3$ group. It is clear that, as for the reactivity, the order of the electronic charges in the excited state is the reverse of the corresponding order for the ground state.

V. General Conclusion

We have seen that in the case of small molecules it has been possible to establish rather complete formulas which, in principle, permit the calculation of the absolute rates of reactions.

Obviously it is not possible to use such elaborate formulas to discuss reactions in which large molecules are involved. However, the general formalism obtained in the case of small molecules has been extended to more complex reactions in such a way that it has been possible to determine what are the main factors which are responsible for the chemical reactivity of such large molecules. The factors are numerous (at least eight for a given conformation and a given elementary process of a reaction). Fortunately, however, in certain cases some of these factors are predominant and others can be neglected. Therefore, rather rough calculations appear to be helpful when we are able to select the important factors. In the case of photochemistry, a priori the situation appears to be more difficult. In fact it turns out that even very rough procedures permit us to predict correctly new kinds of chemical reactivity. This is encouraging. There is no doubt that in the near future quantum chemistry will become a very powerful tool in the interpretation and prediction of the chemical reactivity of large molecules.

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Electronic Theories of Hydrogen Bonding

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I. Introduction

During the last twenty years considerable interest has been manifested in the study of the hydrogen bond. A large number of papers as well as several books (Hadži and Thompson, 1959; Pimentel and McCllelan, 1960; Sokolov and Tschulanovskii, 1964) have been published. In spite of this effort the ideas in this field still seem to be conflicting. Even the basic electronic theory of hydrogen bonding is still discussed although a part at least of the disagreement comes from the differences in emphasis rather than from the divergencies in basic concepts. In these circumstances a critical analysis of the present theory seems useful; the areas in which the agreement has been reached can be recognized. This will be done in what follows. It will be concluded that the overwhelming majority of phenomena connected with hydrogen bonds can be explained if this bond is considered as describing an interaction in which the electrostatic, charge-migration as well as the short-range repulsion effects are simultaneously important. The fundamental similarity between the hydrogen bond and charge-transfer interactions is emphasized.

II. Phenomenology of Hydrogen Bonding

The name hydrogen bond is given to a particular type of strong and specific interaction. The first molecule of the interacting pair, called the proton donor, contains a strongly polar group AH (e.g., FH, OH, NH, ...) and the second, called the proton acceptor, a strongly electronegative atom B (e.g., F, O, N, ...). A hydrogen bond is generally designed by symbols such as AH···B. If this interaction is strong enough, well-defined molecular complexes result. Their geometry is often precisely known; two representative cases are illustrated in Figs. 1(a) and 1(b). The hydrogen bond can be symmetric or asymmetric depending on whether the proton is located midway between the terminal atoms or closer to one of them. Symmetric hydrogen bonds are quite rare, the ion FHF^- being the classical example [Fig. 1(a)]. They are very strong: the dissociation energy of FHF^- to $FH + F^-$ is of the order of 40 kcal/mole although the exact value is uncertain. In the majority of cases, the hydrogen bonds are asymmetric [Fig. 1(b)]. In this case energies are of the order of 5–10 kcal/mole and increase when the distance $R_{AH\cdots B}$ decreases; the smaller $R_{AH\cdots B}$ the larger R_{AH}. Substitution of deuterium causes the AH···B bond to expand (Ubbelohde effect). It is not known whether this comes from the change of the effective surface[1] on substitution, or from other sources.

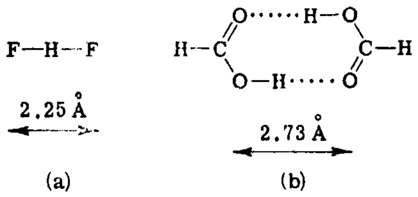

Fig. 1. Two representative systems involving hydrogen bonds: the ion FHF^- represents a symmetric bond (a); $(HCOOH)_2$ represents an asymmetric bond (b).

The spectra of molecules with hydrogen bonds exhibit several unusual features. Their infrared spectra are characterized[2] by (*a*) an important low-frequency shift with respect to those of nonbonded molecules of the 1ν AH stretching bands; (*b*) an increase, with respect to those of nonbonded molecules, of their integrated intensity; (*c*) their abnormal breadth

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[1] If the electronic state considered is nondegenerate, the influence of the term omitted in the Born–Oppenheimer approximation can be accounted for by suitably modifying the Born–Oppenheimer energy surface. This modified surface, called the "effective" energy surface, depends on nuclear mass (Bratož and Daudel, 1956).

[2] Only the most salient features are quoted here.

and, eventually, complicated structure (Fig. 2). In addition, (*d*) new bands appear associated with the low-frequency bridge vibration. These perturbations are astonishingly pronounced when one considers the relative weakness of hydrogen bond. In the ultraviolet spectra both hypsochromic and bathochromic shifts are observed depending on whether the hydrogen bond is stronger in the ground state or in the excited state (Fig. 3). The $n \rightarrow \pi^*$ frequencies are generally displaced to the blue and the $\pi \rightarrow \pi^*$ frequencies shift usually, but not invariably, to the red. The presence of a charge-transfer band has been reported. Finally, in the NMR spectra the proton signal is displaced to lower field although there are also exceptions to this rule.

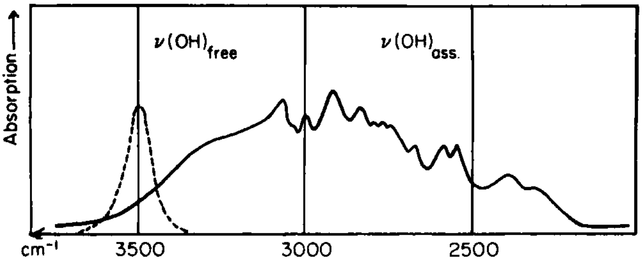


Fig. 2. The infrared spectrum of formic acid in the νOH region (sol. in CCl_4) showing a complicated structure. The breadth of this band is compared with that of free νOH, schematically indicated (Bratož *et al.*, 1956).

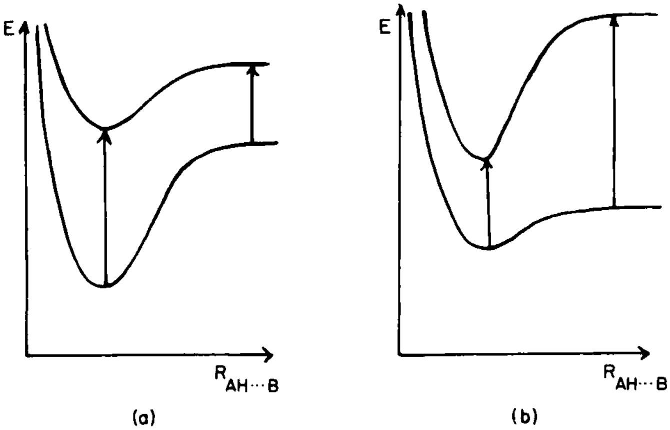


Fig. 3. AH···B energy curves indicating the origin of the UV frequency shifts.

The role of the theory is to explain, qualitatively at least, the data just mentioned.

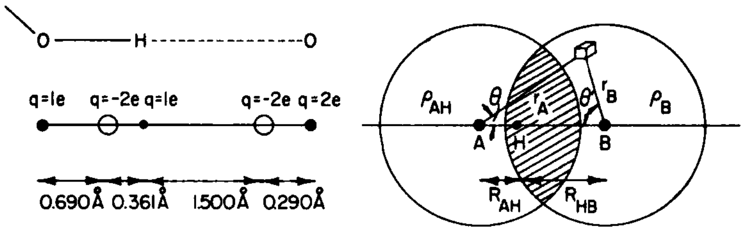
III. Classical Theories

A. Introductory Remarks

The early theoretical work on hydrogen bonding is based on the following argument. The hydrogen atom of the AH···B bond, with its 1*s* orbital, cannot form more than one pure covalent bond. Hydrogen bond formation must therefore be due to ionic forces. This argument, due to Pauling (1929), underlies what are now called electrostatic theories of the hydrogen bond. Two versions of such theories exist: (*a*) an elementary version in which the true charge distribution is approximated by a set of point charges, and (*b*) an elaborate version in which continuous charge distributions are considered. The main work is analyzed in what follows.

B. Elementary Electrostatic Theories

These theories have mainly been developed by Bernal and Fowler (1933), Bauer and Magat (1938), Lennard-Jones and Pople (1951), and Pople (1951). [See also Bourre-Maladière (1950), Briegleb (1941, 1944), Coggeshall (1950), Davies (1947), Harms (1939), Jones *et al.* (1952), Kasper (1931), Maladière and Magat (1947), Maladière (1948), Moelwyn-Hughes (1938), Rowlinson (1951), Sack and Prigogine (1941), Schneider (1955), and Verwey (1941).] Their spirit, and procedures, can conveniently be explained in the example of OH···O′ systems [Fig. 4(a)].



(a) (b)

Fig. 4. The charge distributions used in the (a) elementary and (b) elaborate electrostatic theories. The black points indicate nuclear charges and the circles the electron distributions.

Four electrons are explicitly considered, two from the OH bond and two from the O′ lone pair; all remaining electrons and the nuclei are considered as forming the molecular core. The core is represented by three positive charges located on the nuclei. The electrons are located on the OH···O′ line in such a way as to give the correct values of the OH bond and the O′ lone pair dipole moments. This choice once made, the interaction energy is calculated with the help of the simple Coulomb formula. The energy found in the present case is 6 kcal/mole, a value close to the experimental value. A similar agreement is reached in several other cases. However the quality of the results depends critically on the choice of the point charges and their positions. The electrostatic theories have also been applied, with success, to the calculation of the AH bond expansion on association, to the explanation of the low-frequency shifts of the infrared 1ν AH stretching bands, and to the study of a number of other problems. The main conclusions are as follows. (*a*) The electrostatic energy represents an important component of the hydrogen bond energy. This conclusion is still further supported by the fact that the experimentally known hydrogen bond strengths decrease in the same order as the electronegativities of atoms between which they are formed, i.e., in the order FH···F, OH···O, NH···N, etc. (*b*) The electrostatic forces contribute to the AH bond expansion and to the 1ν AH low-frequency shift on association. In fact, the charge on B exerts a force on the proton which opposes the force acting on the proton in the free molecule. The R_{AH} distance is thus increased and the stretching force constant $K_{\nu AH}$ is decreased.[3]

C. Elaborated Electrostatic Theories

In these theories the charge distribution is represented more carefully, although not necessarily more successfully, than in the elementary electrostatic theories. In the recent Bader's paper (1964) the OH···O′ systems are treated by considering all electrons of this system explicitly. The electronic distribution ρ_{AH} of the acid species AH is described by that of a united atom containing $Z_A + 1$ electrons centered on A. Similarly, the electron distribution ρ_B of the base B is represented by the electron distribution of an atom centered on B. In addition, there are three nuclei with charges Z_A, 1, and Z_B [Fig. 4(b)]. If these distributions are spherical, the resulting force F_Z on the proton is easily calculated by the laws of classical electrostatics. Using the notation of Fig. 4(b) one obtains[4]:

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[3] This conclusion has been strongly criticized by Sokolov (1955a). Nevertheless this criticism seems too severe.

[4] The well-known result of the classical electrostatic is used according to which one has, for a spherical charge distribution, $\int_0^R (\cos\theta\rho/r^2)d\tau = Q_R/R^2$.

$$F_Z = -\frac{\partial V}{\partial z_{AH}} = \frac{Z_A}{R_{AH}^2} - \int \frac{\cos\theta}{r_A{}^2}\rho_{AH}\,d\tau - \frac{Z_B}{R_{HB}^2} + \int \frac{\cos\theta'}{r_B{}^2}\rho_B\,d\tau$$

$$= \frac{1}{R_{AH}^2}(Z_A - Q_A) - \frac{1}{R_{HB}^2}(Z_B - Q_B), \qquad (1)$$

where Q_A, Q_B are the electronic charges contained in the spheres of radii R_{AH}, R_B centered on A, B. The $K_{\nu AH}$ stretching force constant is obtained by differentiating F_Z with respect to z_{AH}. If ρ_{AH} and ρ_B are independent of z_{AH}, one finds

$$K_{\nu AH} = -\frac{\partial^2 V}{\partial z_{AH}^2} = \frac{2}{R_{AH}^3}(Z_A - Q_A) + \frac{2}{R_{HB}^3}(Z_B - Q_B) + 4\pi(\rho_{AH}(H) + \rho_B(H)), \qquad (2)$$

where $\rho_{AH}(H)$ and $\rho_B(H)$ are the electron densities of AH and B at the proton position. These formulas easily explain that the R_{AH} distance is increased and $K_{\nu AH}$ is decreased when a hydrogen bond is formed. Mathematically this can be obtained by putting $F_Z = 0$, resolving this equation for R_{AH}, and inserting R_{AH} into Eq. (2). Physically, the interpretation is just the same as in the case of the elementary electrostatic theories. The AH bonding force constants can be studied in a similar way and are found to be positive. The conclusions of the present theory are thus just the same as those reached by the elementary electrostatic theories. It is satisfactory, however, that they have been obtained by using more realistic charge distributions than those postulated in the elementary electrostatic theories.

D. Critical Survey of Electrostatic Theories

These theories are all based on the hypothesis according to which the hydrogen bond interaction of AH and B reduces to that of two charge distributions associated with *unperturbed* AH and B.[5] In reality, the formation of hydrogen bond perturbs these distributions, e.g., by charge transfer or exchange transfer; all such distortions are neglected. The question to decide is whether such simple theories are, or are not, successful. If they are the hydrogen bond can be said to be ionic.

[5] A confusion may arise by using this terminology. In fact, the forces acting on the nuclei can always be calculated by means of laws of classical electrostatics provided the true charge distribution is known. This is a consequence of a well-known Feynmann–Hellmann theorem. All nonmagnetic chemical forces are electrostatic in a certain sense. In the theory of hydrogen bonding, however, this term refers to the forces originating, not from the true charge density hiding all sorts of quantum mechanical effects, but from the charge density of unperturbed AH and B.

With this in mind it can safely be stated that the hydrogen bond is partially ionic. It should not be concluded, however, that it is entirely ionic. In fact, a number of data reveal nonionic properties of hydrogen bonds. Three such pieces of evidence which are particularly important, are listed here. (*a*) There is no correlation between hydrogen bond strength and dipole moment of the base. If the electrostatic forces were the only forces present, it would be difficult to understand why, for example, acetonitrile and nitromethane, the dipole moments of which are equal to 3.54 D and 3.94 D, respectively, form with phenol the complexes which are less stable than the complexes between phenol and dioxane, the latter having a very small dipole moment of about 0.3 D (Sokolov, 1964). (*b*) The AH···B distances are always much smaller than the sum of the van der Waals radii. Thus strong repulsions arise and the electrostatic forces are not the only forces present. (*c*) The increase of the intensity of the 1ν AH stretching infrared bands is much too large to be accounted for by the electrostatic theory. The existence of charge-transfer forces seems likely. These, and a number of similar data, lead to the following conclusion: the electrostatic theories, in spite of their considerable success, are not entirely satisfactory and must be replaced by more elaborate quantum mechanical theories.

IV. Quantum Theories; Ground State

A. Introductory Remarks

The need for quantum mechanical theories of hydrogen bonding was recognized as early as 1947. In this year Sokolov published the first theory of this type. The later development of the theory was slow because of the relative complexity of the systems connected with hydrogen bonds; nevertheless, in the last few years, more satisfactory progress has been made. Roughly speaking, the existing work can be split into three groups which comprise (*a*) valence-bond theories, (*b*) charge-transfer theories, and (*c*) SCF-MO and CI theories. These theories are described.

B. Valence-Bond Theories

In this group of theories the VB techniques are applied to study hydrogen-bonded systems. As this method is not appropriate for detailed nonempirical calculations, the problem has always been reduced to that of four electrons, two of the acid AH bond and two of the base B lone pair, moving in a molecular core. In this way Sokolov (1947, 1952a) and Coulson–Danielsson (1954b) investigated the systems AH···B and OH···O′

and Tsubomura (1954) investigated $(H_2O)_2$. [See also Coulson (1957, 1959), Sokolov (1955a, 1959), and Sokolov and Tschulanovskii (1964).] The spirit of the method, and the procedures implied, can most easily be explained on the example of the Coulson-Danielsson paper which is now described.

In the Coulson-Danielsson paper (1954b) the O—H···O′ systems are considered. The four electrons involved in the hydrogen bond formation are distributed over the atomic orbitals p_1', h', p_2' (Fig. 5).[6] With the help

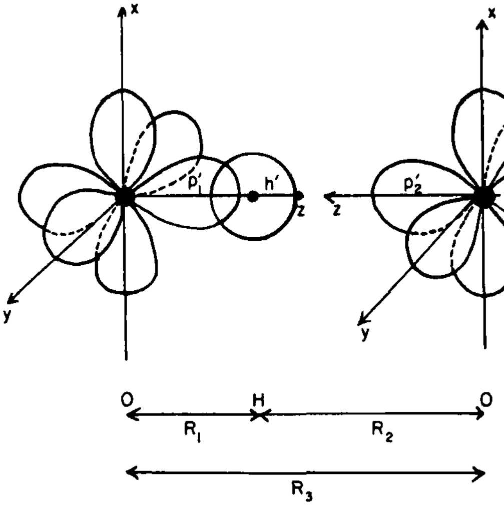

Fig. 5. The orbitals p_1', h', and p_2' involved in an OH···O′ hydrogen bond. The figure gives also the definition of R_1, R_2, and R_3.

of these orbitals, the following wave function Φ is constructed to represent the hydrogen bond:

$$\Phi = C_{\rm I}\Phi_{\rm I} + C_{\rm II}\Phi_{\rm II} + C_{\rm III}\Phi_{\rm III} \tag{3}$$

with

$$\begin{aligned} \Phi_{\rm I} &= N_{\rm I}\{|p_1\bar{h}p_2\bar{p}_2| - |\bar{p}_1 h p_2 \bar{p}_2|\}, \\ \Phi_{\rm I} &= |p_1\bar{p}_1 p_2 \bar{p}_2|, \\ \Phi_{\rm III} &= N_{\rm III}\{|p_1\bar{p}_1 h \bar{p}_2| - |p_1\bar{p}_1\bar{h}p_2|\}. \end{aligned} \tag{4}$$

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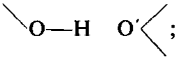
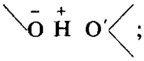
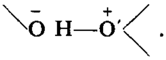
[6] For simplicity, the oxygen orbitals are supposed to be pure p-orbitals. In the original paper, the effect of hydridization was also investigated.

Here, the standard notation is used. The vertical bars indicate normalized determinants, p and h indicate the atomic spin orbitals associated with the orbitals p' and h', and the spin α, $\bar{p}$ and $\bar{h}$ indicate the atomic spin orbitals associated with the orbitals p' and h' and the spin β, and C_{I}, C_{II}, and C_{III} are variational coefficients. The wave function Φ contains three components Φ_{I}, Φ_{II}, and Φ_{III} associated with the following three "mesomeric structures":

(I)

(II)

(III)


Φ_{I} describes a situation in which a covalent bond is formed between O and H, the lone pair being located on O′. Φ_{II} is similarly describing an ionic bond between O and H, the lone pair being still located on O′. Finally, Φ_{III} represents a situation in which a covalent bond is between H and O′, the lone pair now on O. The electronic configurations associated with Φ_{I}, Φ_{II}, and Φ_{III} are given in Table I. This choice of mesomeric structures is one of fundamental characteristic of the VB theory of hydrogen bonding. In fact, if Φ_{I} and Φ_{II} describe ionic interactions between the acid and the base, interactions accounted for by electrostatic theories, Φ_{III} describes a new phenomenon of quantum mechanical origin. This new phenomenon is the charge transfer, from O′ to O, conferring to the hydrogen bond a partially covalent character.

TABLE I

ELECTRONIC CONFIGURATIONS ASSOCIATED WITH $\Phi_{\mathrm{I}}, \Phi_{\mathrm{II}}, \Phi_{\mathrm{III}}$ AND IN THE VB THEORY OF HYDROGEN BONDING

Φ_{I}	$(p_1')(h')(p_2')^2$
Φ_{II}	$(p_1')^2(p_2')^2$
Φ_{III}	$(p_1')^2(h')(p_2')$

The wave function Φ once defined, the techniques of the calculation must still be briefly discussed. The energy E and the coefficients C_{I}, C_{II}, and C_{III} are obtained by solving the secular equation:

$$\begin{vmatrix} H_{\mathrm{I\,I}} - ES_{\mathrm{I\,I}} & H_{\mathrm{I\,II}} - ES_{\mathrm{I\,II}} & H_{\mathrm{I\,III}} - ES_{\mathrm{I\,III}} \\ H_{\mathrm{II\,I}} - ES_{\mathrm{II\,I}} & H_{\mathrm{II\,II}} - ES_{\mathrm{II\,II}} & H_{\mathrm{II\,III}} - ES_{\mathrm{II\,III}} \\ H_{\mathrm{III\,I}} - ES_{\mathrm{III\,I}} & H_{\mathrm{II\,III}} - ES_{\mathrm{II\,III}} & H_{\mathrm{III\,III}} - ES_{\mathrm{III\,III}} \end{vmatrix} = 0. \qquad (5)$$

In this equation, the Hamiltonian matrix H is relative to an effective four-particle Hamiltonian the form of which does not need to be further specified; the overlap matrix S is, on the contrary, perfectly well defined. The calculation is performed as follows. (*a*) The overlap matrix is calculated nonempirically using Slater's orbitals. (*b*) The diagonal elements of the Hamiltonian matrix are calculated semiempirically taking into account the fact that H_{ii} is just the energy of the pure state Φ_i. H_{ii} is composed of the following terms: (1) the covalent bond energy expressed by the familiar Morse formula; (2) the short-range repulsion energy expressed by the help of the empirical formula Ke^{-br}; (3) the energy associated with the transfer of an electron from an atom X to an atom Y (Fig. 6); (4) the polarization energy. In this way and by using the notation of Figs. 5 and 6, the following formulas are easily found:

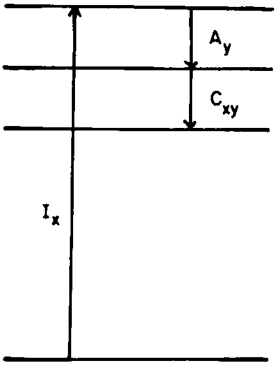


Fig. 6. The energy implied in an electron transfer between X and Y: I_X is the ionization potential of X, A_Y is the electroaffinity of Y, and C_{XY} is the Coulomb attraction of the two ions created by the charge-transfer process. If X and Y are atoms, $C_{XY} = e^2/R_{XY}$.

$$H_{\rm I\,I} = D\{e^{-2a(R_1-R_0)} - 2e^{-a(R_1-R_0)}\}, \tag{6a}$$

$$H_{\rm II\,II} = I_{\rm H} - A_{\rm O} - C_{\rm HO} + Ke^{-bR_1}, \tag{6b}$$

$$H_{\rm III\,III} = D\{e^{-2a(R_2-R_0)} - 2e^{-a(R_2-R_0)}\} + I_{\rm O'} - A_{\rm O} - C_{\rm OO'} - \frac{1}{2}\frac{\alpha}{(R_1 + \frac{1}{2}R_2)^4} \tag{6c}$$

where D, a, K, and b are empirical constants, R_0 is the equilibrium distance of free OH, and α is its polarizability. (*c*) The nondiagonal elements H_{ij} of the Hamiltonian matrix are determined as follows: (1) $H_{\rm I\,II}$ is calculated in such a way that the secular equation constructed on $H_{\rm I\,I}$, $H_{\rm I\,II}$, $H_{\rm II\,II}$, and

$S_{\mathrm{I\,II}}$ gives the exact value E_0 for the free OH bond energy; (2) $H_{\mathrm{I\,III}}$ and $H_{\mathrm{II\,III}}$ are calculated, starting from $H_{\mathrm{I\,II}}$, by approximating the charge distributions $p_1'h'$ and $h'p_2'$ by the well-known Mulliken formula. The result is:

$$H_{\mathrm{I\,II}} = S_{\mathrm{I\,II}}E_0 - \sqrt{(H_{\mathrm{I\,I}} - ES_{\mathrm{I\,I}})(H_{\mathrm{II\,II}} - E_0S_{\mathrm{II\,II}})},$$

$$H_{\mathrm{I\,III}} = \sqrt{\frac{2}{1 - S_1^2 + S_2^2}}\, S_2 H_{\mathrm{I\,II}},$$

$$H_{\mathrm{II\,III}} = \sqrt{\frac{1 + S_1^2 - S_2^2}{1 - S_1^2 + S_2^2}} \cdot \frac{S_2}{S_1} \cdot H_{\mathrm{I\,III}}.$$

Here $S_1 = \langle p_1' \mid h' \rangle$ and $S_2 = \langle p_2' \mid h' \rangle$. If the constants entering into the matrix elements are conveniently chosen, the matrix elements can be calculated and the secular equation (5) resolved. The quality of the results depends critically on the choice of the empirical parameters.

So far we have discussed the Coulson–Danielsson method. The methods used by Sokolov (1947, 1952a) and Tsubomura (1954) as well as the method used in another Coulson–Danielsson's paper (1954a) differ from that described above in many points.[7] Nevertheless, the conclusions reached by all these theories are similar and can be stated as follows. (*a*) The forces implied in hydrogen bonding are (1) the electrostatic forces, (2) short-range repulsion forces, (3) charge-transfer forces, and (4) polarization forces. (*b*) The contributions to the hydrogen bond energy arising from effects (1), (2), and (3) are all of the same order of magnitude, but of different sign (Table II). Often effects (2) and (3) cancel each other which

TABLE II

SEMIEMPIRICAL ESTIMATION OF THE ENERGY CONTRIBUTIONS TO EACH SEPARATE H BOND IN ICE (KCAL/MOLE)[a]

(*a*) Electrostatic	+6
(*b*) Repulsive + dispersion	−5.4
(*c*) Charge transfer	+8
Total	+8.6
Experimental	+6.1

[a] From Coulson (1959).

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[7] In the Tsubomura paper all matrix elements are calculated nonempirically. In the second Coulson–Danielsson paper, the bond orders rather than the matrix elements are empirically estimated.

explains the success of electrostatic theories. (*c*) The amount of charge transferred from O′ to O is measured by the quantity C_{III}^2. C_{III}^2 is found to be nonnegligible (but small) for short bonds and negligible for long bonds; thus the long bonds are essentially electrostatic (Tables III and IV). Although basically correct this conclusion underestimates the importance of the covalent term. There exist intermolecular forces without

TABLE III

The Energy E and The Weights C_I^2, C_{II}^2, and C_{III}^2 as Functions of the Distances R_{OH} and $R_{OO'}$.[a]

$R_{OO'}$ (Å)	R_{OH} (Å)	E (kcal/mole)	C_I^2	C_{II}^2	C_{III}^2
2.50	0.8	−91	0.88	0.10	0.02
	1·0	−120	0.83	0.13	0.04
	1.2	−107	0.81	0.13	0.06
2.65	0.8	−90	0.89	0.10	0.01
	1.0	−117	0.85	0.13	0.03
	1.2	−103	0.83	0.12	0.04
2.80	0.8	−88	0.89	0.10	0.01
	1.0	−114	0.86	0.13	0.02
	1.2	−100	0.85	0.12	0.03

[a] From Coulson and Danielsson (1954b).

TABLE IV

The Stretch of the OH Distance, the Dissociation Energy D, and the Weights C_I^2, C_{II}^2, and C_{III}^2 for the Hydrogen Bond at the Equilibrium Position of the Hydrogen Atom[a]

$R_{OO'}$(Å)	R_{OH}(Å)	$R_{OH}-R_O$ (Å)	E (kcal/mole)	D (kcal/mole)	C_I^2	C_{II}^2	C_{III}^2
2.50	0.994	0.024	−120	9.8	0.83	0.13	0.04
2.65	0.988	0.018	−117	6.4	0.85	0.13	0.02
2.80	0.983	0.013	−115	4.4	0.86	0.12	0.02

[a] From Coulson and Danielsson (1954b).

charge migration, but they do not have properties of hydrogen bonding.[8] (*d*) C_{III}^2 varies rapidly with R_1 and R_2. The astonishingly strong dependence of C_{III}^2 on R_1 must be pointed out.

C. Charge-Transfer Theories

The starting point of the theories of this group is the analogy existing between the charge-transfer interactions (e.g., in the system benzene-iodine) and hydrogen bonding. Since in both cases the charge migration is an important factor it may be hoped that the theories applicable to the study of charge-transfer interactions are, *mutatis mutandis*, applicable to the study of hydrogen bonding. This direction has recently been explored by Puranik and Kumar (1963a) and by Bratož (1966). In these papers the Mulliken theory of charge-transfer interaction (Mulliken, 1952b) has been applied to the study of the systems AH···B and OH···O′. [See also Puranik and Kumar (1963b) and Szczepaniak and Tramer (1965).] The essence of this method, as well as its procedures, can be easily studied in the example of the Bratož paper. It will be described in what follows.

In this paper the O—H···O′ systems are considered. The four electrons involved in the hydrogen bonding are distributed over three orbitals, the bonding and the antibonding OH orbitals χ_1' and χ_2' and the O′ lone pair orbital χ_3' (Fig. 7). Using these orbitals, the following wave function Φ is constructed to represent hydrogen bonds:

$$\Phi = C_1\Phi_1 + C_2\Phi_2 \tag{7}$$

with

$$\Phi_1 = |\chi_1\bar{\chi}_1\chi_3\bar{\chi}_3|, \tag{8a}$$

$$\Phi_2 = N_2\{|\chi_1\bar{\chi}_1\chi_2\bar{\chi}_3| - |\chi_1\bar{\chi}_1\bar{\chi}_2\chi_3|\}. \tag{8b}$$

Here the spin orbitals χ_1, χ_2, and χ_3 are associated with the orbitals $\chi_1', \chi_2', \chi_3'$ and the spin α, the spin orbitals $\bar{\chi}_1, \bar{\chi}_2$, and $\bar{\chi}_3$ are associated with the orbitals $\chi_1', \chi_2', \chi_3'$ and the spin β, and C_1 and C_2 are variational coefficients. The wave function Φ contains two components, Φ_1 and Φ_2. The first term, Φ_1, describes a situation in which two electrons are placed on OH and two on O′. This function, called no bond function (Mulliken, 1952b), accounts for the electrostatic and short-range repulsion interactions. The second function, Φ_2, describes a situation in which charge transfer has

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[8] For a distance of 2.50 Å, an O—H···O bond is not very far from a symmetrical bond and C_{III}^2 is certainly much larger than 0.04 (Table IV). Even long hydrogen bonds are not totally electrostatic. This is indicated by the intensity enhancement of the νOH IR bands.

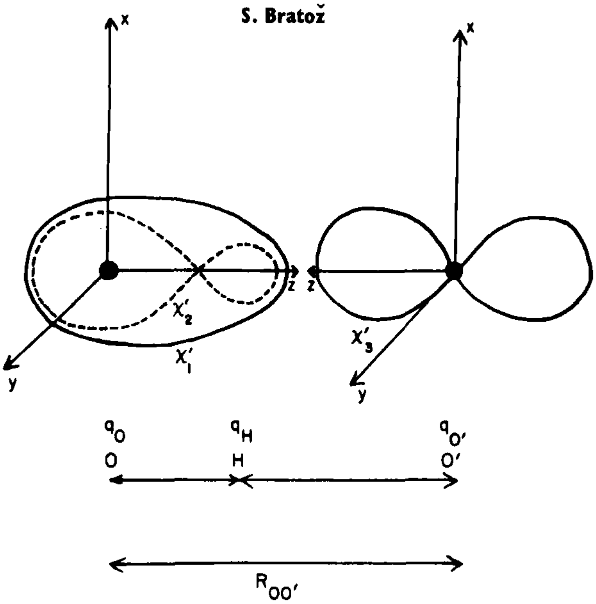

Fig. 7. The orbitals χ_1', χ_2', and χ_3' involved in an OH···O' hydrogen bond. The figure also gives the definition of R_{OH}, $R_{HO'}$ and $R_{OO'}$ as well as that of formal charges $q_{O'}$, q_H, and $q_{O'}$, on O, H, and O'.

taken place from the O' lone pair orbital χ_3' to the antibonding OH orbital χ_2'. This function conferring on the hydrogen bond a partially covalent character is called a dative bond function. The electronic configurations associated with Φ_1 and Φ_2 are given in Table V. This should be compared with Table I.

TABLE V

ELECTRONIC CONFIGURATIONS ASSOCIATED WITH Φ_1 AND Φ_2 IN THE CT THEORY OF HYDROGEN BONDING

Φ_1	$(\chi_1')^2(\chi_3')^2$
Φ_2	$(\chi_1')^2(\chi_2')(\chi_3')$

The wave function Φ once defined, the techniques of the calculation again need to be briefly described. The energy E and the coefficients C_1 and C_2

are obtained by solving the secular equation:

$$\begin{vmatrix} H_{11} - E\,S_{11} & H_{12} - E\,S_{12} \\ H_{21} - E\,S_{21} & H_{22} - E\,S_{22} \end{vmatrix} = 0. \tag{9}$$

In this equation, the Hamiltonian matrix H is relative to an effective four-particle Hamiltonian which does not need to be further specified; the overlap matrix S is, on the contrary, perfectly well defined. Although Eq. (9) can be easily solved, the approximate solution given by the perturbation theory is more convenient. For the ground state one finds[9]:

$$E = H_{11} - \frac{(H_{12} - H_{11}S_{12})^2}{H_{22} - H_{11}}. \tag{10}$$

The matrix elements entering into Eq. (10) are calculated as follows. (*a*) The diagonal elements of the Hamiltonian matrix are calculated semi-empirically by taking into account the fact that H_{ii} is just the energy of the pure state Φ_i. H_{ii} is composed of following terms: (1) the energy E_f of the $\diagdown\mathrm{O{-}H\cdots O'}\!<$ system at infinite separation; (2) the electrostatic energy expressed using the Coulomb formula and the formal charges q_{O}, q_{H}, and $q_{\mathrm{O'}}$ of Fig. 7; (3) the short-range repulsion energy expressed with the help of the empirical formula Ke^{-br}; (4) the energy associated with the transfer of an electron from the lone pair orbital χ_3' of O′ to the antibonding orbital χ_2' of OH (compare with Fig. 6). The following formulas are easily found:

$$H_{11} = E_f - \frac{Q_{\mathrm{H}}Q_{\mathrm{O'}}}{R_{\mathrm{HO'}}} + \frac{Q_{\mathrm{O}}Q_{\mathrm{O'}}}{R_{\mathrm{OO'}}} + Ke^{-bR_{HO'}}, \tag{11}$$

$$H_{22} = H_{11} + I_{\mathrm{O'}} - A_{\mathrm{OH}} - C_{\mathrm{O',OH}}, \tag{12}$$

where K, b, q_{O}, q_{H}, and $q_{\mathrm{O'}}$ are empirical constants. (*b*) The nondiagonal elements of the Hamiltonian and overlap matrices are considered as empirical parameters. One writes β for H_{12} and S for S_{12}. The final formula for the energy is found if (1) the sum of energies of the separate systems is taken as energy zero, (2) Eqs. (11) and (12) are substituted into Eq. (10), and (3) $H_{11}S$ is neglected with respect to H_{12}^*.[10] This gives:

$$E - E_f = -\frac{Q_{\mathrm{O'}}Q_{\mathrm{H}}}{R_{\mathrm{HO'}}} + \frac{Q_{\mathrm{O}}Q_{\mathrm{O'}}}{R_{\mathrm{OO'}}} + Ke^{-bR_{OO'}} - \frac{\beta^2}{I_{\mathrm{O'}} - A_{\mathrm{OH}} - C_{\mathrm{O',OH}}}. \tag{13}$$

[9] This formula is easily obtained by (*a*) replacing E by H_{11} in the elements 12, 21, and 22 of the determinant, (*b*) developing the determinant, and (*c*) solving the resulting equation for E.

[10] With the above choice of energy zero, H_{11} is very small and $H_{11}S_{12}$ is negligible with respect to H_{12}.

The energy of a hydrogen bonded system is thus a sum of the electrostatic, short-range repulsion, and charge-migration energies.

The above is the Bratož procedure. The method used by Puranik–Kumar is not very much different but is less explicit. Nevertheless, the conclusions reached by both theories are similar and can be stated as follows. (*a*) The hydrogen bond energy can be decomposed as postulated by the VB theory. All remarks concerning the relative importance of its components remain valid. (*b*) The charge-transfer component is as much larger as the ionization potential of the lone pair is smaller [compare with Eq. (13)]. This conclusion is supported by experiment (Table VI). (*c*) The special role of the hydrogen in the hydrogen bond formation is due to the smallness of the short-range repulsion term in Eq. (13). This reflects the small "size" of the hydrogen. (*d*) In the charge-transfer process a fraction of an electron is placed on the antibonding OH orbital χ_2'. The OH bond is thus weakened, its length increased, and the force constant $K_{\nu OH}$ decreased. This is just what is observed experimentally. (*e*) The charge migration increases the polarity of the O—H···O systems and intensifies the νOH IR bands. (*f*) Charge-transfer and hydrogen bond interactions are related phenomena. Systems exist in which the binding forces are intermediate between the H bond and CT binding forces (Fig. 8).

TABLE VI

EQUILIBRIUM CONSTANTS FOR THE SYSTEMS β-NAPHTHOL–ACC. COMPARED WITH THE FIRST IONIZATION POTENTIAL OF ACC[a]

Acceptor	Equilibrium constant (25°C)	$I_{O'}$ (eV)
$N(C_2H_5)_3$	103	8.9
$O(C_2H_5)_2$	14.5	9.5
CH_3NO_2	2.6	11.0

[a] From Nagakura and Gouterman (1957).

D. SCF-MO and CI Theories

In these theories the complex AH···B is considered as a single large molecule and is treated by the SCF-MO and CI techniques. The first attempt to apply these methods to the study of hydrogen bonding was made by Pimentel (1951) [See also Nukasawa *et al.* (1953).] In later work a number of papers have been published in which these methods have been applied either relatively accurately (FHF^- : Bessis and Bratož, 1960; Bessis, 1961; Bratož and Bessis, 1959; Clementi, 1961; Clementi and McLean, 1962; Hamano, 1957; Nagahara, 1954) or by introducing drastic approximations [$(H_2O)_2$, $(HF)_2$, $(H_2S)_2$, $(HCl)_2$, and $(H_9O_4)^+$: Fischer-Hjalmars and Grahn, 1958; Grahn, 1959, 1962]. See also Hofacker (1957, 1958, 1959). In the majority of cases, however, the number of electrons is too large to handle and some empirical version of the SCF-MO theory is needed. If the hydrogen bond itself is to be studied a σ-type empirical SCF-MO theory is required. Unfortunately, there exists no generally adopted theory of this kind and some theoretical innovation was necessary in order to make progress [OH···O′: Paoloni, 1959; guanine-cytosine (G-C) base pairs: Rein and Harris, 1964]. The influence of hydrogen bonds on conjugated systems is much easier to study [guanine-cytosine (G-C) pairs and adenine-thymine (A-T) pairs: Hoffman and Ladik, 1964; Ladik, 1964; B. Pullman and Pullman, 1959; A. Pullman, 1963; Rein and Ladik, 1964; proteins: Evans and Gergeley, 1949; Suard *et al.*, 1961; Suard, 1962]. Here, the familiar π-electron theories are successful. These papers are analyzed in what follows.

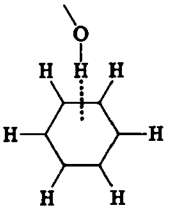

Fig. 8. The systems in which the benzene ring is acceptor can be considered to be either H-bonded or CT-bonded.

(1) FHF^- ion represents the smallest hydrogen-bonded system and contains the shortest hydrogen bond known. It has been studied by Nagahara (1954), Hamano (1957), Bessis and Bratož (1960), Bessis (1961), Bratož and Bessis (1959), Clementi (1961), and Clementi and McLean (1962). The technique of the calculation is the nonempirical SCF-MO technique complemented in some cases by the CI method. In the early work the minimum basic set is used with either Slater or SCF atomic orbitals; some classes of integrals are calculated approximately. In the most recent work by Clementi and McLean several extended basic sets are used constructed on

the Slater atomic orbitals. The calculation is performed without any approximation except those inherent to the SCF-MO method itself. The main conclusions are as follows. (*a*) The nonempirical quantum mechanical calculations confirm the stability of FHF^- against the ionization and the dissociation into FH + F^-. The calculated binding energy is 4.8 eV, a value which agrees favorably with the experimental value of 4.3 eV.[11] (*b*) The hydrogen bond formation is followed by a migration of the electrons from the central region *C* of the molecule to the external region *E* (Fig. 9). In fact, the differential density function (see, e.g., Roux *et al.*, 1956; Löwdin, 1956):

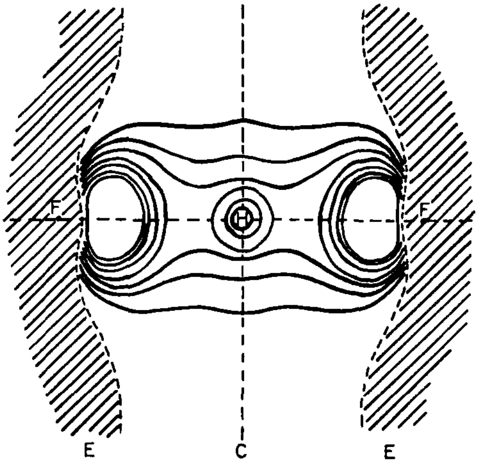

Fig. 9. δ function for FHF^-.

$$\delta(\mathbf{r}) = \rho_{\text{ion}}(\mathbf{r}) - \rho_{\text{free atoms}}(\mathbf{r}) \tag{14}$$

is negative in the first and positive in the second of these regions. The total charge transferred from *C* to *E* is of 0.6 electrons. The hydrogen is about neutral. (*c*) The $2p\pi$ hydrogen orbital occurs, with a nonnegligible coefficient, in the development of the ground state molecular orbitals. This means that there is a small amount of π conjugation across the hydrogen bond.

(2) The second group of papers, still using the nonempirical SCF method, refer to the calculation of the polarization contribution to the hydrogen

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[11] Not too much emphasis should be made of this agreement. The calculation of the binding energies is always exceedingly delicate.

bond energy. The systems $(H_2O)_2$, $(HF)_2$, $(H_2S)_2$, $(HCl)_2$, and $(H_9O_4)^+$ have been studied by Fischer-Hjalmars and Grahn (1958) and Grahn (1959, 1962). The wave functions of free molecules are first determined by the standard SCF-MO technique. The polarization energy E_p is then calculated, e.g., for the system $(OH_2)_2$ (Fig. 10), as follows. (*a*) The molecule $H_2'O'$ is replaced by the atom H_a' nearest to H_2O. (*b*) E_p is split into two parts, the part E_{p_1} arising from the polarization of H_2O in the field of $H_2'O'$ and the part E_{p_2} arising from the polarization of $H_2'O'$ by H_2O. (*c*) E_{p_1} is calculated by considering H_2O as being polarized by a positive point charge and an 1*s*-like negative charge distribution centered on H_a'. Similarly, E_{p_2} is calculated by considering the atom H_a' as being polarized by a charge density associated with free H_2O. The results of the calculation are given in the Table VII and are compared with the roughly estimated electrostatic and the measured hydrogen bond energies. The result is that the polarization and the electrostatic energies are both of the

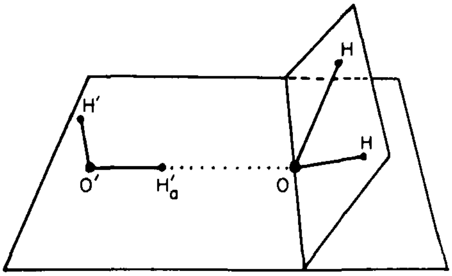

Fig. 10. Nuclear configuration of the system $(H_2O)_2$.

TABLE VII

THE CALCULATED VALUE OF THE POLARIZATION ENERGY COMPARED WITH THE EXPERIMENTAL VALUE OF THE TOTAL H BOND ENERGY (KCAL/MOLE)[a]

	H_2O	HF	H_2S	HCl
Electrostatic energy	5.1	7.5	0.25	0.50
Polarization energy, part E_{p_1}	0.2	—	—	—
Polarization energy, part E_{p_2}	1.2	1.9	~0.05	~0.01
Experimental bond energy	5.8	6.7	—	—

[a] From Grahn (1959).

order of the total bond energy. The polarization process should not therefore be overlooked when studying hydrogen bonds. This result is, of course, entirely expected in view of general properties of the hydrogen bond.

(3) Passing now to the discussion of the results acquired by use of empirical methods, it must first be recalled that no generally accepted empirical SCF-MO theory exists to deal with σ electrons. If, therefore, the hydrogen bond (representing a σ electron system) is to be studied, some kind of theoretical innovation is necessary. Two proposals of this type have been made by Paoloni (1959) concerning the $OH \cdots O'$ systems and by Rein and Harris (1964) concerning the guanine-cytosine (G-C) base pairs. In both papers only those electrons are explicitly considered which are estimated to play an important role. All remaining electrons, and the nuclei, are supposed to form a molecular core. In Paoloni's work the $OH \cdots O'$ system is considered as a four-σ-electron system. The molecular orbitals are written as linear combinations of atomic orbitals ω_1 for O, ω_2 for O', and θ_1 and θ_2 for H. The novelty is to consider two atomic orbitals on H, θ_2 is to allow for a charge migration from O' to H. In the Rein–Harris paper twenty-eight electrons of the G-C base pair (Fig. 11) are explicitly considered; twenty-four of them are π electrons and four are σ electrons of $NH \cdots N$ hydrogen bond. These electrons are fitted into the fourteen lowest molecular orbitals formed from nineteen π-type and three σ-type atomic orbitals. This basic description once chosen, the detailed calculation requires a large number of integrals to be determined. In both papers, they are calculated empirically by using several sets of hypotheses.[12] The essential conclusions are as follows. (*a*) The excited hydrogen orbital θ_2 is found to play a nonnegligible role in describing a hydrogen bond. This

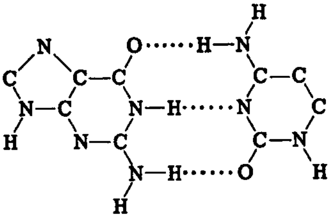

Fig. 11. The guanine-cytosine pair.

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[12] It is extremely difficult, at present, to estimate how justified these hypotheses are. This will only be possible when a certain experience has been acquired with the empirical σ electron SCF-MO methods.

conclusion is similar to that reached by Clementi-McLean.[13] (*b*) The G-C base pair energy surface has two nonequivalent minima corresponding to two different NH distances (Fig. 12). A similar result has been obtained for OH···O′ systems by using a primitive, one-dimensional square-wall model (McKinney and Barrow, 1959). This result, which is further confirmed with the help of the empirical energy expressions (e.g., Lippincott and Schroeder, 1955; Schroeder and Lippincott, 1957; Reid, 1959), probably applies to the majority of hydrogen-bonded systems. It implies that the stretching motion of proton is strongly anharmonic. The abnormal breadth and structure of the 1*ν* AH infrared bands have in fact been explained in these terms (Bratož and Hadži, 1957).[14] The form of the potential energy curve and the height of the barrier separating the two minima are sometimes believed to influence the biological behavior of DNA (Löwdin, 1963, 1964, 1965a,b).

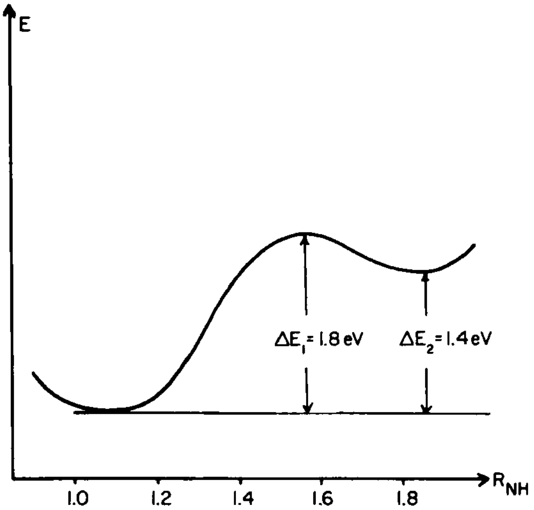

Fig. 12. Double wall potential of the N—H···N hydrogen bond of the C-G base pair.

(4) The last group of papers in which the semiempirical SCF-MO methods are used concerns the study of the influence of the hydrogen bond

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[13] The orbital θ_2 is not the same, however, in both papers. In Paoloni's paper θ_2 is a $2s$-$2p$ hybrid; it is a pure $2p\pi$ hydrogen orbital in the Clementi-MacLean paper.

[14] Curiously enough, the existence of two separate minima in the potential energy surface does not seem to be detectable directly from the IR spectra (Hadži, 1965). The opposite point of view was defended for many years and is still occasionally defended.

on conjugated π electron systems. The systems which have been investigated are some important biological systems: adenine-thymine pairs, guanine-cytosine pairs, and proteins. They have been studied by B. Pullman and Pullman (1959), A. Pullman (1963), Rein and Ladik (1964), Hoffman and Ladik (1964), Ladik (1964), Evans and Gergeley (1949), Suard *et al.* (1961), and Suard (1962). The techniques used are the familiar Hückel and Pariser–Parr–Pople methods as well as the recently proposed Julg method. The presence of a hydrogen bond is then accounted for with the help of either of the following two models (for simplicity of explanation the Hückel method is used). (*a*) In the first model, the hydrogen atoms entering into a hydrogen bond are not considered as active members of the conjugated system. The presence of a hydrogen bond is then accounted for by suitably modifying the Coulomb parameters of hetero atoms united by these bonds and by allotting a small exchange integral to them. The Coulomb integrals of the H donor hetero atoms are uniformly diminished and those of the H acceptors are uniformly increased. (*b*) In the second model, the hydrogen atoms are considered as active parts of the conjugated system. Here, the presence of a hydrogen bond is described by (1) including its $2p\pi_H$ orbital into the calculation, (2) choosing an appropriate set of Coulomb and exchange parameters. Leaving the conclusions of purely biological interest aside, two results which are relevant for the present study appear. (*a*) If the steric conditions are favorable, the hydrogen bonds do not interrupt the conjugated system entirely. A small amount of conjugation persists and can be detected either spectroscopically or by measuring bond distances (e.g., C═O and C—N distances in proteins). (*b*) The $2p\pi_H$ orbital facilitates the transmission of conjugation across the hydrogen bond. Its influence is particularly large for the excited molecular orbitals. Obviously, there is an over-all self-consistency between these results and the similar results discussed in this section.

E. Critical Survey and Possible Developments

There is no doubt that the theories of this section permit the zero-order, or qualitative, understanding of the phenomena connected with hydrogen bonding. Nevertheless, not all of them are suitable for quantitative calculations. The VB theory is useless in this sense and the CT theory, as powerful as it may be from a qualitative point of view, does not lend itself for detailed calculations. The use of the SCF-MO and CI methods is more recommendable. Unfortunately, the systems linked by hydrogen bonds are nearly always too large to be treated in a reasonably complete way.

In these circumstances a further theoretical progress can only be made at the expense of a considerable effort. Admitting this, the following list of problems seems to merit attention. (*a*) FHF^- and $(H_2O)_2$, which are the simplest systems containing a symmetrical and an asymmetrical H bond, respectively, can be studied completely with the help of the nonempirical SCF-MO and CI methods. Such a priori calculations may (1) confirm the basic concepts of the present theory of H bond, (2) indicate the form of the potential energy surface in these two representative cases, (3) give an answer to the question of whether the effects of the D substitution on the (effective) potential energy surface are negligible or not. It is difficult to get a reliable answer to this last question by taking into consideration only the experimental data. (*b*) A number of characteristic hydrogen-bonded systems, e.g., $(HCOOH)_2$, phenol-acetone, ... , can be studied by the help of an approximate SCF-MO theory. This is to suppose that a semiempirical σ electron version of the SCF-MO theory has been definitely established and was found to be satisfactory.[15] Such calculations (1) allow a study of the effects of different functional groups on strength and properties of a hydrogen bond, (2) give a quantitative estimation of the OH bond stretch, the νOH frequency shift, and intensity increment on association, (3) may provide us with a more complete electronic theory of the H bond perturbation of the NMR spectra. (*c*) The influence of a hydrogen bond on the π electron system as well as its reaction on the hydrogen bond merits further discussion. A part of this problem can be studied by the familiar Hückel and Pariser–Parr–Pople theories. (*d*) The cooperative proton motion in multiconnected H bond systems and its coupling with electronic motion play an important role in ferroelectric systems. This problem, which is sometimes believed to influence the behavior of the proteins, certainly merits a thorough investigation.

V. Quantum Theories; Excited State

A. Introductory Remarks

The strength and the properties of hydrogen bonds vary considerably when going from one electronic state of the system to another. As this subject is most easily studied by the help of the ultraviolet spectroscopy (see Section II, Fig. 3), one usually expresses the results in terms of

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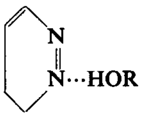
[15] An example of a theory of this kind has been mentioned in connection with the Rein–Harris work (see Section IV,D,3). For some other proposals in this connection, see, e.g., Hall (1951), Sandorfy and Daudel (1954), Del Re (1958), Fukui *et al.* (1961), and Pople (1966). Nevertheless, the properties of these theories are not yet fully understood.

frequency shifts, intensity increments, etc. This terminology will also be followed in this paper. The theory of hydrogen bonding in excited molecular states is at its very beginning; in several practically important cases, only qualitative interpretations have been proposed. The present position is now described.

B. Theory

The first effect to be discussed is the blue shift of the $n \rightarrow \pi^*$ transitions. This effect has been explained, qualitatively, by Brealey and Kasha (1955); their ideas have never been formulated mathematically. See, however, Suard *et al.* (1961) and Suard (1962). The argument is as follows. Consider, e.g., the



complex. In the ground state, two electrons of the N···HO bond are strongly concentrated in the nitrogen lone pair orbital, thus favoring hydrogen bonding in this state. In a $n \rightarrow \pi^*$ transition one of these electrons is promoted to a strongly delocalized π^* orbital of pyridazine. This decreases the charge density on the nitrogen. Thus the electrostatic forces are less important, and the H bond is weaker in the excited state. A blue shift results (Fig. 3). This interpretation is very probably correct from the qualitative point of view. In order to obtain a quantitative agreement (*a*) the σ electron charge migration and (*b*) the π electron density rearrangement following the $n \rightarrow \pi^*$ promotion must be considered.

The next effect to be studied is the red shift of the $\pi \rightarrow \pi^*$ transitions. This effect has been more carefully studied than the one just described. For the preliminary studies, see Baba (1961) and Baba and Suzuki (1961). More recently, a certain amount of work has been done by using the π electron theories of the type described in the Section IV,D,4 in connection with the work by Pullman *et al.* The principal papers are those by Julg and Bonnet (1962; phenol-C_2H_5OH), Besnaïnou *et al.* (1964; phenol-dioxane, α-naphthol-dioxane, β-naphthol-dioxane, crotonaldehyde-C_2H_5OH, mesityl oxide-C_2H_5OH, acetophenone-C_2H_5OH, p-CH_5-acetophenone-C_2H_5OH, p-benzoquinone-C_2H_5OH), and Ponomarev *et al.* (1964; aniline, phenol, nitrobenzene with H_2O, C_2H_5OH, etc.). Somewhat related is the work on the energy bands of proteins by Evans and Gergeley (1949), Suard *et al.* (1961), and Suard (1962). In all these papers, with the exception of that by Suard,[16] the presence of a hydrogen bond is accounted for by suitably modifying the σ core parameters. An attempt has also been made (Besnaïnou *et al.*, 1964) to evaluate separately the contributions to the $\pi \to \pi^*$ frequency shifts arising from the electrostatic and the charge-migration effects. This has been done by (*a*) considering that only the acceptor atom and the donor atom core parameters W are modified by the presence of a hydrogen bond and (*b*) estimating ΔW by means of the electrostatic and the charge-migration model. The following formulas are thus obtained:

$$\Delta W^{\mathrm{ES}}_{\mathrm{ACC}} = -\frac{Q_{\mathrm{H}}}{R_{\mathrm{HO'}}} + \frac{Q_{\mathrm{O}}}{R_{\mathrm{OO'}}}, \tag{15a}$$

$$\Delta W^{\mathrm{ES}}_{\mathrm{DON}} = \frac{Q_{\mathrm{O'}}}{R_{\mathrm{OO'}}}\ ; \tag{15b}$$

$$\Delta W^{\mathrm{CT}}_{\mathrm{ACC}} = \Delta W^{\mathrm{ES}}_{\mathrm{ACC}} - Q_{\mathrm{CT}}(\pi_{\mathrm{O'}}\pi_{\mathrm{O'}} \,|\, \pi_{\mathrm{O'}}\pi_{\mathrm{O'}}), \tag{16a}$$

$$\Delta W^{\mathrm{CT}}_{\mathrm{DON}} = \Delta W^{\mathrm{ES}}_{\mathrm{DON}} + Q_{\mathrm{CT}}(\pi_{\mathrm{O}}\pi_{\mathrm{O}} \,|\, \pi_{\mathrm{O}}\pi_{\mathrm{O}}). \tag{16b}$$

Here, $(\pi\pi \,|\, \pi\pi)$ is the dielectronic interaction integral. The formulas (15a) and (15b) are valid for the electrostatic model. They express the effect of the perturbing potential arising from the formal charges on A, H, and B and acting on a π electron. The formulas (16a) and (16b) apply to the charge-transfer model. In this model, the transfer of a charge Q_{CT} from the proton acceptor to the proton donor makes the first more and the second less attractive with respect to π electrons. The main conclusions of the above theories are as follows. (*a*) The $\pi \to \pi^*$ frequency shifts are expected to be bathochromic although there should be exceptions to this rule. This shift is bathochromic for acceptors and for donors in spite of disymmetric influence of the hydrogen bond ($\Delta W_{\mathrm{ACC}} < 0$, $\Delta W_{\mathrm{DON}} > 0$). In fact, very often the acceptor atom has a larger π-electron charge in the molecular excited state than in its ground state; the opposite is true for the donor atom. The product $\Delta Q \Delta W$ which determines, in the first approximation, the $\pi \to \pi^*$ frequency shifts has therefore the same sign for donors and for acceptors. Final result: the hydrogen bond is often stronger in a ($\pi \to \pi^*$) state than in the ground state of the system. (*b*) If the electrostatic model is used [Eqs. (15a) and (15b)], the agreement between the theory and the experience is much less satisfactory than for the charge-transfer model [Eqs. (16a) and (16b) (compare with Table VIII). One concludes

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[16] In this paper the $2p\pi$ orbital of the hydrogen is explicitly introduced.

TABLE VIII

$\pi \rightarrow \pi^*$ FREQUENCY SHIFTS CALCULATED BY MEANS OF ELECTROSTATIC (THIRD COLUMN) AND CHARGE-TRANSFER (FOURTH COLUMN) MODEL[a]

System	Transition	$\Delta\lambda_{ES}$ (mμ)	$\Delta\lambda_{CT}$ (mμ)	$\Delta\lambda_{EXP}$ (mμ)
Phenol-dioxane	${}^1L_b \leftarrow {}^1A$	+0.2	+6.0	+2.6
	${}^1L_a \leftarrow {}^1A$	+0.2	+3.2	+3.0
α-Naphthol-dioxane	${}^1L_b \leftarrow {}^1A$	0.0	+0.8	+1.4
	${}^1L_a \leftarrow {}^1A$	0.3	+7.4	+6.1
β-Naphthol-dioxane	${}^1L_b \leftarrow {}^1A$	0.3	+4.0	+4.1
	${}^1L_a \leftarrow {}^1A$	0.0	+0.7	+1.0
Crotonaldehyde-C_2H_5OH	$V \leftarrow N$	+1.9	+6.5	?
Mesityl oxide-C_2H_5OH	$V \leftarrow N$	+1.0	+3.7	+7.5
Acetophenone-C_2H_5OH	${}^1L_b \leftarrow {}^1A$	+0.4	+1.4	−1.0
	${}^1L_a \leftarrow {}^1A$	+0.3	×2.3	+4.0
p-CH_3-Acetophenone-C_2H_5OH	${}^1L_b \leftarrow {}^1A$	−0.1	+0.1	—
	${}^1L_a \leftarrow {}^1A$	+0.8	+2.3	+5.0
p-Benzoquinone-C_2H_5OH	${}^1B_{1g} \leftarrow {}^1A$	+3.2	+10.2	+15.0
	${}^1B_{2u} \leftarrow {}^1A_g$	−0.8	−1.4	0.0

[a] From Besnaïnou *et al.* (1964).

that the observed $\pi \rightarrow \pi^*$ frequency shifts arise mainly from the σ electron migration which follows the hydrogen bond formation. This conclusion confirms the results which have been described in Sections IV,C and D.

We shall conclude with some remarks concerning the possible existence of the charge-transfer bands associated with hydrogen bonds. These bands are related to the transitions in which the σ electrons of the H bond itself are excited. If Eq. (9) is solved, two states are found which may be represented, in the zero-order approximation, by the wave functions Φ_1 and Φ_2 [Eqs. (8a) and (8b)].[17] These two states are thus the ground state and the charge-transfer state; their electronic configurations are given in Table V. The existence of such a band has been reported by Nagakura (1964) in the case of the maleic acid anion. This interesting Nagakura

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[17] This is obvious if the nondiagonal elements H_{12} and S_{12} are vanishing, and remains approximately true for $H_{12} - ES_{12}$ small with respect to $H_{22} - H_{11}$.

proposal cannot be as yet considered to be definitely confirmed and the existence of the charge-transfer bands is still an open question.

C. Critical Survey and Possible Developments

Curiously enough, the hydrogen bond is easier to handle theoretically in the excited states of the system than in its ground state. This is due to the fact that a number of well-established π electron theories exist applicable to this problem. It is astonishing that, in these circumstances, the theory is not more advanced in this field than it is. The following problems, at least, can be studied without too many difficulties. (*a*) The Brealey–Kasha qualitative theory of the $n \rightarrow \pi^*$ frequency shifts can be recast into a mathematical theory including all sorts of secondary effects. (*b*) The influence of the chelation on the $\pi \rightarrow \pi^*$ transitions in the systems like *o*-hydroxybenzaldehyde can be studied. The role of the π-conjugation across the H bond can be further investigated at this occasion. (*c*) The problem of the intensity changes of certain electronic bands with hydrogen bond formation (hyperchromic effect) merits attention, particularly in view of its biological implications.

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Molecular Orbital Calculations of Π Electron Systems

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I. Introduction

The aim of this article is to present some (not all!) of the computational methods available at present in the field of molecular orbital theory of π electron systems and to make their theoretical framework clear.

The contents of this article are far from a fair presentation of the present status of the theory. The emphasis is placed on the nonempirical and semiempirical calculational methods (namely Sections II and III of the note). The description of the simple MO theory was grossly condensed and its useful applications have been almost completely neglected. This is partly because the writer is less familiar with these topics and partly because several extremely good books covering this field have been published recently. The readers who are interested in the simple MO theory are referred to the following books (see Daudel *et al.*, 1959; Streitwieser, 1961; Roberts, 1961; Simpson, 1962; Pullman and Pullman, 1963; Coulson and Streitwieser, 1965).

We will start from, and will devote considerable pages to, the standard molecular orbital (MO) method often referred to as the ASP MO LCAO method including CI (Section II). Then we will proceed to a simplified and possibly more useful version of the method due mainly to Pariser, Parr, and Pople. After that comes the still simpler Hückel method. Finally the validity of the σ–π separation will be examined briefly.

In presenting the material, I will try to make it as concrete as possible. In order to illustrate the methods, formulas, and so on, I will apply them to a pet molecule, namely ethylene. I hope that this choice of a specific example will not obscure the generality of our results.

The definition of technical terms is rather important, and we will begin with this.

The molecule we have in mind is planar, or at least the part of the molecular skeleton in which we are interested is in a plane.

A π electron is an electron whose wave function is antisymmetric with respect to the molecular plane; in other words it changes its sign under reflection through the molecular plane.

An orbital means a wave function which contains only the space coordinates of one particle (electron). The definition of a molecular orbital is a little more complicated. There seem to be three possibilities:

(*a*) an orbital which extends throughout the whole molecule, i.e., is not localized on any particular atom or in part of the molecule;
(*b*) an orbital belonging to one of the irreducible representations of the symmetry group of the molecule, if the molecule has any element of symmetry, other than the identity;
(*c*) an orbital which is determined by the requirement that the Hartree–Fock energy matrix is completely reduced to diagonal form. Remember that the Hartree–Fock equation

$$\mathscr{F}\varphi_k' = \sum_h \varepsilon'_{kh}\varphi_h'$$

can be reduced to the form

$$\mathscr{F}\varphi_k = \varepsilon_k\varphi_k$$

by a suitable unitary transformation of the orbitals

$$\varphi_k = \sum_h t_{kh}\varphi'_h.$$

This definition was introduced by Hall and Lennard-Jones (1950). The orbitals which belong to the various irreducible representations of the molecular symmetry group [definition (*b*)] are then called symmetry orbitals.

When the molecule has a symmetry property, definition (*b*) is more precise than (*a*). Definition (*c*) is more restricted than (*b*).

II. The Method of Antisymmetrized Product of Molecular Orbitals in LCAO Approximation, Including Configuration Interaction (ASP MO LCAO CI Method)

1. Hamiltonian

Our problem is to solve the time-independent Schrödinger equation

$$\mathscr{H}\Psi = E\Psi \tag{1.1}$$

for a molecule. If we are interested in time-dependent phenomena, the basic equation is

$$-\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} = \mathscr{H}\Psi, \tag{1.2}$$

but in discussing the theory of molecular electronic structure, we are mainly concerned with the time-independent Schrödinger equation (1.1).

Many essential problems in quantum chemistry arise from the fact that the Schrödinger equations (1.1) and (1.2) are generally much too difficult to solve exactly.

In the time-independent Schrödinger equation (1.1), the form of the Hamiltonian is of primary importance. The theories which will be developed in this article involve two fundamental approximations.

Approximation A. Born–Oppenheimer (or Adiabatic) approximation (Born and Oppenheimer, 1927). By this, nuclear and electronic motion can be treated separately. In dealing with electronic motion, each nucleus is considered to be a point particle at rest with charge *Ze* and infinite mass. This approximation is based on the fact that there is a large difference between the nuclear and electronic masses.

The accuracy of this approximation is usually very high, but we cannot use it in problems dealing with configuration instability (Jahn–Teller distortion) or in problems dealing with the intensity of electronic transitions where an interaction between nuclear vibration and electronic motion plays an important role (see, for example, Liehr, 1957, 1958, 1960, 1961).

Approximation B. All relativistic effects are neglected. Among the relativistic effects, spin-orbit coupling is usually the most important when the ground state is a singlet; e.g., it is responsible for singlet-triplet transitions. Sometimes spin-spin interaction may also cause appreciable effects.

If we adopt the approximations A and B, then the Hamiltonian of a system of electrons has the following form:

$$\mathscr{H} = \sum_i (-\tfrac{1}{2}\Delta_i) - \sum_{i,a} \frac{Z_a}{|\mathbf{r}_i - \mathbf{R}_a|} + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{a<b} \frac{Z_a Z_b}{R_{ab}}, \tag{1.3}$$

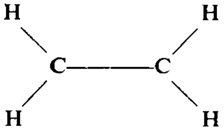
where the suffixes i and j refer to electrons, and a and b to nuclei. Atomic units are used in (1.3).

2. Shape of the Molecule

A lot of information about the shape of molecules has already been published, and we may find it in one of the following very useful books (see Sutton, 1958, 1965; Herzberg, 1945, 1950).

To illustrate the methods which will be explained in the following, we will often take the ethylene molecule as an example. It is the simplest π electron system and is analogous to the simplest σ electron system, the hydrogen molecule. We will see a number of similarities between these two molecules, and the ethylene molecule seems to have the same importance as the hydrogen molecule enjoys.

The shape of C_2H_4 is as follows (Kuchitsu, 1966):



R_{CH}: 1.090 ± 0.003Å
R_{CC}: 1.335 ± 0.003Å
∠HCH: 116.6° ±0.4°

3. Basic Set of Orbitals

In order to describe the electronic structure of a molecule by the MO method, we must know the forms of MO's. As the Hartree–Fock self-consistent field method becomes very complicated when it is applied to a molecular case, it is common to introduce the following:

Approximation C. A molecular orbital is approximated by a linear combination of a finite number of atomic orbitals.[1] This is called the LCAO approximation.

In simple calculations of the electronic structure of small molecules and in practically all calculations of large molecules, we introduce further:

Approximation D. Only AO's which are occupied in the ground state of the free atom are used in the linear combination.

For example, in C_2H_4 we use:

for C, $1s$, $2s$, $2px$, $2py$, $2pz$;
for H, $1s$.

This is a very serious restriction, and when we want to give our molecular orbital description greater flexibility, we have to use orbitals with higher energy, such as $3s$, $3p$, $3d$ ... for C (the importance of the $3p\pi$ orbital of C in the Hückel theory has been discussed and stressed by Hartmann, 1960) or in general orthogonal complements to our already chosen AO's.

Before attacking the problem of constructing MO's from AO's, the symmetry group of the molecule and its irreducible representations should be mentioned.

---

[1] Atomic orbitals are usually determined so as to give the lowest energy for atoms in their ground states. These fixed AO's can be used as basic orbitals. However, sometimes these basic orbitals have some freedom in themselves (e.g., orbital exponent) which is utilized in variational calculations of the molecular energies. When the number of these linearly independent basic orbitals is large enough, they can have little resemblance to the best AO's. For the choice of functional forms, see Section 10.

4. The Symmetry Group and Its Irreducible Representations

Symmetry operations are geometrical operations such as rotations, reflections, inversions, etc., which permute equivalent nuclei among themselves and thus leave the nuclear framework unchanged.

A symmetry group of a molecule is the assembly of all its symmetry operations.

In the case of C_2H_4, the symmetry operations and their effect of permuting equivalent nuclei are as follows (cf. Fig. 1):

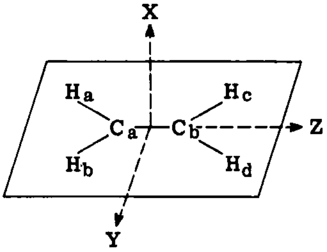


Fig. 1. The coordinate system.

identity, E;

rotation by π around the x, y, and z axes,

C_2^x,	$C_a \leftrightarrow C_b$,	$H_a \leftrightarrow H_d$,	$H_b \leftrightarrow H_c$;
C_2^y,	$C_a \leftrightarrow C_b$,	$H_a \leftrightarrow H_c$,	$H_b \leftrightarrow H_d$;
C_2^z,		$H_a \leftrightarrow H_b$,	$H_c \leftrightarrow H_d$;

inversion through the center of the molecule,

I,	$C_a \leftrightarrow C_b$,	$H_a \leftrightarrow H_d$,	$H_b \leftrightarrow H_c$;

C_2 followed by inversion—this is equivalent to reflexion through a plane,

$IC_2^x = \sigma_{yz}$;			
$IC_2^y = \sigma_{xz}$;		$H_a \leftrightarrow H_b$,	$H_c \leftrightarrow H_d$;
$IC_2^z = \sigma_{xy}$;	$C_a \leftrightarrow C_b$,	$H_a \leftrightarrow H_c$,	$H_b \leftrightarrow H_d$.

The group is called D_{2h}.

We will not go into the general theory of groups and their representations here but will refer the reader to the following textbooks (see Eyring *et al.*, 1944; Cotton, 1963; McWeeny, 1963; Schonland, 1965).

For later use, the character table of the irreducible representations of the group D_{2h} is reproduced in Table I.

TABLE I

Symmetry	E	C_2^x	C_2^y	C_2^z	I	σ_{yz}	σ_{zx}	σ_{xy}
A_g	1	1	1	1	1	1	1	1
A_u	1	1	1	1	−1	−1	−1	−1
B_{1g}	1	−1	−1	1	1	−1	−1	1
B_{1u}	1	−1	−1	1	−1	1	1	−1
B_{2g}	1	−1	1	−1	1	−1	1	−1
B_{2u}	1	−1	1	−1	−1	1	−1	1
B_{3g}	1	1	−1	−1	1	1	−1	−1
B_{3u}	1	1	−1	−1	−1	−1	1	1

Character tables of other molecular symmetry groups will be found in the textbooks mentioned above.

5. Construction of the Basis of the Irreducible Representation

The problem of how to make symmetry orbitals from a given set of AO's will not be treated generally either, but a simple intuitive method is illustrated for the case of C_2H_4.

Consider the AO's of equivalent atoms first. For C—C, we can make two linear combinations from the 1*s* orbitals, which give:

$$\begin{aligned} 1s_{C_a} + 1s_{C_b} &\propto \psi(a_g 1s), \\ 1s_{C_a} - 1s_{C_b} &\propto \psi(b_{1u} 1s). \end{aligned} \tag{5.1}$$

The symmetry classification of the left-hand side can be found by referring to the above character table (Table I). Similarly, from 2*s*, 2*pz*, 2*py*, 2*px*, we obtain:

$$\begin{aligned} 2s_{C_a} + 2s_{C_b} &\propto \psi(a_g 2s), \\ 2s_{C_a} - 2s_{C_b} &\propto \psi(b_{1u} 2s), \\ 2pz_{C_a} + 2pz_{C_b} &\propto \psi(a_g 2pz),^2 \\ 2pz_{C_a} - 2pz_{C_b} &\propto \psi(b_{1u} 2pz), \\ 2py_{C_a} + 2py_{C_b} &\propto \psi(b_{2u} 2py), \\ 2py_{C_a} - 2py_{C_b} &\propto \psi(b_{3g} 2py), \\ 2px_{C_a} + 2px_{C_b} &\propto \psi(b_{3u} 2px), \\ 2px_{C_a} - 2px_{C_b} &\propto \psi(b_{2g} 2px). \end{aligned} \tag{5.2}$$

---

[2] We take the $+z$ axis of each C atom in the direction towards the partner atom.

From the four hydrogen 1*s* orbitals, we get:

$$\begin{aligned} 1s_{\mathrm{H}_a} + 1s_{\mathrm{H}_b} + 1s_{\mathrm{H}_c} + 1s_{\mathrm{H}_d} &\propto \psi(a_g 1s_{\mathrm{H}}), \\ 1s_{\mathrm{H}_a} + 1s_{\mathrm{H}_b} - 1s_{\mathrm{H}_c} - 1s_{\mathrm{H}_d} &\propto \psi(b_{1u} 1s_{\mathrm{H}}), \\ 1s_{\mathrm{H}_a} - 1s_{\mathrm{H}_b} + 1s_{\mathrm{H}_c} - 1s_{\mathrm{H}_d} &\propto \psi(b_{2u} 1s_{\mathrm{H}}), \\ 1s_{\mathrm{H}_a} - 1s_{\mathrm{H}_b} - 1s_{\mathrm{H}_c} + 1s_{\mathrm{H}_d} &\propto \psi(b_{3g} 1s_{\mathrm{H}}). \end{aligned} \tag{5.3}$$

We have, therefore, the following number of symmetry orbitals altogether:

$$4 \times a_g, \quad 4 \times b_{1u}, \quad 2 \times b_{2u}, \quad 2 \times b_{3g}, \quad 1 \times b_{3u}, \quad 1 \times b_{2g}.$$

In order to obtain the molecular orbitals in the sense (*c*) mentioned in the introduction, we have to define the Hartree–Fock single body operator $\mathscr{F}$. This depends upon the electronic wave function, which can only be fixed after we know the molecular orbitals. Thus we must use the iterative procedure in solving the problem. Here let us suppose we find the final $\mathscr{F}$. Usually this operator $\mathscr{F}$ is totally symmetric and thus the orbitals with different symmetries are noninteracting. The resulting orbitals therefore have, for example, the following forms:

$$\begin{aligned} \psi(1a_g) &= c_{11}\psi(a_g 1s) + c_{12}\psi(a_g 2s) + c_{13}\psi(a_g 2pz) + c_{14}\psi(a_g 1s_{\mathrm{H}}), \\ \psi(2a_g) &= c_{21}\psi(a_g 1s) + c_{22}\psi(a_g 2s) + c_{23}\psi(a_g 2pz) + c_{24}\psi(a_g 1s_{\mathrm{H}}), \\ \psi(3a_g) &= c_{31}\psi(a_g 1s) + c_{32}\psi(a_g 2s) + c_{33}\psi(a_g 2pz) + c_{34}\psi(a_g 1s_{\mathrm{H}}), \\ \psi(4a_g) &= c_{41}\psi(a_g 1s) + c_{42}\psi(a_g 2s) + c_{43}\psi(a_g 2pz) + c_{44}\psi(a_g 1s_{\mathrm{H}}). \end{aligned} \tag{5.4}$$

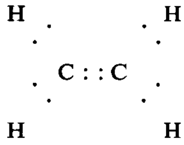
The value of the coefficients c_{ij} can be obtained only by solving the diagonalization problem for the one-electron energy or orbital energy ε.

6. Total Wave Function

In order to write down an approximate total wave function for a state, we need to know its electron configuration; that is, we have to know which orbitals are occupied and which are not. In general this is only possible when we know the orbital energies ε. However, we may guess at the configuration by using physical and chemical intuition. For example in the ground state configuration, we note:

(*a*) the 1*s* shells of both of the carbon atoms are occupied;
(*b*) there is a correspondence between electron configurations and electron pairs located between bonded atoms according to Lewis' idea;
(*c*) the fewer nodes an orbital has, the lower its energy.

Let us apply these observations to C_2H_4. From (*a*), $1a_g$ and $1b_{1u}$ should be occupied. From the following pairing diagram



we infer that $2a_g$ corresponds to one of the C—C bonds.

For the four C—H bonds, we take one each of a_g, b_{1u}, b_{2u}, and b_{3g}, just as we obtained these symmetry orbitals from four hydrogen 1*s* orbitals [cf. (5.3)]. The remaining second C—C bond would correspond to b_{3u}, which has fewer nodes than b_{2g}. Thus we obtain the following configuration,

$$(1a_g)^2(1b_{1u})^2(2a_g)^2(2b_{1u})^2(1b_{2u})^2(1b_{3g})^2(3a_g)^2(1b_{3u})^2.$$

All the orbitals appearing above, except the last, remain invariant when reflected through the molecular plane, the operation in this case being represented by σ_{yz}. On the other hand the sign of the b_{3u} orbital is changed by this operation. The former are called σ orbitals while the latter is called a π orbital.

The usual starting approximation of the ground state of this molecule is

$$\Phi = N\mathscr{A}\{(1a_g)_3\alpha_3(1a_g)_4\beta_4(1b_{1u})_5\alpha_5(1b_{1u})_6\beta_6\cdots$$
$$(3a_g)_{15}\alpha_{15}(3a_g)_{16}\beta_{16}(1b_{3u})_1\alpha_1(1b_{3u})_2\beta_2\}, \qquad (6.1)$$

where N is a normalization constant and $\mathscr{A}$ an antisymmetrizing operator. It is given by

$$\mathscr{A} = \sum_P (-1)^P P, \qquad (6.2)$$

where P represents a permutation operator acting on space and spin coordinates of all the sixteen electrons.

7. σ–π Separation

Almost all of the properties which depend upon the conjugation of an unsaturated molecule are ascribed to the π electrons. These properties include the ultraviolet spectrum, resonance energy, variation in bond order and electron density distribution, chemical reactivity, diamagnetic anisotropy, etc.

As is customary, we shall introduce the following approximation:

Approximation E. The π electrons may be treated quite independently of the σ electrons.

This approximation has been introduced by Hückel (1931, 1932) and turned out to be very successful. The approximation may also be expressed in terms of wave functions as follows. The wave functions, Φ_i, of the various electronic states in which we are interested are

$$\Phi_i \sim \mathscr{A}\{(\Sigma)(\Pi)_i\}, \tag{7.1}$$

where the Σ part is common to all states.

If we adopt this approximation, then we may reduce the problem of the whole molecule to a problem of only π electrons. As for the energy, we can introduce the following effective Hamiltonian (in the case of C_2H_4):

$$\mathscr{H}^{\pi}(1,2) = f^{\pi}(1) + f^{\pi}(2) + \frac{1}{r_{12}}, \tag{7.2}$$

where,

$$\begin{aligned}
&(\psi_{\rm I}(1)|f^{\pi}(1)|\psi_{\rm II}(1)) \\
&= \left(\psi_{\rm I}(1)\right| -\tfrac{1}{2}\Delta_1 - \frac{6}{r_{a1}} - \frac{6}{r_{b1}} - \frac{1}{r_{{\rm H}_a1}} - \frac{1}{r_{{\rm H}_b1}} - \frac{1}{r_{{\rm H}_c1}} - \frac{1}{r_{{\rm H}_d1}} \left|\psi_{\rm II}(1)\right) \\
&\quad + \sum_j \left[2\int \frac{\psi_j^*(2)\psi_j(2)\psi_{\rm I}^*(1)\psi_{\rm II}(1)}{r_{12}}\, dv_1\, dv_2 \right. \\
&\quad \left. - \int \frac{\psi_j^*(2)\psi_{\rm II}(2)\psi_{\rm I}^*(1)\psi_j(1)}{r_{12}}\, dv_1\, dv_2 \right],
\end{aligned} \tag{7.3}$$

and the summation over j is taken over all the occupied σ space orbitals, namely, $1a_g$, $1b_{1u}$, $2a_g$, $2b_{1u}$, $1b_{2u}$, $1b_{3g}$, and $3a_g$. This is a well-defined Hamiltonian when all the occupied σ-type molecular orbitals are doubly filled. We can calculate its matrix elements with respect to any π orbitals if we know the explicit form of ψ_j's.

The total electronic energy E is then given by

$$E = E^{\sigma} + E^{\pi} + E^{N}, \tag{7.4}$$

where E^{π} is the energy from the two π electron problem with the effective Hamiltonian $\mathscr{H}^{\pi}$ and

$$\begin{aligned}
E^{\sigma} &= 2\sum_j \left(\psi_j\right| - \tfrac{1}{2}\Delta - \frac{6}{r_a} - \frac{6}{r_b} - \frac{1}{r_{{\rm H}_a}} - \frac{1}{r_{{\rm H}_b}} - \frac{1}{r_{{\rm H}_c}} - \frac{1}{r_{{\rm H}_d}} \left|\psi_j\right) \\
&\quad + \sum_j (jj\,|\,jj) + 4\sum_{j<k} (jj\,|\,kk) - 2\sum_{j<k} (jk\,|\,kj),
\end{aligned} \tag{7.5}$$

$$(ij\,|\,kl) = \int \frac{\psi_i^*(2)\psi_j(2)\psi_k^*(1)\psi_l(1)}{r_{12}}\, dv_1\, dv_2, \tag{7.6}$$

$$E^N = \sum_{a<b} \frac{Z_a Z_b}{R_{ab}}. \tag{7.7}$$

The last electron interaction integral is sometimes denoted by L_{ikjl} or $(ik|g|jl)$.

This idea of the $\sigma-\pi$ separation has been widely used to obtain numerous results which are in fairly good agreement with experimental observations. However, no one can be sure about the basis of this approximation. Several attempts have been made to see to what extent we can consider σ and π electrons separately. These theoretical treatments show that we cannot get full assurance that we may separate them. We shall come back to this problem in a later section.

8. π Electron States and Their Wave Functions

The π molecular orbitals are [cf. (5.2)]:

$$\begin{aligned} \psi(b_{3u}) &= \frac{1}{\sqrt{2(1+S)}}\,[2px_a + 2px_b] = \frac{1}{\sqrt{2(1+S)}}\,[\pi_a + \pi_b] = \psi_{\mathrm{I}}, \\ \psi(b_{2g}) &= \frac{1}{\sqrt{2(1-S)}}\,[2px_a - 2px_b] = \frac{1}{\sqrt{2(1-S)}}\,[\pi_a - \pi_b] = \psi_{\mathrm{II}}, \end{aligned} \tag{8.1}$$

where S is the overlap integral between π_a and π_b;

$$S = \int 2px_a^*(1) 2px_b(1)\, dv_1 = (2px_a\,|\,2px_b) = (\pi_a\,|\,\pi_b).$$

By assigning two electrons to these two orbitals, we obtain three configurations and four states:

$$\begin{aligned} (b_{3u})^2 &\sim (\psi_{\mathrm{I}})^2 \rightarrow {}^1A_g, \\ (b_{3u})(b_{2g}) &\sim (\psi_{\mathrm{I}})(\psi_{\mathrm{II}}) \rightarrow {}^1B_{1u},\ {}^3B_{1u}, \\ (b_{2g})^2 &\sim (\psi_{\mathrm{II}})^2 \rightarrow {}^1A_g. \end{aligned} \tag{8.2}$$

The fact that we obtain the B_{1u} state from (b_{3u}) (b_{2g}) can be seen from the character table of D_{2h}; by taking the product of the characters of b_{3u} and b_{2g}, we obtain the new characters,

E	C_2^x	C_2^y	C_2^z	I	σ_{yz}	σ_{zx}	σ_{xy}
1	−1	−1	1	−1	1	1	−1

which are the characters of B_{1u}.

Now we can write down the antisymmetrized wave functions for these configurations:

$$\Phi_1({}^1A_g) = \frac{1}{\sqrt{2}}\begin{vmatrix} \psi_{\rm I}(1)\alpha_1 & \psi_{\rm I}(1)\beta_1 \\ \psi_{\rm I}(2)\alpha_2 & \psi_{\rm I}(2)\beta_2 \end{vmatrix} = (\psi_{\rm I}\bar{\psi}_{\rm I}), \tag{8.3}$$

$$\begin{aligned} \Phi_2({}^1B_{1u}) &= \frac{1}{\sqrt{2}}\{\psi_{\rm I}(1)\psi_{\rm II}(2) + \psi_{\rm II}(1)\psi_{\rm I}(2)\}\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2) \\ &= \tfrac{1}{2}\{\psi_{\rm I}(1)\psi_{\rm II}(2)\alpha_1\beta_2 - \psi_{\rm II}(1)\psi_{\rm I}(2)\beta_1\alpha_2\} \\ &\quad + \tfrac{1}{2}\{\psi_{\rm II}(1)\psi_{\rm I}(2)\alpha_1\beta_2 - \psi_{\rm I}(1)\psi_{\rm II}(2)\beta_1\alpha_2\} \\ &= \frac{1}{2}\begin{vmatrix} \psi_{\rm I}(1)\alpha_1 & \psi_{\rm II}(1)\beta_1 \\ \psi_{\rm I}(2)\alpha_2 & \psi_{\rm II}(2)\beta_2 \end{vmatrix} + \frac{1}{2}\begin{vmatrix} \psi_{\rm II}(1)\alpha_1 & \psi_{\rm I}(1)\beta_1 \\ \psi_{\rm II}(2)\alpha_2 & \psi_{\rm I}(2)\beta_2 \end{vmatrix} \\ &= \frac{1}{\sqrt{2}}[(\psi_{\rm I}\bar{\psi}_{\rm II}) + (\psi_{\rm II}\bar{\psi}_{\rm I})]. \end{aligned} \tag{8.4}$$

Similarly, we obtain

$$\begin{aligned} \Phi_3({}^3B_{1u}) &= \frac{1}{\sqrt{2}}\{\psi_{\rm I}(1)\psi_{\rm II}(2) - \psi_{\rm II}(1)\psi_{\rm I}(2)\}\frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2) \\ &= \frac{1}{\sqrt{2}}[(\psi_{\rm I}\bar{\psi}_{\rm II}) - (\psi_{\rm II}\bar{\psi}_{\rm I})], \end{aligned} \tag{8.5}$$

and, finally,

$$\Phi_4({}^1A_g) = (\psi_{\rm II}\bar{\psi}_{\rm II}).$$

There will be interaction between two ${}^1A_g$ wave functions. Taking this into account we arrive at the state functions within the various approximations employed at the present. They are:

$$\begin{aligned} \Phi_N({}^1A_g) &= C_N\Phi_1 + C_N'\Phi_4, \\ \Phi_Z({}^1A_g) &= C_Z\Phi_1 + C_Z'\Phi_4, \\ \Phi_V({}^1B_{1u}) &= \Phi_2({}^1B_{1u}), \\ \Phi_T({}^3B_{1u}) &= \Phi_3({}^3B_{1u}). \end{aligned} \tag{8.6}$$

The symbols N, V, T, and Z are taken from molecular spectroscopy.

9. Energy Calculations; Decomposition into Integrals Which Involve Atomic Orbitals

The Hamiltonian for the π electrons is given by (7.2). Its matrix elements between the configurational wave functions, which are in terms of MO's, can be calculated by remembering that the orbitals $\psi_{\rm I}$ and $\psi_{\rm II}$ are orthogonal to each other. The results are the following (hereafter we shall drop the superscript π from $\mathscr{H}$ and f):

$$\begin{aligned}
&(1\,|\,\mathscr{H}\,|\,1) = 2(\mathrm{I}\,|\,f\,|\,\mathrm{I}) + (\mathrm{I\,I}\,|\,\mathrm{I\,I}),\\
&(2\,|\,\mathscr{H}\,|\,2) = (\mathrm{I}\,|\,f\,|\,\mathrm{I}) + (\mathrm{II}\,|\,f\,|\,\mathrm{II}) + (\mathrm{I\,I}\,|\,\mathrm{II\,II}) + (\mathrm{I\,II}\,|\,\mathrm{II\,I}),\\
&(3\,|\,\mathscr{H}\,|\,3) = (\mathrm{I}\,|\,f\,|\,\mathrm{I}) + (\mathrm{II}\,|\,f\,|\,\mathrm{II}) + (\mathrm{I\,I}\,|\,\mathrm{II\,II}) - (\mathrm{I\,II}\,|\,\mathrm{II\,I}), \qquad (9.1)\\
&(4\,|\,\mathscr{H}\,|\,4) = 2(\mathrm{II}\,|\,f\,|\,\mathrm{II}) + (\mathrm{II\,II}\,|\,\mathrm{II\,II}),
\end{aligned}$$

and

$$(1\,|\,\mathscr{H}\,|\,4) = (\mathrm{I\,II}\,|\,\mathrm{II\,I}),$$

where $(\mathrm{I}\,|\,f\,|\,\mathrm{I})$ is an abbreviation of $(\psi_{\rm I}\,|\,f\,|\,\psi_{\rm I})$, etc. The two-electron integrals can be decomposed into integrals which are defined over atomic orbitals by using (8.1),

$$\begin{aligned}
(\mathrm{I\,I}\,|\,\mathrm{I\,I}) &= \int \psi_{\rm I}{}^*(1)\psi_{\rm I}(1)\frac{1}{r_{12}}\,\psi_{\rm I}^*(2)\psi_{\rm I}(2)\,dv_1\,dv_2\\
&= \frac{1}{4(1+S)^2}\int\{\pi_a(1)\pi_a(1)+\pi_b(1)\pi_b(1)+2\pi_a(1)\pi_b(1)\}\frac{1}{r_{12}}\\
&\quad\times\{\pi_a(2)\pi_a(2)+\pi_b(2)\pi_b(2)+2\pi_a(2)\pi_b(2)\}\,dv_1\,dv_2\\
&= \frac{1}{2(1+S)^2}\{(\pi_a\pi_a\,|\,\pi_a\pi_a)+(\pi_a\pi_a\,|\,\pi_b\pi_b)\\
&\quad+4(\pi_a\pi_a\,|\,\pi_a\pi_b)+2(\pi_a\pi_b\,|\,\pi_a\pi_b)\}. \qquad (9.2)
\end{aligned}$$

The first term is called a one-center Coulomb integral, the second a two-center Coulomb, the third a hybrid or ionic, and the fourth a two-center exchange integral. We obtain, similarly,

$$\begin{aligned}
(\mathrm{II\,II}\,|\,\mathrm{II\,II}) &= \frac{1}{2(1-S)^2}\{(\pi_a\pi_a\,|\,\pi_a\pi_a)+(\pi_a\pi_a\,|\,\pi_b\pi_b)\\
&\quad-4(\pi_a\pi_a\,|\,\pi_a\pi_b)+2(\pi_a\pi_b\,|\,\pi_a\pi_b)\}, \qquad (9.3)
\end{aligned}$$

$$(\mathrm{I\,I}\,|\,\mathrm{II\,II}) = \frac{1}{2(1-S^2)}\{(\pi_a\pi_a\,|\,\pi_a\pi_a)+(\pi_a\pi_a\,|\,\pi_b\pi_b)-2(\pi_a\pi_b\,|\,\pi_a\pi_b)\}, \qquad (9.4)$$

$$\begin{aligned}
(\mathrm{I\,II}\,|\,\mathrm{I\,II}) &= (\mathrm{I\,II}\,|\,\mathrm{II\,I})\\
&= \frac{1}{2(1-S^2)}\{(\pi_a\pi_a\,|\,\pi_a\pi_a)-(\pi_a\pi_a\,|\,\pi_b\pi_b)\}. \qquad (9.5)
\end{aligned}$$

Next we proceed to a similar decomposition of the one-electron part. There are three ways of doing this.

(*a*) *Direct Calculation.* If we know the explicit form of the occupied σ orbitals in terms of AO's, a direct calculation is possible in principle. However, the resulting expression still involves a lot of many-center integrals. Up to the present, the many-center integrals involving σ and π orbitals have not been evaluated exactly, except for the calculation of C_2H_4 carried out by Moskowitz and Harrison (1965) by using Gaussian AO's as bases. Undoubtedly more and more exact values of these many-center integrals will become available; nevertheless rigorous direct calculations will not be easily applied to any π electron systems of considerable size. Therefore, it is often convenient and sometimes necessary to make various simplifications in the calculation. For example, the attached hydrogens may be neglected altogether,[3] thus reducing the C_2H_4 problem to that of two doubly bonded carbon atoms in their valence states. Further, it is often assumed that the three σ orbitals of each carbon are sp^2 hybridized orbitals; thus we neglect any possible deformation of these orbitals due to the molecular formation. If we do this, the result of the decomposition of $(\mathrm{I} \mid f \mid \mathrm{I})$ is as follows:

$$\begin{aligned}(\mathrm{I} \mid f \mid \mathrm{I}) = \frac{1}{1+S} \Big\{ & (\pi_a| -\frac{1}{2}\Delta - \frac{6}{r_a} - \frac{6}{r_b} |\pi_a) + (\pi_a| -\frac{1}{2}\Delta - \frac{6}{r_a} - \frac{6}{r_b} |\pi_b) \\ & + 2(\pi_a\pi_a \mid 1s_a 1s_a) + 2(\pi_a\pi_a \mid 1s_b 1s_b) + 4(\pi_a\pi_b \mid 1s_a 1s_a) \\ & + 3(\pi_a\pi_a \mid \sigma_a\sigma_a) + (\pi_a\pi_a \mid \sigma 1_b \sigma 1_b) + 2(\pi_a\pi_a \mid \sigma 2_b \sigma 2_b) \\ & + 2(\pi_a\pi_b \mid \sigma 1_a \sigma 1_a) + 4(\pi_a\pi_b \mid \sigma 2_a \sigma 2_a) - (\pi_a 1s_a \mid \pi_a 1s_a) \\ & - (\pi_a 1s_b \mid \pi_a 1s_b) - 2(\pi_a 1s_a \mid \pi_b 1s_a) - \tfrac{3}{2}(\pi_a\sigma_a \mid \pi_a\sigma_a) \\ & - \tfrac{1}{2}(\pi_a\sigma 1_b \mid \pi_a \sigma 1_b) - (\pi_a \sigma 2_b \mid \pi_a \sigma 2_b) - (\pi_a \sigma 1_a \mid \pi_b \sigma 1_a) \\ & - 2(\pi_a \sigma 2_a \mid \pi_b \sigma 2_a) \Big\}, \qquad (9.6)\end{aligned}$$

where $\sigma 1_a$, $\sigma 2_a$, $\sigma 3_a$ are the sp^2 hybrids of the carbon atom a which are pointing out towards the other carbon atom b and the hydrogen atoms. Similar expressions can be given for $(\mathrm{II} \mid f \mid \mathrm{II})$.

It may be worth noting that, when we assume spin-pairing for every σ bond, the coefficients of the exchange integrals in (9.6) are always $-\frac{1}{2}$ times those of the corresponding Coulomb integrals.

(*b*) *Ruedenberg's Approximation.* This is another simplified form of the direct calculation proposed by Ruedenberg (1961).

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[3] In other words, we assume complete screening of the protons by their electrons.

The one-electron operator f is supposed to have the following form:

$$f(1) = -\tfrac{1}{2}\Delta_1 + \sum_a v_a(1) + \sum_b u_b(1), \tag{9.7}$$

where v_a is the potential due to the presence of a positively charged atom a, which is formed by taking π electron(s) adiabatically away from a neutral atom in its suitable valence state. The potential u_b is due to the presence of attached atoms which have no π electron; the most common example is the hydrogen atom.

Following the idea of Goeppert-Mayer and Sklar (1938), Ruedenberg then introduces the potential u_a which is a potential of a neutral atom a. The following relation between v_a and u_a is assumed:

$$v_a(1) = u_a(1) - n_a \int \frac{|\pi_a(2)|^2}{r_{12}}\, dv_2, \tag{9.8}$$

where n_a is the number of π electrons which come from the atom a. The use of (9.8) implies that the $\sigma - \pi$ exchange interaction is neglected.

Incorporating (9.8) with (9.7), we obtain

$$f(1) = -\tfrac{1}{2}\Delta_1 + \sum_{\text{all atoms}} u_a(1) - \sum_{\substack{\text{conjugated}\\ \text{atoms}}} n_a \int \frac{|\pi_a(2)|^2}{r_{12}}\, dv_2. \tag{9.9}$$

The first two terms in (9.9) represent comparatively short-range forces while the third term represents the Coulomb interaction which is long-range. In Ruedenberg's approximation, the short-range part is taken into account in the calculation of the integral $(\pi_a \mid f \mid \pi_b)$ only when a and b are the same atom or nearest neighbors. The long-range part is retained for all integrals. For three-center integrals, the following Mulliken approximation is recommended:

$$(\pi_a\pi_a \mid \pi_b\pi_c) = \frac{S_{bc}}{2}\{(\pi_a\pi_a \mid \pi_b\pi_b) + (\pi_a\pi_a \mid \pi_c\pi_c)\}. \tag{9.10}$$

(*c*) *The Goeppert-Mayer–Sklar Approximation.* This was proposed by Goeppert-Mayer and Sklar as early as 1938 and has been used very often. The first step is the assumption (9.7) about the form of the one-electron operator $f(1)$. In the Goeppert-Mayer–Sklar approximation, attached atoms are usually neglected; thus for C_2H_4, we have

$$f = -\tfrac{1}{2}\Delta + v_a + v_b, \tag{9.11}$$

where v_a is the potential of a positively charged carbon atom in its sp^2

valence state. Then comes the crucial point. We assume the following equation,

$$(-\tfrac{1}{2}\Delta + v_a)\pi_a = W_{2p}\pi_a,\text{[4]} \tag{9.12}$$

where W_{2p} is the energy of a $2p\pi$ electron in a carbon atom in its valence state.

If we use this, we obtain

$$\begin{aligned}(\mathrm{I}\,|\,f\,|\,\mathrm{I}) &= \frac{1}{2(1+S)}\int(\pi_a+\pi_b)^*(-\tfrac{1}{2}\Delta + v_a + v_b)(\pi_a+\pi_b)\,dv \\ &= W_{2p} + \frac{1}{1+S}\left\{\int \pi_a{}^* v_b \pi_a\,dv + \int \pi_b{}^* v_b \pi_a\,dv\right\},\end{aligned} \tag{9.13}$$

$$(\mathrm{II}\,|f|\,\mathrm{II}) = W_{2p} + \frac{1}{1-S}\left[\int \pi_a{}^* v_b \pi_a\,dv - \int \pi_b{}^* v_b \pi_a\,dv\right]. \tag{9.14}$$

Thus the problem reduces to the estimation of W_{2p} and the integrals $(\pi_a \mid v_b \mid \pi_a)$ and $(\pi_b \mid v_b \mid \pi_a)$. If we are interested only in excitation energies, we do not need to evaluate W_{2p}. This term appears as a common additional constant in $(\mathrm{I}\,|\,f\,|\,\mathrm{I})$ and $(\mathrm{II}\,|\,f\,|\,\mathrm{II})$ and hence drops out of the calculation. On the other hand, for example, if we are interested in molecular ionization potentials or if the system is not a hydrocarbon but a heterocyclic molecule, the knowledge about W_{2p} is necessary.

Since $-W_{2p}$ is the energy difference between the two valence states $\mathrm{C}^+\ V_3$ and $\mathrm{C}\ V_4$,

$$-W_{2p} = E[\mathrm{C}^+\ V_3] - E[\mathrm{C}\ V_4]. \tag{9.15}$$

We can estimate it if we know the ionization potential (I.P.) of a carbon atom in its ground state,

$$\mathrm{I.P.} = E[\mathrm{C}^+\ {}^2P] - E[\mathrm{C}\ {}^3P], \tag{9.16}$$

and the two energies required to promote the atoms C and C^+ to their valence states (P.E.),

$$\mathrm{P.E.}(\mathrm{C}^+) = E[\mathrm{C}^+\ V_3] - E[\mathrm{C}^+\ {}^2P], \tag{9.17}$$

$$\mathrm{P.E.}(\mathrm{C}) = E[\mathrm{C}\ V_4] - E[\mathrm{C}\ {}^3P]. \tag{9.18}$$

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[4] In general, this may be replaced by the following two equations

$$(\pi_a\,|-\tfrac{1}{2}\Delta + v_a\,|\,\pi_a) = W_{2p},$$

$$(\pi_b\,|-\tfrac{1}{2}\Delta + v_a\,|\,\pi_a) = SW_{2p}.$$

In the case of C_2H_4, the latter is not needed because $(1\,|\,F\,|\,2)$ does not appear in the calculation.

Thus we see from Fig. 2,

$$-W_{2p} = \text{I.P.} + \text{P.E.}(\text{C}^+) - \text{P.E.}(\text{C}). \tag{9.19}$$

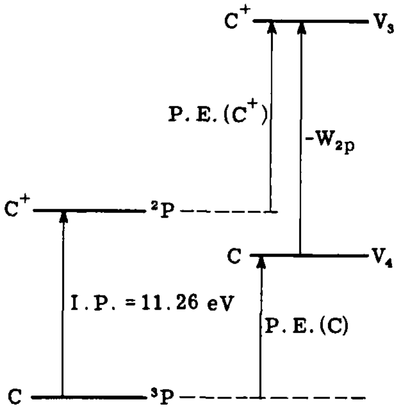

Fig. 2. Schematic diagram of the energy states of C and C$^+$.

The ionization potential of a free carbon atom in the gaseous state is known from experiment to be 11.26 eV.

The valence state energy may be expressed as a weighted mean of spectroscopic term values.[5] How to obtain the weight was discussed by Moffitt (1954). He also gave a useful table of these weights for the configurations $p^2(p^4)$, p^3, $sp(sp^5)$, $sp^2(sp^4)$, and sp^3. He neglected the effect of hybridization. According to his table, we have

$$E(V_4\ sxyz) = \tfrac{5}{16}E(^5S^0) + \tfrac{3}{16}(^3S^0) + \tfrac{3}{8}(^3D^0) + \tfrac{1}{8}(^1D^0), \tag{9.20}$$

$$E(V_3\ sxy) = \tfrac{1}{2}E(^4P) + \tfrac{1}{4}E(^2P) + \tfrac{1}{4}E(^2D). \tag{9.21}$$

The energies of these spectroscopic states can be found in the following extensive tables [see Moore, 1949 (^{1}H—^{23}V), 1952 (^{24}Cr—^{41}Nb), 1958 (^{42}Mo—^{57}La, ^{72}Hf—^{89}Ac)]. We find the following values (in eV):

C:	s^2p^2	^3P	0,	C$^+$:	s^2p	$^2P^0$	0,
	sp^3	$^5S^0$	4.18,		sp^2	^4P	5.33,
	sp^3	$^3D^0$	7.95,		sp^2	^2D	9.29,
	sp^3	$^1D^0$	12.13,		sp^2	^2P	13.71.
	sp^3	$^3S^0$	13.12;				

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[5] One way of seeing this is to note that the wave functions of valence states and spectroscopic states can be constructed from the same set of products of spin-orbitals.

Using these values, we obtain

$$\text{P.E.}(\text{C } V_4\, sxyz) = 8.26\ \text{eV} \tag{9.22}$$

and

$$\text{P.E.}(\text{C}^+\ V_3\, sxy) = 8.42\ \text{eV}. \tag{9.23}$$

Thus we are led to a value

$$-W_{2p} = 11.26 + 8.42 - 8.26 = 11.42\ \text{eV}. \tag{9.24}$$

Energies of valence states calculated in this way have been tabulated by Pritchard and Skinner (1955) in their excellent review article on electronegativity.

Another way of evaluating valence state energies goes back to Van Vleck (1934) and Mulliken (1934) and has been applied extensively by Hinze and Jaffé (1962) and by Pilcher and Skinner (1962). They obtained the valence state energies from Slater–Condon parameters determined using spectroscopic data. Hinze and Jaffé's results are

$$\text{P.E.}(V_4\ \text{C}\ sxyz) = 8.48\ \text{eV} \tag{9.25}$$

and

$$\text{P.E.}(V_3\ \text{C}^+\ sxy) = 8.49\ \text{eV}, \tag{9.26}$$

giving the $-W_{2p}$ value without hybridization,

$$-W_{2p} = 11.26 + 8.49 - 8.48 = 11.27\ \text{eV}. \tag{9.27}$$

With hybridization, these values are

$$\text{P.E.}(V_4\ \text{C}\ (sp^2)^3\pi) = 6.76\ \text{eV}, \tag{9.28}$$

$$\text{P.E.}(V_3\ \text{C}^+\ (sp^2)^3) = 6.67\ \text{eV}, \tag{9.29}$$

$$-W_{2p} = 11.26 + 6.67 - 6.76 = 11.17\ \text{eV}. \tag{9.30}$$

This example shows that, although promotion energies to valence states depend on hybridization, there is little change in W_{2p} even if it is neglected. From the tables of valence state ionization energies given in Hinze and Jaffé's papers (1962, 1963a,b), we can see that this is usually the case.

The calculations of $(\pi_a|v_b|\pi_a)$ and $(\pi_b|v_b|\pi_a)$ were carried out by Goeppert-Mayer and Sklar (1938). They introduced for the first time the potential u which is an assumed spherically symmetric potential of a neutral carbon atom. Using (9.8), we obtain

$$(\pi_a\,|\,v_b\,|\,\pi_a) = (\pi_a\,|\,u_b\,|\,\pi_a) - (\pi_a\pi_a\,|\,\pi_b\pi_b) \tag{9.31}$$

and

$$(\pi_b\,|\,v_b\,|\,\pi_a) = (\pi_b\,|\,u_b\,|\,\pi_a) - (\pi_a\pi_b\,|\,\pi_b\pi_b). \tag{9.32}$$

If we assume that each of the inner shell electrons completely shields one unit of positive nuclear charge, the potential u becomes

$$\begin{aligned} u(1) &= -\frac{4}{r_1} + \int \frac{1}{r_{12}} \{|2s(2)|^2 + |px(2)|^2 + |py(2)|^2 + |pz(2)|^2\}\, dv_2 \\ &= -\frac{4}{r_1} + \frac{1}{r_1}\int_0^{r_1} P(r) r^2\, dr + \int_{r_1}^{\infty} P(r) r\, dr \\ &= -\int_{r_1}^{\infty}\left(\frac{r}{r_1} - 1\right) P(r) r\, dr, \end{aligned} \tag{9.33}$$

where

$$P(r) = 4\pi\{|2s(r)|^2 + |px(r)|^2 + |py(r)|^2 + |pz(r)|^2\} \tag{9.34}$$

and

$$\int_0^{\infty} P(r) r^2\, dr = 4. \tag{9.35}$$

The potential u was later used by other authors too, but it is not essential. We may as well use the formula

$$(\pi_a\,|\,v_b\,|\,\pi_a) = (\pi_a\,|\,-\frac{4}{r_b}\,|\,\pi_a) + (2s_b 2s_b\,|\,\pi_a\pi_a) + (py_b py_b\,|\,\pi_a\pi_a) + (pz_b pz_b\,|\,\pi_a\pi_a) \tag{9.36}$$

and a similar formula for $(\pi_b\,|\,v_b\,|\,\pi_a)$.

What is essential in the Goeppert-Mayer–Sklar approximation is the assumption of (9.12). Although very convenient, the approximation is open to some criticism (Stewart, 1959). The author feels that the direct calculation even in its simplified form is preferable, if it is feasible.

10. Atomic Orbitals

The calculations of molecular energies and wave functions are reduced now to the evaluation of so-called molecular integrals which involve only atomic orbitals. In order to evaluate these integrals, we have to specify the functional form of the atomic orbitals.

There are four types of atomic orbitals which have been used in molecular calculations.

(*a*) *Slater-Type Orbitals.* The functional form is

$$\left\{\frac{2(Z-s)}{n^*}\right\}^{n^*+1/2}[(2n^*)!]^{-1/2}\exp\left(-\frac{Z-s}{n^*}r\right)r^{n^*-1}Y_{lm}(\theta,\varphi),$$

where $Y_{lm}(\theta, \varphi)$ is a normalized spherical harmonic, Z is the nuclear charge, and the atomic unit is used in measuring r. The quantity $(Z - s)/n^*$ is called an orbital exponent and is a very useful parameter in this type of atomic orbitals. When we determine the effective principal number n^* and the shielding constant s according to the following Slater rules, we talk of Slater orbitals:

(α) n^* is determined according to the real principal quantum number n by the following table:

n	1	2	3	4	5	6
n^*	1	2	3	3.7	4.0	4.2

(β) In order to determine the shielding constant s, the electrons are divided into the following groups:

$$\{1s\},\quad \{2s, 2p\},\quad \{3s, 3p\},\quad \{3d\},\quad \{4s, 4p\},\quad \{4d\},\quad \{4f\}, \ldots$$

and s consists of the following contributions:

(*i*) nothing from any group outside the orbital in question;

(*ii*) an amount 0.35 (0.30 for the 1*s* group) per electron in the same group;

(*iii*) an amount 0.85 (in case of *s* and *p* orbitals) or 1.00 (in case of *d* and *f* orbitals) per electron with *n* one less than that for the orbital in question;

(*iv*) an amount 1.00 per electron with *n* still less.

These Slater orbitals are designed to imitate the Hartree–Fock atomic orbitals but have much simpler forms. They are known to be very good for 1*s*, 2*s*, and 2*p*. For the higher orbitals, the deviation from H.F. orbitals becomes rather large.

All the Slater orbitals are nodeless and, as an example, the 2*s* orbital is not orthogonal to the 1*s* orbital. For mathematical convenience, the 2*s* orbital which is orthogonalized to 1*s* by the Schmidt procedure

$$(2s^0) = \frac{1}{\sqrt{1-(1s\,|\,2s)^2}}\{(2s) - (1s\,|\,2s)(1s)\} \qquad (10.1)$$

is used. This has a node and has a finite value at $r = 0$, which is quite important if we want to discuss the local properties of electrons in the vicinity of a nucleus by using these orbitals.

Figure 3 was taken from a paper by Kotani *et al.* (1957) to illustrate how close the radial parts of $(2s^0)$ and H.F. are in the case of oxygen.

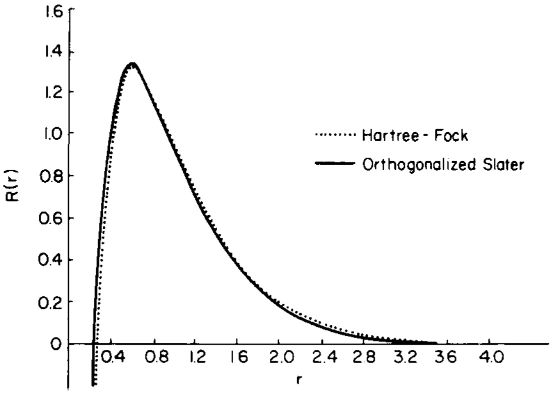

Fig. 3. Comparison of the radial part of H.F. and orthogonalized Slater $2s$ orbitals of the oxygen atom.

(*b*) *Hartree–Fock* (*SCF*) *Atomic Orbitals.* These are surely better than Slater AO's for free atoms. They are usually given only numerically so that the calculation of molecular integrals becomes more tedious and complicated.

A list of atoms whose Hartree or Hartree–Fock orbitals are available and the references can be found in the following: Hartree (1946/1947, 1957), Knox (1957), and Slater (1960).

To give some idea about the accuracy of the energies they give, computed energies and their ratios to the observed values for C, N, and O are listed in Table II.

To circumvent the complexity of calculating molecular integrals from numerical functions, analytical Hartree–Fock AO's are proposed and used for a number of cases (Slater, 1932; Löwdin, 1953, 1954; Löwdin and Appel, 1956). The most usual procedure seems to be to represent an AO by a linear combination of Slater-type orbitals (Roothaan and Bagus, 1963; Clementi, 1965).

(*c*) *Gaussian Atomic Orbitals.* The Gaussian AO's (GO's) have the radial parts of the form $r^n \exp\{-\delta r^2\}$, where n is an integer and $\delta > 0$ is a parameter. The use of the Gaussian orbitals for molecular calculations was

TABLE II

COMPUTED AND OBSERVED ENERGY IN eV

Atom	State	Slater[a]		H.F.[b]		Obs.[c]
C	^3P	-1023.6_3	99.40%	-1025.5_0	99.58%	-1029.8_1
N	^4S	-1476.5_9	99.39%	-1480.2_4	99.64%	-1485.6_4
O	^3P	-2028.1_3	99.26%	-2035.5_4	99.62%	-2043.2_8

[a] Krauss (1958). [b] Clementi (1965). [c] Moore (1949).

proposed and advocated by Boys (1950, 1960). Meckler (1953) and Nesbet (1960) used them in calculations on the oxygen and methane molecules, respectively. The results of these earlier investigations were not satisfactory, because the numbers of GO's used (10 for O_2, 8 for CH_4) were small. A single Gaussian is a very poor approximation to an AO and we have to use at least several GO's to represent an AO reasonably well.

On the other hand, a distinct advantage of the GO's is that all types of molecular integrals can be expressed in analytical closed forms and thus be evaluated more easily. Especially all three- and four-center integrals can be reduced to two-center integrals (see, for example, Shavitt, 1963).

The success of recent uses of GO's is encouraging. Krauss (1963) has reported the calculations on CH_4 and NH_4^+, using nineteen Gaussians as basic functions. He has obtained the total energies better than any previous calculation. Moskowitz and Harrison (1965) have used forty GO's for C_2H_4 and succeeded in performing the first rigorous *ab initio* calculations of this molecule. Their total energy was -77.800 au, which is lower than the sum of experimental atomic energies, and this should be considered highly successful.

Systematic investigations on the usefulness of GO's as bases for polyatomic calculations have begun at various institutes (see, for example, Huzinaga, 1965; Reeves and Fletcher, 1965). It seems that, with the aid of fast electronic computers, *ab initio* calculation of polyatomic molecules using GO's has reached a position at least equivalent to, or possibly better than, the conventional methods using Slater or SCF AO's.

(*d*) *Laguerre Functions*. The radial part has the form of an exponential —common to all—times a polynomial in r. An advantage is that the set is complete. The integral calculations are simplified because of the common exponent.

The Laguerre functions have been successfully used for the helium atom and the negative hydrogen ion (Holøien, 1958). However, if we want to express two atomic orbitals with different exponential behavior at large r, we need perhaps ten Laguerre functions to reach the same accuracy as two Slater AO's give. Unless one is prepared to do a big computation, the outlook for the use of Laguerre functions in complex atoms or molecules is not very bright.

Finally, it is worth mentioning that an excellent article on the choice of basic AO's and its effect on calculated molecular properties (by taking HF as a main example) was written by Mulliken (1962).

11. Molecular Integrals

There are two main lines of approach to the evaluation of molecular integrals involving Slater-type AO's.

(*a*) *Use of Elliptic Coordinates.* One line is to make use of elliptic coordinates

$$\lambda = \frac{r_a + r_b}{2R}, \qquad \mu = \frac{r_a - r_b}{2R}, \qquad \varphi.$$

This line is also characterized by the use of the Neumann expansion of $1/r_{12}$ in evaluating the exchange integral.

One form of the Neumann expansion is

$$\begin{aligned}\frac{1}{r_{12}} &= \frac{2}{R}\sum_{n=0}^{\infty}\sum_{m=0}^{n} D_{nm}Q_n{}^m(\lambda_>)P_n{}^m(\lambda_<)P_n{}^m(\mu_1)\\ &\quad \times P_n{}^m(\mu_2)\cos m(\varphi_1 - \varphi_2), \qquad (11.1)\\ D_{n0} &= 2n+1,\\ D_{nm} &= (-1)^m 2(2n+1)\left\{\frac{(n-m)!}{(n+m)!}\right\}^2,\end{aligned}$$

where $\lambda_>$ and $\lambda_<$ are the larger and the smaller of λ_1 and λ_2, respectively, and $P_n{}^m$ and $Q_n{}^m$ are the associated Legendre function of the first and second kind. This expansion was first used by Sugiura (1927) in evaluating $(1s_a1s_b|1s_a1s_b)$ for the H_2 molecule.

This line of approach has been extensively used for two-center integrals of Slater-type AO's. The following are the standard references.

Formulas.

Two-center overlap, kinetic energy, nuclear attraction, and Coulomb integrals for the AO's with the principal quantum number 1 and 2 (Roothaan, 1951a);

Two-center exchange integrals for the AO's with the principal quantum number 1, 2, and 3 (Ruedenberg, 1951);

Two-center hybrids and a unified treatment of hybrid, Coulomb and

one-electron integrals for the AO's with the principal quantum number 1 and 2 (Ruedenberg *et al.*, 1956);
A new method for auxiliary functions (Roothaan, 1956). More detailed accounts of the third and the fourth papers can be found in the Technical Report from the Laboratory of Molecular Structure and Spectra, Department of Physics, the University of Chicago, 1952–1953 Part II and 1953–1954 Part II, respectively.

Tables.

Integrals between 1*s* and 2*s*, 2*p* and those between 2*s*, 2*p* and 2*s*, 2*p*; in the latter orbital exponents in the AO's on the two centers are equal except for small number of cases (Kotani *et al.*, 1963; Preuss, 1956, 1957, 1960, 1961);
Auxiliary functions needed for the integrals involving 1*s*, 2*s*, and 2*p*σ with two different orbital exponents (Miller *et al.*, 1959);
Nuclear attraction and overlap integrals between the orbitals 1*s*, 2*s*, and 2*p* with different orbital exponents (Sahni and Cooley, 1959); Coulomb integrals between the 1*s*, 2*s*, and 2*p* with different orbital exponents (Sahni and Cooley, 1960); two-center two-electron hybrid integrals between 1*s*, 2*s*, and 2*p* orbitals with different orbital exponents (Sahni and Cooley, 1963).

(*b*) *Use of the Expansion in Spherical Harmonics around One Center.* This line of approach is applicable also to Hartree–Fock AO's and was first used by Coolidge (1932) in his treatment of the water molecule; it was later extended by Landshoff (1936, 1937) and Löwdin (1947, 1948). It is often referred to as the Coulson and Barnett method since the latter authors developed general formulas in the following paper: Barnett and Coulson (1951).

The expansion of an orbital of one center in terms of spherical harmonics around another center was reviewed by Löwdin (1956; see particularly Section 6).

Useful tables of auxiliary functions were compiled by Barnett and Coulson (1956).

Method (*a*) is perhaps more convenient for two-center integrals but its application is restricted to Slater-type functions. Method (*b*) is more convenient for many-center integrals and is applicable to those integrals involving Hartree-Fock AO's as well as those of Slater AO's.

For general reviews, the reader is referred to the following papers: Dalgarno (1954) or to the introductory part of the fourth volume of the Preuss' book (1960).

As was mentioned in the previous section, molecular integrals involving Gaussian AO's are much more easily handled. Adequate references for the evaluation of this type of integrals can be found in Shavitt (1963).

The importance of electronic computers in the calculation of molecular integrals cannot be overstressed. Many extremely useful programs have been written and some of them are available through the Quantum Chemistry Program Exchange, Chemistry Department, Indiana University.

12. Results of Calculations on C_2H_4

Finally we have reached the stage where we discuss the results of various calculations. There have been many investigations on the ethylene molecule since Penny's work in 1934. However, the first calculation performed along the line of LCAO MO CI is that by Hartmann (1943). Unfortunately, there was an error in choosing a spin function and he got a mixture of a singlet and a triplet for an excited state. There are some doubts whether all of his integral values are correct. We do not, therefore, quote his numerical results here.

The next calculation was carried out by Parr and Crawford (1948). Their basic AO's were of Slater type. As very little is known of how to choose the orbital exponent δ of these AO's, they adopted four values, $2\delta = 2.35$, 3.18, 3.27, and 3.91, and carried out the calculation for each of these. Slater's rule gives the value 3.25. In the calculation of the one-electron core integrals, Goeppert-Mayer–Sklar's approximation was used.

Parr and Crawford computed the electronic energy as a function of the twisting angle φ ($\varphi = 0$ corresponds to the planar configuration). When $\varphi \neq 0$, the atomic orbital on the atom b, π_b, should be replaced by π_b', where

$$\pi_b' = \cos\varphi \cdot 2px_b + \sin\varphi \cdot 2py_b. \tag{12.1}$$

Then we can determine the φ dependence of all molecular integrals. Some examples follow:

$$\begin{aligned}
(\pi_a \,|\, \pi_b') &= \cos\varphi(\pi_a \,|\, \pi_b),\\
(\pi_a\pi_a \,|\, \pi_b'\pi_b') &= \cos^2\varphi\,(\pi_a\pi_a \,|\, \pi_b\pi_b) + \sin^2\varphi\,(\pi_a\pi_a \,|\, y_b y_b),\\
(\pi_a\pi_b' \,|\, \pi_a\pi_b') &= \cos^2\varphi\,(\pi_a\pi_b \,|\, \pi_a\pi_b) + \sin^2\varphi\,(\pi_a y_b \,|\, \pi_a y_b),\\
(\pi_a\pi_a \,|\, \pi_a\pi_b') &= \cos\varphi\,(\pi_a\pi_a \,|\, \pi_a\pi_b),\\
(\pi_a \,|\, u_a \,|\, \pi_b') &= \cos\varphi\,(\pi_a \,|\, u_a \,|\, \pi_b).
\end{aligned} \tag{12.2}$$

Using these formulas, we can calculate the twisting force constant k,

$$k = \left(\frac{\partial^2 E}{\partial\varphi^2}\right)_{\varphi=0}. \tag{12.3}$$

The twisting frequency ω (in cm^{-1}) is related to the force constant by

$$\omega = \frac{1}{\pi c}\left(\frac{k}{I}\right)^{1/2}, \tag{12.4}$$

where I is the total moment of inertia around the molecular axis.

Parr and Crawford's results are shown in Table III.

From these results, we can see that:

(*a*) the planar configuration turns out to be more stable, as it should;

(*b*) the order of levels is all right but quantitative agreements with experiment are not satisfactory at all for any choice of the orbital exponent; in particular,the calculated $T-V$ separation is much too large;

(*c*) the agreement of calculated ω_N with the observed one is reasonable; however, the accuracy of the calculation cannot be expected to be of the order 100 cm^{-1};

(*d*) the decrease of ω_N with an increase in the orbital exponent may be explained qualitatively; an increase in δ means a decrease in the overlap of the two π AO's and thus a decrease in the strength of the $\pi-\pi$ bond.

TABLE III

ENERGY LEVELS OF C_2H_4 IN eV

Angle	2δ	2.35	3.18	3.27	3.91	Obs.
$\varphi=0$	Z	19.4	15.0	14.8	14.1	—
	V	12.3	11.5	11.5	12.7	7.6
	T	7.0	3.1	2.8	2.2	4.6[b]
	1[a]	0.3	1.3	1.4	3.0	—
	N	0	0	0	0	0
	$V-T$	5.3	8.4	8.7	10.5	3.0
	$\omega_N(\mathrm{cm}^{-1})$	1140	995	960	715	1027[c]
$\varphi=\pi/2$	Z	8.3	10.1	10.3	12.3	—
	V	8.1	10.0	10.2	12.3	—
	T	3.5	2.1	1.8	0.9	—
	1[a]	6.0	6.2	6.1	6.6	—
	N	3.7	2.2	1.9	0.9	—

[a] This is the configuration $(\psi_1)^2$, namely the ground state wave function without configuration interaction.

[b] The location of this state has long been uncertain. The value 6.4 eV had been used for some time but the band is assigned to the excitation to the triplet $(b_{3u})(3s)$ state by Mulliken [see Evans (1960) and Mulliken (1960)].

[c] Arnett and Crawford (1950).

Parr and Crawford's calculation was extended by Murai (1952). His basic AO's are again Slater-type AO's. A direct calculation of (I | f | I), (II | f | II) [cf. (9.6)] was tried, in which the effect of the hydrogens was neglected. The main point in his calculation is that the orbital exponent of π AO's depends on the state and is determined by minimizing the energy of each state. Thus the orbital exponent for π AO's is not necessarily the same as those for $2s$ and $2p\sigma$. The value $2\delta = 3.20$ is used for the latter in all the states. In Murai's calculation, a slightly different value, 1.323 Å, of the internuclear distance was used instead of 1.353 Å, which was the usual value at that time.

Sponer and Löwdin have tried another kind of calculation on C_2H_4 (Sponer and Löwdin, 1957). Their basic AO's are Hartree–Fock SCF AO's rather than the Slater-type AO's used by Parr, Crawford, and Murai. One effect is the increase of overlap integral to 0.33, the value by Slater-type function with $2\delta = 3.18$ being 0.28. The $1s$ electrons of the four hydrogen atoms are *not* shrunk into the nuclei. The energies of various states were calculated as functions of the twisting angle φ. Goeppert-Mayer–Sklar's approximation was used and a specific approximation (I I | I I) = (I I | II II) = (II II | II II) was employed.

The results of Murai's and Sponer and Löwdin's calculations are compared with the observed values in Table IV.

TABLE IV

ENERGY LEVELS OF C_2H_4 IN eV

Angle	State	Murai[a]	Sponer–Löwdin	Parr–Crawford, $2\delta = 3.18$	Obs.
$\varphi = 0$	Z	15.8 (2.4)	16.8	15.0	—
	V	11.2 (2.4)	12.3	11.5	7.6
	T	4.6 (3.2)	4.4	3.1	4.6
	N	0 (3.2)	0	0	0
	$V - T$	6.6	7.9	8.4	3.0
$\varphi = \pi/2$	Z	8.2 (2.4)	10.0	10.1	—
	V	8.0 (2.4)	10.0	10.0	—
	T	3.0 (3.2)	2.7	2.1	—
	N	3.0 (3.2)	2.7	2.2	—

[a] The values in parentheses indicate twice the optimum orbital exponents among the choice of 3.2, 2.4, and 1.6.

These results are not so different from those of Parr and Crawford. E_V is still too high and the calculated $V - T$ separation is too big.

13. Moffitt's Explanation for the Failure of the Conventional Calculation

The cause of the failure of the usual ASMO CI calculation in predicting the $N - V$ and $V - T$ separations was first ascertained by Moffitt (1951a)—actually for the case of O_2 rather than C_2H_4.

In the following, we shall concentrate our attention on the V and T states. By decomposing the space part of the wave functions for these states into AO's, we obtain

$$\begin{aligned}\Psi_V &= \frac{1}{\sqrt{2}}\{\psi_{\mathrm{I}}(1)\psi_{\mathrm{II}}(2) + \psi_{\mathrm{II}}(1)\psi_{\mathrm{I}}(2)\} \\ &= \frac{1}{2\sqrt{2(1-S^2)}}[\{\pi_a(1) + \pi_b(1)\}\{\pi_a(2) - \pi_b(2)\} \\ &\qquad + \{\pi_a(1) - \pi_b(1)\}\{\pi_a(2) + \pi_b(2)\}] \\ &= \frac{1}{\sqrt{2(1-S^2)}}[\pi_a(1)\pi_a(2) - \pi_b(1)\pi_b(2)], \end{aligned} \tag{13.1}$$

$$\begin{aligned}\Psi_T &= \frac{1}{\sqrt{2}}\{\psi_{\mathrm{I}}(1)\psi_{\mathrm{II}}(2) - \psi_{\mathrm{II}}(1)\psi_{\mathrm{I}}(2)\} \\ &= \frac{1}{\sqrt{2(1-S^2)}}[\pi_b(1)\pi_a(2) - \pi_a(1)\pi_b(2)]. \end{aligned} \tag{13.2}$$

We see that Ψ_V corresponds to a purely ionic or polar structure while Ψ_T corresponds to a covalent or homopolar structure.

The difference of the energies of these states, which is greatly exaggerated by the calculation, is expressed as [cf. (9.1) and (9.5)]

$$\begin{aligned}E_V - E_T &= (2\,|\,\mathscr{H}\,|\,2) - (3\,|\,\mathscr{H}\,|\,3) \\ &= 2(\mathrm{I\,II}\,|\,\mathrm{II\,I}) \\ &= \frac{1}{1-S^2}\{(\pi_a\pi_a\,|\,\pi_a\pi_a) - (\pi_a\pi_a\,|\,\pi_b\pi_b)\}. \end{aligned} \tag{13.3}$$

The next point shows Moffitt's brilliancy. He considered the value of the above quantity for the extreme case of infinite internuclear distance. In that case, $(\pi_a\pi_a\,|\,\pi_b\pi_b)$ is of course zero and the calculated difference is, then, simply

$$\begin{aligned}E_V - E_T(R = \infty) &= (\pi_a\pi_a\,|\,\pi_a\pi_a) \\ &= 17.2\ \mathrm{eV} \qquad (\text{for} \quad 2\delta = 3.25). \end{aligned} \tag{13.4}$$

On the other hand, remembering that the V state corresponds to a purely ionic case—for $R = \infty$, to a positive and a negative ion—and that the T state corresponds to a homopolar state—for $R = \infty$, to a pair of two neutral C atoms—we can express $E_V - E_T(R = \infty)$ as follows:

$$\begin{aligned} E_V - E_T(R = \infty) &= E(\mathrm{C}^+) + E(\mathrm{C}^-) - 2E(\mathrm{C}) \\ &= \{E(\mathrm{C}^+) - E(\mathrm{C})\} - \{E(\mathrm{C}) - E(\mathrm{C}^-)\} \\ &= I - A, \end{aligned} \tag{13.5}$$

where I and A are valence state ionization potential and electron affinity, respectively. A semiempirical estimate by Hinze and Jaffé (1962) gives the value of 11.16 eV for I and 0.03 eV for A. Therefore, $E_V - E_T(R = \infty)$ is only 11.1 eV by the semiempirical estimate in comparison with 17.2 eV by the calculation. In other words, there is an error of 6.1 eV already existing at an infinite internuclear distance. Moffitt reasoned that this difference of 6.1 eV at $R = \infty$ remains more or less the same at the equilibrium internuclear distance R_e and that this is the large portion of the error at R_e (see Fig. 4). That is to say, the failure of the usual theory is

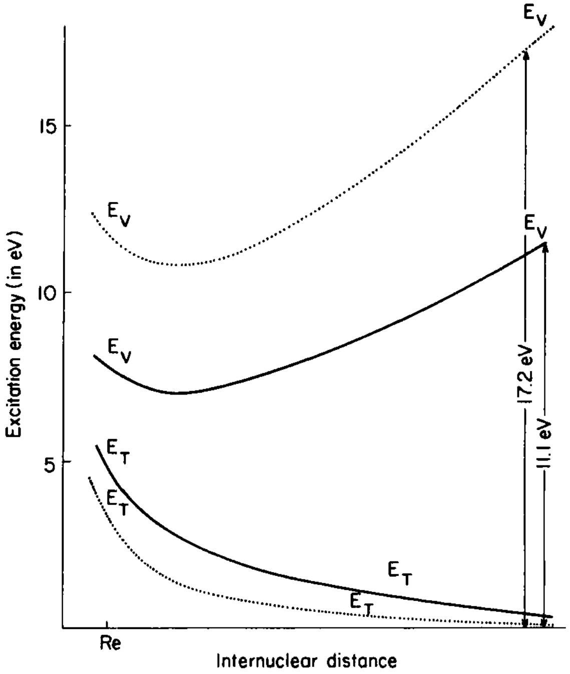

Fig. 4. Schematic diagram of observed (full curve) and calculated (dashed curve) excitation energies.

attributed to its inability in predicting the accurate relative energies of atoms and ions.

Moffitt proposed a new quantitative approach to the problems of the electronic structure of molecules (1951b), based on the above observation. The approach is called the method of atoms in molecules. He observed that the binding energy, namely the change in energy due to molecular formation, is very small as compared with the total energy. In the method of atoms in molecules, a molecule is regarded as an assembly of free atoms plus interaction between them. Then the experimental term values are used as the solution to the former part and the interaction between atoms is treated as a perturbation using the usual orbital approximation.

Moffitt and Scanlan applied this method to C_2H_4 and obtained $E_V = 7.3$ eV (observed 7.6 eV), $E_T = 5.5$ eV (obs. 4.6 eV), and the $V - T$ separation 1.8 eV (obs. 3.0 eV) (Moffitt and Scanlan, 1953). These are in much better agreement with experiment than results of any approach quoted in the previous section.

The method of atoms in molecules was further developed and improved by Hurley (1955, 1956, 1958), Arai (1957, 1960), and others. The method is unfortunately still rather complicated and it is difficult to apply it to larger molecules than say C_6H_6.

14. Use of Different Orbital Exponents for C, C^+, and C^-: a VB Calculation

In the previous section, it was pointed out that the failure of the conventional calculation is due to its inability to make a correct estimate of $I - A$ or $E_V - E_T(R = \infty)$.

There remains one question: Why does the usual calculation give too large an energy separation between two ions—positive and negative—and a pair of two neutral atoms? It is not very difficult to answer this question. The reason is that the same atomic orbital is used to describe a positive or negative ion as well as a neutral atom. As the atomic orbitals usually employed in a calculation are designed so as to give the best description of a neutral atom in its ground state, the consequence is that positive and negative ions are treated by less accurate approximations than is a pair of neutral atoms.

This point may be met at least partly by using different orbital exponents for the ions from the one used for the neutral atom. In negative ions, the charge clouds must be more spread out than those of the neutral atoms owing to the larger interelectronic repulsion. We should, therefore, use a smaller orbital exponent. In the positive ions, on the contrary, the charge clouds must contract due to a decrease in the interelectronic repulsion, and we should use a larger orbital exponent.

We remember, however, that the different orbital exponents depending on the states were used by Murai in the C_2H_4 problem (1952). As we have seen, his results are not much better than the usual treatment. One point may further be improved. The orbital exponents in $2s$ and $2p$ AO's should probably be changed as well according to the ionicity of the atom. If we do this, it means that we abandon the $\sigma - \pi$ separation approximation. The Σ part is no longer common to the N, V, and T states.

Calculations based on the above idea were carried out by Ohno and Itoh (1955, 1958). These calculations are based on the valence bond method but, as we shall see soon, there is a very close relation between the VB and MO methods in this case. The basic AO's are the Slater AO's and the orbital exponents (common to $2s$, $2p\sigma$, and $2p\pi$) are chosen according to the Slater rules:

$$\begin{aligned} 2\delta^{+} &= 3.60 \qquad \text{for C}^{+}, \\ 2\delta\ &= 3.25 \qquad \text{for C}, \\ 2\delta^{-} &= 2.90 \qquad \text{for C}^{-}. \end{aligned} \tag{14.1}$$

Using these values, we obtain $I - A$ of 12.3 eV which seems to be a fairly good estimate. (Remember that $\delta^{+} = \delta = \delta^{-} = 1.625$ gives 17.2 eV and the semiempirical value is 11.1. eV.)

The four valence bond structures shown in Fig. 5 are considered in the calculations. (I) and (IV) are homopolar singlet and triplet structures, respectively, and (II) and (III) are polar singlet structures.

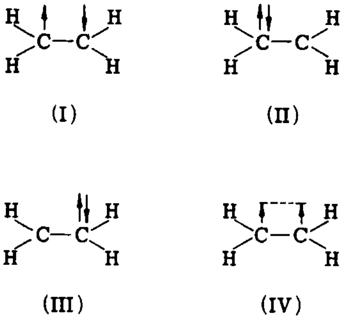

Fig. 5. The valence bond structures of the ethylene molecule.

In order to make the calculation manageable, three assumptions are made:

Assumption 1. All σ bonds are pure electron pair bonds and the σ-bonding orbitals of the carbon atoms are the sp^2 hybridized orbitals.

Assumption 2. The 1*s* electrons of both carbon atoms are shrunk into the respective nuclei.

Assumption 3. The four attached hydrogens are neglected except insofar as they determine the carbon atom valence states.

With these assumptions, the wave functions representing the four structures can be written down:

$$\begin{aligned}\Phi_{\mathrm{I}} = \frac{1}{\sqrt{8!}} \sum_P (-1)^P P \pi_a(1)\pi_b(2) \frac{\alpha_1\beta_2 - \beta_1\alpha_2}{\sqrt{2}}\, \sigma 1_a(3)\sigma 1_b(4) \frac{\alpha_3\beta_4 - \beta_3\alpha_4}{\sqrt{2}} \\ \times \sigma 2_a(5) \frac{\alpha_5\beta_9 - \beta_5\alpha_9}{\sqrt{2}}\, \sigma 3_a(6) \frac{\alpha_6\beta_{10} - \beta_6\alpha_{10}}{\sqrt{2}} \\ \times \sigma 2_b(7) \frac{\alpha_7\beta_{11} - \beta_7\alpha_{11}}{\sqrt{2}}\, \sigma 3_b(8) \frac{\alpha_8\beta_{12} - \beta_8\alpha_{12}}{\sqrt{2}},\end{aligned} \tag{14.2}$$

$$\begin{aligned}\Phi_{\mathrm{II}} = \frac{1}{\sqrt{8!}} \sum_P (-1)^P P \pi_a^-(1)\alpha_1\pi_a^-(2)\beta_2\sigma 1_a^-(3)\sigma 1_b^+(4) \frac{\alpha_3\beta_4 - \beta_3\alpha_4}{\sqrt{2}} \\ \times \sigma 2_a^-(5) \frac{\alpha_5\beta_9 - \beta_5\alpha_9}{\sqrt{2}}\, \sigma 3_a^-(6) \frac{\alpha_6\beta_{10} - \beta_6\alpha_{10}}{\sqrt{2}} \\ \times \sigma 2_b^+(7) \frac{\alpha_7\beta_{11} - \beta_7\alpha_{11}}{\sqrt{2}}\, \sigma 3_b^+(8) \frac{\alpha_8\beta_{12} - \beta_8\alpha_{12}}{\sqrt{2}},\end{aligned} \tag{14.3}$$

$$\begin{aligned}\Phi_{\mathrm{III}} = \frac{1}{\sqrt{8!}} \sum_P (-1)^P P \pi_b^-(1)\alpha_1\pi_b^-(2)\beta_2\sigma 1_a^+(3)\sigma 1_b^-(4) \frac{\alpha_3\beta_4 - \beta_3\alpha_4}{\sqrt{2}} \\ \times \sigma 2_a^+(5) \frac{\alpha_5\beta_9 - \beta_5\alpha_9}{\sqrt{2}}\, \sigma 3_a^+(6) \frac{\alpha_6\beta_{10} - \beta_6\alpha_{10}}{\sqrt{2}} \\ \times \sigma 2_b^-(7) \frac{\alpha_7\beta_{11} - \beta_7\alpha_{11}}{\sqrt{2}}\, \sigma 3_b^-(8) \frac{\alpha_8\beta_{12} - \beta_8\alpha_{12}}{\sqrt{2}},\end{aligned} \tag{14.4}$$

$$\begin{aligned}\Phi_{\mathrm{IV}} = \frac{1}{\sqrt{8!}} \sum_P (-1)^P P \pi_a(1)\pi_b(2) \frac{\alpha_1\beta_2 + \beta_1\alpha_2}{\sqrt{2}}\, \sigma 1_a(3)\sigma 1_b(4) \frac{\alpha_3\beta_4 - \beta_3\alpha_4}{\sqrt{2}} \\ \times \sigma 2_a(5) \frac{\alpha_5\beta_9 - \beta_5\alpha_9}{\sqrt{2}}\, \sigma 3_a(6) \frac{\alpha_6\beta_{10} - \beta_6\alpha_{10}}{\sqrt{2}} \\ \times \sigma 2_b(7) \frac{\alpha_7\beta_{11} - \beta_7\alpha_{11}}{\sqrt{2}}\, \sigma 3_b(8) \frac{\alpha_8\beta_{12} - \beta_8\alpha_{12}}{\sqrt{2}},\end{aligned} \tag{14.5}$$

where $\sigma 1_a$, $\sigma 2_a$, $\sigma 3_a$ are the sp^2 hybridized orbitals of the carbon atom a which are pointing out towards the other carbon atom b and the hydrogen atoms. In (14.2) ~ (14.5), spins of the ghostlike electrons 9–12 are used in order to express the valence state wave function explicitly. In constructing the energy matrix, we have to carry out the summation over these spins as well.

The state functions with correct spin and space symmetries are constructed from these structural functions:

$$\begin{aligned} &\Phi_N(^1A_g) \propto \Phi_{\mathrm{I}} + C(\Phi_{\mathrm{II}} + \Phi_{\mathrm{III}}), \\ &\Phi_V(^1B_{1u}) \propto \Phi_{\mathrm{II}} - \Phi_{\mathrm{III}}, \\ &\Phi_T(^3B_{1u}) = \Phi_{\mathrm{IV}}, \\ &\Phi_Z(^1A_g) \propto \Phi_{\mathrm{I}} + C'(\Phi_{\mathrm{II}} + \Phi_{\mathrm{III}}). \end{aligned} \tag{14.6}$$

Being properly normalized, they are identical with (8.6) if we disregard the differences between $\pi_a{}^+$, π_a, and $\pi_a{}^-$ and σ^+, σ, and σ^-.

In order to simplify the calculation of the energy matrix elements among these four structural functions, it is convenient and almost necessary to introduce further approximations about the overlap integrals. There are five different overlap integrals involved:

$$\begin{aligned} (\pi_a \mid \pi_b) &= 0.267, \\ (\sigma 1_a \mid \sigma 1_b) &= 0.765, \\ (\sigma 1_a \mid \sigma 2_b) &= 0.135, \\ (\sigma 2_a \mid \sigma 2_b) &= 0.128, \\ (\sigma 2_a \mid \sigma 3_b) &= -0.136. \end{aligned} \tag{14.7}$$

Two kinds of calculations were carried out. In the first kind, the overlap integral between the two π orbitals only is taken into account and all the others are neglected. In the second kind, $(\pi_a \mid \pi_a)$ and $(\sigma 1_a \mid \sigma 1_b)$ are retained in the calculations but the others are not. As $(\sigma 1_a \mid \sigma 1_b)$ is the largest among the σ overlap integrals, if the results of these two calculations are found to be fairly close, we may perhaps expect that the results are not sensitive to the values of other overlap integrals.

Each of the energy matrix elements can be separated into three parts:

$$H_{ij} = H_{ij}(\pi) + H_{ij}(\pi - \sigma) + H_{ij}(\sigma), \qquad i, j = \mathrm{I}, \mathrm{II}, \mathrm{III}, \text{ and } \mathrm{IV}. \tag{14.8}$$

We can reduce the part $H_{ij}(\sigma)$ to the form of a constant times the overlap integral between Φ_i and Φ_j, namely,

$$H_{ij}(\sigma) = E(\sigma) S_{ij}, \tag{14.9}$$

by introducing the following approximations concerning integrals which involve AO's σ^+ and σ^-:

$$(\sigma 1_a^- \,|\, f \,|\, \sigma 1_a^-) + (\sigma 1_b^+ \,|\, f \,|\, \sigma 1_b^+) = 2(\sigma 1_a \,|\, f \,|\, \sigma 1_a),$$

$$(\sigma 1_a^- \sigma 1_a^- \,|\, \sigma 1_b^+ \sigma 1_b^+) = (\sigma 1_a \sigma 1_a \,|\, \sigma 1_b \sigma 1_b), \quad (14.10)$$

$$(\sigma 1_a \sigma 1_a^- \,|\, \sigma 2_a \sigma 2_a^-) + (\sigma 1_b \sigma 1_b^+ \,|\, \sigma 2_b \sigma 2_b^+) = 2(\sigma 1_a \sigma 1_a \,|\, \sigma 2_a \sigma 2_a),$$

and so on, where f is any one-electron operator. We also approximate some special intraatomic overlap integrals, for example,

$$T_\sigma^{+-} = (\sigma 1_a^+ \,|\, \sigma 1_a^-),$$

as unity. These approximations mean essentially that we replace the terms involving orbitals for positive and negative ions by the sum of the corresponding neutral ones.

If we do this, then we can leave out the $H_{ij}(\sigma)$ part completely in the calculation of π electron levels. Remember

$$|H_{ij} - S_{ij}E| = |H_{ij}(\pi) + H_{ij}(\pi - \sigma) - S_{ij}\{E - E(\sigma)\}|. \quad (14.11)$$

The result (14.11) conforms to the usual $\sigma - \pi$ separation approximation and we have restored this nice separation at this stage.

Many new heteropolar integrals appear in the calculations. Among them, one-center integrals are large and are calculated rigorously. Others are approximated as follows:

(*i*) Coulomb integrals are calculated by the geometric mean approximation, e.g.,

$$(\pi_a^- \pi_a^- \,|\, \sigma 1_b^+ \sigma 1_b^+) = [(\pi_a^- \pi_a^- \,|\, \sigma 1_b^- \sigma 1_b^-)(\pi_a^+ \pi_a^+ \,|\, \sigma 1_b^+ \sigma 1_b^+)]^{1/2}; \quad (14.12)$$

(*ii*) hybrid and exchange integrals are evaluated by the Mulligan approximation (1951), e.g.,

$$(\pi_a^- \pi_b^- \,|\, \sigma 1_b^- \sigma 1_b^+) = T_\sigma^{+-} \frac{S^{--}}{S} (\pi_a \pi_b \,|\, \sigma 1_b \sigma 1_b); \quad (14.13)$$

(*iii*) $\sigma - \pi$ exchange integrals are small and so are approximated by the corresponding homopolar ones.

The results of the calculations are shown and compared with experimental data and other calculations in Table V.

The agreement with experiment is quite satisfactory. However, it is rather fortuitous. It seems that the errors from the many simplifying

TABLE V

THE π ELECTRON STATES OF C_2H_4

State	I[a]	II[b]	III[c]	IV[d]	Obs.	Moffitt	Murai	Sp–Lö	Pa–Cr
Z	13.6	13.1	14.9	14.7	—	—	15.8	16.8	15.0
V	7.7	7.5	8.6	8.5	7.6	7.3	11.2	12.3	11.5
T	5.4	5.2	5.8	5.8	4.6	5.5	4.6	4.4	3.1
N	0	0	0	0	0	0	0	0	0
$V-T$	2.3	2.3	2.8	2.7	3.0	1.8	6.6	7.9	8.4

[a] I: the σ—π exchange is neglected; $(\sigma 1_a | \sigma 1_b) = 0$.
[b] II: the σ—π exchange is neglected; $(\sigma 1_a | \sigma 1_b) \neq 0$.
[c] III: the σ—π exchange is included; $(\sigma 1_a | \sigma 1_b) = 0$.
[d] IV: the σ—π exchange is included; $(\sigma 1_a | \sigma 1_b) \neq 0$.

approximations tend to cancel out. For example, one of the biggest errors comes from the approximation (14.10):

$$(\sigma_a{}^+ \,|\, f \,|\, \sigma_a{}^+) + (\sigma_a{}^- \,|\, f \,|\, \sigma_a{}^-) = 2(\sigma_a \,|\, f \,|\, \sigma_a),$$

where

$$f = -\frac{1}{2}\Delta - \frac{4}{r_a} - \frac{4}{r_b}. \tag{14.14}$$

The integral due to the second term in f, namely the one-center nuclear attraction, is linear in the orbital exponent, and, as the Slater rules give $2\delta = \delta^+ + \delta^-$, the above equality is exact as far as this term is concerned. However, the kinetic energy integral is proportional to δ^2. The estimate of the energy of the ion pair by using (14.10) is too low by about 1.9 eV due to this kinetic energy part. On the other hand, the present estimate of $I - A$ is too high by 1.2 eV ($= 12.3 - 11.1$). These two errors cancel each other to a considerable extent.

The results of calculations I and II, and III and IV are very close so that we may say the effect of σ overlapping on the π electron states is rather small. We also observe that the $\sigma - \pi$ exchange effect is not negligible.

A subtle point in this type of calculations is the choice of the orbital exponent. The Slater rules may not be used in this context. Altmann and Cohan (1954) have calculated the energy of the hydrogen molecule using the ionic wave function:

$$\Psi \propto a(1)a(2) + b(1)b(2),$$

where a and b are the $1s$ orbitals of the hydrogen atoms a and b, respectively. Varying the orbital exponent, they reached the energy minimum at $\delta = 1.08$ rather than the Slater value $\delta = 0.7$. The evidence is strong enough to throw some doubts upon, but not completely to deny, the desirability of using AO's determined by the Slater rules in molecular calculations.

15. Calculation by Huzinaga

Extensive ASMO LCAO calculations on C_2H_4 have been carried out by Huzinaga (1962).

The basic assumptions involved in his calculations are as follows:

(*i*) The nucleus and the $1s$ electrons of each carbon atom are taken together as a point charge of $4e$.
(*ii*) The σ wave function consists of six sp^2 hybrids of the carbon atoms and four $1s$ orbitals of the four attached hydrogen atoms. A possible deformation of the σ wave function due to bonding is neglected.
(*iii*) The $\sigma - \pi$ exchange interaction is neglected.

The main point of his calculations lies in the fact that he uses different orbital exponents for bonding and antibonding MO's. The exponents depend on the states too. They are determined so as to minimize the energies of the states N, T, and V, for a fixed δ_σ. The whole calculations are repeated three times for three values of δ_σ: 1.4, 1.59, and 1.8.

Slater-type AO's are the basic orbitals. One- and two-center integrals are evaluated rigorously while three-center integrals are estimated by use of the Mulliken approximation:

$$(\chi_a\chi_a \mid \chi_b\chi_c) = \tfrac{1}{2}S_{bc}[(\chi_a\chi_a \mid \chi_b\chi_b) + (\chi_a\chi_a \mid \chi_c\chi_c)]. \tag{15.1}$$

The results of the calculations are summarized in Table VI, in which δ_b and δ_a mean orbital exponents for the bonding and antibonding MO's, respectively, for each state. We can see that, among the three values of δ_σ, $\delta_\sigma = 1.59$ gives the best $V - N$, $T - N$ separations.

Huzinaga has also carried out the calculation neglecting the attached hydrogen atoms to see their effects. For $\delta_\sigma = 1.59$, the energies of V and T states turn out to be 6.32 and 4.31, respectively, with that approximation. Therefore the effect of attached atoms is not negligible at least on the $V - N$ separation. If we compare these results with those of the Parr–Crawford calculation ($\delta_b = \delta_a = 1.59$), the effect of adopting separate values for δ_b and δ_a is quite obvious, especially on the $V - T$ separation.

TABLE VI

ENERGY LEVELS AND IONIZATION POTENTIAL OF C_2H_4 (IN eV)

δ_σ	1.4			1.59			1.8			Obs.
	Energy	δ_b	δ_a	Energy	δ_b	δ_a	Energy	δ_b	δ_a	
V	10.06	1.6	0.4	7.28	1.6	0.4	5.45	1.4	0.4	7.6
T	3.82	1.6	1.6	4.45	1.4	1.2	4.17	1.4	1.0	4.6
N	0.0	1.6	1.6	0.0	1.4	1.4	0.0	1.2	1.2	0.0
$V-T$	6.24	—		2.83	—		1.28	—		3.0
I.P.	11.54	—		8.52	—		6.51	—		10.52

The calculated value of the ionization potential does not agree very well with the experimental value, which is possibly due to approximation (*i*) mentioned above.

A remarkable and somewhat disturbing result is that the optimum δ_a value for the V state is as small as 0.4. Whether this has a genuine meaning or is simply an outcome of some inadequacies in the present form of the π electron wave functions remains to be seen.

There are more investigations on the C_2H_4 molecule. Barriol and Regnier (1958) have used wave functions which contain electron coordinates as a factor. A simplest example of the ground state wave function is given by

$$\Phi' = C(z_1 + z_2)\Phi_1(^1A_g), \tag{15.2}$$

where C is a normalization constant. They have obtained good $N-V$ and $V-T$ separations using such wave functions. Kolos (1957) has employed a wave function which contains the distance r_{12} between two electrons explicitly. An interesting approach has been used by Dewar and Hojvat (1961), who imposed the condition that two π electrons should not be on one side (up or down) of the molecular plane simultaneously. The method is called the split p orbital method and has been critically reviewed by Coulson and Sharma (1963) recently. We shall not go into details of these approaches and the reader is referred to the original papers.

16. Self-Consistent LCAO Method

The whole idea of this method is based on the well-known Hartree–Fock method. Thus a total wave function of an electron system is approximated by a single Slater determinant:

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\xi_1) & \varphi_2(\xi_1) & \cdots & \varphi_N(\xi_1) \\ \varphi_1(\xi_2) & \varphi_2(\xi_2) & \cdots & \varphi_N(\xi_2) \\ \vdots & \vdots & & \vdots \\ \varphi_1(\xi_N) & \varphi_2(\xi_N) & \cdots & \varphi_N(\xi_N) \end{vmatrix} \tag{16.1}$$

where φ_i is a spin orbital,

$$\varphi_i(\xi) = \psi_i(\mathbf{r})\begin{cases}\alpha(\sigma) \\ \beta(\sigma)\end{cases}, \tag{16.2}$$

and ξ stands for the spacial coordinate $\mathbf{r}$ and the spin coordinate σ.

When the number of electrons is even, the ground state of the system can often be approximated reasonably well by a closed shell configuration. Each of the occupied space orbitals $\psi_1, \psi_2, \ldots \psi_n$ $(2n = N)$ is occupied by two electrons with spins α and β. Then the lowest energy of the system is obtained when the orbitals satisfy the following equations,

$$\mathscr{F}(\mathbf{r})\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}), \qquad i = 1, 2, \ldots n, \tag{16.3}$$

where the Hartree–Fock *single-body* operator $\mathscr{F}$ has the following form:

$$\mathscr{F} = -\tfrac{1}{2}\Delta + \sum_a \frac{Z_a}{|\mathbf{r} - \mathbf{R}_a|} + \sum_{j=1}^{n} 2\int \frac{|\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}\, dv' - \mathscr{A}. \tag{16.4}$$

The operator $\mathscr{A}$ represents the exchange interaction and is defined as

$$\mathscr{A}\psi_i(\mathbf{r}) = \sum_{j=1}^{n} \int \frac{\psi_j(\mathbf{r}')^*\psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, dv'\psi_j(\mathbf{r}). \tag{16.5}$$

It should be remembered that the Hartree–Fock operator $\mathscr{F}$ is common to all the space orbitals. The resulting space orbitals are orthogonal to each other.

The total energy E is expressed as

$$\begin{aligned} E = \sum_i 2\varepsilon_i - \sum_i \iint \frac{|\psi_i(\mathbf{r})|^2\,|\psi_i(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}\, dv\, dv' \\ - 4\sum_{i<j} \iint \frac{|\psi_i(\mathbf{r})|^2|\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}\, dv\, dv' \\ + 2\sum_{i<j} \iint \frac{\psi_i(\mathbf{r})^*\psi_j(\mathbf{r})\psi_j(\mathbf{r}')^*\psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, dv\, dv'. \end{aligned} \tag{16.6}$$

The ionization energy (I.P.) of removing an electron from a space orbital ψ_i is

$$(\text{I.P.})_i = -\varepsilon_i, \tag{16.7}$$

if we neglect changes of the orbitals due to ionization. According to Koopmans' theorem, this will be a good approximation to the true ionization potential.

An unoccupied orbital ψ_p is defined by the following equation:

$$\mathscr{F}(\mathbf{r})\psi_p(\mathbf{r}) = \varepsilon_p\psi_p(\mathbf{r}), \qquad p = n+1, n+2, \ldots . \tag{16.8}$$

When excitation of the system can be interpreted as a transition of an electron from an occupied orbital ψ_i to an unoccupied one ψ_p, then excitation energies to the singlet and triplet states are given by

$$\begin{aligned} E^s_{\text{exc}} &= \varepsilon_p - \varepsilon_i - (ii \mid pp) + 2(ip \mid ip), \\ E^t_{\text{exc}} &= \varepsilon_p - \varepsilon_i - (ii \mid pp), \end{aligned} \tag{16.9}$$

respectively.

So much for the general Hartree–Fock self-consistent field method,[6] we now turn to its limited form, the self-consistent LCAO method.

As its name shows, a fundamental approximation in the method is the LCAO approximation:

$$\psi_i = \sum_{a=1}^{h} c_{ai}\chi_a \qquad (i = 1, \ldots n). \tag{16.10}$$

The problem is to find out the best set of coefficients within the limit of a single-determinant wave function. The analysis goes quite parallel to the general case and the equation corresponding to (16.3) is obtained in a matrix form:

$$\mathscr{F}\mathbf{c}_i = \varepsilon_i\mathbf{S}\mathbf{c}_i, \tag{16.11}$$

where $\mathbf{c}_i$ is a column vector,

$$\mathbf{c}_i = \begin{pmatrix} c_{1i} \\ c_{2i} \\ \vdots \\ c_{hi} \end{pmatrix}, \tag{16.12}$$

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[6] For derivations of formulas (16.3)–(16.9) and detailed discussion of the method, the reader is referred to, for example, Kotani *et al.* (1961) and Daudel *et al.* (1959, Chapter XIX, Section 11).

S is an overlap matrix,

$$\mathbf{S} = \begin{pmatrix} (\chi_1 | \chi_1) & (\chi_1 | \chi_2) & \cdots & (\chi_1 | \chi_h) \\ (\chi_2 | \chi_1) & (\chi_2 | \chi_2) & \cdots & (\chi_2 | \chi_h) \\ \vdots & \vdots & & \vdots \\ (\chi_h | \chi_1) & (\chi_h | \chi_2) & \cdots & (\chi_h | \chi_h) \end{pmatrix}, \tag{16.13}$$

and the matrix elements of $\mathscr{F}$ are given by

$$(\mathscr{F})_{bc} = (\chi_b | -\tfrac{1}{2}\Delta + \sum_a \frac{Z_a}{|\mathbf{r} - \mathbf{R}_a|} | \chi_c) + \sum_{i=1}^{n} \sum_{d,e=1}^{h} c_{ei}^* c_{di} [2(ed | bc) - (ec | bd)]. \tag{16.14}$$

The equation was obtained by Roothaan (1951b) and Hall (1951) independently. As the Hartree–Fock operator involves the unknown $\mathbf{c}$, trial and error is a usual technique to solve (16.11). Namely, one assumes certain values for $\mathbf{c}_i$'s, solves the equation, and compares the results with the assumed values. If they disagree, one puts the new values into (16.14) and repeats the procedure until self-consistency is attained.

The self-consistent LCAO method for an open shell is more complicated and we will not go into this. The reader is referred to the original references (Pople and Nesbet, 1954; Nesbet, 1955; Lefebvre, 1957, 1959; Roothaan, 1960; Huzinaga, 1960, 1961; Roothaan and Bagus, 1963; Birss and Fraga, 1963; for a review, see Berthier, 1964).

This procedure (SC LCAO) is not necessary for the π MO's of such molecules as C_2H_4, C_2H_2, C_6H_6 where the molecular symmetries alone determine the coefficients in (16.10) uniquely. It is also unnecessary if we are prepared to do a full configuration interaction calculation. In that case whether the basic MO's are good or not does not matter. On the other hand, the self-consistent LCAO method is quite useful for molecules which do not have a very high symmetry and are big enough to discourage full configuration interaction. At present, all molecules except a few special ones such as mentioned above fall in this category. The method is also useful if we want to take into account σ electrons explicitly. Such calculations will be mentioned in the next section.

17. Self-Consistent LCAO Calculations on C_2H_4

The first application of the self-consistent LCAO method to C_2H_4 was performed by Berthod (1959). Her basic orbitals were Slater AO's. All

16 electrons were explicitly considered. Many-center integrals were approximated. The main aim of the calculation was to find the LCAO form of the occupied σ orbitals and their orbital energies, which are shown in Table VII.

TABLE VII

THE FORM OF MO'S AND ORBITAL ENERGIES OF C_2H_4[a]

Symmetry	LCAO form	Orbital energy (eV)
$1a_g$	$0.707(1s_a + 1s_b)$	-310.4
$1b_{1u}$	$0.707(1s_a - 1s_b)$	-310.2
$2a_g$	$0.052(h_a + h_b + h_c + h_d) + 0.494(2s_a + 2s_b) + 0.088(2pz_a + 2pz_b)$	-24.5
$2b_{1u}$	$0.223(h_a + h_b - h_c - h_d) + 0.546(2s_a - 2s_b) - 0.047(2pz_a - 2pz_b)$	-20.7
$1b_{2u}$	$0.189(h_a - h_b + h_c - h_d) - 0.463(2py_a + 2py_b)$	-20.5
$1b_{3g}$	$0.219(h_a - h_b - h_c + h_d) - 0.600(2py_a - 2py_b)$	-18.9
$3a_g$	$0.333(h_a + h_b + h_c + h_d) - 0.208(2s_a + 2s_b) - 0.413(2pz_a + 2pz_b)$	-15.1
$1b_{3u}$	$0.629(2px_a + 2px_b)$	-8.74

[a] In this table, h_a stands for $1s_{Ha}$. The function $2s_a$ means the $2s_a$ function orthogonalized to $1s_a$.

Only the excitation energy $N \rightarrow V$ was calculated by using formula (16.9), the value being 11.65 eV. The agreement with the experimental value of 7.6 eV was only fair.

The most recent and most extensive self-consistent LCAO calculation on C_2H_4 is the one carried out by Moskowitz and Harrison (1965). The molecule was again treated as a full 16-electron problem.

As was mentioned in Section 10, the basis set was a set of Gaussian orbitals. Ten basis sets of varying size were tried. The biggest set by which excitation energies were calculated consisted of five Gaussians (orbital exponents δ being 0.32, 1.6, 8.0, 40.0, 200.0) for carbon s-type orbitals,[7] three each ($\delta = 0.1852, 0.9259, 4.63$) for carbon py-, pz-, and px-type orbitals, and two ($\delta = 0.27, 1.8$) for hydrogen s-type orbitals. These GO's give -37.45032 and -0.48581 au as the energy of the ground states of the carbon and hydrogen atoms, respectively. The experimental values

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[7] There is no need for the distinction between $1s$ and $2s$ when we use Gaussians as basic functions.

are -37.857 and -0.5 au, respectively. The total number of the basic GO's was thus 36. Many-center integrals were evaluated rigorously.

The resulting orbital energies are collected and compared with Berthod's value in Table VIII. The agreement between two sets of calculated values is fairly good except that the order of orbital energies of $3a_g$ and $1b_{3g}$ is reversed.

TABLE VIII

ORBITAL ENERGIES OF C_2H_4

Symmetry	Orbital energy (eV)	
	Moskowitz–Harrison	Berthod
$1a_g$	−305.1	−310.4
$1b_{1u}$	−305.1	−310.2
$2a_g$	−28.5	−24.5
$2b_{1u}$	−21.8	−20.7
$1b_{2u}$	−17.9	−20.5
$3a_g$	−15.9	−15.1
$1b_{3g}$	−14.0	−18.9
$1b_{3u}$	−10.4	−8.74
$1b_{2g}$	4.18	—

Calculated excitation energies are listed in Table IX which also shows results and characteristic approximations of various nonempirical approaches explained so far.[8]

Moskowitz and Harrison's calculations gave only fair agreement with experiment, the *V* state being too high. On the other hand the calculated ionization potentials showed excellent agreement with experiment. These authors are planning to extend this work to invoke large configuration interactions, the result of which will be of great importance in the π electron theory.[9]

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[8] Moffitt and Scanlan's approach may be regarded as semiempirical, since empirical atomic term values were used in the calculation.

[9] Of interest in this connection is also the recent paper by Hart and Robin (1965).

TABLE IX

CALCULATIONS ON THE ETHYLENE MOLECULE[a]

Author	Parr–Crawford (1948)	Murai (1952)	Sponer–Löwdin (1954)	Ohno (*i*) (1958)	Itoh (*ii*)	Huzinaga (*i*) (1962)	Huzinaga (*ii*)	Huzinaga (*iii*)	Moskowitz–Harrison (1965)	Obs.	Moffitt–Scanlan (1953)
V	11.5	11.2	12.3	7.5	8.5	12.7	6.3	7.3	10.4	7.6	7.3
T	3.1	4.6	4.4	5.2	5.8	4.4	4.3	4.5	4.3	4.6	5.5
N	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$V-T$	8.4	6.6	7.9	2.3	2.7	8.4	2.0	2.8	6.1	3.0	1.8
I.P.	—	8.8	—	—	—	8.0	7.4	8.5	10.35	10.52	—
Method	MO	MO	MO	VB		MO			MO	—	Atoms in mols.
Basic AO	Slater	Slater	SCF	Slater		Slater			Gaussian	—	—
Core	Mayer–Sklar app.	Direct calc.	Mayer–Sklar for C, direct for H	Direct calc.		Direct calc.			Self-consistent LCAO	—	—
σ–π exchange	X	X	X	X	O	X			O	—	—
δ_σ	1.59	1.60	—	$\delta_\sigma = \delta_\pi$		1.59			—	—	—
							δ_b	δ_a			
δ_π	1.59	1.60 (N, T) 1.20 (V)	—	1.625 (C) 1.80 (C^+) 1.45 (C^-)		1.59	1.4 1.4 1.6	1.4 (N) 1.2 (T) 0.4 (V)	—	— —	— —
Hydrogens	X	X	O	X		X	X	O	O	—	X

---

[a] The sign O means the effect is included. The sign X means the effect is not included.

III. Semiempirical Theory of Pariser, Parr, and Pople

18. Need for a Semiempirical Theory

The orthodox procedure explained in Section II involves quite a lot of labor. Setting up and solving secular equations of high dimensions is difficult in itself, but the most laborious part of the whole calculation is undoubtedly the evaluation of numerous molecular integrals. Even with modern electronic computers, there is great difficulty in dealing with molecules bigger than benzene. On the other hand, we have seen that the results of this type of calculation are not necessarily in good agreement with experiment. It seems highly desirable, therefore, to have a simpler method which gives better agreement with experiment. This is almost necessary if our calculations are to be extended to larger molecules.

Introducing some experimentally known quantities into the theory in certain nice ways, Pariser and Parr (1953; Fumi and Parr, 1953; Parr and Pariser, 1955) and Pople (1953) have independently presented such methods. These two very similar methods will be explained in the following sections.[10]

The Pariser–Parr–Pople method may also be regarded as a more advanced theory than the simple molecular orbital method such as the Hückel method. Electron interaction is explicitly taken into account in the Pariser–Parr–Pople theory, while it is taken into account only in an averaged form in the simple molecular orbital theory.

19. Characteristic Approximations

The theoretical framework of the Pariser–Parr–Pople method is quite the same as that of ASMO LCAO CI. There are three fundamental approximations in the method concerning how to treat molecular integrals.

(*i*) The first basic approximation is called the approximation of zero differential overlap. Whenever the expression

$$\pi_a(1)\pi_b(1)\,dv_1 \qquad (a \neq b)$$

appears in molecular integrals (except core resonance integrals β_{ab}^{core} which will be explained in due course), the integrals are put equal to zero.

This means that all overlap integrals are zero, i.e.,

$$S_{ab} = (\pi_a \mid \pi_b) = \delta_{ab}, \tag{19.1}$$

---

[10] The difference is that Pariser and Parr proposed to estimate one-center Coulomb integrals in a semiempirical way while Pople did not. Pariser and Parr's emphasis was on configuration interaction and Pople's on the self-consistent LCAO method.

and all electron interaction integrals vanish except for those of Coulomb type:

$$(ab \mid cd) \equiv \int a^*(1)b(1)\frac{1}{r_{12}}\,c^*(2)d(2)\,dv_1\,dv_2$$
$$= (aa \mid cc)\delta_{ab}\delta_{cd}. \tag{19.2}$$

Hybrid $(aa \mid ab)$, exchange $(ab \mid ab)$, and many-center $(ab \mid cd)$ integrals all disappear.

Before we introduce the second characteristic approximation, we have to define the core Coulomb and resonance integrals. The Hamiltonian $\mathscr{H}^\pi$ of the π electron system we are considering may be written as

$$\mathscr{H}^\pi = \sum_i^{(\pi)} f^\pi(i) + \sum_{i<j}^{(\pi)} \frac{1}{r_{ij}}, \tag{19.3}$$

where f^π includes kinetic energy, potential energy due to nuclear attraction, and electron repulsion from the σ charge cloud [cf. (7.2) and (7.3)].

The core Coulomb and resonance integrals are then defined as

$$\alpha_a^{\text{core}} \equiv (\chi_a \mid f^\pi \mid \chi_a) \tag{19.4}$$

and

$$\beta_{ab}^{\text{core}} \equiv (\chi_a \mid f^\pi \mid \chi_b), \tag{19.5}$$

respectively. We shall drop the superscript π from f hereafter.

(*ii*) The second basic approximation is to treat the core resonance integral β_{ab}^{core} as an empirical parameter. Its value is determined to fit a certain property to an experimental datum, usually the lowest singlet-singlet transition energy. If the atoms a and b are not neighbors, β_{ab}^{core} is taken to be zero.

(*iii*) The last basic approximation is concerned with one-center Coulomb integrals:

$$(aa \mid aa) = I_a - A_a, \tag{19.6}$$

where I_a and A_a are the valence state ionization potential and the electron affinity, respectively, of the orbital π of atom a. As we have seen in Section 13, this assumption takes care of the relative energies of polar and homopolar states at $R = \infty$.

The other kinds of molecular integrals are evaluated more or less conventionally.

(*a*) Core Coulomb integrals, α_a^{core}. The operator f may be regarded as having the following form:

$$f = -\tfrac{1}{2}\Delta + v_a + \sum_{b \neq a} v_b + \sum_c u_c, \tag{19.7}$$

where the potential v is that of a positive ion which is formed from the atom by taking π electron(s) away, and the potential u is due to a neutral attached atom. It should be clear that the summation over b runs over the atoms which contribute π electrons and the summation over c runs over the atoms which have no π electron (e.g., hydrogen atoms in C_2H_4).

We use the Goeppert-Mayer–Sklar approximations:

$$(a \mid -\tfrac{1}{2}\Delta + v_a \mid a) = -I_a, \tag{19.8}$$

where W_{2p} is replaced by the valence state ionization potential, then

$$\alpha_a^{\text{core}} = -I_a + \sum_{b(\neq a)} (a|\, v_b \,|a) + \sum_c (a|\, u_c \,|a). \tag{19.9}$$

If the atoms contribute one π electron each to the system and if we neglect the σ–π exchange interaction, we obtain from (9.8),

$$(a|\, v_b \,|a) = (a|\, u_b \,|a) - (aa \mid bb), \tag{19.10}$$

where u_b is the potential due to the presence of the neutral atom. In that case, α_a^{core} becomes

$$\alpha_a^{\text{core}} = -I_a + \sum_{b(\neq a)} \{(a|\, u_b \,|a) - (aa|\, bb)\} + \sum_c (a|\, u_c \,|a). \tag{19.11}$$

(*b*) Two-center Coulomb integrals. There are several ways of evaluating these integrals.

(*b*1) For $R \geq 2.80$ Å, values calculated with Slater AO's are used. For $R < 2.80$ Å, the formula

$$\begin{aligned}(aa|\, bb) &= \tfrac{1}{2}[(aa \mid aa) + (bb \mid bb)] - \lambda R - \mu R^2 \\ &= \tfrac{1}{2}[I_a - A_a + I_b - A_b] - \lambda R - \mu R^2 \end{aligned} \tag{19.12}$$

is used, where λ and μ are determined by fitting values for $R = 2.80$ Å and $R = 3.70$ Å to the computed values. This is an interpolation which goes (smoothly) into the zero distance value given by $I - A$.

(*b*2) An alternative is to use the so-called uniformly charged sphere approximation (Parr, 1952) for $R \geq 2.80$ Å. In this approximation, the charge cloud of the $2p\pi$ orbital is replaced by two uniformly charged spheres in contact. The diameter d of these charged spheres is given by the formula

$$d = \frac{9.194}{\delta} \text{ Å}, \tag{19.13}$$

where δ is the orbital exponent usually determined by Slater's rules. Equation (19.13) is derived so as to give the one-center Coulomb integral the same value as is calculated by using the $2p\pi$ Slater orbital.

By using this model, we obtain the following formula for $(aa\,|\,bb)$ from classical electrostatic theory:

$$(aa\,|\,bb) = \frac{7.1957}{R_{ab}}\left[\left\{1 + \left(\frac{d_a - d_b}{2R_{ab}}\right)^2\right\}^{-1/2} + \left\{1 + \left(\frac{d_a + d_b}{2R_{ab}}\right)^2\right\}^{-1/2}\right] \text{ eV}, \tag{19.14}$$

where R_{ab} is the distance in angstroms between the nuclei of atoms a and b. The formula holds only when $2R \geq d_a + d_b$. For $R \leq 2.80$ Å, an interpolation formula similar to (19.12) is used.

(*b*3) A third alternative, first proposed by Pople (1953), is very simple:

$$(aa\,|\,bb) = \frac{14.3986}{R_{ab}} \text{ eV}, \tag{19.15}$$

where R is in angstroms.

(*b*4) A fourth alternative, due to Mataga and Nishimoto (1957), is as follows:

$$(aa\,|\,bb) = \frac{14.3986}{R_{ab} + \gamma} \text{ eV}, \tag{19.16}$$

where

$$\gamma = \frac{14.3986}{\frac{1}{2}(I_a - A_a) + \frac{1}{2})I_b - A_b)} \tag{19.17}$$

and R_{ab} is in angstroms. It is often claimed that results of calculations are in good agreement with experiment, if we use (19.16).

(*b*5) We can further modify Eq. (19.16) and obtain

$$(aa\,|\,bb) = \frac{14.3986}{\sqrt{R_{ab}^2 + \gamma^2}} \tag{19.18}$$

where γ is given by (19.17) and R_{ab} is in angstroms.

We can see that (19.14) and (19.18) have a very similar R dependence when R is large.

The results of these estimates in the case of carbon-carbon are illustrated in Fig. 6.

(*c*) Penetration integrals $(a\,|\,u_b\,|\,a)$ which appear in (19.11) are either calculated using Slater AO's, or estimated, or quite often neglected.

(*d*) The valence state ionization potentials and electron affinities which appear in (19.6) and (19.11) are estimated from experimental data as was explained in Section 9.

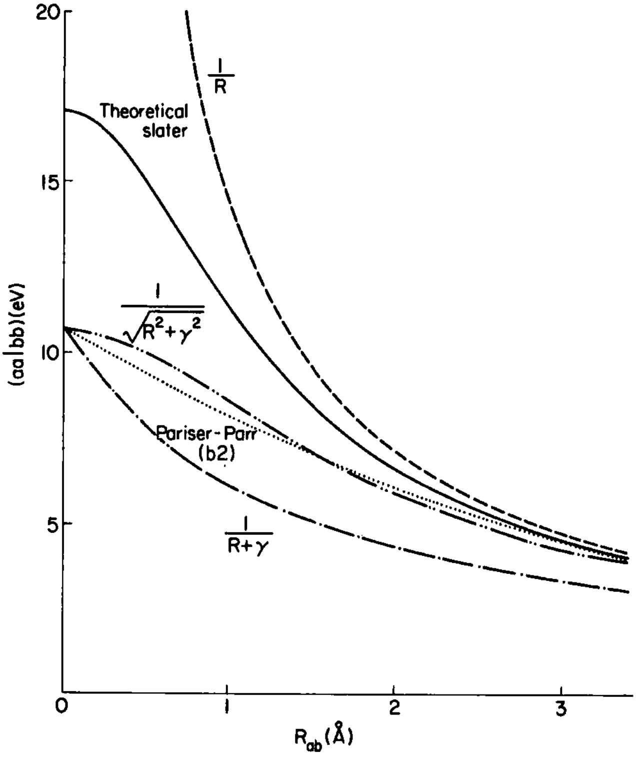

Fig. 6. Coulomb integral as a function of R.

Thus we have formulas for all integrals needed in a calculation.

20. Application to Ethylene

In order to make the merits and limitations of the method clear, it is applied to our pet molecule, C_2H_4.

The π molecular orbitals are [cf. (8.1)]

$$\psi_{\mathrm{I}} = \frac{1}{\sqrt{2}}(\pi_a + \pi_b),$$
$$\psi_{\mathrm{II}} = \frac{1}{\sqrt{2}}(\pi_a - \pi_b). \tag{20.1}$$

The reduction of two-electron integrals defined in terms of the molecular orbitals to integrals defined over AO's is very much simplified by the neglect of differential overlap. The results are as follows [cf. (9.2), (9.3), (9.4), and (9.5)]:

$$
\begin{aligned}
(\mathrm{I\,I}\mid \mathrm{I\,I}) = (\mathrm{II\,II}\mid \mathrm{II\,II}) &= (\mathrm{I\,I}\mid \mathrm{II\,II}) \\
&= \tfrac{1}{2}\{(aa\mid aa) + (aa\mid bb)\} \equiv J, \qquad (20.2)\\
(\mathrm{I\,II}\mid \mathrm{I\,II}) &= \tfrac{1}{2}\{(aa\mid aa) - (aa\mid bb)\} \equiv K. \qquad (20.3)
\end{aligned}
$$

The one-electron parts are

$$
\begin{aligned}
(\mathrm{I}\mid f\mid \mathrm{I}) &= \alpha^{\mathrm{core}} + \beta^{\mathrm{core}},\\
(\mathrm{II}\mid f\mid \mathrm{II}) &= \alpha^{\mathrm{core}} - \beta^{\mathrm{core}}.
\end{aligned}
\qquad (20.4)
$$

From these and (8.6) and (9.1), we obtain

$$
\begin{aligned}
E_1 &= (1\mid \mathscr{H}\mid 1) = 2\alpha^{\mathrm{core}} + 2\beta^{\mathrm{core}} + J, \qquad (20.5)\\
E_V({}^1B_{1u}) &= (2\mid \mathscr{H}\mid 2) = 2\alpha^{\mathrm{core}} + J + K\\
&= 2\alpha^{\mathrm{core}} + (aa\mid aa), \qquad (20.6)\\
E_T({}^3B_{1u}) &= (3\mid \mathscr{H}\mid 3) = 2\alpha^{\mathrm{core}} + J - K\\
&= 2\alpha^{\mathrm{core}} + (aa\mid bb), \qquad (20.7)
\end{aligned}
$$

and

$$
E_4 = (4\mid \mathscr{H}\mid 4) = 2\alpha^{\mathrm{core}} - 2\beta^{\mathrm{core}} + J. \qquad (20.8)
$$

The secular equation which determines the mixing of $\Phi_4 = (\psi_{\mathrm{II}}\bar{\psi}_{\mathrm{II}})$ with $\Phi_1 = (\psi_{\mathrm{I}}\bar{\psi}_{\mathrm{I}})$ is as follows:

$$
\begin{vmatrix}
2\alpha^{\mathrm{core}} + 2\beta^{\mathrm{core}} + J - E & K\\
K & 2\alpha^{\mathrm{core}} - 2\beta^{\mathrm{core}} + J - E
\end{vmatrix} = 0.
$$

Introducing a new energy $E' = E - E_1$, we get

$$
\begin{vmatrix}
-E' & K\\
K & -4\beta^{\mathrm{core}} - E'
\end{vmatrix} = 0, \qquad (20.9)
$$

which gives the roots

$$
E' = -2\beta^{\mathrm{core}} \pm \sqrt{4(\beta^{\mathrm{core}})^2 + K^2}.
$$

The energies of the four states, N, T, V, and Z, are thus obtained:

$$
\begin{aligned}
E_N &= 2\alpha^{\mathrm{core}} + J - \sqrt{4(\beta^{\mathrm{core}})^2 + K^2},\\
E_T &= 2\alpha^{\mathrm{core}} + J - K,\\
E_V &= 2\alpha^{\mathrm{core}} + J + K,\\
E_Z &= 2\alpha^{\mathrm{core}} + J + \sqrt{4(\beta^{\mathrm{core}})^2 + K^2}.
\end{aligned}
\qquad (20.10)
$$

We see that the quantity $2\alpha^{\text{core}}+J$ enters all electronic levels additively and so drops out completely in the computation of excitation energies.

The one-center Coulomb integral is the difference between the ionization potential I_v and the electron affinity A_v of the carbon valence state (tr tr tr π); here tr means the trigonal or sp^2 hybridized orbital,

$$(aa\,|\,aa) = I_v - A_v = 11.54 - 0.46 = 11.08\ \text{eV}.^{11} \tag{20.11}$$

For the two-center integral $(aa\,|\,bb)$, we use either an interpolated value of 7.38 eV [cf. (b1) in Section 19] or a calculated value of 9.26 eV by using the Slater-type $2p\pi$ AO's with the orbital exponent of 1.59 at the internuclear distance of 1.353 Å.

For each case, the parameter β^{core} is determined by fitting the calculated $E_V - E_N$ separation to the observed value of 7.6 eV.

The results thus obtained by Pariser and Parr (1953) are shown in Table X.

TABLE X

PARISER AND PARR'S CALCULATIONS ON C_2H_4

	(*i*)	(*ii*)	Obs.
$(aa\,\|\,bb)$	7.38	9.26	—
β^{core}	−2.92	−3.31	—
Z	—	13.3	—
V	$\underline{7.6}$	$\underline{7.6}$	7.6
T	4.5	5.8	4.6
N	0.0	0.0	0.0
$V-T$	3.1	1.8	3.0

Agreement with experimental results is excellent. The first kind of calculation with an interpolated two-center Coulomb integral seems to give a slightly better result.

Next we discuss the ionization potential and the electron affinity.

The π electron energy of $C_2H_4^+$, C_2H_4, and $C_2H_4^-$ are expressed as [cf. (20.4), (20.5), (20.2), and (20.3)]:

---

[11] This value is due to Parr and Pariser (1953), and is slightly different from the values given in Hinze and Jaffé (1962).

$$E^{\pi}(C_2H_4{}^+) = (\mathrm{I}\,|f|\,\mathrm{I}) = \alpha^{\text{core}} + \beta^{\text{core}}, \tag{20.12}$$

$$E^{\pi}(C_2H_4) \fallingdotseq E_1 = 2\alpha^{\text{core}} + 2\beta^{\text{core}} + J, \tag{20.13}$$

$$\begin{aligned} E^{\pi}(C_2H_4{}^-) &= 2(\mathrm{I}\,|f|\,\mathrm{I}) + (\mathrm{II}\,|f|\,\mathrm{II}) + (\mathrm{I\ I}\,|\,\mathrm{I\ I}) + 2(\mathrm{I\ I}\,|\,\mathrm{IIII}) - (\mathrm{I\ II}\,|\,\mathrm{I\ \ II}) \\ &= 3\alpha^{\text{core}} + \beta^{\text{core}} + 3J - K, \end{aligned} \tag{20.14}$$

where we neglected the small effect of configuration interaction on $E^{\pi}(C_2H_4)$. Then by assuming the σ part is common to C_2H_4 and $C_2H_4{}^+$,

$$I = E(C_2H_4{}^+) - E(C_2H_4) = -\{\alpha^{\text{core}} + \beta^{\text{core}} + J\}. \tag{20.15}$$

If we write down the Hartree–Fock single-body operator (16.4), regarding the π electron interaction with the σ charge cloud as a part of the core Hamiltonian, we obtain

$$\mathscr{F} = f + 2\int \frac{|\psi_{\mathrm{I}}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}\, dv' - \mathscr{A}, \tag{20.16}$$

where $\mathscr{A}$ is the exchange interaction operator with $|\psi_{\mathrm{I}}(\mathbf{r}')|^2$. The orbital energy of the bonding orbital ψ_{I} is thus [cf. (20.2) and (20.4)]:

$$\begin{aligned} \varepsilon_{\mathrm{I}} = (\,\mathrm{I}\,|\,\mathscr{F}\,|\,\mathrm{I}\,) &= (\,\mathrm{I}\,|\,f\,|\,\mathrm{I}\,) + 2(\,\mathrm{II}\,|\,\mathrm{II}\,) - (\,\mathrm{II}\,|\,\mathrm{II}\,) \\ &= \alpha^{\text{core}} + \beta^{\text{core}} + J. \end{aligned} \tag{20.17}$$

Comparing this with (20.15), we see that

$$I = -\varepsilon_{\mathrm{I}}. \tag{20.18}$$

This is nothing but the prediction of Koopmans' theorem.

The electron affinity of the molecule is

$$A = E(C_2H_4) - E(C_2H_4{}^-) = -\alpha^{\text{core}} + \beta^{\text{core}} - 2J + K, \tag{20.19}$$

again by assuming the energy of the σ part is unchanged by adding an electron to the system. We can easily check that

$$\begin{aligned} A = -\varepsilon_{\mathrm{II}} &= -(\mathrm{II}\,|\,\mathscr{F}\,|\,\mathrm{II}\,) \\ &= -\{(\,\mathrm{II}\,|\,f\,|\,\mathrm{II}\,) + 2(\,\mathrm{I\ I}\,|\,\mathrm{II\,II}\,) - (\,\mathrm{I\,II}\,|\,\mathrm{I\,II}\,)\}. \end{aligned} \tag{20.20}$$

This means that electron affinity of a molecule is approximately equal to the orbital energy of the lowest unoccupied orbital with its sign reversed.

Values of various integrals and the calculated ionization energy are collected in Table XI.

TABLE XI

CALCULATED VALUES OF SOME INTEGRALS AND IONIZATION ENERGY OF C_2H_4

	(*i*)	(*ii*)
$(aa\|bb)$	7.38	9.26
β^{core}	−2.92	−3.31
α^{core}	−19.79	−21.67
J	9.11	10.17
K	1.73	0.91
I	13.60	14.81
A	0.38	−1.07

The observed value of the ionization potential of C_2H_4 is 10.62 eV (Honig, 1948). Both of the calculated values come out much too high. It seems that this is a general tendency of the Pariser–Parr–Pople type calculations.

The reason for this was attributed by Hoyland and Goodman (1962) to the deformation of both σ and π charge clouds due to ionization. As the phenomenon is fairly complicated, their treatment seems to the writer not yet conclusive.

21. Justification of the Scheme

The assumption of zero differential overlap is certainly drastic. Overlaps between neighboring π orbitals in usual hydrocarbons are about 0.25. We cannot neglect this in comparison with 1 when we are discussing excitation energies which are, after all, very small compared with the total energy. We should remember further that if we assume orthogonality between AO's consistently in the usual type of calculation, we do not get binding at all.

We need some justification of the basic assumptions of the Pariser–Parr–Pople theory.

(*a*) *Empirical Justification*. Strictly speaking, this is not justification, but the flexibility of the method and its success in reproducing the purely theoretical as well as observed data are very impressive.

In the previous section, we have seen that the P–P–P method reproduces observed transition energies of C_2H_4 quite well (with the $I-A$ correction). Without the $I-A$ correction it can also reproduce the theoretically computed results. Table XII shows this.

TABLE XII

THE π ELECTRONIC LEVELS of C_2H_4 IN eV

Method	Purely theoretical Slater orbital	P–P–P $\beta^{\text{core}} = -3.125^a$
$(aa\|bb)$	9.26	9.26
Z	15.0	14.7
V	11.5	11.2
T	3.1	3.5
N	0.0	0.0

[a] The value was determined to fit the energy of the state $(\psi_{\text{II}})^2$ to the purely theoretical value.

Table XIII confirms the reproducibility of theoretical and experimental values in the case of C_6H_6.

TABLE XIII

THE π ELECTRONIC LEVELS OF C_6H_6 IN eV

Method	Purely theoretical Slater AO without CI	P–P–P	Purely theoretical Slater AO with CI	Obs.	P–P–P
β^{core}	—	-2.79^a	—	—	-2.39^a
$^1E_{1u}$	9.8	9.9	9.9	7.0	7.0
$^1B_{1u}$	7.3	7.3	9.0	6.0	5.3
$^1B_{2u}$	5.9	$\underline{5.9}$	4.4	4.9	$\underline{4.9}$
$^3B_{2u}$	5.8	5.9	8.2	—	4.9
$^3E_{1u}$	4.4	4.5	4.7	—	4.45
$^3B_{1u}$	3.1	3.2	6.4	3.8	4.0
$^1A_{1g}$	0.0	0.0	0.0	0.0	0.0

[a] The value of β^{core} was determined to fit the energy of $^1B_{2u}$ state to a desired value.

Even for the N-containing heterocyclic molecules calculated values not only of the excitation energies but also of the oscillator strengths are in excellent agreement with experiment [cf. Table XIV which is also taken from Pariser and Parr's paper (1953)].

TABLE XIV

LOWEST SINGLET AND TRIPLET EXCITED STATES

Molecule	Symmetry	State	Calculated energy[a]	Obs.	Calculated f	Obs.
Pyridine	C_{2v}	$^3A_1$	4.08	—	0	—
		$^1B_1$	4.90	4.95	0.046	0.041
Pyradine	D_{2h}	$^3B_{3u}$	3.85	3.35	0	~ 0
		$^1B_{3u}$	4.71	4.77	0.121	0.130
Pyrimidine	C_{2v}	$^3A_1$	4.16	—	0	—
		$^1B_1$	5.05	5.15	0.038	—
s-Triazine	D_{3h}	$^3A_{1'}$	4.26	—	0	—
		$^1A_{2'}$	$\underline{5.29}$	5.29	0	~ 0

[a] The value of $\beta_{\mathrm{CC}}^{\mathrm{core}}$ was taken over from C_6H_6: $\beta_{\mathrm{CC}}^{\mathrm{core}} = -2.39$ eV. The value of $\beta_{\mathrm{CN}}^{\mathrm{core}}$ was determined as -2.576 eV so as to fit the calculated lowest singlet of *s*-triazine to the observed value. The value used for $\alpha_{\mathrm{N}}^{\mathrm{core}} - \alpha_{\mathrm{C}}^{\mathrm{core}}$ and how it is obtained are not clear.

(*b*) *Theoretical Justification.* One attempt to justify the zero differential overlap approximation is to assume that we are using orthogonalized AO's as the basic functions instead of usual overlapping AO's (Löwdin, 1955; Parr, 1960).

For the sake of simplicity, let us consider the two π orbitals of C_2H_4 again. Starting from the AO's π_a and π_b which are usual Slater or Hartree–Fock AO's, we can make orthogonalized AO's, $\bar{\pi}_a$ and $\bar{\pi}_b$, by the symmetric orthogonalization procedure[12]:

$$\begin{aligned} \bar{\pi}_a &= \lambda\pi_a - \mu\pi_b, \\ \bar{\pi}_b &= -\mu\pi_a + \lambda\pi_b, \end{aligned} \tag{21.1}$$

---

[12] In general,

$$\bar{\pi} = \pi(1 + \mathrm{S})^{-1/2},$$

where $\bar{\pi} = (\bar{\pi}_a \bar{\pi}_b \bar{\pi}_c \cdots)$ and S is the overlap matrix

$$\mathrm{S} = \begin{pmatrix} 0 & (\pi_a|\pi_b) & (\pi_a|\pi_c) \cdots \\ (\pi_b|\pi_a) & 0 & (\pi_b|\pi_c) \cdots \\ \vdots & \vdots & \vdots \quad \vdots\vdots\vdots \end{pmatrix}.$$

This procedure was first proposed by Löwdin (1950).

where

$$\begin{aligned} \lambda &= \tfrac{1}{2}\{(1-S)^{-1/2} + (1+S)^{-1/2}\}, \\ \mu &= \tfrac{1}{2}\{(1-S)^{-1/2} - (1+S)^{-1/2}\}. \end{aligned} \tag{21.2}$$

If we expand $\bar{\pi}_a$ in terms of S, we get

$$\bar{\pi}_a = (1 + \tfrac{3}{8}S^2)\pi_a - \tfrac{1}{2}S\pi_b + O(S^3). \tag{21.3}$$

When $S = (\pi_a \mid \pi_b) = \frac{1}{4}$, we have

$$\bar{\pi}_a = 1.0245\pi_a - 0.1301\,\pi_b.$$

If we assume that we are using these orthogonalized AO's as our basis, then the overlap integrals are strictly vanishing. How about the electron interaction integrals? Roughly speaking, two-center Coulomb integrals $(\bar{a}\bar{a} \mid \bar{b}\bar{b})$ retain values similar to those calculated using the original overlapping AO's. On the other hand all others—hybrid type $(\bar{a}\bar{a} \mid \bar{a}\bar{b})$, exchange type $(\bar{a}\bar{b} \mid \bar{a}\bar{b})$, and many-center type $(\bar{a}\bar{b} \mid \bar{c}\bar{d})$—which contain at least one $\bar{a}\bar{b}$-type charge distribution become very small.

Table XV shows the situation in the case of C_6H_6. In this table, the orbitals a, b, c, and d are situated along the ring in this order.

TABLE XV

ELECTRON INTERACTION INTEGRALS OF C_6H_6 (IN eV)[a]

Electron interaction integrals	AO	$\overline{\text{AO}}$
$(aa \mid aa)$	16.930	17.618
$(aa \mid bb)$	9.027	8.924
$(aa \mid cc)$	5.668	5.574
$(aa \mid dd)$	4.968	4.876
$(aa \mid ab)$	3.313	−0.115
$(aa \mid bc)$	1.870	−0.048
$(aa \mid cd)$	1.421	0.036
$(ab \mid ab)$	0.923	0.088
$(ab \mid bc)$	0.677	0.017

[a] From McWeeny (1955).

We can interpret the situation in the following way. Since the Coulomb integral $(aa \mid bb)$ represents the interaction between two more-or-less localized unit charges, the value does not depend too strongly on the shape of the charge distribution. Other types of integrals involve at least one charge distribution $\bar{a}\bar{b}$ which has zero net charge; therefore the values are small.

The situation is also connected with the remarkable success of the Mulliken approximation in the evaluation of molecular integrals, i.e.,

$$(ab \mid \rho(2)) = \tfrac{1}{2}S_{ab}\{(aa \mid \rho(2)) + (bb \mid \rho(2)\}, \qquad (21.4)$$

where ρ can be any charge distribution.

Using (21.3), we have the expansion

$$\bar{\pi}_a\bar{\pi}_b = (1 + \tfrac{1}{2}S^2)\pi_a\pi_b - \tfrac{1}{2}S(\pi_a\pi_a + \pi_b\pi_b) + O(S^3), \qquad (21.5)$$

so that

$$(\bar{a}\bar{b} \mid \rho) \fallingdotseq (1 + \tfrac{1}{2}S^2)(ab \mid \rho) - \tfrac{1}{2}S\{(aa \mid \rho) + (bb \mid \rho)\}.$$

By using the Mulliken approximation (21.4), we get

$$(\bar{a}\bar{b} \mid \rho) = \tfrac{1}{2}S^2(ab \mid \rho), \qquad (21.6)$$

which is much smaller than $(ab \mid \rho)$.

On the other hand, a similar expansion gives

$$\bar{\pi}_a\bar{\pi}_a = (1 + \tfrac{3}{4}S^2)\pi_a\pi_a - S\pi_a\pi_b + \tfrac{1}{4}S^2\pi_b\pi_b + O(S^3). \qquad (21.7)$$

Then

$$\begin{aligned}(\bar{a}\bar{a} \mid \bar{b}\bar{b}) \fallingdotseq{} & (1 + \tfrac{3}{2}S^2)(aa \mid bb) - S(aa \mid ab) \\ & - S(ab \mid aa) + \tfrac{1}{4}S^2(aa \mid aa) \\ & + \tfrac{1}{4}S^2(bb \mid bb) + S^2(aa \mid bb). \qquad (21.8)\end{aligned}$$

If we use the Mulliken approximation, $(\bar{a}\bar{a} \mid \bar{b}\bar{b})$ reduces to

$$(\bar{a}\bar{a} \mid \bar{b}\bar{b}) = (1 + \tfrac{1}{2}S^2)(aa \mid bb) - \tfrac{1}{4}S^2\{(aa \mid aa) + (bb \mid bb)\}. \qquad (21.9)$$

This is expected to be not so different from $(aa \mid bb)$. Thus, once the Mulliken approximation is accepted, the Coulomb-type integrals defined over $\overline{\text{AO}}$'s are shown to be much greater than other types of integrals.

The zero differential overlap approximation used in overlap and electron-interaction integrals is not an unreasonable one if our basis is a set of properly orthogonalized AO's ($\overline{\text{AO}}$'s).

The core resonance integral should be interpreted as

$$\bar{\beta}_{ab}^{\text{core}} = (\bar{\chi}_a \mid f \mid \bar{\chi}_b), \qquad (21.10)$$

but, as it is treated as a parameter, there is no problem about this.

The third basic approximation is about the one-center Coulomb integral (19.6). The reason for this approximation can be found in Moffitt's argument explained in Section 13. Does the interpretation that our basic orbitals are $\overline{\text{AO}}$'s affect the argument? In order to answer this question, we express the original AO's in terms of $\overline{\text{AO}}$'s, again considering a two-center problem:

$$\begin{aligned} \pi_a &= \lambda'\bar{\pi}_a - \mu'\bar{\pi}_b, \\ \pi_b &= -\mu'\bar{\pi}_a + \lambda'\bar{\pi}_b, \end{aligned} \tag{21.11}$$

where

$$\begin{aligned} \lambda' &= \tfrac{1}{2}\{(1+S)^{1/2} + (1-S)^{1/2}\}, \\ \mu' &= -\tfrac{1}{2}\{(1+S)^{1/2} - (1-S)^{1/2}\}. \end{aligned} \tag{21.12}$$

Using (21.11), we obtain

$$\begin{aligned} (aa\,|\,aa) = {} & \lambda'^4(\bar{a}\bar{a}\,|\,\bar{a}\bar{a}) - 4\lambda'^3\mu'(\bar{b}\bar{a}\,|\,\bar{a}\bar{a}) \\ & + 2\lambda'^2\mu'^2\{2(\bar{b}\bar{a}\,|\,\bar{b}\bar{a}) + (\bar{b}\bar{b}\,|\,\bar{a}\bar{a})\} \\ & - 4\lambda'\mu'^3(\bar{a}\bar{a}\,|\,\bar{a}\bar{b}) + \mu'^4(\bar{b}\bar{b}\,|\,\bar{b}\bar{b}). \end{aligned} \tag{21.13}$$

On the right-hand side, we retain only Coulomb integrals, because they are much bigger than the others,

$$(aa\,|\,aa) = \lambda'^4(\bar{a}\bar{a}\,|\,\bar{a}\bar{a}) + 2\lambda'^2\mu'^2(\bar{b}\bar{b}\,|\,\bar{a}\bar{a}) + \mu'^4(\bar{b}\bar{b}\,|\,\bar{b}\bar{b}). \tag{21.14}$$

If the two atoms a and b are the same, we have

$$(aa\,|\,aa) = (\bar{a}\bar{a}\,|\,\bar{a}\bar{a}) - \tfrac{1}{2}S^2\{(aa\,|\,aa) - (aa\,|\,bb)\}. \tag{21.15}$$

The second term is estimated to be around 0.3 eV; therefore $(\bar{a}\bar{a}\,|\,\bar{a}\bar{a})$ is slightly bigger but not so different from $(aa\,|\,aa)$. We may conclude that interpreting $\overline{\text{AO}}$'s as our basis does not conflict with the $I - A$ approximation.

How about the core Coulomb integral α^{core}? For the homopolar two-center case, we obtain in a similar manner:

$$\bar{\alpha}^{\text{core}} = (1+S^2)\alpha^{\text{core}} - S\beta^{\text{core}} + O(S^3). \tag{21.16}$$

On the other hand,

$$\bar{\beta}^{\text{core}} = (1+S^2)\beta^{\text{core}} - S\alpha^{\text{core}} + O(S^3). \tag{21.17}$$

Eliminating β^{core} from (21.16) and (21.17) we get

$$\bar{\alpha}^{\text{core}} = \alpha^{\text{core}} - S\bar{\beta}^{\text{core}}. \tag{21.18}$$

The second term $-S\bar{\beta}^{\text{core}}$ is about $\frac{3}{4}$ eV in C_2H_4 and C_6H_6. Although it is the largest correction we have met in changing our basis from AO's to $\overline{\text{AO}}$'s, this is again not so big.[13]

In conclusion, we can perhaps say that, by interpreting the basic AO's used in the Pariser–Parr–Pople calculation as the properly orthogonalized AO's, we can justify the zero differential overlap approximation (at least to some extent) and the other basic assumptions are unaffected.

22. Simplified SC LCAO Scheme

By adopting the formulas of the Pariser–Parr–Pople method, Eq. (16.14) of the self-consistent LCAO method is very much simplified.

Remembering that the Hamiltonian is given by (19.3) and that

$$(ab \mid cd) = \delta_{ab}\delta_{cd}(aa \mid cc)$$

under the zero differential overlap approximation, we obtain

$$\begin{aligned}(\overline{\mathscr{F}})_{aa} &\equiv (\bar{\chi}_a \mid \mathscr{F} \mid \bar{\chi}_a)\\ &= (\bar{\chi}_a \mid f \mid \bar{\chi}_a) + \sum_{i=1}^{n} \sum_{b} c_{bi}^{*} c_{bi} [2(\bar{b}\bar{b} \mid \bar{a}\bar{a}) - (\bar{a}\bar{a} \mid \bar{a}\bar{a})\delta_{ab}]\\ &= \bar{\alpha}_a^{\text{core}} + (\bar{a}\bar{a} \mid \bar{a}\bar{a}) \sum_{i=1}^{n} |c_{ai}|^2 + \sum_{b \neq a} (\bar{b}\bar{b} \mid \bar{a}\bar{a}) \sum_{i=1}^{n} 2|c_{bi}|^2 \qquad (22.1)\end{aligned}$$

and

$$\begin{aligned}(\overline{\mathscr{F}})_{ab} &\equiv (\bar{\chi}_a \mid \mathscr{F} \mid \bar{\chi}_b)\\ &= (\bar{\chi}_a \mid f \mid \bar{\chi}_b) - (\bar{a}\bar{a} \mid \bar{b}\bar{b}) \sum_{i=1}^{n} c_{ai}^{*} c_{bi}\\ &= \bar{\beta}_{ab}^{\text{core}} - (\bar{a}\bar{a} \mid \bar{b}\bar{b}) \sum_{i=1}^{n} c_{ai}^{*} c_{bi}. \qquad (22.2)\end{aligned}$$

The summation over *i* is to be taken over all occupied π molecular orbitals and it is tacitly assumed that each atom has one π AO.

As we shall see later, the quantity $\sum_i 2|c_{ai}|^2$ is called the π electron density on atom *a* and is often denoted by q_a. The quantity $\sum_i (c_{ai}^{*} c_{bi} + c_{ai} c_{bi}^{*})$ is called the bond order between atoms *a* and *b* and is denoted by p_{ab}.

Using (19.11), that is to say using (19.7), (19.8), and (19.10)—all three

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[13] Taking the correction $-S\bar{\beta}^{\text{core}}$ to $\bar{\alpha}^{\text{core}}$ into account, we get, as the ionization potential for C_2H_4, 12.9 eV instead of 13.6 eV. The improvement is not sufficient, the observed value being 10.6 eV.

being approximations—we obtain

$$(\overline{\mathscr{F}})_{aa} = -I_a + \tfrac{1}{2}q_a(\bar{a}\bar{a}\,|\,\bar{a}\bar{a}) + \sum_c (\bar{a}\,|\,u_c\,|\,\bar{a})$$
$$+ \sum_{b\neq a} \{(q_b - 1)(\bar{a}\bar{a}\,|\,\bar{b}\bar{b}) + (\bar{a}\,|\,u_b\,|\,\bar{a})\}. \tag{22.3}$$

Introducing the $I - A$ approximation,

$$(\bar{a}\bar{a}\,|\,\bar{a}\bar{a}) = I_a - A_a, \tag{22.4}$$

and neglecting the penetration integrals,

$$(\bar{a}\,|\,u_b\,|\,\bar{a}) = 0,^{14} \tag{22.5}$$

we reach the equation

$$(\overline{\mathscr{F}})_{aa} = -I_a + \tfrac{1}{2}q_a(I_a - A_a) + \sum_{b\neq a} (q_b - 1)(\bar{a}\bar{a}\,|\,\bar{b}\bar{b}). \tag{22.6}$$

The notation becomes more compact by denoting the Coulomb integral $(aa\,|\,bb)$ by γ_{ab}:

$$(\overline{\mathscr{F}})_{aa} = -(1 - \tfrac{1}{2}q_a)I_a - \tfrac{1}{2}q_aA_a + \sum_{b\neq a} (q_b - 1)\gamma_{ab}. \tag{22.7}$$

For the off-diagonal element of $\overline{\mathscr{F}}$, we have

$$\begin{aligned}(\overline{\mathscr{F}})_{ab} &= \beta_{ab}^{\text{core}} - \tfrac{1}{2}p_{ab}\gamma_{ab} && \text{for neighbors,}\\ &= -\tfrac{1}{2}p_{ab}\gamma_{ab} && \text{for nonneighbors.}\end{aligned} \tag{22.8}$$

Equations (22.7) and (22.8) are the basic equations for the self-consistent LCAO method in the Pariser–Parr–Pople approximation. The equation to solve is [cf. (16.11)]

$$\overline{\mathscr{F}}\mathbf{c}_i = \varepsilon_i\mathbf{c}_i. \tag{22.9}$$

23. General Remarks

The Pariser–Parr–Pople method is not very complicated. The only molecular integrals which must be evaluated are of Coulomb type. Theoretical values of these between $2p\pi - 2p\pi$ evaluated by using Slater-type

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[14] Some numerical examples of penetration integrals are as follows:

-0.989 eV in C_2H_4,

$$\left.\begin{array}{l}-0.856 \text{ eV for the nearest neighbors}\\ -0.013 \text{ eV for the next neighbors}\\ -0.003 \text{ eV for the third neighbors}\end{array}\right\} \text{in } C_6H_6.$$

Although they themselves are not negligible, we may reasonably hope that their effects on spectra and other molecular properties are quite small.

orbitals are available in the existing tables. When $3p\pi$ and $3d\pi$ orbitals are present, the problem is a little more difficult, not only because we have to calculate additional molecular integrals with them, but also because we know less about the shape of these AO's.

The P–P–P method works very well for hydrocarbons and simple heterocyclic molecules in predicting energies and intensities of their spectral lines. However, it still causes considerable error in predicting ionization potentials and electron affinities of those molecules unless we treat the α^{core} as parameters. In the latter type of problems, absolute values of α come in, while we do not need them in discussing spectra.

Applications of the method to various heteropolar and bigger molecules and to $n \rightarrow \pi^*$ transitions are being actively explored [see, for example, Parr, 1963; Lykos, 1964; I'Haya, 1964; Gimarc and Parr, 1965 (esp. refs. 173–191)]. There is the difficulty that the number of parameters increases rapidly with the size of the molecule and the variety of atoms involved. Several investigators (see, for example, Berthier *et al.*, 1963; Ellison and Huff, 1963; Leroy, 1963; Ohno, 1964; Fischer-Hjalmars, 1964) have looked into the problem of choosing these parameters but we do not seem to have a unified way yet. The extension of the P–P–P method to make it applicable to the σ system as well is also under vigorous investigation.

At present, the P–P–P method seems to be the best compromise between accuracy and ease of use in the π electron calculation of moderate-size molecules.

IV. Simple Molecular Orbital Theory

24. Basic Assumptions

The simple molecular orbital theory which will be dealt with in this section was originated by Hückel (1931, 1932) and is sometimes referred to as the Hückel MO method.

The first basic assumption is that of the σ–π separation, which is common to all the methods treated in this note.

The second basic assumption, which is characteristic of the simple MO theory, is

$$\mathscr{H}(1, 2, \ldots N) = \sum_{i=1}^{N} h_{\text{eff}}(i). \tag{24.1}$$

This means that the electrons are supposed to move independently in a potential field in which electron interactions are taken care of in an averaged form. A one-electron operator h_{eff} describes their behavior. This statement applies to the Hartree–Fock method and its single-body operator $\mathscr{F}$. However, there is a difference between the two operators h_{eff} and $\mathscr{F}$ (see below).

If we adopted assumption (24.1), then the many-body Schrödinger equation can be separated to a set of one-electron equations. A total wave function is expressed as a simple product of molecular orbitals ψ_i:

$$\Psi(1, 2, \ldots N) = \prod_{i=1}^{N} \psi_i(i). \tag{24.2}$$

Each molecular orbital is an eigenfunction of h_{eff},

$$h_{\mathrm{eff}}\psi_i = \varepsilon_i\psi_i. \tag{24.3}$$

The π electron total energy E^π is

$$E^\pi = \sum_i n_i\varepsilon_i, \tag{24.4}$$

where n_i is the occupation number of orbital ψ_i and can take the values 0, 1, or 2.

When an electron is excited from ψ_i to ψ_j, the excitation energy E_{exc} is given by

$$E_{\mathrm{exc}} = \varepsilon_j - \varepsilon_i. \tag{24.5}$$

Although (24.3) has a form similar to (16.3), the total energy (24.4) and the excitation energy (24.5) are given by expressions different from (16.6) and (16.9). In the latter, there are electron interaction terms as big as the orbital energy difference.

As electron interaction is not explicitly taken into account in the simple MO theory, there is no energy difference between singlet and triplet states. There is no possibility of having a high spin state ($S \geq 1$) unless there is a degeneracy in the highest occupied level.

As far as the writer knows there has been no rigorous argument justifying assumption (24.1) and also no suggestion about the nature and the form of h_{eff}. Nevertheless, the theory has been quite succesful in describing (ground state) properties such as charge densities, bond order, dipole moment, and even resonance energy, etc. The theory is known to be less successful in the discussion of ionization potentials, electron affinities, and excitation energies.

Let us turn to the third basic assumption. This is quite familiar; the MO's are expressed as LCAO's:

$$\psi_i = \sum_a c_{ai}\chi_a. \tag{24.6}$$

The coefficients c_{ai} are determined so as to minimize the orbital energy ε_i.

Let us assume that all the AO's are real. This is allowed except when the original Hamiltonian contains i. Then all coefficients are also real.

Introducing so-called Coulomb and resonance integrals,

$$\begin{aligned}\alpha_a &= (\chi_a | h_{\text{eff}} | \chi_a),\\ \beta_{ab} &= (\chi_a | h_{\text{eff}} | \chi_b), \qquad a \neq b,\end{aligned} \tag{24.7}$$

we can write the orbital energy ε_i in the following form:

$$\begin{aligned}\varepsilon_i &= (\psi_i | h_{\text{eff}} | \psi_i)\\ &= \sum_a c_{ai}^2 \alpha_a + \sum_{a<b} 2c_{ai}c_{bi}\beta_{ab}.\end{aligned} \tag{24.8}$$

Instead of finding a minimum of ε_i with respect to variations of the c_{ai} under the constraint that the MO is normalized, we may take free variation of the following quantity:

$$\begin{aligned}I &= (\psi_i | h_{\text{eff}} | \psi_i) - \varepsilon(\psi_i | \psi_i)\\ &= \sum_a (\alpha_a - \varepsilon)c_{ai}^2 + \sum_{a<b} (2\beta_{ab} - 2\varepsilon S_{ab})c_{ai}c_{bi},\end{aligned}$$

where S_{ab} is the overlap integral between atomic orbitals a and b. The condition $\delta I = 0$ with respect to variations of c_a leads to

$$(\alpha_a - \varepsilon)c_{ai} + \sum_{b \neq a} (\beta_{ab} - \varepsilon S_{ab})c_{bi} = 0. \tag{24.9}$$

The orbital energies ε_i are determined from the secular determinant

$$\begin{vmatrix} \alpha_1 - \varepsilon & \beta_{12} - S_{12}\varepsilon & \cdot & \cdot & \cdot \\ \beta_{21} - S_{21}\varepsilon & \alpha_2 - \varepsilon & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} = 0 \tag{24.10}$$

Putting a value of ε_i into (24.9), we obtain the ratios c_{ai}/c_{bi} and adding the normalization condition we can determine the values of the c_{ai}'s.

In the simple MO theory α and β are usually treated as empirical parameters, but often they are considered to be characteristic to atoms and bonds. In other words, they are supposed not to depend on the environment but only on the atom or the bond itself.

25. Neglect of Overlap Integrals between AO's

The overlap integrals which appear in (24.9) and (24.10) may be calculated and a number of calculations by the simple MO theory include overlap. On the other hand, quite often they are simply neglected.

As the relation between the two types of calculation, with and without overlap, has not always been clear in the literature, we shall examine it in the case of C_2H_4.

The idea is again to note that we are using orthogonalized AO's as our basis in the calculation without overlaps and usual overlapping AO's in the calculation with overlaps. As they differ only in the choice of basis of representation, physical quantities like orbital energies must be the same in these calculations if we choose suitable parameters.

With the nonorthogonal basis, the secular determinant for C_2H_4 is

$$\begin{vmatrix} \alpha - \varepsilon & \beta - S\varepsilon \\ \beta - S\varepsilon & \alpha - \varepsilon \end{vmatrix} = 0, \tag{25.1}$$

and the solutions are

$$\begin{aligned} \varepsilon_1 &= \frac{\alpha + \beta}{1 + S} = \alpha + \frac{\beta - \alpha S}{1 + S}, \\ \varepsilon_2 &= \frac{\alpha - \beta}{1 - S} = \alpha - \frac{\beta - \alpha S}{1 - S}. \end{aligned} \tag{25.2}$$

With the orthogonal basis, the secular determinant is

$$\begin{vmatrix} \bar{\alpha} - \varepsilon & \bar{\beta} \\ \bar{\beta} & \bar{\alpha} - \varepsilon \end{vmatrix} = 0, \tag{25.3}$$

and the solutions are simply

$$\begin{aligned} \varepsilon_1 &= \bar{\alpha}_1 + \bar{\beta}_1, \\ \varepsilon_2 &= \bar{\alpha}_1 - \bar{\beta}_1. \end{aligned} \tag{25.4}$$

From the relation (21.1) between AO's and $\overline{\text{AO}}$'s we obtain

$$\bar{\alpha} = \frac{\alpha - \beta S}{1 - S^2}, \qquad \bar{\beta} = \frac{\beta - \alpha S}{1 - S^2} \tag{25.5}$$

and

$$\alpha = \bar{\alpha} + \bar{\beta} S, \qquad \beta = \bar{\beta} + \bar{\alpha} S. \tag{25.6}$$

If we determine the $\bar{\beta}$ value by fitting it to the mean value of observed singlet and triplet excitation energies, we have

$$-2\bar{\beta} = \tfrac{1}{2}(7.6 + 4.6)\ \text{eV},$$

$$\bar{\beta} = -3.05\ \text{eV}.$$

By equating $-(\bar{\alpha} + \bar{\beta})$ to the observed ionization potential of 10.62 eV, $\bar{\alpha}$ is determined as

$$\bar{\alpha} = -7.57\ \text{eV}.$$

Assuming $S = 0.25$, we obtain

$$\alpha = -8.33\ \text{eV}, \qquad \beta = -4.94\ \text{eV}.$$

The levels are illustrated in Fig. 7. Although the above choice of parameters is certainly arbitrary, it should be noted that considerably larger resonance integrals must be used in the calculation with overlaps than those in the calculation without overlaps. We cannot carry parameter values over from one to the other. On the other hand, the difference between α and $\bar{\alpha}$ is not so large.

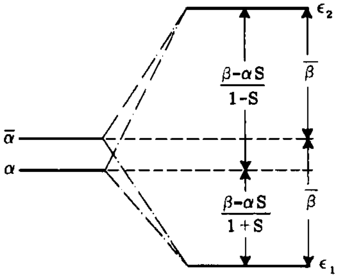

Fig. 7. Schematic energy levels of C_2H_4 by the simple molecular orbital theory.

26. Bond Order and Charge Density

When molecular orbitals are expressed as LCAO's,

$$\psi_i = \sum_a c_{ai}\chi_a, \tag{26.1}$$

the π electron charge density on atom a is defined as

$$q_a = \sum_i n_i c_{ai}^2, \tag{26.2}$$

and the bond order between atoms a and b is defined as

$$p_{ab} = \sum_i n_i c_{ai} c_{bi}, \tag{26.3}$$

when overlaps between AO's are neglected. When overlaps are not neglected, (26.2) and (26.3) are replaced by

$$q_a = \sum_i n_i \left\{ c_{ai}^2 + c_{ai} \sum_{b(\neq a)} c_{bi} S_{ab} \right\} \tag{26.4}$$

and

$$p_{ab} = \sum_i n_i \left\{ c_{ai} c_{bi} + \tfrac{1}{2} c_{ai} \sum_{d(\neq a)} c_{di} S_{ad} + \tfrac{1}{2} c_{bi} \sum_{e(\neq b)} c_{ei} S_{be} \right\}, \tag{26.5}$$

respectively.

If a and b are not neighbors, the bond order is usually taken to be zero. In (26.2) ~ (26.5) n_i, the number of electrons in the MO ψ_i, is 0 or 1 or 2.

If the electronic state we are considering is a closed-shell state, namely each occupied MO has two electrons and overlaps are neglected, then

$$\begin{aligned} q_a &= 2 \sum_{i=1}^{n} (c_{ai})^2, \\ p_{ab} &= 2 \sum_{i=1}^{n} c_{ai} c_{bi}. \end{aligned} \tag{26.6}$$

Example 1. The simplest example is C_2H_4. In this case $n = 1$ and

$$\psi = \frac{1}{\sqrt{2}} (\pi_a + \pi_b),$$

the overlap integral being neglected. We have

$$q_a = q_b = 1$$

and

$$p_{ab} = 1.$$

Example 2. In the case of C_6H_6, by neglecting β for nonneighboring atoms, the secular equation has the following form

$$\beta c_{k-1} + (\alpha - \varepsilon) c_k + \beta c_{k+1} = 0, \qquad k = 1, \ldots 6. \tag{26.7}$$

Let us assume

$$c_k = e^{ik\theta}.$ [15]$$

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[15] In this argument it is more convenient to allow for complex values of c_k. We could transform them to real numbers by making use of degeneracies of orbital energies.

From the condition $c_7 \equiv c_1$, $\theta = n\pi/3$, n being an integer. Equation (26.7) then takes the form

$$\alpha - \varepsilon_n + 2\beta \cos \frac{n\pi}{3} = 0,$$

$$\varepsilon_n = \alpha + 2\beta \cos \frac{n\pi}{3}.$$

We obtain the following three lowest eigenvalues and eigenfunctions:

$$n = 0, \qquad \varepsilon_0 = \alpha + 2\beta, \qquad \psi_0 = \frac{1}{\sqrt{6}}(\pi_1 + \pi_2 + \pi_3 + \pi_4 + \pi_5 + \pi_6),$$

$$n = \pm 1, \qquad \varepsilon_{\pm 1} = \alpha + \beta, \qquad \psi_1 = \frac{1}{\sqrt{6}}(\pi_1 + e^{i(\pi/3)}\pi_2 + e^{i(2\pi/3)}\pi_3 - \pi_4 - e^{i(\pi/3)}\pi_5 - e^{i(2\pi/3)}\pi_6),$$

$$\psi_{-1} = \frac{1}{\sqrt{6}}(\pi_1 + e^{-i(\pi/3)}\pi_2 + e^{-i(2\pi/3)}\pi_3 - \pi_4 - e^{-i(\pi/3)}\pi_5 - e^{-i(2\pi/3)}\pi_6).$$

From these we obtain

$$q_1 = q_2 = q_3 = q_4 = q_5 = q_6 = 1,$$

$$p_{12} = p_{23} = p_{34} = p_{45} = p_{56} = p_{61} = \tfrac{2}{3}.$$

The total π electron energy E^{π} is, under the present approximation, given by

$$E^{\pi} = 2 \sum_i \varepsilon_i. \tag{26.8}$$

Inserting the expression of orbital energies (24.8) into (26.8), we obtain

$$\begin{aligned} E^{\pi} &= \sum_a \alpha_a \sum_i 2c_{ai}^2 + 2 \sum_{a<b} \beta_{ab} \sum_i 2c_{ai}c_{bi} \\ &= \sum_a \alpha_a q_a + 2 \sum_{a<b} \beta_{ab} p_{ab}. \end{aligned} \tag{26.9}$$

As E^{π} is stationary with respect to variations of the c_{ai}'s, for any small changes of α and β, we have

$$\delta E^{\pi} = \sum_a q_a \delta\alpha_a + 2 \sum_{a<b} p_{ab} \delta\beta_{ab} \tag{26.10}$$

or

$$q_a = \frac{\partial E^\pi}{\partial \alpha_a}, \qquad p_{ab} = \frac{1}{2}\frac{\partial E^\pi}{\partial \beta_{ab}}. \tag{26.11}$$

The π bond order is considered to be a measure of bond strength, and there is a relation between bond orders and bond lengths. The bond length depends, of course, on the type of σ bond between the two atoms and it is known that hybridization plays quite an important role in deciding the equilibrium internuclear distance (Coulson, 1948). Let us take, for example, the C—C bonds where both C atoms are in the sp^2 hybridized state. Molecules such as C_2H_4 or C_6H_6 and graphite belong to this category. The bond length R_{ab} is expressed as a function of bond order p_{ab} as follows:

$$R_{ab} = S_{ab} - \frac{S_{ab} - D_{ab}}{1 + K_{ab}\dfrac{1 - p_{ab}}{p_{ab}}}, \tag{26.12}$$

where S_{ab} and D_{ab} are the lengths of single and double bonds, respectively, between atoms a and b and K_{ab} is a constant. This formula was proposed by Coulson (1939) and derived by him as follows. For the equilibrium bond length R_{ab}, the following equation should be satisfied:

$$\frac{\partial E}{\partial R_{ab}} = \frac{\partial(E^\sigma + E^\pi)}{\partial R_{ab}} = \frac{\partial E^\sigma}{\partial R_{ab}} + \frac{\partial E^\pi}{\partial \beta_{ab}}\frac{d\beta_{ab}}{dR_{ab}} = 0, \tag{26.13}$$

where we assume that $E = E^\sigma + E^\pi$, that α is independent of R_{ab}, and also that β_{ab} is a function of R_{ab}. Let us express E^σ as a sum of σ bond energies,

$$E^\sigma = \text{const} + \sum_{a<b} \frac{k_{ab}^s}{2}(R_{ab} - S_{ab})^2, \tag{26.14}$$

where k_{ab}^s is a force constant for a σ bond. Then we obtain

$$\frac{\partial E^\sigma}{\partial R_{ab}} = k_{ab}^s(R_{ab} - S_{ab}). \tag{26.15}$$

Similarly for a double bond we have

$$\frac{\partial E}{\partial R_{ab}} = k_{ab}^d(R_{ab} - D_{ab}). \tag{26.16}$$

For a typical double bond like the one in C_2H_4, we have, from (26.9),

$$E^{\pi} = 2\alpha + 2\beta = E - E^{\sigma}. \tag{26.17}$$

By differentiating (26.17) by R, we have

$$\frac{d\beta_{ab}}{dR_{ab}} = \frac{1}{2}\left(\frac{\partial E}{\partial R_{ab}} - \frac{\partial E^{\sigma}}{\partial R_{ab}}\right).$$

By making use of (26.16) and (26.15) we can transform the right-hand side of the above equation; the result is as follows:

$$\frac{d\beta_{ab}}{dR_{ab}} = \tfrac{1}{2}k^{d}_{ab}(R_{ab} - D_{ab}) - \tfrac{1}{2}k^{s}_{ab}(R_{ab} - S_{ab}).$$

Putting this expression into (26.13) and using (26.15) and (26.11), we obtain

$$k^{s}_{ab}(R_{ab} - S_{ab}) + p_{ab}\{k^{d}_{ab}(R_{ab} - D_{ab}) - k^{s}_{ab}(R_{ab} - S_{ab})\} = 0.$$

Solving this equation for R_{ab}, and denoting k^{s}_{ab}/k^{d}_{ab} by K_{ab}, we reach (26.12).

27. Alternant Hydrocarbons

A hydrocarbon molecule which does not contain a ring composed of an odd number of unsaturated carbon atoms belongs to the class of alternant hydrocarbons. For such molecules, we can divide the unsaturated carbon atoms into two sets in such a way that any two adjacent carbon atoms belong to different sets. This is illustrated for benzene and phenanthrene in Fig. 8.

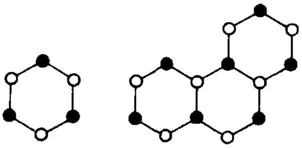


Fig. 8. Benzene and phenanthrene.

We number all the atoms of one set from 1 to h and all the atoms of the other set from $h + 1$ to m. We neglect overlaps and β's between non-neighboring atoms and, since α's are supposed to be the same, (24.9) becomes

$$\begin{aligned} &(\alpha - \varepsilon)c_a + \sum_{b=h+1}^{m} \beta_{ab}c_b = 0, \qquad a = 1, 2, \ldots h, \\ &(\alpha - \varepsilon)c_a + \sum_{b=1}^{h} \beta_{ab}c_b = 0, \qquad a = h + 1, h + 2, \ldots m. \end{aligned} \tag{27.1}$$

Putting $\varepsilon' = \varepsilon - \alpha$, we obtain a secular determinant of the following form:

$$\Delta(\varepsilon') = \begin{vmatrix} -\varepsilon'\mathbf{I} & \boldsymbol{\beta} \\ \bar{\boldsymbol{\beta}} & -\varepsilon'\mathbf{J} \end{vmatrix} = 0, \tag{27.2}$$

where $\mathbf{I}$ and $\mathbf{J}$ are the unit matrices of dimension h and $m - h$, respectively, and $\boldsymbol{\beta}$ and $\bar{\boldsymbol{\beta}}$ are rectangular matrices of dimension h and $m - h$. Multiplying the first h rows by (-1), and then the last $m - h$ columns by (-1), we obtain

$$\begin{aligned} \Delta(\varepsilon') = (-1)^h \begin{vmatrix} \varepsilon'\mathbf{I} & -\boldsymbol{\beta} \\ \bar{\boldsymbol{\beta}} & -\varepsilon'\mathbf{J} \end{vmatrix} &= (-1)^m \begin{vmatrix} \varepsilon'\mathbf{I} & \boldsymbol{\beta} \\ \bar{\boldsymbol{\beta}} & \varepsilon'\mathbf{J} \end{vmatrix} \\ &= (-1)^m \Delta(-\varepsilon'). \end{aligned} \tag{27.3}$$

This means that when ε_i is a root of $\Delta(\varepsilon') = 0$, $-\varepsilon_i$ is also a root.

When the number of atoms (= the number of roots) m is even, all the roots of $\Delta(\varepsilon') = 0$ occur in pairs of equal absolute magnitude and with opposite signs. We will assume that the ε_j's are all distinct and will discuss only closed-shell states in which each occupied MO contains two electrons. Since we assumed no degeneracy exists, $\varepsilon' = 0$ cannot be a root of the secular equation, and the above result tells that

$$\begin{gathered} \varepsilon_1' < \varepsilon_2' < \cdots < \varepsilon_{m/2}' < 0 < \varepsilon_{m/2+1}' < \varepsilon_{m/2+2}' < \cdots < \varepsilon_m', \\ \varepsilon_{m-i+1}' = -\varepsilon_i'. \end{gathered} \tag{27.4}$$

This is called the pairing theorem. All orbitals with negative ε' are doubly occupied and those with positive ε' are unoccupied.

If we replace ε' by $-\varepsilon'$ and c_a by $-c_a$ for $a = 1, 2, \ldots, h$, the secular equations (27.1) remain unchanged. Therefore, we obtain

$$\begin{aligned} c_{a,m-i+1} &= -c_{a,i}, \qquad a = 1, \ldots, h, \\ c_{a,m-i+1} &= c_{a,i}, \qquad a = h+1, \ldots, m. \end{aligned} \tag{27.5}$$

These relations tell us that if we excite an electron from ψ_i to ψ_{m-i+1}, the contribution of that electron to any bond order is reversed in sign but unaltered in magnitude.

When the number of atoms m is odd (we still assume that ε_j''s are all distinct), all the MO's except one occur in pairs with orbital energies ε_i' and $-\varepsilon_i'$; the remaining one must have energy zero. We have, therefore,

$$\begin{gathered} \varepsilon_1' < \varepsilon_2' < \cdots < \varepsilon_{\frac{1}{2}(m-1)}' < \varepsilon_{\frac{1}{2}(m+1)}' = 0 < \varepsilon_{\frac{1}{2}(m+3)}' < \cdots < \varepsilon_m', \\ \varepsilon_{m-i+1}' = -\varepsilon_i'. \end{gathered} \tag{27.6}$$

All the orbitals with negative ε's are doubly occupied and the $\psi_{\frac{1}{2}(m+1)}$ is singly occupied in the ground state. For orbitals ψ_i and ψ_{m-i+1} which makes a pair, the relations (27.5) hold.

Let us consider the nonbonding MO $\psi_{\frac{1}{2}(m+1)}$. For this orbital, the orbital energy ε is equal to α ($\varepsilon' = 0$), and from (27.1) we obtain the following two sets of equations:

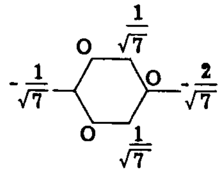
$$\sum_{b=h+1}^{m} \beta_{ab} c_b = 0, \qquad a = 1, 2, \cdots, h,$$

$$\sum_{b=1}^{h} \beta_{ab} c_b = 0, \qquad a = h+1, h+2, \ldots, m.$$

For the first set of equations, there are h equations for $m - h$ unknown c's, and in the latter, there are $m - h$ equations for h unknown c's. Without loss of generality, we can assume $h > m - h$, because otherwise we can simply interchange the name of the two sets of carbon atoms. Then for the first set of equations, the number of equations is greater than the number of unknowns, and in general the only solution is

$$c_{h+1} = c_{h+2} = \cdots = c_m = 0.$$

Thus the nonbonding MO has vanishing coefficients for all the atoms belonging to the set which contains less carbon atoms than the other. Thus the contribution of the odd electron in $\psi_{\frac{1}{2}(m+1)}$ to the bond order of any bond is zero. In the case of benzyl radical, the coefficients of nonbonding MO are as follows:



There are some simple rules about the charge densities and the bond orders in alternant hydrocarbons. First of all, when m is even, we have

$$q_a = 2 \sum_i^{\text{occ}} c_{ai}^2 = \sum_i^{\text{all}} c_{ai}^2, \tag{27.7}$$

where the second equal sign holds because of (27.5). Since both AO's $\{\chi_a\}$ and MO's $\{\psi_i\}$ are orthonormalized, the coefficients c_{ia} in

$$\psi_i = \sum_a c_{ai} \chi_a \tag{26.1}$$

can be regarded as the directional cosine between ψ_i and χ_a. We now reverse the role of ψ_i and χ_a; then we have

$$\chi_a = \sum_i^{\text{all}} c_{ia}\psi_i.$$

Since χ_a is normalized,

$$1 = (\chi_a \mid \chi_a) = \sum_i c_{ia}^2.$$

Combining this relation with (27.7), we obtain the important relation

$$q_a = 1. \tag{27.8}$$

It is easy to see that this relation holds also when m is odd. This also holds even if we do not neglect the overlaps between AO's. Therefore, in alternant hydrocarbons, every carbon atom has exactly unit π electron charge according to the simple Hückel theory.

From Cauchy's inequality

$$\left(\sum_i^{\text{occ}} c_{ai}c_{bi}\right)^2 \leqq \left(\sum_i^{\text{occ}} c_{ai}^2\right)\left(\sum_i^{\text{occ}} c_{bi}^2\right),$$

we obtain

$$p_{ab}^2 \leqq q_a q_b = 1,$$

namely

$$|p_{ab}| \leqq 1. \tag{27.9}$$

This means that no bond in an alternant hydrocarbon can have more double-bond character than the C—C bond in ethylene.

Now let us consider the effect of a small change of the Coulomb integral of atom a in an alternant hydrocarbon. This change

$$\alpha_a \rightarrow \alpha_a + \delta\alpha_a$$

can be caused by a change of attached atom or group (e.g., $H \rightarrow CH_3$) or by introduction of a hetero atom in the ring (e.g., $CH \rightarrow N$). This causes a change of electron density on atom b and this is given, to the first order, by

$$\delta q_b = \frac{\partial q_b}{\partial \alpha_a}\,\delta\alpha_a \equiv \pi_{ba}\delta\alpha_a. \tag{27.10}$$

The newly defined quantity π_{ba} is called the mutual atom polarizability and the following relation holds [cf. (26.11)]:

$$\pi_{ba} \equiv \frac{\partial q_b}{\partial \alpha_a} = \frac{\partial^2 E}{\partial \alpha_a\,\partial \alpha_b} = \frac{\partial q_a}{\partial \alpha_b} \equiv \pi_{ab}. \tag{27.11}$$

In words, a change in α_a produces the same change in charge density at atom b as a similar change at atom b would produce at atom a.

By the perturbation calculation, we can calculate δq_b or π_{ba}. When the one-electron operator is changed from h_{eff} to $h_{\text{eff}} + \Delta V$, the new MO can be expressed as

$$\psi_i = \psi_i{}^0 + \sum_{j(\neq i)} \lambda_{ij} \psi_j{}^0, \tag{27.12}$$

where $\psi_j{}^0$'s are unperturbed MO's and

$$\lambda_{ij} = \frac{(\psi_j{}^0 | \Delta V | \psi_i{}^0)}{\varepsilon_i{}^0 - \varepsilon_j{}^0} = \sum_{b,c} c_{bj}^0 c_{ci}^0 \frac{(\chi_b | \Delta V | \chi_c)}{\varepsilon_i{}^0 - \varepsilon_j{}^0}. \tag{27.13}$$

We assume that we may neglect the effect of ΔV except that on α_a and thus we write

$$(\chi_b | \Delta V | \chi_c) = \delta\alpha_a \delta_{ab} \delta_{ac}, \tag{27.14}$$

$$\lambda_{ij} = c_{aj}^0 c_{ai}^0 \frac{\delta\alpha_a}{\varepsilon_i{}^0 - \varepsilon_j{}^0}. \tag{27.15}$$

The perturbed charge density at atom b is expressed as

$$q_b = \sum_i^{\text{occ}} 2[c_{bi}^0 + \sum_j \lambda_{ij} c_{bj}^0]^2.$$

The change in the charge density becomes, to the first order,

$$\delta q_b \equiv q_b - q_b{}^0 = 4 \sum_i^{\text{occ}} \sum_{j(\neq i)}^{\text{all}} \lambda_{ij} c_{bi}^0 c_{bj}^0.$$

Using (27.15), we obtain

$$\begin{aligned} \delta q_b &= 4\delta\alpha \sum_i^{\text{occ}} \sum_{j(\neq i)}^{\text{all}} \frac{c_{ai}^0 c_{aj}^0 c_{bi}^0 c_{bj}^0}{\varepsilon_i{}^0 - \varepsilon_j{}^0} \\ &= 4\delta\alpha \sum_i^{\text{occ}} \sum_{j(\neq i)}^{\text{occ}} \frac{c_{ai}^0 c_{aj}^0 c_{bi}^0 c_{bj}^0}{\varepsilon_i{}^0 - \varepsilon_j{}^0} \\ &\quad + 4\delta\alpha \sum_i^{\text{occ}} \sum_{j \neq i}^{\text{unocc}} \frac{c_{ai}^0 c_{aj}^0 c_{bi}^0 c_{bj}^0}{\varepsilon_i{}^0 - \varepsilon_j{}^0}. \end{aligned}$$

The first summation $\sum_i^{\text{occ}} \sum_{j \neq i}^{\text{occ}}$ vanishes, because $(c_{ai}^0 c_{aj}^0 c_{bi}^0 c_{bj}^0)/\varepsilon_i{}^0 - \varepsilon_j{}^0$ is antisymmetric with respect to the interchange $i \leftrightarrow j$. Therefore,

$$\delta q_b = 4\delta\alpha_a \sum_i^{\text{occ}} \sum_j^{\text{unocc}} \frac{c_{ai}^0 c_{aj}^0 c_{bi}^0 c_{bj}^0}{\varepsilon_i{}^0 - \varepsilon_j{}^0}. \tag{27.16}$$

As we have seen in (27.4) and (27.6), there is a one to one correspondence between occupied and unoccupied orbitals. Making use of this we can change the summation $\sum_i^{\text{occ}}\sum_j^{\text{unocc}}$ in (27.16) to the summation $\sum_i^{\text{occ}}\sum_k^{\text{unocc}}$. If atoms a and b belong to the same set, we have

$$\varepsilon_j{}^0 = -\varepsilon_k{}^0,$$

$$c_{aj}^0 c_{bj}^0 = c_{ak}^0 c_{bk}^0;$$

thus we obtain

$$\delta q_b = 4\delta\alpha_a \sum_i^{\text{occ}} \sum_k^{\text{occ}} \frac{c_{ai}^0 c_{bi}^0 c_{ak}^0 c_{bk}^0}{\varepsilon_i{}^0 + \varepsilon_k{}^0} = 4\delta\alpha_a F(c_{ai}^0 c_{bi}^0 c_{ak}^0 c_{bk}^0). \qquad (27.17)$$

Writing $c_{ai}^0 c_{bi}^0 = \xi_i$ and noticing

$$F = \frac{1}{2}\sum_i \xi_i \sum_k \frac{\partial F}{\partial \xi_k}$$

and

$$\frac{\partial^2 F}{\partial \xi_i \partial \xi_k} = \frac{1}{\varepsilon_i{}^0 + \varepsilon_k{}^0} < 0,$$

we can deduce that

$$F \equiv \sum_i^{\text{occ}} \sum_k^{\text{occ}} \frac{c_{ai}^0 c_{bi}^0 c_{ak}^0 c_{bk}^0}{\varepsilon_i{}^0 + \varepsilon_k{}^0} < 0.$$

This means

$$\delta q_b \gtrless 0, \qquad \text{when} \quad \delta\alpha_a \lessgtr 0. \qquad (27.18)$$

When atoms a and b belong to different sets,

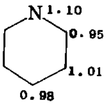
$$c_{aj}^0 c_{bj}^0 = -c_{ak}^0 c_{bk}^0,$$

and we obtain the result

$$\delta q_b \gtrless 0, \qquad \text{when} \quad \delta\alpha_a \gtrless 0. \qquad (27.19)$$

By replacing CH by more electronegative N, we have $\delta\alpha_a < 0$. Therefore the charge densities on atoms belonging to the same set as a increase, $\delta q > 0$, but on the other atoms decrease, $\delta q < 0$.

The π electron charge distribution of pyridine is illustrated below as an example:



The above result about the alternating sign of δq provides a theoretical basis for the law of alternating polarity. The latter says that, in a conjugated molecule containing one hetero atom or substituent, the atoms are alternatively more and less susceptible to anionoid or cationoid reagents.

The concepts and theories explained in Sections 26 and 27 have been developed largely by Coulson and Longuet-Higgins. For more detailed discussions, the reader is referred to their original papers (Coulson, 1940; Coulson and Rushbrooke, 1940; Coulson and Longuet-Higgins, 1947a,b; 1948a,b; Longuet-Higgins, 1950a,b).

28. Estimate of Coulomb Integrals α

As we have seen in Section 24, the basic equations in the simple Hückel theory are the secular equation (24.9) and the determinant (24.10). Once we choose our α and β parameters—evaluation of S, if we do it, being not so difficult—calculations can go straightforwards. The crucial point in this method, therefore, is how to choose α and β integrals.

Although α's and β's are usually treated as semiempirical parameters, the number of them becomes too great for this to be done if we want to deal with a fairly big heterocyclic molecule. It would be very nice if we could have an equation which predicts at least approximate values for these parameters. It may be impossible to have such an equation. At any rate, it will be worth reviewing some presently available methods to determine α's and β's.

We will take up the Coulomb integral in this section. Usually α for the carbon $2p\pi$ orbital in benzene or similar hydrocarbons is taken to be a reference point. The deviation is expressed in units of the resonance integral for such systems:

$$\alpha_a = \alpha_C + \delta_a \beta_{CC}. \tag{28.1}$$

As we have seen in (27.2), α_C can be absorbed in the orbital energy ε' when the overlap integrals are neglected.

(*a*) *Purely Empirical Method.* Let us take the nitrogen atom as our example.

(*a*1) The original suggestion was made by Wheland and Pauling (1935),

$$\delta_N \fallingdotseq 2;$$

(*a*2) Löwdin (1951) recomended the value

$$\delta_N = 0.6$$

on the ground that it leads to the correct dipole moment of pyridine;

(*a*3) Orgel and others (1951) reached

$$\delta_N = 1.0$$

on the same ground as Löwdin's; this criterion is not decisive, for it depends on the value assigned to the dipole moment due to the σ electrons;

(*a*4) Hameka and Liquori (1958) proposed

$$\delta_N = 0.4,$$

by estimating the σ contributions to dipole moments carefully and fitting their value for a number of N-containing heterocyclics;

(*a*5) Lofthus (1959) concluded that

$$\delta_N = 0.9 \sim 1.0, \qquad \text{for nitrogen in six-membered ring,}$$

and

$$\delta_N = 1.8 \sim 2.0, \qquad \text{for nitrogen in pyrrole,}$$

by using the bond-order bond-length relation in fitting calculated bond-length with observed data.

(*b*) *Estimate from Electronegativities.*

(*b*1) Sandorfy (1949) proposed the formula

$$\alpha_a = \alpha_C \frac{\chi_a}{\chi_c},$$

where χ denotes the electronegativity of the atom; if we assume $\alpha_C = -11.4$ eV, $\beta_{CC} = -2.8$ eV, this relation gives $\delta_N \fallingdotseq 0.8$;

(*b*2) Mulliken (1949) suggested the relation

$$\delta_a = K(\chi_a - \chi_c)$$

where K is a constant;

(*b*3) Laforgue (1949) claimed that if we take Pauling's scale for electronegativities, we can take $K = 1$, namely

$$\delta_a = \chi_a - \chi_c;$$

according to this, we get $\delta_N = 0.5$.

(*c*) *Estimate from Ionization Potentials.* Spanjaard and Berthier (1961) made an estimate of α by simply putting it equal to the ionization potential with sign reversed of an electron in that orbital,

$$\alpha_a = -I_a.$$

The ionization potential of a π electron in the valence state (tr tr tr π) was taken to be 11.54 eV and the standard C—C resonance integral to be -2.06 eV. Thus we have

$$\delta_a = \frac{I_a - 11.54}{2.06}.$$

This gives

$$\delta_N \text{ (pyridine)} \fallingdotseq 0.4$$

and

$$\delta_N \text{ (pyrrole)} \fallingdotseq 1.0.$$

Ohno and others (1963) modified the above procedure slightly and α was equated to an electron affinity for empty AO's (e.g., $4s$ and $4p$ of Fe^{++}).

If we try to sum up the situation in a word, it is a mess. In 1947, Coulson and Longuet-Higgins (1947a) stated: "α_r is the energy of an electron confined to nucleus r. ... It is not possible at present to calculate this energy with any accuracy." In 1965, the situation has hardly changed. The difficulty arises from the fact that we do not know the exact nature of h_{eff}. Sometimes it is assumed that h_{eff} is a Hartree–Fock single-body operator for a molecule. This would certainly give a rather good charge distribution in the molecule. However, as we have seen in Section 16, the total energy and excitation energies cannot be expressed as the simple forms of (24.4) and (24.5). The safest way is to treat them as purely empirical parameters and to be prepared to use different values for discussing different molecular properties.

29. Estimate of Resonance Integrals β

The situation here seems to be a little better. One reason is that molecular properties such as charge distribution depend less sharply on β than on differences in α.

(*a*) *Purely Empirical Method.* A typical example of this is due to Hückel himself (1931, 1932). He calculated resonance energies[16] of some

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[16] The resonance energy is defined as the amount of energy lowering of a molecule below that of its most stable valence bond structure. It is a widely used and useful quantity but is not physically observable. In comparing the resonance energy with experimental data, the compression energy due to the change of bond length should also be taken into account.

hydrocarbon molecules and obtained the results shown in Table XVI.

TABLE XVI

RESONANCE ENERGIES OF SOME HYDROCARBONS

Molecule	Empirical[a] (kcal/mole)	Calculated	β (kcal/mole)
Benzene	37	-2.00β	-19
Naphthalene	75	-3.68β	-20
Anthracene	105	-5.32β	-20
Phenanthrene	111	-5.45β	-20

[a] Empirical resonance energies can be estimated by using the heats of combustion of the molecule and an assigned bond energy of each bond.

(*b*) *Estimate from Overlap Integrals.* Wheland (1942) proposed the formulas:

$$\beta_{ab} = \beta_{\mathrm{CC}} \frac{S_{ab}}{S_{\mathrm{CC}}}. \tag{29.1}$$

The AO's χ_a and χ_b should not differ too much from the carbon $2p\pi$ orbital. The definition of β_{ab} itself suggests the proportionality

$$\beta_{ab} = \int \chi_a h_{\mathrm{eff}} \chi_b \, dv \sim \int \chi_a \chi_b \, dv = S_{ab},$$

and (29.1) is used very widely.

(*c*) *Estimate from the Bond Energies of Single and Double Bonds.* This is due to Lennard-Jones (1931) and is based on the idea that 2β is a measure of the difference between the energy of a double bond and a single bond.

Denoting the bond energy of a single bond between atoms *a* and *b* as E_{ab}^s and so on, we have the formula

$$\beta_{ab} = \frac{E_{ab}^d - E_{ab}^s}{E_{\mathrm{CC}}^d - E_{\mathrm{CC}}^s} \beta_{\mathrm{CC}}. \tag{29.2}$$

If we apply this to a C—N bond, we obtain the result $\beta_{\mathrm{CN}} \approx \beta_{\mathrm{CC}}$.

(*d*) *The Wolfsberg-Helmholz Approximation.* In this approximation, the resonance integrals are estimated by

$$\beta_{ab} = K S_{ab} \frac{\alpha_a + \alpha_b}{2}, \tag{29.3}$$

where the constant K is 2 for a π bond and 1.67 for a σ bond. Wolfsberg and Helmholz (1952) found this formula adequate in their study of the energy levels of homonuclear diatomic molecules of first- and second-row elements. Unfortunately the details of the calculations are not published. The basis of this approximation therefore remains not quite clear but this is certainly very convenient in reducing the number of unknown parameters. One difficulty about this formula is that the resulting orbital energies depend on the choice of the reference point in energy. In other words, the transformation

$$h_{\text{eff}} \rightarrow h_{\text{eff}} + k,$$

where k is a constant, does not cause the result

$$\varepsilon_l \rightarrow \varepsilon_l + k$$

as it should. If we require this property, the constant K should be unity.

In conclusion, we have to say again that the method of estimating resonance integrals has not been established.

V. The Validity of the σ–π Separation

30. Charge Distribution of σ and π Electrons

Coulson *et al.* (1952) calculated the electron density in benzene in the plane 0.35 Å above the molecular plane. They did it for σ electrons and π electrons separately and compared the results. They found that there is only a very small region, directly above each of the six carbon nuclei, where the charge density of the π electrons is as great as that of the σ electrons. This means that the π electron charge cloud does overlap considerably with that of σ electrons. Under these circumstances, it is very natural to think that any change of π electronic state—e.g., excitation of an electron to a higher orbital—would cause some change of the σ part. Thus this calculation threw a considerable doubt on the validity of the σ–π separation.

31. Calculations without the σ–π Separation

Altmann (1952) made a calculation on C_2H_4 without the σ–π separation. His calculation is based on the valence bond method or the Heitler–London–Slater–Pauling method and the σ–π resonance effect is taken into account. The 1*s* electrons of carbon are shrunk into the nuclei as usual. More drastic approximations are that ionic structures are neglected and orthogonality between AO's is assumed.

His conclusion is that the usual π electron approximation is by no means satisfactory. He observed that the σ–π resonance effect is particularly important in the excited states. However, since his calculations are so approximate, especially in that no ionic structures are included, it is difficult to judge whether his conclusions can be trusted.

The contrary conclusion was reached by Moser (1953). Again the ethylene molecule is treated but by the MO method this time. Besides two π electrons, two σ electrons which take part in the C—C bonding are taken into account. Assigning the four electrons in the four MO's available, eight wave functions belonging to ^1A_g are obtained. Estimating the diagonal elements of the Hamiltonian with respect to these eight wave functions, Moser concluded that the effect of σ excitations should be very small in the ground state. Ross (1952) made a similar investigation on C_2H_2. He also concluded that the effect of σ excitation is small.

Parks and Parr (1960) made a detailed investigation on H_2CO, treating it as a six-electron problem. They adjusted the σ wave function to the π wave function and then vice versa until they reached self-consistency. Their conclusion is that the fixed σ part assumption may lead to only small errors in energies but is not always good in determining wave functions.

All these investigations have been carried out on simple molecules. The σ–π configuration interaction would become more important when the number of atoms in the system becomes large. This means the σ–π separation is more doubtful for bigger molecules.

The soundness of π electron approximation which is accepted and proved to be so useful in organic chemistry remains to be justified theoretically in the future.

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Quantum Theory of Time-Dependent Phenomena Treated by the Evolution Operator Technique*

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I. Introduction

In science one of the most important goals is to explain all the numerous phenomena in nature of varying character by means of a few basic principles, i.e., to reduce complexity to simplicity. Several times in history, the development of science has reached such stages that one has believed that the highest degree of simplicity has actually been achieved. Two important examples are provided by Aristotle's philosophy and Newton's mechanics, but further development has shown that these epochs did not represent final stages but essential "plateaus" in the development of science. The natural sciences of today are essentially built on modern quantum theory and, even if the basic principles have now a higher degree of simplicity than ever before, there are no real reasons for believing that one has actually reached the "final" stage. Keeping this important fact in mind, one may still find it very interesting to investigate the present "plateau" and to study how far modern quantum theory is able to explain the basic phenomena in nature.

A. Classical Mechanics

In order to understand the principles of modern quantum theory, it may be worthwhile to study the breakdown of classical physics and the development of the new ideas. At the end of the last century, the mechanical model of the world was dominating physics, and the universe was assumed to consist of a number of particles moving with respect to each other in accordance with the laws of Newton's dynamics:

$$m_k \frac{d^2\mathbf{r}_k}{dt^2} - \mathbf{K}_k, \tag{1}$$

where t is the time, m_k and $\mathbf{r}_k = (x_k, y_k, z_k)$ are the mass and position of particle k, respectively, whereas $\mathbf{K}_k$ is the force on this particle. The basic laws are hence second-order differential equations in time. Introducing the velocity $\mathbf{v}_k = d\mathbf{r}_k/dt$ and the momentum $\mathbf{p}_k = m_k\mathbf{v}_k$, one can also write (1) in the form:

$$\mathbf{p}_k = m_k \frac{d\mathbf{r}_k}{dt}, \qquad \frac{d\mathbf{p}_k}{dt} = \mathbf{K}_k, \tag{2}$$

i.e., as a system of first-order equations in time. If in a given moment $t = t_0$, one knew the position and the momentum of each one of the particles:

$$\mathbf{r}_k = \mathbf{r}_k(0), \qquad \mathbf{p}_k = \mathbf{p}_k(0), \tag{3}$$

it would be possible to predict the future of the entire universe as well as its past history. This is the basis for the completely deterministic mechanical model of the physical world, which left a very small margin for man and his free will—if any margin at all.

If the system has a potential $U = U(\mathbf{r}_1, \mathbf{r}_2, \ldots)$ from which the forces may be derived so that $\mathbf{K}_k = -\text{grad}_k U = -\nabla_k U$, the classical Hamiltonian takes the form

$$H = \sum_k \frac{\mathbf{p}_k{}^2}{2m_k} + U, \tag{4}$$

and the equations of motion (2) may then be written in the form

$$\frac{d\mathbf{r}_k}{dt} = \frac{\partial H}{\partial \mathbf{p}_k}, \qquad \frac{d\mathbf{p}_k}{dt} = -\frac{\partial H}{\partial \mathbf{r}_k}, \tag{5}$$

which may be extended also to more general coordinates. The Hamiltonian $H = H(\mathbf{r}_k, \mathbf{p}_k)$ satisfies the relation $dH/dt = 0$ and is hence a constant of motion representing the total energy E of the system:

$$H = E. \tag{6}$$

B. Maxwell's Equations

During the nineteenth century, the theory of electricity and magnetism went through a rapid development leading to the establishment of Maxwells' equations:

$$\begin{aligned} \operatorname{div} \mathbf{E} &= 4\pi\rho, & \operatorname{div} \mathbf{H} &= 0, \\ \operatorname{curl} \mathbf{E} &= -\frac{1}{c}\frac{\partial \mathbf{H}}{\partial t}, & \operatorname{curl} \mathbf{H} &= \frac{4\pi}{c}\mathbf{j} + \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t}, \end{aligned} \tag{7}$$

where ρ and $\mathbf{j}$ are the charge and current density, respectively. The force on a volume element exerted by the electromagnetic field is given by the force density:

$$\mathbf{k} = \rho\mathbf{E} + \frac{1}{c}\mathbf{j} \times \mathbf{H}, \tag{8}$$

and the behavior of a system of charged particles is then regulated by a combination of Maxwell's equations and the classical laws of motion.

C. The Quantum Postulate

The success of this electrodynamics was enormous and of essential importance not only for the scientific but also for the technical development. Under these circumstances, it is rather remarkable that, at the end of the century, there was still a rather simple phenomenon to be explained, namely the temperature radiation from an ordinary black body. It was shown by Max Planck in 1900 that all the various experimental experiences could be explained from one and the same formula, if one made the rather drastic assumption that the energy of an oscillating electric particle had to be an integer multiple of a "quantum of energy" $h\nu$ proportional to the frequency ν of the particle. The proportionality factor h has been called Planck's constant and has the value $h = 6.625_2 \times 10^{-27}$ erg sec, which is an exceedingly small number from the macroscopic point of view. Planck soon realized that the quantum postulate would lead to a new way of thinking in physics and that a complete reformulation of the basic laws would be needed.

The next step in the development followed when Albert Einstein in 1905 in one and the same volume of *Annalen der Physik* published three papers in three different fields, each one representing a more or less complete turning point in its area. The papers treated the special theory of relativity including the law of the equivalence between mass and energy, $E = mc^2$, the photoelectric effect, and the Brownian motion. In connection with the explanation of the threshold phenomenon in the photoelectric effect, Einstein assumed that the electromagnetic field was quantized and occurred in the form of "wave packets" or photons having the energy $E = h\nu$, where ν is the frequency of the radiation.

D. Bohr's Atomic Model

The success of these ideas made it likely that the quantum postulate would be of importance also in many other phenomena associated with the atomic structure of matter. It should be remembered that, for both chemists and physicists, the atom had until the end of the nineteenth century been "undividable" by definition. However, after the discovery of radioactive decay and the transformation of one atom into another, the circumstances were changed. Thomson's discovery of the electron cathode rays in 1897 and Rutherford's results as to the scattering of alpha particles in matter in 1911 led the latter to propose a model in which an atom consists of electrons moving around a small positively charged "nucleus" carrying the main part of the atomic mass.

The quantum postulate was introduced into this atomic model by Niels Bohr in 1913. He had discovered that an angular momentum has the same dimensions ML^2T^{-1} as Planck's quantum of action h, and he introduced the postulate that the electrons in an atom could move only in certain selected circles around the nucleus fulfilling the condition

$$pa = n\frac{h}{2\pi}, \tag{9}$$

where p is the momentum of the electron, a is the radius of the circle, and $n = 1, 2, 3, \ldots$. Bohr assumed that each circle represented a "stationary state," with a specific energy, in which the electron does not emit any electromagnetic radiation, and further that, if the electron jumps from one circle to another, the atom emits radiation with a frequency ν determined by Planck's law, i.e., $h\nu = E_1 - E_2$. This simple picture combined with the laws of classical mechanics:

$$\frac{e^2}{a^2} = \frac{p}{ma}, \qquad E = \frac{p_2}{2m} - \frac{e^2}{a}, \tag{10}$$

where e is the fundamental charge, leads immediately to an explanation of the spectrum of the hydrogen atom, to a derivation of the famous Rydberg constant in spectroscopy, and to an understanding of many related phenomena. Bohr's discovery opened the new field of atomic structure, and its importance for the development of modern science can hardly be overestimated.

Bohr later generalized his atomic model so that it became similar to a planetary system in miniature with the electrons moving in ellipses characterized by three quantum numbers (n, l, m). In 1918 Sommerfeld studied the corrections in this model required by the special theory of relativity and could explain also the fine structure of the hydrogen spectrum. This is a good example of a "perfect model" which still has only limited validity.

Using the three quantum numbers (n, l, m), the rules

$$\begin{aligned} n &= 1, 2, 3, 4, \ldots, \\ l &= 0, 1, 2, \ldots n-1, \\ m &= l, l-1, l-2, \ldots -l+1, -l, \end{aligned} \tag{11}$$

and Pauli's exclusion principle saying that each ellipse (n, l, m) could contain a maximum of two electrons, Bohr and his Copenhagen school reached in the beginning of the 1920's a new understanding of the periodic system of the elements which led, among other things, to the discovery of a new element (Hf). Using the simple rules that, with increasing atomic number the ellipses are filled by one and two electrons after increasing values of first $(n + l)$ and then n, one could also explain the occurrence of the groups of transition metals and rare earth metals which differ only in so-called "inner shells."

Bohr's atomic model was constructed for the hydrogen atom and, even if all attempts to generalize it to give a reasonable quantitative treatment of even the helium atom so far have failed, it gives apparently a good qualitative understanding of the entire periodic system.

E. Matter Waves

A second epoch in quantum mechanics started in 1924 with the introduction of the "matter waves" by Louis de Broglie. In his theory of the photoelectric effect, Einstein had in 1905 assumed that the electromagnetic waves were quantized in form of "wave packets" or photons having the energy $E = h\nu$, so that there existed a wave-corpuscle parallellism. Each photon has a vanishing rest mass and a relativistic mass m determined by Einstein's relation $E = mc^2$, where c is the velocity of light. Since $c = \nu\lambda$ is also the velocity of the wave packet, the photon has a momentum $p = mc$, for which one obtains the transformation

$$p = mc = \frac{mc^2}{c} = \frac{E}{c} = \frac{h\nu}{\lambda\nu} = \frac{h}{\lambda}, \tag{12}$$

where λ is the wavelength of the radiation. Generalizing this idea, de Broglie assumed that the wave-corpuscle parallellism was universal, and that the frequency ν and the wavelength λ of the "matter waves" were given by the same relations:

$$E = h\nu, \qquad p = h/\lambda. \tag{13}$$

He showed that these relations are relativistically invariant and further that they lead to a new understanding of Bohr's quantum condition (9), since substitution of $p = h/\lambda$ into (9) gives $2\pi a = n\lambda$; i.e., a circle will be associated with a stationary state if and only if it contains an integer number of waves, so that the wave pattern is unique. In this way, de Broglie obtained an explanation of Bohr's otherwise rather arbitrary "quantum rule."

Introducing the relativistic mass m and the velocity v of the particle and using the relations $E = mc^2$ and $p = mv$, one finds that matter waves have a phase velocity $\omega = \nu\lambda = E/p = c^2/v$, which must necessarily exceed the speed of light. The phase α of a de Broglie wave traveling along an x axis at the time t is given by the expression

$$\alpha = 2\pi\left(\frac{x}{\lambda} - \nu t\right). \tag{14}$$

For a wave packet having reciprocal wavelengths or wave numbers $k = 1/\lambda$ in the interval (k; $k + dk$) and frequencies in the interval (ν; $\nu + d\nu$), the phases are situated in the interval (α; $\alpha + d\alpha$) with $d\alpha = 2\pi(x dk - t d\nu)$. A "group" of waves is essentially characterized by the relation $d\alpha = 0$; i.e., it travels along the x axis with a constant phase. For the "group velocity" $g = x/t$, one obtains directly

$$g = \frac{d\nu}{dk} = \frac{d(\omega/\lambda)}{d(1/\lambda)} = \omega - \lambda\frac{d\omega}{d\lambda}, \tag{15}$$

which is a classical formula used also in hydrodynamics, in studying ocean waves, for example. Using (13), one can also write it in the simple form $g = dE/dp$. From the relation $m = m_0(1 - v^2/c^2)^{-1/2}$, where m_0 is the rest mass of the particle, follows the relativistic identity $(E/c)^2 - p^2 = m_0c^2$ and, further,

$$g = \frac{dE}{dp} = \frac{pc^2}{E} = \frac{mvc^2}{mc^2} = v. \tag{16}$$

Hence the group velocity of the de Broglie waves is identical with the velocity of the particle.

F. Wave Mechanics

In 1925 modern quantum theory was introduced independently in three different ways by Schrödinger, Heisenberg, and Dirac, respectively. In generalizing de Broglie's ideas, Schrödinger pointed out that the behavior of waves is usually regulated by a wave equation. According to (14) and (13), the phase of a matter wave is given by the expression

$$\alpha = 2\pi(px - Et)/h. \tag{17}$$

The physicists and engineers had previously been interested essentially in "real waves" of the type cos α or sin α, but, in many fields, e.g., the theory of alternating currents, it had turned out to be mathematically convenient to deal with "complex waves" according to Euler's formula $e^{i\alpha} = \cos\alpha + i\sin\alpha$ and to take the real component only at the end. Anyway, Schrödinger started his work by considering the *complex wave*:

$$\Psi(x, t) = A\exp(i\alpha) = A\exp\left[\frac{2\pi i}{h}(px - Et)\right]. \tag{18}$$

Taking the partial derivatives with respect to x and t, he obtained the relations

$$\frac{\partial\psi}{\partial x} = \frac{2\pi i}{h}p\psi, \qquad \frac{\partial\psi}{\partial t} = -\frac{2\pi i}{h}E\psi, \tag{19}$$

which led him to postulate the connections

$$p \rightarrow \frac{h}{2\pi i}\frac{\partial}{\partial x}, \qquad E \rightarrow -\frac{h}{2\pi i}\frac{\partial}{\partial t}, \tag{20}$$

representing physical quantities by *linear operators*. In order to proceed, Schrödinger started from the classical laws of motion in the Hamiltonian form (6) or $(H - E) = 0$ and postulated the existence of a *wave equation* of the form $(H - E)\Psi = 0$, where the classical quantities are replaced by operators according to (20). The basic Schrödinger equation hence has the form

$$\boxed{H_{\text{op}}\Psi = -\frac{h}{2\pi i}\frac{\partial\Psi}{\partial t}} \tag{21}$$

where H_{op} is the Hamiltonian operator obtained from the classical Hamiltonian by means of (20) or the more general relation:

$$\mathbf{p} \rightarrow \frac{h}{2\pi i}\left(\frac{\partial}{\partial x_k}, \frac{\partial}{\partial y_k}, \frac{\partial}{\partial z_k}\right) = \frac{h}{2\pi i}\nabla_k, \tag{22}$$

and Ψ is the "wave function" in the configuration space $(\mathbf{r}_1, \mathbf{r}_2, \ldots)$. Hence from (4) one obtains the following operator:

$$H_{\text{op}} = \sum_k \frac{1}{2m_k} \nabla_k{}^2 + U, \tag{23}$$

where $\nabla_k{}^2 = \partial^2/\partial x_k{}^2 + \partial^2/\partial y_k{}^2 + \partial^2/\partial z_k{}^2$ is the Laplace operator for the particle k.

The Schrödinger equation (21) is a "diffusion equation" of a type studied also for a long time in classical physics, and it permits separation of the coordinates $\mathbf{r}_1, \mathbf{r}_2, \ldots$ from the time variable t. Putting $\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots; t) = \Phi(\mathbf{r}_1, \mathbf{r}_2, \ldots)g(t)$, one obtains $[H\Phi]g = \Phi[-(h/2\pi i)(\partial g/\partial t)]$ and, after division by Ψ,

$$\frac{H\Phi}{\Phi} = -\frac{\dfrac{h}{2\pi i}\dfrac{dg}{dt}}{g}, \tag{24}$$

where the left-hand member depends only on the coordinates and the right-hand member only on the time variable t; both must hence be equal to a constant E'. The function g has consequently the form $g(t) = g_0 \exp(-2\pi i E't/h)$, whereas Φ must satisfy the differential equation

$$H\Phi = E'\Phi, \tag{25}$$

which has the form of an *eigenvalue problem*. The intensity $|\Psi|^2$ of the wave was interpreted by Schrödinger as proportional to the particle density of the system in the configuration space $(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots)$ at the time t, and this quantity should hence be integrable over the entire space or, at least, stay finite even at infinity. The differential equation (25) certainly has solutions for all values of E' but, of all these solutions, only a few satisfy the physical *boundary conditions* associated with Schrödinger's interpretation of Ψ. This leads to a natural quantization of the energy E' without any integer rules.

The solutions connected with the separability condition have the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots; t) = \Phi(\mathbf{r}_1, \mathbf{r}_2, \ldots)g_0 \exp\left(-\frac{2\pi i}{h} E't\right), \tag{26}$$

and, for the associated intensity, one obtains

$$|\Psi(r_1, \mathbf{r}_2, \ldots; t)|^2 = |g_0|^2 \, |\Phi(\mathbf{r}_1, \mathbf{r}_2, \ldots)|^2, \tag{27}$$

which implies that the particle density is *independent of time* and that the solutions correspond to "stationary states" in the sense of Bohr. From the Schrödinger equation (21) follows hence the existence of the stationary states provided that the eigenvalue problem (25) has solutions corresponding to the proper physical boundary conditions which apparently replace the previous "quantum conditions."

One of the most interesting aspects of the Schrödinger equation (21) is the fact that it is of *first order* in the time variable t in contrast to the second-order Newton equation (1). In some way, it must instead be analogous to the classical first-order system (2) in the variables $\mathbf{r}_1, \mathbf{r}_2, \ldots$ and $\mathbf{p}_1, \mathbf{p}_2, \ldots$, and it seems likely that the complex wave function $\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots; t)$, which consists of a pair of real functions, will give information about the physical situation not only in the coordinate space $(\mathbf{r}_1, \mathbf{r}_2, \ldots)$ but also in the momentum space $(\mathbf{p}_1, \mathbf{p}_2, \ldots)$. This problem will be discussed in greater detail in the following section.

The existence of the "matter waves" was shown experimentally in 1926 by Davison and Germer. Schrödinger showed further that his momentum operator $p = (h/2\pi i)(\partial/\partial x)$ satisfied the commutation relation

$$px - xp = \frac{h}{2\pi i}, \tag{28}$$

which had basic importance in the matrix mechanics developed by Heisenberg, Born, and Jordan and in the q number theory developed by Dirac, and that the three formulations of the new quantum theory were essentially equivalent. The time had now come for a complete reformation of the basic laws of physics and chemistry.

II. Coordinate Space and Momentum Space; Phase Problem in Quantum Mechanics

A. Fourier Transformation

Let us start by considering a single particle in a one-dimensional space with the coordinate x. The physical situation is characterized by a complex wave function $\psi = \psi(x, t)$, in which the variable t will be temporarily suppressed. Such a wave function may be resolved into harmonic waves with the wave number $k = 1/\lambda$ by means of the formulas

$$\begin{aligned} \psi(x) &= \int_{-\infty}^{+\infty} \eta(k) e^{2\pi i k x}\, dk, \\ \eta(k) &= \int_{-\infty}^{+\infty} \psi(x) e^{-2\pi i k x}\, dx, \end{aligned} \tag{29}$$

and the functions $\psi(x)$ and $\eta(k)$ are said to be related by a Fourier transformation. According to the de Broglie relations (13), one may introduce the momentum p by the formula $p = h/\lambda = hk$ and, putting $\varphi(p) = h^{-1/2}\eta(k)$ one obtains

$$\begin{aligned} \psi(x) &= h^{-1/2} \int_{-\infty}^{+\infty} \varphi(p) \exp\left(\frac{2\pi i}{h} px\right) dp, \\ \varphi(p) &= h^{-1/2} \int_{-\infty}^{+\infty} \psi(x) \exp\left(-\frac{2\pi i}{h} px\right) dx. \end{aligned} \tag{30}$$

It is evident that $\psi(x)$ and $\varphi(p)$ in these reciprocal formulas are completely equivalent and, since $|\psi(x)|^2$ is assumed to be proportional to the particle or "probability" density in the x space, it seems natural to interpret $|\varphi(p)|^2$ as proportional to the probability density in the p space.

From the Fourier transformation (3) follows immediately

$$\int_{-\infty}^{+\infty} |\varphi(p)|^2 \, dp = \int_{-\infty}^{+\infty} |\psi(x)|^2 \, dx; \tag{31}$$

i.e., the normalization integrals in the x space and the p space are the same. In the following, we will assume that these quantities are equal to unity. The average position x of the particle is then given by the expression

$$\bar{x} = \int_{-\infty}^{+\infty} x|\psi|^2 \, dx = \int_{-\infty}^{+\infty} \psi^* x \psi \, dx, \tag{32}$$

and, for an arbitrary function $f(x)$, one has similarly

$$f(x) = \int_{-\infty}^{+\infty} f(x)|\psi|^2 \, dx = \int_{-\infty}^{+\infty} \psi^* f(x) \psi \, dx. \tag{33}$$

The probability that the particle has a momentum in the interval $(p, p + dp)$ is given by the quantity $|\varphi(p)|^2 dp$, and the average momentum p is defined by the relation:

$$\bar{p} = \int_{-\infty}^{+\infty} p|\varphi(p)|^2 \, dp = \int_{-\infty}^{+\infty} \varphi^* p \varphi \, dp. \tag{34}$$

From the Fourier transformation (30) follows:

$$\frac{\partial \psi(x)}{\partial x} = h^{-1/2} \int_{-\infty}^{+\infty} \frac{2\pi i}{h} p\varphi(p) \exp\left(\frac{2\pi i}{h} px\right) dp, \tag{35}$$

and further

$$\begin{aligned}\int_{-\infty}^{+\infty} \psi^*(x) \frac{h}{2\pi i} \frac{\partial\psi(x)}{\partial x} \frac{dx}{xp} \\ &= h^{-1/2} \int_{-\infty}^{+\infty} p\varphi(p)\, dp \int_{-\infty}^{+\infty} \psi^*(x) \exp\left(\frac{2\pi i}{h} px\right) dx \\ &= \int_{-\infty}^{+\infty} \varphi^*(p) p \varphi(p)\, dp = \bar{p}.\end{aligned} \tag{36}$$

This gives the formula

$$\bar{p} = \int_{-\infty}^{+\infty} \psi^* \left(\frac{h}{2\pi i} \frac{\partial}{\partial x}\right) \psi\, dx, \tag{37}$$

which implies that p may be calculated as an average value in the x space according to (33), provided that p is replaced by an operator $(h/2\pi i)(\partial/\partial x)$ in agreement with (20). For any polynomial function $f(p)$, one finds similarly

$$\overline{f(p)} = \int_{-\infty}^{+\infty} \psi^* f\left(\frac{h}{2\pi i} \frac{\partial}{\partial x}\right) \psi\, dx. \tag{38}$$

By using the same technique, one can further show that any average value $f(x)$ in the x space may be evaluated in the p space by using the formula

$$\overline{f(x)} = \int_{-\infty}^{+\infty} \varphi^*(p) f\left(-\frac{h}{2\pi i} \frac{\partial}{\partial p}\right) \varphi(p)\, dp, \tag{39}$$

which implies that the coordinate x in the momentum space may be represented by the operator

$$x \rightarrow -\frac{h}{2\pi i} \frac{\partial}{\partial p} \tag{40}$$

in analogy to the first relation in (20).

Using the operator relations, one may finally define the average value of a polynomial function $f(x; p)$ of both variables x and p, and it turns out that it is irrelevant if the evaluation is carried out in the x space or in the p space as long as one strictly observes the order of all factors and the validity of the commutation relation (28).

B. Scalar Products and Adjoint Operators

If F is a linear operator in the symbols x and p, one defines finally its *expectation value* in the physical situation characterized by the normalized wave function ψ by the relation

$$\bar{F} = \int_{-\infty}^{+\infty} \psi^* F_{\text{op}} \psi \, dx. \tag{41}$$

For the sake of brevity we will in the following use the Dirac bracket symbol for the "scalar product" of two wave functions ψ_1 and ψ_2 considered as "vectors":

$$\langle \psi_1 | \psi_2 \rangle = \int_{-\infty}^{+\infty} \psi_1^* \psi_2 \, dx, \tag{42}$$

and remember that the same quantity by the mathematicians are denoted by (ψ_2, ψ_1), so that one has the translation $(\psi_2, \psi_1) = \langle \psi_1 \mid \psi_2 \rangle$.

The quantity $\|\psi\| = \langle \psi \mid \psi \rangle^{1/2}$ is said to represent the *length* of the vector ψ, and one has $\|\psi\| \geq 0$. The normalization implies $\|\psi\| = 1$. By considering the discriminant of the quadratic form $\|\psi_1 + \mu\psi_2\|^2 \geq 0$ in the real variable μ, one can easily prove Schwarz's inequality

$$|\langle \psi_1 | \psi_2 \rangle|^2 \leq \langle \psi_1 | \psi_1 \rangle \langle \psi_2 | \psi_2 \rangle. \tag{43}$$

Instead of (41), one can now write

$$\bar{F} = \langle \psi | F\psi \rangle = \langle \psi | F | \psi \rangle, \tag{44}$$

where, in the last form, one has introduced a "dummy" bar for the sake of symmetry. A wave function ψ for which $\|F\psi\|$ exists is said to belong to the *domain* D_F of the operator F.

Expectation values are in general complex quantities. Two operators F and $F^\dagger$ with the same domain which always have *complex conjugate* expectation values, so that

$$\langle \psi | F^\dagger | \psi \rangle = \langle \psi | F | \psi \rangle^* \tag{45}$$

for all ψ in D_F, are said to form *a pair of adjoint operators*. From definition (45), one obtains after some simple algebraic manipulations, the "turnover rule":

$$\begin{aligned} \langle \psi_1 \mid F^\dagger \mid \psi_2 \rangle &= \langle \psi_2 \mid F \mid \psi_1 \rangle^* \\ &= \langle F\psi_1 \mid \psi_2 \rangle, \end{aligned} \tag{46}$$

provided that both ψ_1 and ψ_2 belong to the domain of F. By means of (46), it is then easy to prove the two basic rules $(F_1 + F_2)^\dagger = F_1{}^\dagger + F_2{}^\dagger$ and $(F_1 F_2)^\dagger = F_2{}^\dagger F_1{}^\dagger$.

Of particular importance in physics are such operators A as always have *real expectation values*. In such a case, the operator is identical with its adjoint so that $A^\dagger = A$, and such an operator is said to be self-adjoint or hermitean. It is easily shown that both the position x and the momentum p are represented by hermitean operators and, by using the rules for forming the adjoint, one can then test whether an operator $F = F(x, p)$ is self-adjoint or not.

The properties of the scalar product and the concept of adjoint and self-adjoint operators are here only briefly reviewed, and for a more complete treatment we will instead refer to the many special papers on these subjects (von Neuman, 1932; Stone, 1932; Riesz and Sz.-Nagy, 1955).

C. Uncertainty Relations

The accuracy of a simultaneous measurement of the position x and the momentum p of a particle in a physical situation characterized by the wave function $\psi(x)$ in x space or its analog $\varphi(p)$ in p space may be characterized by the two quantities Δx and Δp defined by the relations

$$(\Delta x)^2 = \int_{-\infty}^{+\infty} (x - \bar{x})^2 |\psi|^2 \, dx, \tag{47}$$

$$(\Delta p)^2 = \int_{-\infty}^{+\infty} (p - \bar{p})^2 |\varphi|^2 \, dx. \tag{48}$$

They give a measure of the quadratic deviation of x and p from the average values $\bar{x}$ and $\bar{p}$, respectively.

Let us now consider the integral

$$I \equiv \int_{-\infty}^{+\infty} |(x - \bar{x})\psi + i\mu(p_{\mathrm{op}} - \bar{p})\psi|^2 \, dx \geq 0, \tag{49}$$

which is positive for any value of the real parameter μ. By using (20), partial integration, and the commutation relation (28), one finds the transformation

$$I = (\Delta x)^2 - \frac{h}{2\pi}\mu + \mu^2(\Delta p)^2 \geq 0. \tag{50}$$

This is a quadratic form in μ which is never negative, and its discriminant $D = (h/2\pi)^2 - 4(\Delta x)^2(\Delta p)^2$ is hence always negative: $D \leq 0$. This gives the inequality

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}, \tag{51}$$

which is the famous Heisenberg's uncertainty relation for the simultaneous measurement of the position x and the momentum p of a particle.

Let us now consider two general physical quantities represented by the self-adjoint operators A and B having the expectation values $\bar{A} = \langle \psi | A | \psi \rangle$ and $\bar{B} = \langle \psi | B | \psi \rangle$, and the "uncertainties" or widths

$$\begin{aligned} \Delta A &= \|(A - \bar{A})\psi\|, \\ \Delta B &= \|(B - \bar{B})\psi\|, \end{aligned} \tag{52}$$

respectively. We note that $\Delta A = 0$ if and only if $(A - \bar{A})\psi = 0$, i.e., if ψ is a proper eigenfunction to the operator A. By using Schwarz's inequality (43) and the turnover rule (46), one obtains directly

$$\begin{aligned} \Delta A \cdot \Delta B &= \|(A - \bar{A})\psi\| \cdot \|(B - \bar{B})\psi\| \\ &\geq | \langle (A - \bar{A})\psi | (B - \bar{B})\psi \rangle | \\ &\geq | \mathscr{Im} \langle (A - \bar{A})\psi | (B - \bar{B})\psi \rangle | \\ &= \tfrac{1}{2} | (\langle A - \bar{A})\psi | (B - \bar{B})\psi \rangle - \langle (B - \bar{B})\psi | (A - \bar{A})\psi \rangle | \\ &= \tfrac{1}{2} | \langle A\psi | B\psi \rangle - \langle B\psi | A\psi \rangle | \\ &= \tfrac{1}{2} | \langle \psi | AB - BA | \psi \rangle |, \end{aligned} \tag{53}$$

which leads to the general uncertainty relation for any pair of operators A and B:

$$\Delta A \cdot \Delta B \geq \tfrac{1}{2} |\overline{(AB - BA)}|, \tag{54}$$

of which (51) is a special case. In quantum mechanics, one can hence not expect that two quantities should be simultaneously measurable unless the associated operators commute, so that $AB = BA$. However, even if the operators do not commute, there may exist special situations in which A and B are simultaneously measurable, provided that the expectation value of the commutator $(AB - BA)$ vanishes in these situations.

D. Generalizations to Several Variables

In this section, we have so far considered only a one-dimensional system, but it is now easy to generalize the results to three-dimensional systems and to several variables to treat a many-particle system in a configuration space having the composite position vector $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ and the composite momentum vector $\mathbf{P} = (\mathbf{p}_1, \mathbf{p}_2, \ldots \mathbf{p}_n)$. The Fourier transformation of the wave function $\Psi = \Psi(\mathbf{R}, t)$ is obtained by repeated use of (30) for each one of the $3N$ variables leading to the formulas

$$\begin{aligned}\Psi(\mathbf{R}, t) &= h^{-3N/2}\int_{-\infty}^{+\infty}\Phi(\mathbf{P}, t)\exp\left(\frac{2\pi i}{h}\mathbf{R}\cdot\mathbf{P}\right)(d\mathbf{P}),\\ \Phi(\mathbf{P}, t) &= h^{-3N/2}\int_{-\infty}^{+\infty}\Psi(\mathbf{R}, t)\exp\left(-\frac{2\pi i}{h}\mathbf{R}\cdot\mathbf{P}\right)(d\mathbf{R}),\end{aligned} \tag{55}$$

where

$$\begin{aligned}\mathbf{R}\cdot\mathbf{P} &= \sum_{k=1}^{N}\mathbf{r}_k\cdot\mathbf{p}_k,\\ (d\mathbf{R}) &= (d\mathbf{r}_1)(d\mathbf{r}_2)\cdots(d\mathbf{r}_N),\\ (d\mathbf{P}) &= (d\mathbf{p}_1)(d\mathbf{p}_2)\ldots(d\mathbf{p}_N).\end{aligned} \tag{56}$$

In analogy to (42), the scalar product is now defined by the relation

$$\langle\Psi_1|\Psi_2\rangle = \int_{-\infty}^{+\infty}\Psi_1^*(\mathbf{R}, t)\Psi_2(\mathbf{R}, t)(d\mathbf{R}), \tag{57}$$

where the single integral sign indicates a $3N$-dimensional integration over the entire position space. All the previous results about expectation values are now easily generalized to many-particle systems.

E. Phase Problem in Quantum Mechanics

After this preliminary discussion of the relation between the position space and momentum space, it is easier to compare the bases for classical physics and quantum mechanics. It has previously been pointed out that the Schrödinger equation (21) is a first-order differential equation in time for a complex function $\Psi = \Psi(\mathbf{R}, t)$ which depends on the position coordinate $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ alone and the time t, whereas the classical analog (2) or (5) is a system of first-order equations dealing with both $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ and $\mathbf{P} = (\mathbf{p}_1, \mathbf{p}_2, \ldots \mathbf{p}_N)$. The physical situation in the position space is fully characterized by the probability density $|\Psi(\mathbf{R}, t)|^2$, but it is clear that, at the same time, the wave function $\Psi(\mathbf{R}, t)$ must contain information about the physical situation in the momentum space. This is apparently achieved by the complex character of Ψ, i.e., by the fact that it contains two real functions, for instance, the absolute value $|\Psi|$ and the "phase" arg Ψ. This "pair" character of the wave function permits transformations between different reference schemes, and a typical example is provided by the Fourier transformation (55) which connects the **R** space with the **P** space according to the following diagram:

$$\begin{tikzcd}
 & \text{position space} & & \text{momentum space} \\
\text{Wave functions:} & \Psi(\mathbf{R},t) \arrow[rr, leftrightarrow, "\text{Fourier transformation}"] \arrow[d, dash] & & \Phi(\mathbf{P},t) \arrow[d, dash] \\
\text{Probabilities:} & |\Psi(\mathbf{R},t)|^2 \arrow[dr, dash] & & |\Phi(\mathbf{P},t)|^2 \arrow[dl, dash] \\
 & & \text{inequalities} &
\end{tikzcd} \tag{58}$$

It should be observed that, even if the wave functions Ψ and Φ are directly and uniquely connected, this is not true for the corresponding probability densities, $|\Psi|^2$ and $|\Phi|^2$, which are interrelated only through certain inequalities of the type Heisenberg's uncertainty relation (51). Since one can only measure probability distributions, one has the fundamental problem how wave functions can be determined experimentally, i. e., how one can calculate the wave function $\Psi(\mathbf{R}, t)$—or the equivalent function $\Phi(\mathbf{P}, t)$—from two compatible distributions $|\Psi(\mathbf{R}, t)|^2$ and $|\Phi(\mathbf{P}, t)|^2$. This important problem was once stated by Pauli (1933, particularly p. 98), but it does not seem to have been fully solved. One can also ask how one can measure the "phase" of the wave function, i.e., the quantity $\arg \Psi$, in a uniquely defined physical situation. We note that the classical initial condition (3), i.e., $\mathbf{R} = \mathbf{R}(0)$, $\mathbf{P} = \mathbf{P}(0)$, for $t = t_0$, in quantum mechanics corresponds to the knowledge of the complex wave function $\Psi = \Psi_0(\mathbf{R})$ for $t = t_0$.

In many situations in physics, e.g., in the treatment of stationary states with real Hamiltonians, the eigenfunctions Ψ turn out to be *real*, and the question is whether this means any loss of information. The answer is no, since the Fourier transformation (55) is still valid and leads to uniquely defined momentum functions Φ. However, since $\Psi^* = \Psi$, the second relation (55) gives $\Phi^*(\mathbf{P}) = \Phi(-\mathbf{P})$, and vice versa:

$$\Psi^*(\mathbf{R}) = \Psi(\mathbf{R}), \tag{59}$$

$$\Phi^*(\mathbf{P}) = \Phi(-\mathbf{P}). \tag{60}$$

These relations show that, for real wave functions, the probability distribution in momentum space is necessarily inversion symmetric around origin, i.e., $|\Phi(-\mathbf{P})|^2 = |\Phi(\mathbf{P})|^2$. One immediate consequence of this is, of course,

$$\overline{\mathbf{P}} = 0, \tag{61}$$

showing that the average momentum is vanishing. The use of real wave functions thus has important physical consequences and should, by no means, be considered as a matter of convenience. In connection with scattering problems and particle beams, one should observe the importance of the plane wave (18) and the de Broglie phase (17).

The phase problem is well-known from many experimental fields involving radiation, as, for example, X-ray crystallography or laser and maser technique, and it is probably of still greater importance than is now realized. In this connection, it is often convenient to distinguish between coherent and incoherent phenomena, depending on whether the relative phase differences involved are essential or not.

Let us consider a wave function $\Psi = \Psi_1 + \Psi_2$ which is a superposition of two terms, Ψ_1 and Ψ_2. For the associated probability density, one has

$$|\Psi|^2 = |\Psi_1|^2 + |\Psi_2|^2 + 2\,\mathcal{Re}\{\Psi_1{}^*\Psi_2\}, \tag{62}$$

which means that, in coherent phenomena, the probabilities are usually not additive. The last term is called the interference term and, as a typical example of coherent superposition, one can mention the diffraction patterns of electromagnetic waves in gratings, etc. In quantum chemistry, a typical example of coherent superposition of wave patterns is offered by the molecular-orbital theory of the homopolar bond (e.g., the H_2 molecule) in which the bonding orbital $(a + b)$ is the sum of the atomic orbitals involved, whereas the antibonding orbital has the form $(a - b)$. Even the change of sign of the π orbital in conjugated systems under reflection in the molecular plane is a typical phase effect.

As a contrast to the coherent phenomena, one may consider an *assembly* of similar systems having different phases. If the average value of the interference term in (62) vanishes over the assembly, one obtains

$$|\tilde{\Psi}|^2 = |\tilde{\Psi}_1|^2 + |\tilde{\Psi}_2|^2, \tag{63}$$

showing that even the probabilities in such a case become additive. Here the symbol $\sim$ indicate the formation of an average over the entire assembly. The assumption of "random phases" is of particular importance in treating the so-called transition probabilities, and we will return to these problems below.

III. Schrödinger Equation

A. Superposition Principle

A basic assumption about the Hamiltonian H in the Schrödinger equation (21) is that it is a *linear operator* satisfying the relations

$$\begin{aligned} H(\Psi_1 + \Psi_2) &= H\Psi_1 + H\Psi_2, \\ H(\alpha\Psi) &= \alpha H\Psi, \end{aligned} \tag{64}$$

where α is a complex constant. This leads to an important consequence for the solutions to (21) known as the *superposition principle*, which says that if $\Psi_1(t)$ and $\Psi_2(t)$ are two solutions corresponding to the initial function $\Psi_1(0)$ and $\Psi_2(0)$ at $t = 0$, then

$$\Psi(t) = \Psi_1(t\Psi+)_2(t) \tag{65}$$

is another solution corresponding to the initial function $\Psi(0) = \Psi_1(0) + \Psi_2(0)$. The proof follows immediately from (21) and (64). The superposition principle emphasizes a very important aspect of modern quantum mechanics, and Dirac (1935) has chosen it as the fundamental introductory principle in his book. It is essential for the interference phenomena connected with the basic properties of the "matter waves," and it will be further discussed below.

B. Continuity Equation

Let us start by considering a single particle with the charge e in a physical situation characterized by the wave function $\Psi = \Psi(\mathbf{r}, t)$. In Schrödinger's interpretation of quantum mechanics, the quantity $\rho = e|\Psi|^2$ represents the *charge density*, whereas, in Born's interpretation, the quantity $|\psi|^2$ represents the *probability density*. In both interpretations, it seems natural to require that the quantity $|\Psi(\mathbf{r}, t)|^2$ vary continuously with position and time and that, in analogy with hydrodynamics, there exist a continuity equation of the form

$$\frac{\partial|\Psi|^2}{\partial t} + \operatorname{div} \mathbf{s} = 0, \tag{66}$$

where $\mathbf{s}$ is said to be the probability density current. From the Schrödinger equation and its complex conjugate:

$$\begin{aligned} -\frac{h}{2\pi i}\frac{\partial\Psi}{\partial t} &= H\psi, \\ +\frac{h}{2\pi i}\frac{\partial\psi^*}{\partial t} &= (H\psi)^*, \end{aligned} \tag{67}$$

follows immediately

$$\begin{aligned} \frac{\partial|\psi|^2}{\partial t} &= \frac{\partial\psi^*}{\partial t}\psi + \psi^*\frac{\partial\psi}{\partial t} \\ &= \frac{2\pi i}{h}\{\psi(H\psi)^* - \psi^*(H\psi)\}, \end{aligned} \tag{68}$$

and the condition that the right-hand member should be a "divergence" puts a rather severe constraint on the form of the Hamiltonian H.

In the case when the particle moves under the influence of a potential $U = U(\mathbf{r})$, the Hamiltonian has the form $H = (p^2/2m) + U$ and, from (68), one obtains particularly

$$\frac{\partial|\psi|^2}{\partial t} = -\frac{h}{4\pi i m}\operatorname{div}(\psi^* \operatorname{grad}\psi - \psi \operatorname{grad}\psi^*), \tag{69}$$

showing that the continuity requirement is fulfilled and that the probability density current $\mathbf{s}$ has the form

$$\begin{aligned}\mathbf{s} &= \frac{h}{4\pi i m}(\psi^* \operatorname{grad}\psi - \psi \operatorname{grad}\psi^*)\\ &= \frac{1}{2m}\{\psi^* \mathbf{p}_{\mathrm{op}}\psi + \psi(\mathbf{p}_{\mathrm{op}}\psi)^*\}.\end{aligned} \tag{70}$$

If instead one uses Schrödinger's interpretation, the quantity $\mathbf{j} = e\mathbf{s}$ represents the charge density current. In both cases, the continuity equation is interpreted in the same way as in hydrodynamics, and we note particularly the relation

$$\frac{\partial}{\partial t}\int_V |\psi|^2\, dv = -\int_F \mathbf{s}\cdot\mathbf{n}\, dF, \tag{71}$$

where V is an arbitrary volume enclosed within the surface F with the outer normal $\mathbf{n}$. If the surface is put at infinity, one obtains

$$\frac{\partial}{\partial t}\int |\psi|^2\, dv = 0, \tag{72}$$

showing that the normalization integral $\langle\psi|\psi\rangle$ over the entire volume is independent of time. Analogous discussions may also be carried out for many-particle systems.

C. Heisenberg's Equation of Motion

Let us now consider an arbitrary many-particle system having the wave function $\Psi = \Psi(\mathbf{R}, t)$, where $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$, and let F be a linear operator representing a physical or chemical quantity. Using the notations (42) and (44), we will now study the quantity

$$\langle\Psi_1|F|\Psi_2\rangle = \int \Psi_1^* F \Psi_2 (d\mathbf{R}), \tag{73}$$

where Ψ_1 and Ψ_2 are wave functions taken at the same time t. The "matrix element" (73) is hence also a function of time, and, by using the Schrödinger equation (21) and its complex conjugate together with the "turnover rule" (46), one obtains

$$\begin{aligned}\frac{d}{dt}&\langle\Psi_1|F|\Psi_2\rangle\\&=\langle\frac{\partial\Psi_1}{\partial t}|F|\Psi_2\rangle+\langle\Psi_1|F|\frac{\partial\Psi_2}{\partial t}\rangle+\langle\Psi_1|\frac{\partial F}{\partial t}|\Psi_2\rangle\\&=\frac{2\pi i}{h}\langle H\Psi_1|F|\Psi_2\rangle-\frac{2\pi i}{h}\langle\Psi_1|F|H\Psi_2\rangle+\langle\Psi_1|\frac{\partial F}{\partial t}|\Psi_2\rangle\\&=\langle\Psi_1|\frac{2\pi i}{h}(H^\dagger F-FH)+\frac{\partial F}{\partial t}|\Psi_2\rangle,\end{aligned}\tag{74}$$

which is often called Heisenberg's law of motion. Putting $F=1$, one gets the special result that all scalar products $\langle\Psi_1|\Psi_2\rangle$ are independent of time if and only if $H^\dagger=H$, i.e., H is self-adjoint or hermitean:

$$\frac{d}{dt}\langle\Psi_1|\Psi_2\rangle=\frac{2\pi i}{h}\langle\Psi_1|H^\dagger-H|\Psi_2\rangle.\tag{75}$$

We note that the condition $H^\dagger=H$ is related to but somewhat weaker than the continuity requirement discussed in the previous section. In the following, we will always assume that the Hamiltonian is self-adjoint:

$$H^\dagger=H.\tag{76}$$

This is also consistent with the requirement that H is the "energy operator" and that $\bar{H}$ always should be real.

Assuming the normalization $\langle\Psi|\Psi\rangle=1$, we will now study the time variation of the expectation value F of the operator F in the physical situation characterized by the wave function Ψ:

$$\bar{F}=\langle\Psi|F|\Psi\rangle.\tag{77}$$

Putting $\Psi_1=\Psi_2=\Psi$ into (74), one obtains particularly

$$\frac{d\bar{F}}{dt}=\frac{2\pi i}{h}\overline{(HF-FH)}+\overline{\frac{\partial F}{\partial t}},\tag{78}$$

which is the law of motion in Heisenberg's matrix mechanics.

D. Ehrenfest's Relations

Let us now assume that the system has a potential $U=U(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_N)$ and a Hamiltonian of the form (23):

$$H=\sum_k\frac{p_k{}^2}{2m_k}+U.\tag{79}$$

The operator $\mathbf{K}_k = -\text{grad}_k U = -\nabla_k U$ corresponds to the classical force on particle k and is called the "force operator." From commutation relations of type (28) it follows further that

$$\begin{aligned} H\mathbf{r}_k - \mathbf{r}_k H &= \frac{h}{2\pi i}\frac{\mathbf{p}_k}{m_k}, \\ H\mathbf{p}_k - \mathbf{p}_k H &= \frac{h}{2\pi i}\mathbf{K}_k. \end{aligned} \tag{80}$$

Putting $F = \mathbf{r}_k$ and $F = \mathbf{p}_k$ into (78) and using (80), one obtains

$$\begin{aligned} \frac{d\bar{\mathbf{r}}_k}{dt} &= \frac{1}{m_k}\bar{\mathbf{p}}_k, \\ \frac{d\bar{\mathbf{p}}_k}{dt} &= \overline{\mathbf{K}}_k, \end{aligned} \tag{81}$$

which are known as Ehrenfest's relations. The formulas for the expectation values are closely analogous to the classical laws of motion (2), and one may wonder whether the "center" of a wave packet moves like a classical particle. Substitution of the first relation (81) into the second gives

$$m_k \frac{d^2\bar{\mathbf{r}}_k}{dt^2} = \overline{\mathbf{K}}_k, \tag{82}$$

in close analogy to (1), but we note that the "center" represented by the average position vector $\bar{\mathbf{r}}_k$ moves like a classical particle, if and only if

$$\overline{\mathbf{K}}_k = \mathbf{K}_k(\bar{\mathbf{r}}_k). \tag{83}$$

This occurs only for forces which are linear in the positions, i.e., for potentials U which are quadratic in the same quantities. This implies that, in a harmonic oscillator field, the center of a quantum-mechanical wave packet moves as a classical particle. However, in general, one has $\overline{\mathbf{K}}_k \neq \mathbf{K}_k(\bar{\mathbf{r}}_k)$, and the center of the wave packet moves in a way which is characteristic for the quantum-mechanical problem.

We note particularly that, for the *stationary states* defined by the relations (25) and (26), all expectation values $\bar{\mathbf{r}}_k$ and $\bar{\mathbf{p}}_k$ are independent of time. Since the associated time derivatives are vanishing, one obtains from (81) the relations

$$\bar{\mathbf{p}}_k = 0, \qquad \overline{\mathbf{K}}_k = 0, \tag{84}$$

showing that the average momentum and the average force are zero for these states. Such general relations are often very useful.

As an example, we will consider a single particle in one dimension with the position coordinate x. The kinetic energy has the form $T = p^2/2m$ and, according to (84), one obtains for the square of the width Δp in a stationary state:

$$(\Delta p)^2 = \overline{p^2} - (\bar{p})^2 = \overline{p^2} = 2m\overline{T}. \tag{85}$$

The uncertainty relation (51) takes then the form $\Delta x \cdot (2m\overline{T})^{1/2} \geq h/4\pi$ or

$$\overline{T} \geq \frac{h^2}{32\pi^2 m(\Delta x)^2}, \tag{86}$$

showing an important connection between the kinetic energy and the linear dimension Δx of the system. Since the kinetic energy is related to the total energy through the virial theorem (for references, see e.g. Löwdin, 1959), one obtains information about the system as to important orders of magnitude which sometimes are remarkably exact. For a three-dimensional isotropic system, one has instead $(\Delta p)^2 = 2m\overline{T}/3$ and

$$\overline{T} \geq \frac{9h^2}{32\pi^2 m\overline{r^2}}, \tag{87}$$

etc. It is interesting to study how close these relations are fulfilled for the ground state of simple quantum-mechanical systems, as the harmonic oscillator or the hydrogen atom, and to investigate the modifications required to treat excited states also.

Finally, let F be an arbitrary linear operator which does not contain the time t explicitly. For a stationary state, the expectation value F is then independent of time and, according to (78), one has the relation

$$\overline{(HF - FH)} = 0, \tag{88}$$

which is a generalization of (84). For convenient choices of F, one obtains the virial theorem and many other interesting consequences (Hirschfelder, 1960; Epstein and Hirschfelder, 1961; Hirschfelder and Coulson, 1962; and other papers).

E. Time Reversal

It is a characteristic feature of the classical law of motion (1) in Newton's mechanics that it is invariant against reversal of the time axis:

$$t' = -t. \tag{89}$$

If one takes a movie of a system of classical particles and later runs the movie "backwards," the motions of the particles are still in accordance with the laws of dynamics and make sense. This does not apply to movies in general which usually become absurd when run backwards, since everything seems to be in conflict with both "common sense" and the laws of nature. Physical laws which are invariant against time reversal are often called *primary laws*, in contrast to such laws as require a definite time direction which are called *secondary laws.*

Let us consider the classical laws of motion in greater detail in the form (2) or

$$\mathbf{p}_k = m_k \frac{d\mathbf{r}_k}{dt}, \qquad \frac{d\mathbf{p}_k}{dt} = -\mathrm{grad}_k\, U, \tag{90}$$

with the initial condition $\mathbf{r}_k = \mathbf{r}_k(0)$, $\mathbf{p}_k = \mathbf{p}_k(0)$ for $t = 0$. Putting $t' = -t$, one finds that one has also the reverse solution

$$\mathbf{r}_k'(t') = \mathbf{r}_k(-t), \qquad \mathbf{p}_k'(t') = -\mathbf{p}_k(-t), \tag{91}$$

corresponding to the initial condition $\mathbf{r}_k' = \mathbf{r}_k(0)$, $\mathbf{p}_k'(0) = -\mathbf{p}_k(0)$ for $t = 0$. We note particularly that all the momenta have reverse direction after the time reversal, but the energy (4) of the system stays the same.

Even in quantum mechanics, the transformation (89) is of fundamental importance. The physical situation is now described by a wave function $\Psi = \Psi(\mathbf{R}, t)$ which is a function of t and the coordinates $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ alone. In order to study the situation in momentum space $\mathbf{p} = (\mathbf{p}_1, \mathbf{p}_2, \ldots \mathbf{p}_N)$, one should consider the Fourier transformation (55) which defines the associated wave function $\Phi = \Phi(\mathbf{P}, t)$ in momentum space. By taking the conjugate complex, one obtains directly the connections

$$\begin{aligned} \Psi(\mathbf{R},t) &\leftrightarrow \Phi(\mathbf{P}, t), \\ \Psi^*(\mathbf{R}, t) &\leftrightarrow \Phi^*(-\mathbf{P}, t), \end{aligned} \tag{92}$$

showing that this operation also leads to a reversal of the directions of all the moments; compare (59) and (60).

Let us now consider the Hamiltonian (23) which corresponds to the classical case with a potential U. This Hamiltonian is not only self-adjoint ($H^\dagger = H$) but even real ($H^* = H$) which means that it stays the same when i is replaced by $-i$. From the Schrödinger equation (21) and its complex conjugate, one obtains

$$\begin{aligned} H_{\mathrm{op}}\Psi &= -\frac{h}{2\pi i}\frac{\partial\Psi}{\partial t}, \\ H_{\mathrm{op}}\Psi^* &= +\frac{h}{2\pi i}\frac{\partial\Psi^*}{\partial t}. \end{aligned} \tag{93}$$

If $\Psi = \Psi(\mathbf{R}, t)$ is a solution to the first equation corresponding to the initial condition $\Psi = \Psi_0$ for $t = 0$, one finds from the second equation by putting $t' = -t$ that one has also the solution

$$\Psi'(\mathbf{R}, t') = \Psi^*(\mathbf{R}, -t) \tag{94}$$

corresponding to the initial condition $\Psi' = \Psi_0{}^*$ for $t = 0$. Relation (94) is the quantum-mechanical analog to the classical formula (91), and it shows that the Schrödinger equation for *real* Hamiltonians is invariant against time reversal; i.e., it is a primary physical law.

IV. Schrödinger Equation for Particles in Electromagnetic Field

A. Electromagnetic Potentials

Maxwell's equations (7) also form in quantum mechanics the basis for the treatment of all electromagnetic phenomena. Let us start our brief review by introducing the electromagnetic potentials ϕ and $\mathbf{A}$.

From the equation $\operatorname{div} \mathbf{H} = 0$ follows the existence of a vector field $\mathbf{A} = \mathbf{A}(x, y, z, t)$ such that $\mathbf{H} = \operatorname{curl} \mathbf{A}$. From the equation $\operatorname{curl} \mathbf{E} + (1/c)\partial\mathbf{H}/\partial t = \operatorname{curl}\{\mathbf{E} + (1/c)\partial\mathbf{A}/\partial t\} = 0$ follows further the existence of a scalar field $\phi = \phi(x, y, z, t)$ such that $\mathbf{E} + (1/c)\partial\mathbf{A}/\partial t = -\operatorname{grad} \phi$. Hence one has the relations

$$\begin{aligned} \mathbf{H} &= \operatorname{curl} \mathbf{A}, \\ \mathbf{E} &= -\operatorname{grad} \phi - \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}, \end{aligned} \tag{95}$$

which define the field strengths $\mathbf{E}$ and $\mathbf{H}$ in terms of the scalar potential ϕ and the vector potential $\mathbf{A}$. It should be observed that the potentials ϕ and $\mathbf{A}$ are auxiliary quantities which are not directly physically measurable. For our discussion, it is convenient to introduce the notation

$$S = \operatorname{div} \mathbf{A} + \frac{1}{c}\frac{\partial \phi}{\partial t}, \tag{96}$$

where S is a four-dimensional scalar.

Substitution of the expressions (95) into the Maxwell equations $\operatorname{div} \mathbf{E} = 4\pi\rho$ and $\operatorname{curl} \mathbf{H} = (4\pi/c)\mathbf{j} + (1/c)\partial\mathbf{E}/\partial t$ and using the fact that, in Cartesian coordinates, div grad $= \nabla^2$ and curl curl $= -\nabla^2 +$ grad div gives immediately:

$$\begin{aligned} \Box\, \phi + \frac{1}{c}\frac{\partial S}{\partial t} &= -4\pi\rho, \\ \Box\, \mathbf{A} - \operatorname{grad} S &= -\frac{4\pi}{c}\mathbf{j}, \end{aligned} \tag{97}$$

where

$$\Box = \nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} = \sum_{k=1}^{4} \frac{\partial^2}{\partial x_k^2} \tag{98}$$

is the four-dimensional wave operator with $x_1 = x$, $x_2 = y$, $x_3 = z$, and $x_4 = ict$.

At this point, it is convenient to introduce the so-called *gauge transformation*:

$$\begin{aligned} \phi' &= \phi + \frac{1}{c}\frac{\partial \chi}{\partial t}, \\ \mathbf{A}' &= \mathbf{A} - \operatorname{grad} \chi, \end{aligned} \tag{99}$$

where $\chi = \chi(x, y, z, t)$ is a completely arbitrary real function. Substitution into (95) and (96) gives

$$\mathbf{H}' = \mathbf{H}, \qquad \mathbf{E}' = \mathbf{E}, \qquad S' = S - \Box\,\chi, \tag{100}$$

showing that the field strengths are *gauge-invariant*, whereas the scalar S undergoes a transformation. If one chooses the gauge function χ so that $\Box\,\chi = S$ one obtains particularly $S' = 0$ showing that there always exists a choice of potentials for which one has

$$\operatorname{div} \mathbf{A} + \frac{1}{c}\frac{\partial \phi}{\partial t} = 0, \tag{101}$$

which is the so-called Lorentz condition. In the following, we will always assume that this condition is valid. We note that the gauge transformations (99) are then restricted to functions χ satisfying the relation

$$\Box\,\chi = 0. \tag{102}$$

Equations (97) are now simplified to the form

$$\Box\,\phi = -4\pi\rho, \qquad \Box\,\mathbf{A} = -\frac{4\pi}{c}\mathbf{j}. \tag{103}$$

Of particular importance are the solutions known as *retarded potentials*:

$$\begin{aligned} \phi(P, t) &= \int \frac{\rho(Q, t - r_{PQ}/c)}{r_{PQ}}\, dv_Q, \\ \mathbf{A}(P, t) &= \frac{1}{c}\int \frac{\mathbf{j}(Q, t - r_{PQ}/c)}{r_{PQ}}\, dv_Q. \end{aligned} \tag{104}$$

Since the wave operator $\Box$ is invariant against the transformation $c \rightarrow -c$, one has also *advanced potentials* containing the time variable

$(t + r_{PQ}/c)$ and "symmetric potentials" obtained by averaging over the retarded and the advanced potentials. The general solution to (103) is obtained by taking any special solution and adding solutions ϕ_0 and $\mathbf{A}_0$ to the homogeneous wave equations $\Box\,\phi_0 = 0$ and $\Box\,\mathbf{A}_0 = \mathbf{0}$.

B. Single Particle in an Outer Electromagnetic Field

Let us first consider a single particle with charge e in an outer electromagnetic field. In classical mechanics, there is a simple rule for introducing an electromagnetic field into the Hamiltonian which may be directly taken over into quantum mechanics. The rule is most easily understood by considering the relation

$$\mathbf{p} = \boldsymbol{\pi} + \frac{e}{c}\,\mathbf{A}, \tag{105}$$

which says that the total momentum $\mathbf{p}$ is the sum of the kinetic momentum $\boldsymbol{\pi}$ and the electromagnetic momentum $(e/c)\mathbf{A}$. Since the total energy is the sum of the kinetic energy and the electromagnetic contribution $e\phi$, one has further

$$\begin{aligned} H &= \frac{1}{2m}\,\pi^2 + e\phi \\ &= \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\,\mathbf{A}\right)^2 + e\phi, \end{aligned} \tag{106}$$

which is the classical Hamiltonian desired. By putting $\mathbf{p} = (h/2\pi i)\nabla$, one obtains the quantum-mechanical analog. We note that the Hamiltonian operator is self-adjoint $(H^\dagger = H)$, but that it is no longer real $(H^* \neq H)$, which is of importance in discussing time reversal.

It is interesting to observe that the Schrödinger equation (21) for a Hamiltonian of the type (106) leads to a continuity equation of the form (66) having the probability density current

$$\mathbf{s} = \frac{1}{2m}\,\{\psi^*\boldsymbol{\pi}\psi + \psi(\boldsymbol{\pi}\psi)^*\}, \tag{107}$$

which is obtained from (70) by replacing $\mathbf{p}$ by $\boldsymbol{\pi}$. Using Schrödinger's interpretation of quantum mechanics, one has the identifications

$$\begin{aligned} \rho &= e|\psi|^2, \\ \mathbf{j} &= \frac{e}{2m}\,(\psi^*\boldsymbol{\pi}\psi + \psi\boldsymbol{\pi}^*\psi^*), \end{aligned} \tag{108}$$

leading to the quantum-mechanical expressions for the charge density ρ and the current density $\mathbf{j}$. By using these expressions in the wave equations

(103) for the potentials, one can then derive the electromagnetic field created by the "matter wave" associated with the particle.

The operator $\boldsymbol{\pi}$ for the kinetic momentum $\boldsymbol{\pi} = \mathbf{p} - (e/c)\mathbf{A}$ is of fundamental importance in the theory, and we note that it has the commutation relations

$$\boldsymbol{\pi} \times \boldsymbol{\pi} = i(eh/2\pi c)\mathbf{H}. \tag{109}$$

Using Heisenberg's law of motion (78), it is now interesting to study the time dependence of the expectation values $\bar{\mathbf{r}}$ and $\bar{\boldsymbol{\pi}}$. One obtains

$$\begin{aligned} \frac{d\bar{\mathbf{r}}}{dt} &= \frac{1}{m}\bar{\boldsymbol{\pi}}, \\ \frac{d\bar{\boldsymbol{\pi}}}{dt} &= e\bar{\mathbf{E}} + \frac{e}{2mc}\overline{(\boldsymbol{\pi} \times \mathbf{H} - \mathbf{H} \times \boldsymbol{\pi})}, \end{aligned} \tag{110}$$

where the right-hand member of the second relation is the quantum-mechanical analog to the classical Lorentz force (8) in hermitean form:

$$\frac{d\bar{\boldsymbol{\pi}}}{dt} = \int \left[\rho\mathbf{E} + \frac{1}{2c}(\mathbf{j} \times \mathbf{H} - \mathbf{H} \times \mathbf{j})\right] dv. \tag{111}$$

Equations (110) correspond to the Ehrenfest's relations (81) in the case of an outer electromagnetic field.

Let us now study the behavior of the Schrödinger equation for a Hamiltonian of the type (106) under a *gauge transformation* (99) characterized by the real function $\chi = \chi(x, y, z, t)$. For the basic operators, one obtains the following transformations:

$$\boldsymbol{\pi}' = \boldsymbol{\pi} + \frac{e}{c}\operatorname{grad}\chi, \qquad \phi' = \phi + \frac{1}{c}\frac{\partial\chi}{\partial t}, \tag{112}$$

and for the Hamiltonian:

$$\begin{aligned} H' &= \frac{1}{2m}(\boldsymbol{\pi}')^2 + e\phi' \\ &= \frac{1}{2m}\left(\boldsymbol{\pi}' + \frac{e}{c}\operatorname{grad}\chi\right)^2 + e\phi + \frac{e}{c}\frac{\partial\chi}{\partial t}. \end{aligned} \tag{113}$$

Let $\psi = \psi(\mathbf{r}, t)$ be a solution to the original Schrödinger equation corresponding to the initial condition $\psi = \psi_0$ for $t = 0$. It is now easily shown that the function

$$\psi' = \psi e^{-(2\pi i e/hc)\chi} \tag{114}$$

is a solution to the transformed Schrödinger equation

$$H'_{\text{op}}\,\psi' = -\frac{h}{2\pi i}\frac{\partial\psi'}{\partial t}, \tag{115}$$

corresponding to the initial condition $\psi_0' = \psi_0 \exp\{-(2\pi ie/hc)\chi_0\}$ for $t = 0$. The proof follows from the fact that

$$\left.\begin{aligned} \pi'\psi' &= e^{-(2\pi ie/hc)\chi}(\pi\psi), \\ -\frac{h}{2\pi i}\frac{\partial\psi'}{\partial t} &= e^{-(2\pi ie/hc)\chi}\left\{-\frac{h}{2\pi i}\frac{\partial\psi}{\partial t} + \frac{e}{c}\frac{\partial\chi}{\partial t}\psi\right\}, \end{aligned}\right. \tag{116}$$

and substitution of these relations into (113) verifies the statement.

Relation (114) is called the gauge transformation of the wave function. It follows immediately that

$$|\psi'(\mathbf{r}, t)|^2 = |\psi(\mathbf{r}, t)|^2, \tag{117}$$

showing that the probability density in the coordinate space stays invariant under a gauge transformation. For the kinetic momentum one has the commutation relation

$$\boldsymbol{\pi}' e^{-(2\pi ie/hc)\chi} = e^{-(2\pi ie/hc)\chi}\boldsymbol{\pi}, \tag{118}$$

and more generally for any polynomial function $f = f(\pi_1, \pi_2, \pi_3)$:

$$f(\pi_1', \pi_2', \pi_3')e^{-(2\pi ie/hc)\chi} = e^{-(2\pi ie/hc)\chi}f(\pi_1, \pi_2, \pi_3). \tag{119}$$

This leads to the relation

$$(\psi')^* f(\pi_1', \pi_2', \pi_3')\psi' = \psi^* f(\pi_1, \pi_2, \pi_3)\psi, \tag{120}$$

showing that all expectation values of the kinetic momentum will be gauge-invariant. The formulas (117) and (120) show that the quantum mechanics based on the Schrödinger equation (115) fulfils the basic requirement that *all physically measurable quantities should in principle be gauge-invariant.* In this connection, it should be observed that the Hamiltonian H is an auxiliary quantity which undergoes the gauge transformation (113). Using (114) and (120), one obtains further

$$(\psi')^* H'_{\text{op}}\,\psi' = \psi^*\left(H_{\text{op}} + \frac{e}{c}\frac{\partial\chi}{\partial t}\right)\psi. \tag{121}$$

This relation implies that, in order to discuss "stationary states" and properties of energy levels, etc., it is convenient to restrict the permissible gauge transformation so that χ is independent of time.

Let us now make a few comments about the effect of a *time reversal* of the type (89). Equations (93) were based on the assumption that the Hamiltonian was real, i.e., $H_{\text{op}}^* = H_{\text{op}}$, which follows directly from (23) and the fact that $\mathbf{p}_{\text{op}} = -\mathbf{p}_{\text{op}}^*$ according to (22). This does not apply to the Hamiltonian (106), for which one obtains

$$H_{\text{op}}^* = \frac{1}{2m}\left(\mathbf{p} + \frac{e}{c}\,\mathbf{A}\right)^2 + e\phi. \tag{122}$$

Even if the outer magnetic field were static, its presence would prevent the simple time reversal previously discussed, unless the currents producing the vector potential **A** would also be reversed in accordance with the general rule that all momenta should change direction. The nonstatic case is much more cumbersome for, if one uses retarded potentials, they go under time reversal over into advanced potentials, and vice versa. This means that, in order to keep the primary character of the basic laws of quantum mechanics, it would be necessary to use *symmetric potentials* which are the average of retarded and advanced potentials. We will discuss these questions further below in connection with radiation theory.

C. Many-Particle System in an Outer Electromagnetic Field

Let us now consider a system of particles having the charges $e_k (k = 1, 2, \ldots N)$ under the influence of an internal potential $U = U(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ and an outer electromagnetic field with the potentials $\phi = \phi(\mathbf{r}, t)$ and $\mathbf{A} = \mathbf{A}(\mathbf{r}, t)$. The Schrödinger equation for the wave function $\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N; t)$ again takes the form

$$-\frac{h}{2\pi i}\frac{\partial \Psi}{\partial t} = H_{\text{op}}\,\Psi, \tag{123}$$

with the Hamiltonian

$$H_{\text{op}} = U(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) + \sum_{k=1}^{N}\left\{\frac{1}{2m_k}\left(\mathbf{p}_k - \frac{e_k}{c}\,\mathbf{A}_k\right)^2 + e_k\phi_k\right\}, \tag{124}$$

which is formed by a generalization of the simple rule given in the previous section; here we have used the abbreviations

$$\phi_k = \phi(\mathbf{r}_k, t), \qquad \mathbf{A}_k = \mathbf{A}(\mathbf{r}_k, t). \tag{125}$$

By using Heisenberg's law of motion (78), one obtains in analogy to (110) the Ehrenfest's relations:

$$\begin{aligned} \frac{d\bar{\mathbf{r}}_k}{dt} &= \frac{1}{m_k}\,\bar{\boldsymbol{\pi}}_k, \\ \frac{d\bar{\boldsymbol{\pi}}_k}{dt} &= -\,\overline{\text{grad}_k\,U} + \overline{e_k\mathbf{E}_k + \frac{e_k}{2m_k c}(\boldsymbol{\pi}_k \times \mathbf{H}_k - \mathbf{H}_k \times \boldsymbol{\pi}_k)}, \end{aligned} \tag{126}$$

where $\boldsymbol{\pi}_k = \mathbf{p}_k - (e/c)_k\mathbf{A}_k$ is the kinetic momentum for particle k. It is also interesting to observe that the Schrödinger equation (123) leads to a continuity equation for the total probability density $|\Psi|^2$ of the form

$$\begin{aligned} \frac{\partial|\Psi|^2}{\partial t} &= -\sum_{k=1}^{N} \operatorname{div}_k \mathbf{s}_k, \\ \mathbf{s}_k &= \frac{1}{2m_k}(\Psi^*\boldsymbol{\pi}_k\Psi + \Psi\boldsymbol{\pi}_k{}^*\Psi^*), \end{aligned} \tag{127}$$

in analogy to (70) and (107). This continuity equation is valid within the $3N$-dimensional configuration space, but we note that there exists also a continuity equation in a three-dimensional space for each one of the particles separately.

If $(dv) = dv_1dv_2 \cdots dv_N$ is the total volume element in the configuration space, it is convenient to introduce the notation

$$(dv_k') = dv_1\, dv_2 \cdots dv_{k-1}\, dv_{k+1} \cdots dv_N, \tag{128}$$

which goes over all particles *except particle k*. The probability density for finding particle k in the point $\mathbf{r}_k$ at the time t, when all the other particles have arbitrary positions, is then given by the quantity

$$\gamma_k(\mathbf{r}_k, t) = \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_k, \ldots \mathbf{r}_N; t)|^2 (dv_k'). \tag{129}$$

In a similar way, one introduces the probability density current $\mathbf{s}_k'$ for the particle k alone when all the other particles have arbitrary motions through the relation

$$\mathbf{s}_k'(\mathbf{r}_k, t) = \int \mathbf{s}_k(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_k, \ldots \mathbf{r}_N; t)(dv_k'). \tag{130}$$

Integrating the continuity equation (127) over the coordinates $\mathbf{r}_1$, $\mathbf{r}_2$, $\ldots \mathbf{r}_{k-1}, \mathbf{r}_{k+1} \ldots \mathbf{r}_N$, one obtains

$$\frac{\partial\gamma_k}{\partial t} = -\operatorname{div}_k \mathbf{s}_k'. \tag{131}$$

So far everything is simple and straightforward. The crucial problem is to find the true charge density ρ and current density $\mathbf{j}$ of the many-particle system to be used in evaluating the electromagnetic potentials created by the $3N$-dimensional matter waves. In the historical development of quantum mechanics (Pauli, 1933, p. 201), it seemed natural to assume that $e_k\gamma_k$ and $e_k\mathbf{s}_k'$ would be the contributions from particle k to the charge density and current density, respectively, and to make tentatively the identifications

$$\begin{aligned} \rho(\mathbf{r}, t) &= \sum_{k=1}^{N} e_k \gamma_k(\mathbf{r}, t), \\ \mathbf{j}(\mathbf{r}, t) &= \sum_{k=1}^{N} e_k \mathbf{s}_k'(\mathbf{r}, t). \end{aligned} \tag{132}$$

We note that, for $e_1 = e_2 = \cdots = e_N$, the charge density ρ is essentially identical to the diagonal element of the reduced first-order density matrix treated in modern many-particle theory.

By combination of (132) and (103), one can hence study the electromagnetic field created by a system of matter waves and, by introducing the potentials ϕ and $\mathbf{A}$ into the Schrödinger equation (123) with the Hamiltonian (124), one can investigate the effect of the field on the matter waves. This coupling of the equations leads necessarily to a problem which is formally of a nonlinear character.

So far, there are only a few many-particle systems which have been treated with sufficient accuracy to permit a real comparison between theory and experimental experience. The theoretical data for the ground state and lowest excited states of the helium atom and the hydrogen molecule obtained by Hylleraas (1928, 1929, 1930a,b), Kinoshita (1957, 1959), Pekeris (1958, 1959, 1962), etc., and by James and Coolidge (1933), Kolos and Roothaan (1960), Kolos and Wolniewicz (1963), etc., respectively, show that Schrödinger's idea about a wave equation in configuration space seems to lead to results in complete agreement with experimental experience. At the same time, the form of the Coulomb potential is no longer derived from the average charge density ρ defined in (132). Hence it seems evident that the question of the nature of the electromagnetic field generated by the matter waves has a more complicated character than is indicated above. Using the formulism of second quantization, these problems are treated in the new field of *quantum electrodynamics* (for references, see, e.g., Schwinger, 1958; Feynman, 1961) which deals with modern radiation theory as well as the very difficult problem of the nature of the elementary particles themselves and their "self-interaction." Even if progress in this area has been considerable during the last two decades, there are still many fundamental problems to be solved, particularly in connection with the relativistic formulation of the theory.

In this paper, we will confine our interest to the much simpler problem of solving the Schrödinger equation for a given fixed Hamiltonian. This

Hamiltonian may contain an outer magnetic field and a given interaction between the particles, and it is assumed that the problem has strictly a linear character.

V. Evolution Operator

The main problem in the quantum theory of a time-dependent system is to find the solution $\Psi = \Psi(\mathbf{R}, t)$ to the Schrödinger equation

$$-\frac{h}{2\pi i}\frac{\partial \Psi}{\partial t} = H_{\text{op}}\Psi \tag{133}$$

which corresponds to the initial condition $\Psi = \Psi_0$ at $t = t_0$. Here $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ is the space coordinate of the many-particle system, but the problem can, of course, also be treated equally well in the momentum space. The space coordinate will in the following often be supressed, and the main emphasis is put on the time dependence of the wave function. One can write the connection between $\Psi(t)$ and Ψ_0 symbolically in the form

$$\Psi(t) = U(t, t_0)\Psi_0. \tag{134}$$

Since the Schrödinger equation (133) is linear and there exists a superposition principle (65), one can conclude that U must be a *linear operator.*

Since U describes the time dependence of the system completely, it is called the "evolution operator." From the definition follows immediately the relation

$$U(t_2; t_0) = U(t_2; t_1)U(t_1; t_0) \tag{135}$$

for $t_0 \leq t_1 \leq t_2$, which is the multiplication law characteristic for the evolution operator. One has further $U(t_0, t_0) = 1$, where the symbol 1 means the identity operator.

The Hamiltonian is assumed to be self-adjoint, $H^\dagger = H$, and this implies according to (75) that the normalization integral is independent of time. This gives

$$\begin{aligned}\langle\Psi\,|\,\Psi\rangle - \langle\Psi_0\,|\,\Psi_0\rangle &= \langle U\Psi_0\,|\,U\Psi_0\rangle - \langle\Psi_0\,|\,\Psi_0\rangle \\ &= \langle\Psi_0\,|\,U_\dagger U - 1\,|\,\Psi_0\rangle = 0\end{aligned} \tag{136}$$

for all Ψ_0, which leads to the conclusion $U^\dagger U = 1$. Letting $U^\dagger$ work on the relation $\Psi = U\Psi_0$, one obtains $\Psi_0 = U^\dagger\Psi$. We will now make the specific assumption that not only the initial state Ψ_0 but also the final state Ψ may be chosen quite arbitrarily, i.e., that there always exists a Ψ_0 so that a given Ψ may be obtained. Since one has now

$$\begin{aligned}\langle\Psi_0|\Psi_0\rangle - \langle\Psi|\Psi\rangle &= \langle U^\dagger\Psi|U^\dagger\Psi\rangle - \langle\Psi|\Psi\rangle \\ &= \langle\Psi|UU^\dagger - 1|\Psi\rangle = 0\end{aligned} \tag{137}$$

for all Ψ, one is lead to the conclusion $UU^\dagger = 1$. Under these assumptions, the evolution operator is hence a *unitary operator*:

$$U^\dagger U = UU^\dagger = 1. \tag{138}$$

Substitution of the relation $\Psi = U\Psi_0$ into the Schrödinger equation (133) gives

$$\left(-\frac{h}{2\pi i}\frac{\partial U}{\partial t} - H_{\text{op}}\,U\right)\Psi_0 = 0 \tag{139}$$

for all Ψ_0, and the evolution operator fulfils hence the differential equation

$$-\frac{h}{2\pi i}\frac{\partial U}{\partial t} = H_{\text{op}}\,U, \tag{140}$$

with the initial condition $U = 1$ for $t = 0$. In order to solve this equation, it is convenient to distinguish between three cases:

(1) H is independent of time;
(2) H depends on the time, but in a commutative way so that $H(t_1)H(t_2) = H(t_2)H(t_1)$ for all pairs (t_1, t_2) in the interval concerned;
(3) H depends on the time in a noncommutative way, so that in general $H(t_1)H(t_2) \neq H(t_2)H(t_1)$.

A. Hamiltonian Independent of Time

In the case when the Hamiltonian H does not contain the time t explicitly, one can immediately solve (140) and represent the evolution operator symbolically in the form

$$U(t; t_0) = \exp\left[-\frac{2\pi i}{h}\,H_{\text{op}}(t - t_0)\right]. \tag{141}$$

In this case, the evolution operator is translationally invariant on the time axis, i.e., $U(t + \tau; t_0 + \tau) = U(t; t_0)$, and it is easily shown that the reverse is also true. For the sake of simplicity, we will now put $t_0 = 0$, and the solution (134) may then be written in the form

$$\Psi(t) = \exp\left[-\frac{2\pi i}{h}\,H_{\text{op}}\,t\right]\Psi_0. \tag{142}$$

Introducing the normalized eigenstates $\Phi_k(\mathbf{R})$ of H satisfying the relation $H\Phi_k = E_k\Phi_k$ as a basis, and assuming that this basis is complete so that one has the following resolution of the identity

$$1 = \sum_k |\Phi_k\rangle\langle\Phi_k|, \tag{143}$$

where one sums the discrete eigenvalues and integrates over the continuous eigenvalues, one obtains the spectral resolution $H = \Sigma_k E_k|\Phi_k\rangle\langle\Phi_k|$, and more generally for an arbitrary function f:

$$f(H) = \sum_k f(E_k)\,|\Phi_k\rangle\langle\Phi_k|. \tag{144}$$

This gives particularly for the evolution operator (141):

$$U = \sum_k \exp\left(-\frac{2\pi i}{h}E_k t\right)|\Phi_k\rangle\langle\Phi_k|, \tag{145}$$

In ordinary space, one has the identifications $|\Phi_k\rangle = \Phi_k(\mathbf{R})$ and $\langle\Phi_k| = \int(dv)\Phi_k{}^*(\mathbf{R})$. Substitution of the sum (145) into (142) gives the formula

$$\Psi(\mathbf{R}, t) = \sum_k \exp\left(-\frac{2\pi i}{h}E_k t\right)|\Phi_k\rangle\langle\Phi_k|\Psi_0\rangle, \tag{146}$$

which is the famous expansion of the solution into stationary states. Hence, one can determine the time dependence of a solution by a study of the stationary states, and vice versa.

B. Hamiltonian Dependent on Time in a Commutative Way

In this case, the Hamiltonian $H = H(t)$ is assumed to fulfill the commutation relation

$$H(t_1)H(t_2) = H(t_2)H(t_1) \tag{147}$$

for any pair (t_1, t_2) within the time interval under consideration. Starting from (140), it is easily shown that the evolution operator may be written symbolically in the form

$$U(t; t_0) = \exp\left[-\frac{2\pi i}{h}\int_{t_0}^{t} H(t_1)dt_1\right]. \tag{148}$$

The operator is no longer translationally invariant. However, since all the operators $H(t)$ commute, it is possible to introduce the normalized eigenstates $\Phi_k(\mathbf{R})$ of the operator $H(0)$ in such a way that they become simultaneous eigenstates to all the operators $H(t)$ satisfying the relations

$$H(t)\Phi_k(\mathbf{R}) = E_k(t)\Phi_k(\mathbf{R}), \tag{149}$$

where the eigenvalues $E_k = E_k(t)$ are now functions of time t. From the resolution of identity $1 = \Sigma_k|\Phi_k\rangle\langle\Phi_k|$, one obtains according to (148) the following spectral resolution of the evolution operator:

$$U(t; 0) = \sum_k \exp\left[-\frac{2\pi i}{h}\int_0^t E_k(t_1)\,dt_1\right]|\Phi_k\rangle\langle\Phi_k|, \tag{150}$$

which gives the following solution to the Schrödinger equation:

$$\Psi(\mathbf{R}; t) = \sum_k \exp\left[-\frac{2\pi i}{h}\int_0^t E_k(t_1)\,dt_1\right]\Phi_k(\mathbf{R})\,\langle\Phi_k|\Psi_0\rangle. \tag{151}$$

This is a trivial extension of formula (146). We note that there still exist "stationary states" associated with the eigenfunctions $\Phi_k(\mathbf{R})$ but that the energy values are now functions of time.

C. Hamiltonian Dependent on Time in a General Way

In this case, the Hamiltonian $H = H(t)$ is assumed to be of such a general character that the commutation relation (147) is no longer valid, i.e.,

$$H(t_1)H(t_2) \neq H(t_2)H(t_1). \tag{152}$$

In order to treat this case, it is convenient to transform the differential equation (140) into the associated integral equation:

$$U(t) = 1 - \frac{2\pi i}{h}\int_0^t H(t_1)U(t_1)dt_1, \tag{153}$$

where we have used the abbreviation $U(t; 0) = U(t)$ and the initial condition $U(0) = 1$. This is a "Volterra equation of the second kind," except that the kernel $H(t_1)$ is not a simple function of t but a linear operator acting on functions of the space coordinate $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N)$. By substituting the left-hand member of (153) for $t = t_1$ into the right-hand member, one obtains by iteration:

$$\begin{aligned} U(t) &= 1 - \frac{2\pi i}{h}\int_0^1 H(t_1)dt_1 + \left(-\frac{2\pi i}{h}\right)^2 \int_0^t H(t_1)\,dt_1 \int_0^{t_1} H(t_2)U(t_2)\,dt_2 \\ &= \sum_{n=0}^{\infty}\left(-\frac{2\pi i}{h}\right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n\, H(t_1)H(t_2)\cdots H(t_n). \end{aligned} \tag{154}$$

In the integrand of each term in this formal series, one has the condition $t \geq t_1 \geq t_2 \geq \cdots \geq t_n$ and one says the factors in the product $H(t_1)H(t_2)\cdots H(t_n)$ are arranged in "chronological order."

Let us now study the connection between the series (154) and the expression (148) which is obtained under the special assumption (147). For a series of symmetrical terms u_{ij}, u_{ijk}, ... one has the general transformation formulas

$$\sum_{i<j} u_{ij} = \frac{1}{2!}\sum_{i,j}{}' u_{ij}, \qquad \sum_{i<j<k} u_{ijk} = \frac{1}{3!}\sum_{i,j,k}{}' u_{ijk}, \tag{155}$$

and similar relations are also valid for integrals. If P is the "Dyson chronological-order operator" which has the property that it permutes the time variables in any product $H(t_1')H(t_2') \cdots H(t_n')$, so that they occur in chronological sequence after decreasing order, one has

$$\begin{aligned}\int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \cdots \int_0^{t_{n-1}} dt_n H(t_t)H(t_2)H(t_3) \cdots H(t_n)\\ = \frac{1}{n!}\int_0^t dt_1 \int_0^t dt_2 \cdots \int_0^t dt_n P\{H(t_1)H(t_2) \cdots H(t_n)\}.\end{aligned} \tag{156}$$

According to (154), this gives

$$\begin{aligned}U(t) &= P\sum_{n=0}^{\infty} \frac{1}{n!}\left(-\frac{2\pi i}{h}\right)^n \int_0^t dt_1 H(t_1) \int_0^t dt_2 H(t_2) \cdots \int_0^t dt_n H(t_n)\\ &= P\exp[-(2\pi i/h)\int_0^t dt_1 H(t_1)],\end{aligned} \tag{157}$$

in analogy to (148), which gives the connection desired. It is evident that the series (154) is convergent only under rather limited conditions, and it will now be transformed into more useful forms.

D. Interaction Representation

Let us assume that the Hamiltonian $H = H(t)$ may be written in the form

$$H = H_0 + V(t), \tag{158}$$

where H_0 is the "unperturbed Hamiltonian" and $V = V(t)$ is a comparatively small "perturbation." The operator H_0 is further assumed to be independent of time t and to have well-known eigenfunctions $\Phi_k^0 = \Phi_k^0(\mathbf{R})$ and eigenvalues E_k^0. The associated evolution operator U_0 has the form

$$U_0 = \exp\left(-\frac{2\pi i}{h} H_0 t\right)$$
$$= \sum_k \exp\left(-\frac{2\pi i}{h} E_k^0 t\right) |\Phi_k^0\rangle \langle\Phi_k^0| \tag{159}$$

and satisfies the differential equation (140) for $H = H_0$. In order to proceed, we will now introduce the substitution

$$U = U_0 \cdot U_V, \tag{160}$$

where U_V is a unitary operator to be determined. According to (140), one obtains the differential equation

$$-\frac{h}{2\pi i}\frac{\partial U_0}{\partial t} \cdot U_V - \frac{h}{2\pi i} U_0 \cdot \frac{\partial U_V}{\partial t} = (H_0 + V) U_0 \cdot U_V;$$
$$-\frac{h}{2\pi i} U_0 \cdot \frac{\partial U_V}{\partial t} = V U_0 \cdot U_V; \tag{161}$$
$$-\frac{h}{2\pi i}\frac{\partial U_V}{\partial t} = (U_0^\dagger V U_0) \cdot U_V.$$

It is clear that U_V satisfies a differential equation of exactly the same type as U but with the Hamiltonian H replaced by the operator

$$V_H = U_0^\dagger V U_0$$
$$= \exp\left(\frac{2\pi i}{h} H_0 t\right) V \exp\left(-\frac{2\pi i}{h} H_0 t\right). \tag{162}$$

The operator V_H is said to represent the perturbation in the "interaction representation." Since U_V satisfies the initial condition $U_V(0) = 1$, one obtains from (161) the integral equation

$$U_V(t) = 1 - \frac{2\pi i}{h}\int_0^t V_H(t_1) U_V(t_1)\, dt_1. \tag{163}$$

Iteration leads to the series expansion

$$U_V(t) = 1 - \frac{2\pi i}{h}\int_0^t V_H(t_1)\, dt_1 + \left(-\frac{2\pi i}{h}\right)^2 \int_0^t V_H(t_1)\, dt_1 \int_0^t V_H(t_2) U_V(t_2)\, dt_2$$
$$= \sum_{n=0}^{\infty} \left(-\frac{2\pi i}{h}\right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n V_H(t_1) V_H(t_2) \cdots V_H(t_n), \tag{164}$$

which is fundamental for the so-called *time-dependent perturbation theory.* In analogy to (157), one obtains the following form for the total evolution operator:

$$\begin{aligned} U(t) &= P\exp\left[-\frac{2\pi i}{h}\int_0^t \{H_0 + V(t_1)\}\,dt_1\right] \\ &= \exp\left(-\frac{2\pi i}{h}H_0 t\right) P\exp\left[-\frac{2\pi i}{h}\int_0^t V_H(t_1)\,dt_1\right] \\ &= \exp\left(-\frac{2\pi i}{h}H_0 t\right)\sum_{n=0}^{\infty}\left(-\frac{2\pi i}{h}\right)^n \int_0^t dt_1\int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \\ &\quad \times V_H(t_1)V_H(t_2)\cdots V_H(t_n). \end{aligned} \tag{165}$$

The various terms in this expansion will be further discussed below.

VI. Reformulation of Quantum Theory

So far the evolution operator U has been expressed in terms of a given Hamiltonian H, but sometimes it seems more convenient to turn things around and reformulate the fundamentals of quantum mechanics with $U = U(t; t_0)$ as the basic operator. This may also be of importance from philosophical point of view, since the evolution operator U is defined with respect to a finite time interval $(t_0; t)$, whereas H is associated with a differential equation of type (21).

Let us now assume that the relation

$$\Psi(t) = U(t; t_0)\Psi_0 \tag{166}$$

is the fundamental law for the time evolution of a quantum-mechanical system, and that U is linear and unitary:

$$U^\dagger U = UU^\dagger = 1. \tag{167}$$

The evolution operator has an eigenvalue problem of the form

$$U\eta_k = \lambda_k\eta_k, \tag{168}$$

where the eigenfunctions $\eta_k = \eta_k(\mathbf{R}, t)$ depend on $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ and t. The eigenvalues $\lambda_k = \lambda_k(t)$ are situated on the unit circle $|\lambda_k| = 1$ and have the form $\lambda_k = \exp(i\alpha_k)$, where α_k is real. Since the operator is normal, one has also $U^\dagger\eta_k = \lambda_k^*\eta_k$, and the eigenfunctions form an orthogonal system which is assumed to be normalized so that $\langle\eta_k|\eta_l\rangle = \delta_{kl}$. The system is further assumed to be complete, so that $1 = \Sigma_k |\eta_k\rangle\langle\eta_k|$. This gives the spectral resolution

$$U = \sum_k \lambda_k |\eta_k\rangle\langle\eta_k|, \tag{169}$$

which substituted into (166) gives the expansion

$$\Psi(t) = \sum_k e^{i\alpha_k}\eta_k\langle\eta_k|\Psi_0\rangle, \tag{170}$$

corresponding to the expansion in "stationary states" (146).

Let us now consider an operator Λ which commutes with U so that

$$U\Lambda = \Lambda U. \tag{171}$$

For the expectation value of Λ, one obtains $\langle\Psi|\Lambda|\Psi\rangle = \langle U\Psi_0|\Lambda|U\Psi_0\rangle = \langle\Psi_0|U^\dagger\Lambda U|\Psi_0\rangle = \langle\Psi_0|\Lambda|\Psi_0\rangle$; i.e., the expectation value $\langle\Lambda\rangle_{Av}$ is the same for the times t_0 and t. Such an operator Λ will be called a "constant of evolution," and its eigenprojectors may be used to classify the degeneracies of the eigenstates of U.

If the evolution operator U exists in the interval $(t; t + dt)$ and has a first derivative, one can show the existence of a specific Hamiltonian H. Differentiating relation (166) with respect to t, one obtains

$$-\frac{h}{2\pi i}\frac{\partial\Psi}{\partial t} = -\frac{h}{2\pi i}\frac{\partial U}{\partial t}\Psi_0 = -\frac{h}{2\pi i}\frac{\partial U}{\partial t}U^\dagger\Psi, \tag{172}$$

i.e., the connection

$$H_{\text{op}} = -\frac{h}{2\pi i}\frac{\partial U}{\partial t}U^\dagger, \tag{173}$$

which defines the Hamiltonian. Taking the time derivative of the relation $UU^\dagger = 1$, one obtains the alternative form

$$H_{\text{op}} = +\frac{h}{2\pi i}U\frac{\partial U^\dagger}{\partial t}, \tag{174}$$

and combination of (173) and (174) gives finally $H^\dagger = H$. If the evolution operator is unitary, the associated Hamiltonian is hence self-adjoint.

The eigenfunctions η_k of the evolution operator U are usually not eigenfunctions of the Hamiltonian H, and it is instructive to derive the matrix representation of H with respect to the basis η_k. From the relation

$(U^\dagger - \lambda_k^*)\eta_k = 0$, by taking the time derivative and using (174), one has

$$\left(\frac{\partial U^\dagger}{\partial s} - \frac{\partial \lambda_k^*}{\partial t}\right)\eta_k + (U^\dagger - \lambda_k^*)\frac{\partial \eta_k}{\partial t} = 0;$$

$$\left(H - \frac{h}{2\pi i}\lambda_k \frac{\partial \lambda_k^*}{\partial t}\right)\eta_k = \frac{h}{2\pi i}(1 - U\lambda_k^*)\frac{\partial \eta_k}{\partial t}; \tag{175}$$

$$\langle \eta_k | H | \eta_l \rangle = \frac{h}{2\pi i}\lambda_k \frac{\partial \lambda_k^*}{\partial t}\delta_{kl} + \frac{h}{2\pi i}(1 - \lambda_k \lambda_l^*)\left\langle \eta_k \middle| \frac{\partial \eta_l}{\partial t}\right\rangle;$$

and further

$$\langle \eta_k | H | \eta_k \rangle = -\frac{h}{2\pi}\frac{\partial \alpha_k}{\partial t}; \tag{176}$$

$$\langle \eta_k | H | \eta_l \rangle = \frac{h}{2\pi i}\{1 - e^{(\alpha_k - \alpha_l)}\}\left\langle \eta_k \middle| \frac{\partial \eta_l}{\partial t}\right\rangle. \tag{177}$$

Hence one has

$$\alpha_k = -\frac{2\pi}{h}\int_0^t \langle \eta_k | H | \eta_k \rangle \, dt_1, \tag{178}$$

and substitution of this expression into (170) leads to an expansion closely analogous to (151).

The matrix representation $\langle \eta_k | H | \eta_l \rangle$ will be strictly diagonal if and only if $HU = UH$, i.e., if H is a constant of evolution. By using (173) and (167) this condition may also be written

$$\frac{\partial U}{\partial t} U = U \frac{\partial U}{\partial t}, \tag{179}$$

which implies that $U(t)$ should commute with $U(t + dt)$; i.e., the evolution operator should commute with itself in the extended interval $(t; t + dt)$. In this latter case, H and U have simultaneous eigenfunctions at the time t, and the eigenvalues of the Hamiltonian are given by (176). The evolution operator description has many advantages, but so far the Hamiltonian description has been dominating in quantum mechanics particularly for systems where H is easily constructed from classical analogs.

VII. Transition Probabilities

In order to study the probability distribution over a set of discrete states as a function of time, we will introduce a complete set of orthonormal functions $f_k = f_k(\mathbf{R})$ as a basis:

$$\langle f_k | f_l \rangle = \delta_{kl}; \qquad 1 = \sum_k | f_k \rangle \langle f_k |. \tag{180}$$

Expanding the wave function $\Psi = \Psi(\mathbf{R}, t)$ in this basis, one obtains $\Psi = \Sigma_k |f_k\rangle\langle f_k|\Psi\rangle$, i.e.,

$$\Psi(\mathbf{R}, t) = \sum_k f_k(\mathbf{R})C_k(t), \tag{181}$$

where $C_k(t) = \langle f_k | \Psi\rangle$ is a time-dependent coefficient. Introducing the relation $\Psi(t) = U\Psi_0$, the expansion $\Psi_0 = \Sigma_l f_l(\mathbf{R})C_l(0)$, and the notation $U_{kl} = \langle f_k | U | f_l\rangle$, one obtains directly

$$\begin{aligned} C_k(t) &= \langle f_k | \Psi\rangle = \langle f_k | U\Psi_0\rangle \\ &= \langle f_k | U | \sum_l f_l C_l(0)\rangle \\ &= \sum_l \langle f_k | U | f_l\rangle\, C_l(0) \\ &= \sum_l U_{kl} C_l(0), \end{aligned} \tag{182}$$

which formula describes the time evolution of the coefficients. The quantities $P_k(t) = |C_k(t)|^2$ are conventionally interpreted as the probability for finding the quantum-mechanical system in the state k characterized by the wave function f_k at the time t. From (182) we get further

$$\begin{aligned} P_k(t) &= C_k^*(t)C_k(t) = \{\sum_l U_{kl}C_l(0)\}^*\{\sum_m U_{km}C_m(0)\} \\ &= \sum_{l,m} U_{kl}^* U_{km} C_l^*(0)C_m(0) \\ &= \sum_l |U_{kl}|^2 P_l(0) + \sum_{l \neq m} U_{kl}^* U_{km} C_l^*(0)C_m(0), \end{aligned} \tag{183}$$

where the last term may be characterized as an "interference term" between the various states. Using the unitary property of the operator U expressed in the relations

$$\sum_k |U_{kl}|^2 = \sum_l |U_{kl}|^2 = 1 \tag{184}$$

and

$$\sum_k U_{kl}^* U_{km} = \sum_k U_{lk}^* U_{mk} = 0 \qquad (l \neq m), \tag{185}$$

one finds that

$$\sum_k P_k(t) = \sum_l P_l(0) = 1. \tag{186}$$

A. Transition Probabilities

Let us start the discussion of the interpretation of Eq. (183) by assuming that at $t = t_0$ the system is completely in the state characterized by the wave function f_n, so that $P_n(0) = 1$, whereas all other $P_l(0) = 0$. From (183), it follows that

$$P_k(t) = |U_{kn}|^2, \tag{187}$$

and the quantity $|U_{kn}(t; t_0)|^2$ is then interpreted as the probability that the system jumps from the original state n to the state k during the time interval $(t_0; t)$. This interpretation is obtained in a very special physical situation, and it is then generalized to more complicated situations:

$$S_{n\to k}(t_0; t) = |U_{kn}(t; t_0)|^2. \tag{188}$$

From the unitary properties (184) of the evolution operator it follows that

$$\sum_k S_{n\to k}(t_0; t) = \sum_k |U_{kn}|^2 = 1, \tag{189}$$

showing that the total probability that the system either stays in the state n or leaves this state equals 1. Since all the quantities S are positive, one has further

$$0 \leq S_{n\to k}(t_0; t) \leq 1, \tag{190}$$

which means that transition probabilities can never "blow up." If this is the case in an approximate treatment, e.g., in perturbation theory, the phenomenon must hence depend on a defect in the approximation itself.

One should observe that the question of the transition probabilities depends essentially on the reference system $\{f_k\}$ chosen. For instance, if one chooses the eigenfunctions η_k of the evolution operator as a basis, one has $\langle \eta_k | U | \eta_l \rangle = \lambda_l \delta_{kl}$, and

$$|\langle \eta_k | U | \eta_l \rangle|^2 = \begin{cases} 1, & \lambda_k = \lambda_l, \\ 0, & \lambda_k \neq \lambda_l, \end{cases} \tag{191}$$

which relation shows that the probability distribution over this specific basis is the same at the times t_0 and t, i.e., remains stationary. However, the system as a whole is by no means stationary, and the evolution from t_0 to t is instead described by the phase changes in the coefficients C_k in (182). Hence, in general, the phases play a key role in the description of the time dependence, as one could also expect from the discussion in Section II.

B. Random-Phase Systems

It has been emphasized in connection with the quantum-mechanical superposition principle that the interference term in (62) plays a fundamental role in many basic phenomena in physics and chemistry. However, there are also situations where it is of interest to study assemblies of systems having different phases, where probabilities are additive in accordance with (63).

Let us introduce an assembly of systems having the same probability distribution $P_l(0)$ at the time $t = t_0$, whereas the phases are distributed at random so that, in average over the assembly, one has

$$\overline{C_l^*(0)C_m(0)} = 0, \qquad l \neq m. \tag{192}$$

By applying this averaging procedure to (183), one obtains

$$P_k(t) = \sum_l |U_{kl}|^2 P_l(0), \tag{193}$$

which is the fundamental equation in the random-phase systems. Using the fact that U is a unitary operator and the definition (188) of the transition probabilities, one can write relation (193) in the form

$$P_k(t) = P_k(0) + \sum_{l \neq k} P_l(0) S_{l\to k}(t) - P_k(0) \sum_{l \neq k} S_{k\to l}(t), \tag{194}$$

showing that the probability for the occurrence of the system in the state k at time t equals the probability at $t = t_0$, plus the probability that the system would jump from any other state l to the state k under the time interval $(t_0; t)$, minus the probability that the system would leave the original state k and go over to another state during the same period. In random-phase systems, the transition probabilities are hence truly additive, as one could expect in an incoherent phenomenon.

In a conventional treatment of (194), one would proceed by assuming the existence of a law of "microscopic reversibility" saying that $S_{n\to k} = S_{k\to n}$ for the time interval $(t_0; t)$. In the general case, however, one has usually for the unitary operator U:

$$|U_{kn}|^2 \neq |U_{nk}|^2, \tag{195}$$

except in special cases which will be further discussed below. Even in the general case, one can now proceed by noting the existence of the relation

$$1 - \sum_{l \neq k} S_{k\to l}(t) = |U_{kk}|^2 = 1 - \sum_{l \neq k} S_{l\to k}(t), \tag{196}$$

which follows directly from (184). Introducing this relation into (194), we obtain

$$Pk(t) = P_k(0) + \sum_{l \neq k} \{P_l(0) - P_k(0)\} S_{l\to k}(t), \tag{197}$$

which is exactly the relation one usually derives by means of the law of microscopic reversibility. This equation shows that, in general, there is a flow of probability from levels of higher probability to levels of lower probability, and, since this flow is always going in one and the same direction, one can expect that the process should be irreversible. This is also the case, as we will see below.

C. Reversible Processes

The problem of time reversal has previously been discussed in some detail, and it has been emphasized that the basic laws in classical mechanics as well as in quantum mechanics are reversible in time under certain general conditions and are hence "primary laws" of physics. According to (93), this applies in the latter case if a time-independent Hamiltonian H is not only self-adjoint ($H^\dagger = H$) but also real:

$$H^* = H, \tag{198}$$

in which case the process $\Psi_0 \rightarrow \Psi$ has the reverse process $\Psi^* \rightarrow \Psi_0{}^*$ as outlined in (94).

This problem can now be treated by means of the evolution operator. From the definition $\Psi = U\Psi_0$ it follows directly that $\Psi_0 = U^\dagger\Psi$ and

$$\Psi_0{}^* = (U^\dagger)^*\Psi^*. \tag{199}$$

In the special case when the evolution operator has the simple form (141), one obtains

$$(U^\dagger)^* = U, \tag{200}$$

showing that the reverse process $\Psi^* \rightarrow \Psi_0{}^*$ is associated with the same evolution operator and the same Hamiltonian as the original process $\Psi_0 \rightarrow \Psi$.

This result is of interest also for studying the principle of "microscopic reversibility." If the Hamiltonian is real according to (198), its eigenfunctions may also be chosen real, and we will now choose even the basis $\{f_k\}$ to consist of only *real* functions. Using the relation $U^\dagger = U^*$, one obtains

$$\begin{aligned} U_{kl} = U^\dagger_{lk} &= \langle f_l | U^\dagger | f_k \rangle = \langle f_l | U^* | f_k \rangle \\ &= \langle f_l | U | f_k \rangle^* = U^*_{lk} \end{aligned} \tag{201}$$

and

$$|U_{kl}|^2 = |U_{lk}|^2, \tag{202}$$

which means that, under these specific assumptions, the principle of microscopic reversibility is strictly valid.

It should be observed, however, that the wave functions themselves have in general *complex character* in order to describe the probability distributions in both ordinary position space and momentum space as outlined in Section II. If one has insufficient information about the phases, one has also insufficient information about the physical situation in general, and any averaging procedure will then usually lead to equations which are no longer reversible in time, and which are hence characterized as "secondary laws."

D. Irreversible Processes

As a simple example of an irreversible process, we will study the behavior of a random-phase system based on assumption (192). The random-phase postulate was first clearly stated by Pauli (1928) in connection with a study of irreversible processes, but it was also used by Dirac (1927, 1935) in his formulation of the time-dependent perturbation theory.

In order to study some of the consequences of the random-phase postulate (192), we will introduce an arbitrary function $L(x)$ which is convex in the interval $0 \leq x \leq 1$ so that $L''(x) > 0$. According to Lagrange's mean-value formula, one has

$$L(x+h) - L(x) - hL'(x) = \frac{h^2}{2!} L''(x + \theta h) \geq 0, \tag{203}$$

where $0 \leq \theta \leq 1$. Putting $x + h = P_l(0)$ and $x = P_k(t)$, we obtain

$$Q_{kl} \equiv L\{P_l(0)\} - L\{P_k(t)\} - \{P_l(0) - P_k(t)\}L'\{P_k(t)\} \geq 0, \tag{204}$$

where the equality is valid only if $h = 0$. Using the fundamental relation (193) and the unitary properties (184) of the evolution operator, one finds

$$\begin{aligned} 0 &\leq \sum_{kl} Q_{kl}|U_{kl}|^2 \\ &= \sum_l L\{P_l(0)\} \sum_k |U_{kl}|^2 - \sum_k L\{P_k(t)\} \sum_l |U_{kl}|^2 \\ &\quad - \sum_k \Big[\sum_l |U_{kl}|^2 P_l(0)\Big] L'\{P_k(t)\} + \sum_k P_k(t) L'\{P_k(t)\} \sum_l |U_{kl}|^2 \\ &= \sum_l L\{P_l(0)\} - \sum_k L\{P_k(t)\}, \end{aligned} \tag{205}$$

$$\sum_k L\{P_k(0)\} \geq \sum_k L\{P_k(t)\}. \tag{206}$$

Here the equality sign holds only if the initial probabilities $P_k(0)$ are all the same. The relation indicates hence that, in general, the time evolution of a random-phase system from t_0 to t is irreversible and that the quantity $\Sigma_k L\{P_k\}$ has decreased.

There are many possible choices of the convex function L, and the particular form $L = x \log x$ is characterized by the fact that $\Sigma_k P_k \log P_k$ is additive over independent subsystems. The quantity

$$S = -k \sum_k P_k \log P_k, \tag{207}$$

where the coefficient k is Boltzmann's constant, is such that $S(0) \leq S(t)$ and is sometimes characterized as the "microentropy." It is defined over the configuration space associated with all the particles of the system, whereas the conventional entropy refers to the ordinary space and may be obtained by a reduction procedure.

As mentioned above, the random-phase postulate has been used to a large extent in modern quantum mechanics, particularly by Dirac (1927, 1935). However, it has considerable weaknesses, since it can be valid only in a specific reference system and only at a specific time t_0. With the evolution in time, the system leaves the pure random-phase situation, and the same happens if one goes over to another basis.

In conclusion, it should be observed that the Schrödinger equation itself may contain irreversible elements in the form of time-dependent electromagnetic potentials, e.g., retarded potentials. However, even in the case when the Schrödinger equation is fully reversible in time, a study of the probability properties of assemblies may show irreversible features depending on the fact that one has not complete knowledge of the entire physical situation, i.e., the wave function including its phase. The question is how these uncertainties should be properly described. Important work on the irreversibility problem has during the last decades been carried out by Kirkwood (1946, 1947), Prigogine (1947), and Bogoliubov (1946).

E. Time Dependence of Density Matrices

In concluding this section, it should be observed that the evolution operator formalism is particularly useful in treating statistical assemblies described by density matrices. In the terminology of von Neumann (1932), a system characterized by a wave function Ψ corresponds to a "pure state" and is associated with a *homogeneous assembly* which has a density matrix Γ defined by the relation $\Gamma = \Psi\Psi^\dagger$ or

$$\Gamma(\mathbf{R}, t \mid \mathbf{R}', t') = \Psi(\mathbf{R}, t)\Psi^\dagger(\mathbf{R}', t'), \tag{208}$$

where, for the sake of simplicity, we will choose $t' = t$. Since the wave functions have a time evolution of the type $\Psi = U\Psi_0$, $\Psi^\dagger = \Psi_0{}^\dagger U^\dagger$, one obtains

$$\Gamma(t) = U\Gamma(0)U^\dagger \tag{209}$$

for the density matrix of the homogeneous assembly. This relation is then generalized to define the time behavior of density matrices in general. A density matrix $\Gamma = \Gamma(\mathbf{R}, t|\mathbf{R}', t)$ is essentially characterized by the following three conditions:

$$\Gamma^\dagger = \Gamma, \qquad \Gamma \geq 0, \qquad \mathrm{Tr}(\Gamma) = 1, \tag{210}$$

and it usually represents a "mixture" of physical situations associated with wave functions.

In order to study the properties of density matrices in greater detail, it is convenient to introduce a complete orthonormal basis $\{f_k\}$ fulfilling the relations (180). In considering the initial time $t = t_0$, one obtains the expansion

$$\Gamma(\mathbf{R}, t_0|\mathbf{R}', t_0) = \sum_{kl} f_k(\mathbf{R})\Gamma_{kl}(0)f_l^*(\mathbf{R}'), \tag{211}$$

or, in matrix form, $\Gamma_0 = \mathbf{f}\boldsymbol{\Gamma}(0)\mathbf{f}^\dagger$. In analogy to (210), the discrete matrix $\boldsymbol{\Gamma}(0) = \{\Gamma_{kl}(0)\}$ has the properties $\boldsymbol{\Gamma}^\dagger = \boldsymbol{\Gamma}$, $\boldsymbol{\Gamma} \geq 0$, $\mathrm{Tr}(\boldsymbol{\Gamma}) = 1$. There exists hence a unitary transformation $\mathbf{V}$ which brings $\boldsymbol{\Gamma}(0)$ to diagonal form $\mathbf{n}(0)$:

$$\mathbf{V}^\dagger\boldsymbol{\Gamma}(0)\mathbf{V} = \mathbf{n}(0), \tag{212}$$

where the eigenvalues $n_k(0)$ are real and satisfy the relations

$$n_k(0) \geq 0, \qquad \sum_k n_k(0) = 1. \tag{213}$$

One has further $\boldsymbol{\Gamma}(0) = \mathbf{V}\mathbf{n}(0)\mathbf{V}^\dagger$ and, introducing the wave functions $\chi_k(\mathbf{R})$ through the transformation

$$\chi = \mathbf{f}\mathbf{V}, \tag{214}$$

one obtains $\Gamma_0 = \mathbf{f}\boldsymbol{\Gamma}(0)\mathbf{f}^\dagger = \mathbf{f}\mathbf{V}\mathbf{n}(0)\mathbf{V}^\dagger\mathbf{f}^\dagger = \chi\mathbf{n}(0)\chi^\dagger$, i.e.,

$$\Gamma(\mathbf{R}, t_0\,|\,\mathbf{R}', t_0) = \sum_k \chi_k(\mathbf{R})n_k(0)\chi_k^*(\mathbf{R}'), \tag{215}$$

which relation may be considered as the "spectral resolution" of the density matrix Γ for $t = t_0$; the functions $\chi_k(\mathbf{R})$ are its eigenfunctions and the numbers $n_k(0)$ its eigenvalues, and one has $\Gamma\chi_k = n_k\chi_k$. Each one of the terms $\chi_k(\mathbf{R})\chi_k^*(\mathbf{R}')$ represents the density matrix for a "pure state" having the wave function $\chi_k(\mathbf{R})$, and the sum (215) hence represents a "mixture" of such pure states with the weights $n_k(0)$. We note the essential physical difference between the expansion (215) which is used in analyzing a general assembly and the expansion (181) which is used in studying the wave function associated with a "pure state."

The sum (215) contains usually many terms, and it is reduced to a single term if and only if $n_p(0) = 1$ and $n_k(0) = 0$ for $k \neq p$, in which case one has

$$\Gamma(\mathbf{R}, t_0 \,|\, \mathbf{R}', t_0) = \chi_p(\mathbf{R})\chi_p^*(\mathbf{R}'); \tag{216}$$

i.e., the assembly is homogeneous and corresponds to a pure state with the wave function $\chi_p(\mathbf{R})$. It is easily shown that an assembly corresponds to a pure state if and only if the density matrix is idempotent, so that $\Gamma^2 = \Gamma$.

After this analysis of the density matrix at $t = t_0$, we will now study the time dependence defined through the relation (209). Introducing the time-dependent basis

$$\chi_k(\mathbf{R}, t) = U(t)\chi_k(\mathbf{R}), \tag{217}$$

one obtains directly

$$\begin{aligned}\Gamma(t) &= U\Gamma(0)U^\dagger = U\chi n(0)\chi^\dagger U^\dagger \\ &= \chi(t)\mathbf{n}(0)\chi^\dagger(t),\end{aligned} \tag{218}$$

and the spectral resolution

$$\Gamma(\mathbf{R}, t \,|\, \mathbf{R}', t) = \sum_k \chi_k(\mathbf{R}, t)n_k(0)\chi_k^*(\mathbf{R}', t), \tag{219}$$

which shows that the weight factors n_k and hence the character of the mixture are independent of time.

For a more detailed study of the properties of the density matrices and their use in physics and chemistry, we will refer to von Neumann (1932) and to Husimi (1940).

VIII. Time-Dependent Perturbation Theory

Let us now consider the case when the Hamiltonian $H = H(t)$ may conveniently be written in the form

$$H = H_0 + V(t), \tag{220}$$

where V is a small perturbation to the unperturbed system characterized by the Hamiltonian H_0 having the normalized eigenfunctions Φ_k^0 and the eigenvalues E_k^0. In the following, we will make the choice $f_k = \Phi_k^0$ and introduce the unperturbed eigenfunctions as a basis and reference system.

The transition probabilities caused by the perturbation V are given by the general formula (188):

$$S_{n\to k}(t_0; t) = |U_{kn}(t; t_0)|^2, \tag{221}$$

and we note that, depending on the condition (190), these quantities can never "blow up." The absolute values of the unitary matrix **U** are always well-behaved, whereas the phases may turn out to be "dangerous" quantities involving some of the divergence difficulties still associated with modern quantum mechanics.

It is convenient to treat the perturbation problem in the "interaction representation" and to express the evolution operator U in the product form $U = U_0 \cdot U_V$, where U_V is given by expansion (164):

$$U_V(t) = \sum_{n=0}^{\infty} \left(-\frac{2\pi i}{h}\right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n V_H(t_1) V_H(t_2) \cdots V_H(t_n), \tag{222}$$

where

$$V_H = U_0{}^{\dagger} V U_0 = e^{+(2\pi i/h)H_0 t}\, V e^{-(2\pi i/h)H_0 t}. \tag{223}$$

For the matrix elements of U, one obtains directly:

$$\langle \Phi_k{}^0 \mid U \mid \Phi_l{}^0 \rangle = \exp[(2\pi_i/h)E_k{}^0 t] \langle \Phi_k{}^0 \mid U_V \mid \Phi_l{}^0 \rangle, \tag{224}$$

and consequently

$$S_{n\to k}(t_0; t) = |\langle \Phi_k{}^0 | \, U_V \, | \Phi_l{}^0 \rangle|^2, \tag{225}$$

which is a considerable simplification. Introducing the "Bohr frequency"

$$\nu_{kl}^0 = (E_k{}^0 - E_l{}^0)/h, \tag{226}$$

one obtains similarly for the matrix elements of V_H:

$$\langle \Phi_k{}^0 \mid V_H \mid \Phi_l{}^0 \rangle = \exp(2\pi i \nu_{kl}^0 t) \langle \Phi_k{}^0 \mid V \mid \Phi_l{}^0 \rangle. \tag{227}$$

Using the expansion (222), we will now study the matrix elements of the operator U_V:

$$\begin{aligned} \langle \Phi_k{}^0 \mid U_V \mid \Phi_l{}^0 \rangle = \delta_{kl} &- \frac{2\pi i}{h} \int_0^t dt_1 \{V_H(t_1)\}_{kl} \\ &+ \sum_{\alpha} \left(-\frac{2\pi i}{h}\right)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \{V_H(t_1)\}_{k\alpha} \{V_H(t_2)\}_{\alpha l} \\ &+ \sum_{\alpha\beta} \left(-\frac{2\pi i}{h}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \{V_H(t_1)\}_{k\alpha} \\ &\times \{V_H(t_2)\}_{\alpha\beta} \{V_H(t_3)\}_{\beta l} + \cdots \end{aligned} \tag{228}$$

for various forms of the perturbation V. The indices α, β, ... are said to refer to so-called "intermediate states."

A. Time-Independent Perturbation

Let us start by considering the simplest case when the perturbation is a constant in time, $V(t) = V$. Using (227) and (228), one obtains directly

$$\begin{aligned}\langle \Phi_k{}^0 | U_V | \Phi_l{}^0 \rangle = {} & \delta_{kl} - \frac{2\pi i}{h} V_{kl} \frac{\exp(2\pi i \nu^0_{kl} t) - 1}{2\pi i \nu^0_{kl}} \\ & + \left(-\frac{2\pi i}{h}\right)^2 \sum_\alpha V_{k\alpha} V_{\alpha l} \\ & \times \left\{ \frac{e^{2\pi i \nu^0_{kl} t} - 1}{2\pi i \nu^0_{kl} \cdot 2\pi i \nu^0_{\alpha l}} - \frac{\exp(2\pi i \nu^0_{k\alpha} t) - 1}{2\pi i \nu^0_{k\alpha} \cdot 2\pi i \nu^0_{\alpha l}} \right\} \\ & + \cdots . \end{aligned} \tag{229}$$

For $\nu^0_{kl} = 0$, one obtains so-called "resonance denominators," but we note that all terms are still regular according to formulas of the type

$$\lim_{\nu \to 0} \frac{\exp(2\pi i \nu t) - 1}{2\pi i \nu} = t. \tag{230}$$

In the special case when V commutes with H_0, the matrix V_{kl} is diagonal, and one has further the explicit solution

$$U_V = e^{-(2\pi i/h)Vt} = 1 - \frac{2\pi i}{h} V t + \left(-\frac{2\pi i}{h} V\right)^2 \frac{t^2}{2!} + \cdots, \tag{231}$$

which often serves as a convenient check.

Following Dirac (1927, 1935), we will now study the first-order term in (229) for $k \neq l$ in greater detail:

$$\langle \Phi_k{}^0 | U_V | \Phi_l{}^0 \rangle \approx \Gamma \frac{2\pi i}{h} V_{kl} \frac{\exp(2\pi i \nu^0_{kl} t) - 1}{2\pi i \nu^0_{kl}} . \tag{232}$$

Substitution into (225) gives the transition probability

$$S^{(1)}_{l \to k}(t) = \frac{2}{h^2} |V_{kl}|^2 \frac{1 - \cos 2\pi \nu^0_{kl} t}{(\nu^0_{kl})^2} . \tag{233}$$

This quantity oscillates a great deal with time and we observe that, for a small $t \approx 0$, one has a quadratic behavior $S^{(1)}_{l \to k}(t) = (4\pi^2/h^2)|V_{kl}|^2 t^2$.

Of particular importance in physics and chemistry are the time-proportional transition probabilities, and one may wonder how they are related to perturbation theory. It turns out (Dirac, 1927, 1935) that they are characteristic for transitions from a discrete level l to a series of levels k which are so tight-lying that they form a continuous band (see Fig. 1).

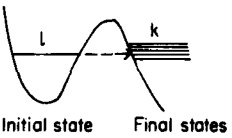

Fig. 1. Transition from a discrete level to a series of levels in the continuum.

Such transitions occur, e.g., in phenomena where a free particle is emitted, for instance radioactivity. Let us assume that the "band" for the final state $E_k{}^0$ covers the energy interval $(E - \Delta E;\ E + \Delta E)$ and that the density of states is given by the quantity $\rho(E)$. Assuming that the probabilities are additive, one obtains for the total transition probability:

$$S^{(1)}_{l\to\mathrm{cont}}(t) = \sum_k S^{(1)}_{l\to k}(t) = \int_{E-\Delta E}^{E+\Delta E} S^{(1)}_{l\to k}(t)\rho(E_k{}^0)\, dE_k{}^0$$
$$= \frac{2}{h^2}\int_{E-\Delta E}^{E+\Delta E} |\langle \Phi_k{}^0 | V | \Phi_l{}^0\rangle|^2 \, \frac{1 - \cos 2\pi(E_k{}^0 - E_l{}^0)t/h}{(E_k^0 - E_l)^2/h^2}$$
$$\times\ \rho(E_k{}^0)\, dE_k{}^0. \tag{234}$$

We will assume that the quantities $|\langle \Phi_k{}^0 | V | \Phi_l{}^0\rangle|$ and $\rho(E_k{}^0)$ are slowly varying functions of $E_k{}^0$ which may be taken outside the integration. Making the substitution

$$\frac{2\pi}{h}(E_k{}^0 - E_l{}^0)t = \xi, \qquad \frac{2\pi}{h}\, t\, dE_k{}^0 = d\xi, \tag{235}$$

one obtains

$$S^{(1)}_{l\to\mathrm{cont}}(t) = \frac{4\pi t}{h}\, |V_{kl}|^2 \rho(E) \int_{-2\pi t\cdot\Delta E/h}^{+2\pi t\cdot\Delta E/h} \frac{1 - \cos\xi}{\xi^2}\, d\xi. \tag{236}$$

The integrand is plotted in Fig. 2 and given by the following equation (see Appendix):

$$\int_{-\infty}^{+\infty} \frac{1 - \cos\xi}{\xi^2}\, d\xi = \pi. \tag{237}$$

We note that the main contribution to the integral comes from the environment of the point $\xi = 0$, which corresponds to the energy resonance

$E_k^0 \approx E_l^0$ between the initial and final states. This resonance is never completely sharp, however, depending on the uncertainty relation for the energy and time.

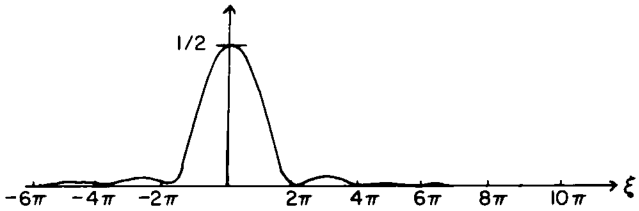

Fig. 2. Diagram of the function $(1-\cos\xi)/\xi^2$.

All energy measurements involve some interaction between the object and the apparatus which is carried by at least one elementary particle in the form of a wave packet having the kinetic energy $E = p^2/2m$ and the extension Δx. The time Δt needed for the entire wave packet to enter the measuring device is approximately the same as the time needed to pass through a plane separating the object from the apparatus, perpendicular to the motion of the wave packet (see Fig. 3). Since the velocity is p/m, one has

$$(p/m)\Delta t \approx \Delta x. \tag{238}$$

From $E = p^2/2m$ follows further $\Delta E = p\Delta p/m$, which gives $\Delta E \cdot \Delta t = \Delta p(p/m)\Delta t = \Delta p \cdot \Delta x \geq h/4\pi$, and the uncertainty relation

$$\Delta E \cdot \Delta t \geq \frac{h}{4\pi}. \tag{239}$$

This implies that, in order to make a measurement of the energy with a certain accuracy ΔE, a certain minimum time interval Δt is always needed.

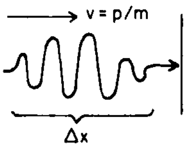

Fig. 3. Passage of a wave packet through a plane.

Let us now return to relation (236). It is clear that this formula has a meaning only if the time interval t is not too short with reference to the uncertainty relation (239), i.e.,

$$t \geq \frac{h}{4\pi\Delta E}, \tag{240}$$

which implies that $2\pi t\Delta E/h > +\frac{1}{2}$. With increasing t, the integral takes quickly its full value according to (237), and one obtains the final formula

$$S^{(1)}_{l\to\mathrm{cont}}(t) = \frac{4\pi^2}{h}\,|V_{kl}|^2\rho(E)\cdot t, \tag{241}$$

which is a time-proportional transition probability. Because of (190), it can only be valid for times t which are not too large, and formula (241) gives essentially the transition coefficient $\gamma = (4\pi^2/h)|V_{kl}|^2\rho$, which enters the decay relation

$$\frac{dP_l}{dt} = -\gamma P_l, \tag{242}$$

with the solution $P_l(t) = P_l(0)e^{-\gamma t}$. The probability of the levels k in the "band" increases further according to the rule

$$P_k(t) = P_l(0)\{1 - e^{-\gamma t}\}, \tag{243}$$

and we note that the term γt in the right-hand member (241) may be considered as the first term in the expansion of $(1 - e^{-\gamma t})$. The relations (242) and (243) may be obtained by considering also the higher terms in the expansion (228), but, in reality, the situation is usually more complicated than indicated here.

B. Oscillatory Perturbation

Let us now consider a general perturbation V, which is a function of time, and let us assume that it may be expressed as a Fourier series:

$$V(t) = \sum_{\kappa} \exp(-2\pi i\nu_\kappa t)v_\kappa, \tag{244}$$

where the coefficients v_κ are linear operators working on the functions in the **R** space. According to (227), one obtains for the matrix elements of V_H:

$$\langle\Phi_k{}^0\,|\,V_H\,|\,\Phi_l{}^0\rangle = \sum_{\kappa} \exp[2\pi i(\nu^0_{kl} - \nu_\kappa)t]\langle k\,|\,v_\kappa\,|\,l\rangle. \tag{245}$$

The matrix elements of the operator U_V are again given by formula (228), and we note that, for a perturbation of the form (244), the time integrations are of an elementary nature and are easily carried out explicitly. One obtains

$$\begin{aligned}\langle \Phi_k{}^0 \,|\, U_V \,|\, \Phi_l{}^0 \rangle = \delta_{kl} &- \frac{2\pi i}{h} \sum_{\kappa} \frac{\exp[2\pi i(\nu_{kl}^0 - \nu_\kappa)t] - 1}{2\pi i(\nu_{kl}^0 - \nu_\kappa)} \langle k \,|\, \nu_\kappa \,|\, l \rangle \\ &+ \left(-\frac{2\pi i}{h}\right)^2 \sum_{\kappa,\lambda} \sum_{\alpha} \left\{ \frac{\exp[2\pi i(\nu_{kl}^0 - \nu_\kappa - \nu_\lambda)t] - 1}{2\pi i(\nu_{kl}^0 - \nu_\kappa - \nu_\lambda) 2\pi i(\nu_{\alpha l}^0 - \nu_\lambda)} \right. \\ &\left. - \frac{\exp[2\pi i(\nu_{k\alpha}^0 - \nu_\kappa)t] - 1}{2\pi i(\nu_{k\alpha}^0 - \nu_\kappa) 2\pi i(\nu_{\alpha l}^0 - \nu_\lambda)} \right\} \\ &\times \langle k \,|\, \nu_\kappa \,|\, \alpha \rangle \langle \alpha \,|\, \nu_\lambda \,|\, l \rangle + \cdots . \end{aligned} \tag{246}$$

It is interesting to observe that "resonance denominators" occur for $\nu_\kappa = \nu_{kl}^0$ and, in the second-order terms, also for $\nu_\kappa + \nu_\lambda = \nu_{kl}^0$, etc., corresponding to one- and two-quantum processes, etc. These terms are of essential interest in studying time-proportional transition probabilities, and the treatment follows essentially the same lines as given in the previous section.

For the sake of simplicity, we will study a single oscillatory term in greater detail:

$$V = e^{-2\pi i \nu t} v. \tag{247}$$

Such a perturbation is not self-adjoint, but the result is still typical for the terms occurring in this connection. Using (246), one obtains through the first order

$$\langle \Phi_k{}^0 \,|\, U_V \,|\, \Phi_l{}^0 \rangle \approx -\frac{2\pi i}{h} v_{kl} \frac{\exp[\ \pi i(\nu_{kl}^0 - \nu)t] - 1}{2\pi i(\nu_{kl}^0 - \nu)}, \tag{248}$$

in complete analogy to (232). This gives for the associated transition probability

$$S_{l \to k}^{(1)}(t) = \frac{2}{h^2} |v_{kl}|^2 \frac{1 - \cos 2\pi(\nu_{kl}^0 - \nu)t}{(\nu_{kl}^0 - \nu)^2}, \tag{249}$$

and, by studying the transitions from the discrete level l to the continuous levels k having the energy

$$E_k{}^0 \approx E_l{}^0 + h\nu, \tag{250}$$

one obtains in analogy to (241)

$$S_{l \to \mathrm{cont}}^{(1)}(t) = \frac{4\pi^2}{h} |v_{kl}|^2 \rho(E_k{}^0) t, \tag{251}$$

which is the formula desired. According to (250), one finds that, from the point of view of the unperturbed system, this transition involves the absorption of the energy $h\nu$ from the oscillatory field associated with the perturbation V. By studying the self-adjoint perturbation

$$V = v \exp(-2\pi i\nu t) + v^{\dagger} \exp(+2\pi i\nu t), \tag{252}$$

one finds also the transition probability for the corresponding emission process.

It is clear that, since the evolution operator in principle describes all the various time-dependent phenomena in physics and chemistry, we have here only touched a very small field of applications. The further study of the evolution operator and its matrix elements is probably one of the most important current research problems and, even if very important progress has been made during the last two decades particularly in connection with the so-called diagram technique, the study is still far from being concluded.

IX. Discussion

The purpose of this paper is to give a brief discussion of the treatment of time-dependent phenomena in the nonrelativistic quantum theory. In many of the applications, the theory has been quite successful and has led to results in complete agreement with experimental experience, but there are still certain difficulties connected with the concept of a complex wave function and particularly the evaluation of its phase. In the formula for time evolution $\Psi(t) = U\Psi_0$, it may be possible to calculate the evolution operator U but considerably more difficult to determine the wave function Ψ_0 for the initial state. The phase problem has been discussed in some detail in Section II.

The problem of the behavior of a many-particle system under the influence of an outer electromagnetic field can be treated in principle, but it is more difficult to study the interaction between a system of matter waves and their own electromagnetic field. The problem of the self-interactions leads to divergence difficulties in both the nonrelativistic and relativistic formulations of quantum theory, and the nature of the elementary particles themselves is still completely unknown. For some time, one hoped that the evolution-operator formalism would be helpful in solving these problems, particularly since the absolute values of the matrix elements of U can never blow up, but it turned out that the difficulties were again connected with the phases. In scattering theory, the S matrix given by the relation

$$S = U(+\infty, -\infty) \tag{253}$$

has been studied in many papers with interesting results, but the main problems associated with the basic divergence difficulties seem still to be unsolved.

One way out of the difficulties would be to quantize the space-time coordinates and to introduce a minimum length and a minimum time. In such a case, one would have to give up the differential form of the laws of nature which has been characteristic for classical mechanics (2) as well as wave mechanics (21). We note, however, that the evolution-operator formalism is based on the use of a *finite* time interval (t_0; t). If the Hamiltonian H is time-independent, the evolution operator takes the form

$$U = \exp[-(2\pi i/h)H_{\text{op}}t] = \sum_k \exp[-(2\pi i/h)E_k t]\,|\Phi_k\rangle\langle\Phi_k|, \tag{254}$$

where Φ_k and E_k are the eigenfunctions and eigenvalues of H, respectively. The eigenvalue relation $H\Phi_k = E_k\Phi_k$ is certainly a differential equation, but the quantities Φ_k and E_k entering (254) may instead be found by considering the variational integral:

$$I = \frac{\langle\Phi|H|\Phi\rangle}{\langle\Phi|\Phi\rangle}. \tag{255}$$

Since the expectation value of the differential operator $\Sigma_k \mathbf{p}_k{}^2/2m_k$ may be evaluated in momentum space according to (38), it is not necessary to use any derivatives whatsoever—all the results may be obtained by integration only. In this way, wave mechanics may be formulated entirely in terms of integral calculus. Instead of requesting the wave functions to be continuous and differentiable, it is now sufficient to require that they should be quadratically integrable. Whether this change in the character of the theory gives a better fundament for solving the basic difficulties as to the nature of the elementary particles remains to be seen.

The time-dependent Schrödinger equation (21) has deepened the understanding of physics, and it has further rendered a unification of physics and chemistry which was previously inconceivable. It has led to a new model of the inner structure of atoms, molecules, and the solid state in excellent agreement with experience. Even if the remaining difficulties indicate that the theory is still not in its final form, it is highly useful as a tool for a unified description of numerous phenomena in nature.

Appendix. Evaluation of Certain Integrals

In time-dependent perturbation theory, there are certain definite integrals which often occur and have to be evaluated. It is convenient to start from the formula

$$\int_0^{\xi} e^{-x} \cos tx \, dx = \frac{1}{1+t^2} - e^{-\xi} \frac{\cos t\xi - t \sin t\xi}{1+t^2}, \tag{A1}$$

which is easily proven by differentiation. Integration over t between the limits 0 and t gives further:

$$\int_0^{\xi} e^{-x} \frac{\sin tx}{x} \, dx = \arctan t - e^{-\xi} \int_0^{t} \frac{\cos t\xi - t \sin t\xi}{1+t^2} \, dt. \tag{A2}$$

By letting $\xi \to +\infty$, one obtains

$$\int_0^{+\infty} e^{-x} \frac{\sin tx}{x} \, dx = \arctan t \, . \tag{A3}$$

Putting x instead of xt and $t = 1/u$, one has, for $t > 0$,

$$\int_0^{+\infty} e^{-ux} \frac{\sin x}{x} \, dx = \arctan \frac{1}{u}. \tag{A4}$$

Because of the uniform convergence of the integral, one can easily put $u \to +0$, which gives the result

$$\int_0^{+\infty} \frac{\sin x}{x} \, dx = \frac{\pi}{2}. \tag{A5}$$

Let us now return to the relation (A3). Integrating t over the interval between 0 and t, one obtains

$$\int_0^{+\infty} e^{-x} \frac{1 - \cos tx}{x^2} \, dx = t \arctan t - \tfrac{1}{2} \log(1 + t^2). \tag{A6}$$

Putting x instead of xt and $t = 1/u$, one gets immediately

$$\int_0^{+\infty} e^{-ux} \frac{1 - \cos x}{x^2} \, dx = \arctan \frac{1}{u} - \frac{u}{2} \log\left(1 + \frac{1}{u^2}\right), \tag{A7}$$

which, for $u \to +0$, gives

$$\int_0^{+\infty} \frac{1 - \cos x}{x^2} \, dx = \frac{\pi}{2}. \tag{A8}$$

One has $1 - \cos x = 2 \sin^2 x/2$ and, substituting x instead of $x/2$, one obtains finally

$$\int_0^{+\infty} \left(\frac{\sin x}{x}\right)^2 dx = \frac{\pi}{2}. \tag{A9}$$

These examples may be sufficient to illustrate a general technique for evaluating definite integrals of this specific type.

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