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PREFACE

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

Quantum chemistry deals particularly with the electronic structure of atoms, molecules, and crystalline matter and 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 for both the expert and the nonexpert to follow the rapid development in this new borderline area.

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

The editor would like to thank the authors for their contributions which give an interesting picture of the current status of selected parts of quantum chemistry. The topics covered in this volume range from the treatment of band theory of solids, mobile electrons in organic molecules, over studies of fundamental concepts in valence theory and intermolecular forces to chemical kinetics. Some of the papers emphasize studies in fundamental quantum theory and others computational techniques.

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

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Statistical Exchange-Correlation in the Self-Consistent Field

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I. The Derivation of the Xα Self-Consistent Method by Variations

In 1951, the author (Slater, 1951a, b) suggested the use of an approximate exchange term proportional to the one-third power of the local electronic density to replace the exact exchange in the self-consistent field for atoms, molecules, and crystals. The use of this simplified exchange, combined with the various approximate methods which had been worked out for solving Schrödinger's equation in a periodic potential, made possible a very extensive development of the theory of energy bands. Thus, in a book published by the author in 1965, it was possible to list a great many energy-band calculations which had been made up to that time (Slater, 1965a, Sect. 10-8), many of them using the approximate exchange method.

During the years since 1965, there has been greatly expanded activity in the way of treating the theory, calculation, and application of energy bands. In the references at the end of the present paper we list approximately a thousand papers which have appeared since the publication of the book cited above, dealing with subjects closely related to the self-consistent field for crystals. Some 450 of these papers, listed in the " Key to the References," describe energy-band calculations, and some 180 energy-band calculations out of this number, indicated by italicized references in the key, make some use of the approximate exchange. As one will see from this list of references and key, the energy bands of most of the crystalline elements, and of many important compounds, have been treated, many of them by several different methods. There is furthermore a large literature, not included in our list of references, concerning experimental work on energy bands and related topics, making connections between these bands and experiment.

There are two sides to a self-consistent field calculation: the determination of the potential, and the solution of Schrödinger's equation for the one-electron problem. The solution of Schrödinger's equation has fortunately advanced far enough, through the application of the electronic digital computer, so that it can be regarded for most purposes as being a standardized technique. A number of books or review articles dealing with this part of the problem have appeared since 1965. Thus there is the volume entitled " Energy Bands in Solids," forming Volume 8 of *Methods in Computational Physics*, edited by Alder *et al.* (1968). This contains papers (listed separately in our list of references) dealing with various computational methods including the augmented plane wave (APW), orthogonalized plane wave (OPW), Korringa–Kohn–Rostoker (KKR), linear combination of atomic orbitals or tight-binding (LCAO), pseudopotential, and others.

Individual methods have been handled in separate books. These include Loucks (1967a), Callaway (1964), Harrison (1966b). A recent survey, a report of a conference held in the spring of 1970, with articles by many workers, listed separately among our list of references, is *Computational Methods in Band Theory*, edited by Marcus *et al.* (1971). A number of individual papers dealing with the problems are collected in the Sanibel Symposium issues of the *International Journal of Quantum Chemistry*, including issues 1, 1967; 2, 1968; 3, 1970; and 4, 1971. With all of this review literature available, it has not seemed necessary to cover this side of the problem in the present review. Many of the applications of the energy-band calculations to problems of the Fermi surface, optical properties, etc., were taken up in a volume by the author in 1967 (Slater, 1967a).

The other side of the problem, the determination of the potential, and particularly the treatment of exchange and correlation, has not advanced nearly as far, and there has been more development of technique during the period since 1965. Consequently, we make this the main topic of the present paper. It should be stated that the author is engaged in writing Volume 4 of the series *Quantum Theory of Molecules and Solids,* which will handle the same type of material taken up in the present paper, but presented in detail, which it is hoped will answer many of the questions which the reader is likely to feel when reading the present abbreviated treatment. Let us now go on to describe some of the developments of the theory of the approximate statistical exchange as presented by the author in 1951, in the papers cited above.

Shortly after 1951, Gaspar (1954) observed that there was some theoretical justification for using an exchange of the same form as that suggested by the author, but with a coefficient two-thirds times as great. Kohn and Sham (1965), who had not noticed Gaspar's paper, pointed out the same fact later. Following the paper of Kohn and Sham, those who were calculating energy bands in crystals by use of the statistical approximation took to making the calculations both for the original exchange, and for that two-thirds as great. More generally, it began to be of interest to try intermediate values for the exchange, equal to α times the value originally suggested (so that $\alpha = \frac{2}{3}$ for the Gaspar–Kohn–Sham method), and by now it is clear that a value of α somewhat greater than two-thirds, generally of the order of magnitude of 0.7, is better than either $\alpha = 1$ or $\frac{2}{3}$. This method, with α determined as will be described in Section III, is now generally called the Xα method, and it is the method that we shall describe and advocate in the present review article. Our object will be to understand the situation in a fairly fundamental way, rather than to examine the effect of varying α empirically, as has been done by many of the authors quoted in the references.

The main point of the method of Gaspar, Kohn, and Sham is that they derive the approximate exchange correction from an approximate Hamiltonian for the system by varying the spin-orbitals to minimize the average value of this Hamiltonian for the ground state. The approximate Hamiltonian has many important and valuable features, which we shall describe in Sections III–VI. To have the situation well in mind, let us describe the method, which has been discussed by Slater and Wood (1971). We set up the problem in terms of a set of orthonormal spin-orbitals u_i, each associated with either spin up or down. We assume that there is an occupation number n_i for the ith spin-orbital; i.e., the ith spin-orbital is occupied by n_i electrons, where on account of the exclusion principle n_i must be between zero and unity. The Hartree–Fock case is one in which all n_i's are either zero or unity. We shall come later, in Sections IV and V, to the case of partially filled shells, as in the 3d transition elements, where we shall introduce q_i's, the total number of electrons in a shell in an isolated atom, which can go from zero to the total number of electrons that a closed shell can contain.

We shall define charge densities of electrons with spin up and spin down by the equations

$$\rho\uparrow = \sum_{j\uparrow} n_j u_j^* u_j, \qquad \rho\downarrow = \sum_{j\downarrow} n_j u_j^* u_j, \qquad \rho = \rho\uparrow + \rho\downarrow, \tag{I.1}$$

where the summation of $\rho\uparrow$ is carried over those spin-orbitals with spin up, that in $\rho\downarrow$ over those with spin down. The formula for total energy of the system, suggested in the Xα method (Slater and Wood, 1971) is

$$\langle EX\alpha\rangle = \sum_i n_i \int u_i^*(1) f_1 u_i(1)\, dv_1 + \tfrac{1}{2}\int \rho(1)\rho(2) g_{12}\, dv_1\, dv_2 + \tfrac{1}{2}\int [\rho\uparrow(1) U_{X\alpha\uparrow}(1) + \rho\downarrow(1) U_{X\alpha\downarrow}(1)]\, dv_1. \tag{I.2}$$

In this expression, f_1 is the one-electron operator associated with the first electron, the sum of its kinetic energy and the potential energy in the field of all nuclei. The quantity g_{12} is the Coulomb interaction energy between the first and second electrons. Thus the second term of Eq. (I.2) is the complete Coulomb interaction energy between the classical electronic charge distribution and itself, including self-interaction energy of an electron in the ith spin-orbital with itself, which of course should not be present in the total energy. The last term in Eq. (I.2) is the exchange term, which cancels the self-interaction terms just mentioned, as well as including characteristic exchange effects. Thus this last term is really an exchange-correlation term, and we shall use this name for it in the future, though in past papers it has been denoted as an exchange term. In addition to the energy of Eq. (I.2), we should also add the Coulomb interactions between all pairs of nuclei, but since this is a constant we shall omit it and understand that it must be added to the energy at the end of the calculation.

The exchange-correlation potential $U_{X\alpha\uparrow}(1)$ of Eq. (I.2) is written explicitly as

$$U_{X\alpha\uparrow}(1) = -9\alpha[(3/4\pi)\rho\uparrow]^{1/3} \tag{I.3}$$

with a corresponding formula for $U_{X\alpha\downarrow}(1)$. In this expression, energies are measured in rydbergs, distances in Bohr hydrogen radii, as they will be throughout this paper. We can now take the energy expression of Eq. (I.2), and vary the spin-orbitals to minimize this statistical total energy. When we do this, we find that the one-electron equation is

$$[-\nabla_1{}^2 + V_C(1) + V_{X\alpha\uparrow}(1)]u_i\uparrow(1) = \varepsilon_{iX\alpha\uparrow}\, u_i\uparrow(1), \tag{I.4}$$

where $V_C(1)$ is the Coulomb potential acting on electron 1 as a result of the total electronic and nuclear charge density (including the charge density of the ith spin-orbital), and

$$V_{X\alpha\uparrow}(1) = \tfrac{2}{3}U_{X\alpha\uparrow} = -6\alpha[(3/4\pi)\rho\uparrow]^{1/3}, \tag{I.5}$$

which is α times the exchange proposed by the author (Slater, 1951a, b).

The eigenvalue $\varepsilon_{iX\alpha\uparrow}$ can be found by multiplying Eq. (I.4) on the left by $u_{i\uparrow}(1)$, and integrating over the electron coordinates, taking advantage of the orthonormal nature of the u_i's. We can then prove that it is given by

$$\varepsilon_{iX\alpha\uparrow} = \partial\langle E_{X\alpha}\rangle/\partial n_i, \tag{I.6}$$

where we are to differentiate the expression of Eq. (I.2) with respect to n_i, the occupation number of a spin-orbital with spin up, expressing the various terms of this equation by use of Eqs. (I.1) and (I.2). This expression for the eigenvalue, as we shall see later in Eq. (III.2), is quite different from that given by the Hartree–Fock method, and we shall point out the significance of this fact later in Sections VI–IX.

To get a self-consistent solution for the ground state of the system using the Xα method, we proceed in the standard way. We solve Eqs. (I.4), assuming trial values of $V_C(1)$ and $V_{X\alpha\uparrow}(1)$. We then assume occupation numbers n_i of unity for all spin-orbitals with lower eigenvalues $\varepsilon_{iX\alpha}$, zero for all higher ones, filling enough to account for the number of electrons in the system. We justify filling only the lower spin-orbitals in the ground state by noting that Eq. (I.6) shows that one lowers the total energy $\langle E_{X\alpha}\rangle$ by shifting electrons from higher to lower spin-orbitals. When we have carried this out, we iterate, modifying both spin-orbitals and occupation numbers at each stage of the iteration, until self-consistency is achieved. As mentioned earlier, we shall not discuss the methods used to solve Eq. (I.4) in the present article.

II. Common Misconceptions Regarding the Statistical Exchange-Correlation

When we have carried out this self-consistent calculation, we must ask how the results are to be interpreted in terms of calculations of physical properties. In this interpretation, many misconceptions have been encountered by various readers, and we shall now attempt to clear up some of them, before going on to the detailed discussion. First is the impression which some readers have had, that the self-interaction energy is disregarded in this method. We have pointed out in the preceding section that this is not the case, the self-interaction being in fact the major part of the last term of Eq. (I.2), the exchange-correlation term. This has been discussed quantitatively by Slater and Wood (1971); see Table 1 of that paper.

Next is the misconception that the argument is essentially tied to the treatment of a free-electron gas of constant density. One can get the general idea of an exchange-correlation term varying as the one-third power of the charge density by very simple dimensional arguments. Thus, on account of the antisymmetry ofthe many-electron wave function Ψ, the electrostatic interaction energy between the electrons of an N-electron system can be exactly written in the form

$$\tfrac{1}{2}N(N-1)\int\cdots\int \Psi^*(1,\ldots,N)g_{12}\Psi(1,\ldots,N)\,dv_1\cdots dv_N. \qquad \text{(II.1)}$$

Here the integral is the interaction between electron 1 and 2, which must equal the interaction between any pair of electrons, and $N(N-1)/2$ is the number of pairs. In this expression, integrations over the volume elements are understood to include also summations over the spins.

We can now rewrite this electrostatic interaction energy in the form

$$\tfrac{1}{2}\int \rho(1)W(1)\,dv_1 \qquad \text{(II.2)}$$

where the charge density $\rho(1)$ is given by

$$\rho(1) = N\int\cdots\int \Psi^*(1,\ldots,N)\Psi(1,\ldots,N)\,dv_2\cdots dv_N \qquad \text{(II.3)}$$

and the electrostatic potential of interaction $W(1)$ takes the form

$$W(1) = (N-1)\frac{\int\cdots\int g_{12}\Psi^*(1,\ldots,N)\Psi(1,\ldots,N)\,dv_2\cdots dv_N}{\int\cdots\int\Psi^*(1,\ldots,N)\Psi(1,\ldots,N)\,dv_2\cdots d_N} \qquad \text{(II.4)}$$

This is the familiar argument in terms of the first- and second-order density matrices. The potential $W(1)$ at position 1 is the electrostatic potential at this point of a charge distribution

$$(N-1)\frac{\int\cdots\int\Psi^*(1,\ldots,N)\Psi(1,\ldots,N)\,dv_3\cdots dv_N}{\int\cdots\int\Psi^*(1,\ldots,N)\Psi(1,\ldots,N)\,dv_2\cdots dv_N} \qquad \text{(II.5)}$$

located at position 2.

The total amount of this charge distribution is found by integrating the charge density of Eq. (II.5) over dv_2, and is obviously $N-1$ electrons. We may expect that at large distances from the electron 1, this charge density will reduce to the value $\rho(2)$ of Eq. (II.3) (written as a function of the position 2, rather than 1), which is the density of the whole system of N electrons. The difference between these two charge densities is the density of the exchange-correlation hole, amounting to one electron. Its density, as a function of the position 2, when electron 1 is located at position 1, is

$$\begin{aligned} &N\int\cdots\int\Psi^*(1,\ldots,N)\Psi(1,\ldots,N)\,dv_1\,dv_3\cdots dv_N \\ &\quad -(N-1)\frac{\int\cdots\int\Psi^*(1,\ldots,N)\Psi(1,\ldots,N)\,dv_3\cdots dv_N}{\int\cdots\int\Psi^*(1,\ldots,N)\Psi(1,\ldots,N)\,dv_2\cdots dv_N}. \end{aligned} \qquad \text{(II.6)}$$

When position 2 equals position 1 (which implies that the two electrons have the same spin, as well as being located at the same point of space), the density of the exchange-correlation hole, from Eq. (II.6), reduces to the first term in the equation, since the second term vanishes on account of the antisymmetry of the wave function. Thus the density of the exchange-correlation hole charge of the same spin as that of electron 1 must be equal to the total density $\rho\uparrow(1)$ at that point (for the case of spin up).

If we had a uniform charge density $\rho\uparrow(1)$ for this exchange-correlation hole, throughout a sphere of radius R, and zero outside, we should have

$$\tfrac{4}{3}\pi R^3\rho\uparrow(1) = 1, \qquad R = (3/4\pi\rho\uparrow)^{1/3}. \qquad \text{(II.7)}$$

The electrostatic potential at the center of a uniformly charged sphere, in the units we are using, is $3/R$. Thus the potential at the point 1 would be

$$-3[(4\pi/3)\rho\uparrow]^{1/3}. \qquad \text{(II.8)}$$

This is a potential proportional to the one-third power of the charge density, which we have derived by simple dimensional arguments, quite independently of a perfect-gas model. Only the numerical value must be adjusted to get from this simple dimensional argument to our Xα approximation, and as we shall explain in Section III, the method we use to derive it is based on the wave functions of isolated atoms and has no direct connection with the free-electron gas.

We have been enumerating various misconceptions concerning the Xα method. One very important one, which in fact underlies a great deal of thinking concerning the electronic structure of solids, is the belief that the charge distribution in an actual solid is only a small modification of a free-electron gas. This notion arose historically from the success of the free-electron theory of metals of Sommerfeld, and the fact that the work of Wigner and Seitz was on the sodium crystal, in which a free-electron approximation is in fact rather a good assumption throughout the whole unit cell except for rather small spheres surrounding the nuclei. But in general it is a very poor approximation. It is much closer to the truth to regard the crystal as being simply a superposition of undistorted atoms. For this reason, much of the work which has been done to verify the general correctness of the Xα method, and which will be discussed in later sections of this paper, has been carried out on isolated atoms. The author regards pseudopotential methods and similar treatments, which focus one's attention on the supposed region where a free-electron treatment is almost correct rather than on the much more important region where the atomic behavior is of paramount importance, as being rather misleading and undesirable.

Closely allied with this notion that the real crystal is a small modification of a free-electron gas is the attempt to derive a more elaborate statistical exchange-correlation correction from the case of an electron gas showing small variations of density from point to point. In such a case one might expect to use an exchange-correlation potential involving not only the electronic density, but its derivatives with respect to the coordinates. Such an attempt is that of Herman *et al.* (1969, 1970). It does not appear to the author that this procedure is desirable. As has been pointed out by Slater and Wood (1971), the function $U_{X\alpha\beta}(1)$ which one obtains by this method in place of the function of Eq. (I.3) is in fact further from the Hartree–Fock value than is the function of Eq. (I.3). Furthermore, discussion of the convergence of a series expansion of the exchange-correlation potential in terms of derivatives of higher and higher order, held informally at various Sanibel Symposia, indicates that the series is probably divergent, so that it is not legitimate to break it off after a given number of terms. It is the author's belief that the expression of Eq. (I.3), using no derivatives at all, is preferable to the more elaborate treatments.

On the whole, the most serious of the misconceptions regarding the statistical exchange-correlation method is a fundamental one: This is the idea that some localized potential can be found for use in Eq. (I.4) that will convert it into an exact treatment, in perfect agreement with experiment. These experiments can include both those relating to the Fermi surface, and those involving optical absorption and emission, as well as electronic and spin densities, and a variety of other properties of a crystal. There is no reason for thinking that such a treatment is possible, and in fact excellent reason for thinking that it is not. The statistical exchange-correlation method, like all self-consistent-field approximations, is only an approximation, though it can be quite a good one. The workers in the field of atomic and molecular theory are well aware of this fact.

One can use a self-consistent field to generate a set of one-electron basis functions, from which one can set up antisymmetric many-electron functions of a determinantal type. In the most elementary atomic theory of multiplets, one makes linear combinations of a number of such determinantal functions to describe the various multiplet states. In more elaborate treatments of atoms, and in most treatments of molecules, one makes similar linear combinations of much larger numbers of determinantal functions, and it is well known that if a complete set of such functions is used, the resulting configuration interaction approaches the true solution of the many-body problem in the limit of large numbers of determinants.

The same situation must be assumed to hold for solids, but this fact is not nearly as familiar to the workers in the solid-state field as it is to those in atomic and molecular theory. The solid-state theorists in many cases seem reluctant to accept the prospect of the future computational effort which is demanded by the view that the one-electron approximation is only a first step toward a final theory. The author feels that it is time to accept this fact, and believes that the major object of the statistical exchange-correlation correction is to lead to a set of one electron basis functions, from which such a configuration interaction can be set up. By using a sufficiently good set of basis functions, the convergence of the process can be improved, and the Xα method seems to give a good starting point for further computation.

In connection with this procedure, there is one matter of notation which it is worthwhile to mention. Many workers, particularly those trained in field theory, advocate the language of second quantization. The author does not favor this method, and it will not be used in this article. He wishes to point out that nothing is accomplished by use of the second quantization formalism except to express in more compact language results which we meet in an equivalent way in the determinantal method. Furthermore, he feels that the language of second quantization is likely to hide essential features, such as the fundamentally nonlinear nature of the total energy when expressed in terms of the occupation numbers, which are of primary importance, and which can be easily overlooked by one whose only training is in field theory.

III. Specific Advantages of the Xα Method. Total Energy and Value of α

We now come to a more detailed discussion of the properties and particular advantages of the Xα method. There are two very important advantages connected with the use of the method, as outlined in Section I. First, the virial theorem is satisfied exactly by the resulting potential and kinetic energies. Secondly, Eq. (I.6) leads to the result that if the energy is defined by use of Eqs. (I.2) and (I.3), the Fermi statistics are obeyed precisely by the model.

As for the virial theorem, this has been discussed by Ross (1969) and Sham (1970), and it is not necessary to reproduce the argument here. The virial theorem holds independently of the value of the parameter α assumed in Eq. (I.3). Slater and Wood (1971) have suggested making this the basis of a method of choosing an optimum value of α. The energy $\langle E_{X\alpha} \rangle$ of Eqs. (I.2) and (I.3) depends strongly on α, and one can choose α so that it exactly agrees with the Hartree–Fock value of the energy of a closed-shell atom (or with the average energy of the multiplets arising from the ground-state configuration for an open-shell atom). The exact wave function, as well as a Hartree–Fock or equivalent function, satisfies the virial theorem. Thus, if the total energy $\langle E_{X\alpha} \rangle$ agrees with the energy of the exact wave function, or with the Hartree–Fock energy, the kinetic energies will also agree. This is a rather sensitive test for the accuracy of the spin-orbitals, and it is found that if α is chosen so that the Xα energy equals the Hartree–Fock energy, the Xα spin-orbitals of the atom agree closely with the Hartree–Fock spin-orbitals. Thus the charge densities agree closely, which means that the second term of Eq. (I.2), as well as the first, agrees well. Consequently, the third term, the exchange-correlation energy, will also agree closely.

Schwarz (unpublished, presented at the 1971 Sanibel Symposium) has applied this condition to a series of the lighter atoms, and has shown that the resulting α decreases from about 0.77 for two-electron atoms, to about 0.70 for atoms with atomic number in the neighborhood of 40. It is to be expected that it will continue to decrease somewhat further for the heavier elements. The values of α as a function of atomic number found in this way lie on a much smoother curve than the values given earlier by Kmetko (1970) by a somewhat different method. Schwarz has shown that the value of α varies only slightly as one goes from one atomic configuration to another (as in shifting an electron from the s to the d shell in a transition element, or in removing an outer electron). This leads one to hope that it will not be too inaccurate to use the same value of α for an isolated atom and for the same atom incorporated into a crystal.

The reasonableness of this view is demonstrated by unpublished work of Averill (discussed at the 1971 Sanibel Symposium) on the crystal of cesium, and of Hattox (presented at the 1971 Sanibel Symposium) on the crystal of vanadium. In each case, they have assumed the total energy expression of Eqs. (I.2) and (I.3) for the crystal, and have calculated the total energy as a function of volume, as well as finding the energies of the isolated atoms. The cohesive energy, as indicated by the lattice spacing of minimum energy; energy difference between crystal and separated atoms; and the compressibility, calculated from this statistical expression for total energy, show qualitative agreement with experiment. These calculations form more recent and accurate applications of methods suggested earlier by Ross (1969) and by Rudge (1969a, b, c). There are thus grounds for hoping that the use of the statistical total energy may give a first approximation to the calculation of cohesive energy, though of course a configuration interaction based on the spin-orbitals found from the Xα method will be required to get a reliable value of cohesive energy

For the crystal of a compound, there is the difficulty that the α's indicated by Schwarz's calculation for the various atoms of the crystal will not be identical. However, Schwarz and Conklin (unpublished, presented at the 1971 Sanibel Symposium) have studied the effect of changing the value of α on the energy bands of TiC, and have found in this case that the effect is small. This suggests that it may be possible in a compound to use for the whole crystal a value of α which is a compromise between those indicated for the various atoms of which it is composed. This might be the α which would lead to a sum of $\langle E_{X\alpha} \rangle$ values for the various atoms composing the crystal which would precisely equal the Hartree–Fock energy of the crystal in the state of separated atoms. This procedure has not yet been applied in an actual case, but it seems very promising.

Next we come to the fact that the Fermi statistics are obeyed precisely by the model. This arises from the validity of Eq. (I.6), which states that the change of statistical total energy, when the occupation numbers change, is

$$d\langle E_{X\alpha}\rangle = \sum_i \frac{\partial\langle E_{X\alpha}\rangle}{\partial n_i}\, dn_i = \sum_i \varepsilon_{iX\alpha}\, dn_i \tag{III.1}$$

up to the first order of small quantities. This is the assumption made in the derivation of the Fermi statistics. The situation is so important that we take it up in detail in the next section. We point out here that the validity of the Fermi statistics is the foundation of the whole modern theory of solid-state electronics, and that a great industry has grown up based on the accuracy of this approximation method.

On the other hand, the one-electron energy or eigenvalue of the Hartree–Fock method is not given by a partial derivative, as in Eq. (I.6), but by a finite difference. Namely, if $\langle E_{\mathrm{HF}}\rangle$ is the total energy as computed by the Hartree–Fock method, it is familiar that the eigenvalue is given by

$$\varepsilon_{i\mathrm{HF}} = \langle E_{\mathrm{HF}}(n_i = 1)\rangle - \langle E_{\mathrm{HF}}(n_i = 0)\rangle, \tag{III.2}$$

or the difference of total energy computed for the case where the ith spin-orbital is occupied, minus that where it is empty (where the latter is to be computed without modification or relaxation of the remaining spin-orbitals when the ith electron is removed). In other words, one has a finite difference of energies rather than the partial derivative of Eq. (I.6), and these quantities will not be equal unless the total energy can be approximated by a linear function of the occupation numbers. This is not possible for an isolated atom, though the nonlinear terms can be disregarded in a crystal. We shall discuss this important question later in Sections VII–X.

IV. The Xα Method and the Fermi Statistics

Obviously an important feature of the Xα method is the use of nonintegral occupation numbers n_i, since in Eq. (I.6) we encounter the derivative of the total energy with respect to these occupation numbers, a concept which has a meaning only in case the energy is a continuous function of the occupation numbers (though limited by the exclusion principle to the range $0 \le n_i \le 1$). It is no accident that the Fermi statistics, which prove to be exactly satisfied by our statistical approximation, also are based on the use of such fractional occupation numbers. Let us therefore go somewhat more carefully into the basis of the Fermi statistics than we otherwise would do, in order to explain just what is meant by fractional or nonintegral occupation numbers. The method of discussion that we shall use is not a standard one in statistical mechanics, but is one which was given in a textbook by the author (Slater, 1939), as representing a derivation which fitted in with the general background of determinantal functions and quantum mechanics.

In the derivation quoted, one uses the principle that the most stable distribution of a system at a given temperature will be that which minimizes the free energy $A = U - TS$, where U is the internal energy, T, the temperature, S, the entropy. If the state of the system is described by occupation numbers n_i, as we are doing, and if we identify the internal energy with our total energy $\langle E_{X\alpha} \rangle$, or a similar quantity, we must find the entropy in order to apply this principle. We use Boltzmann's relation

$$S = k \ln W, \qquad \text{(IV.1)}$$

where k is Boltzmann's constant, and W is the so-called thermodynamic probability, the number of states of the system consistent with the given assignment of n_i's [not to be confused with the quantity W of Eqs. (II.2) and (II.4)]. We are assuming a system with a large number of one-electron energy levels, such as an electron gas; if we are handling isolated atoms, we may set up an equivalent crystal with an infinite number of atoms, but with infinite interatomic distances, which will then have an infinite number of energy levels. The Xα method for such a crystal gives results which are identical with those for individual atoms. We interpret an individual state as having integral occupation numbers, unity or zero, as in a single determinantal function; the quantities n_i which take on nonintegral values are averages, of the sort to be described next.

Let us subdivide our infinite number of one-electron energy levels into individual groups of levels, one group having G levels in it, a number large compared to unity, but still finite. We assume that all G of these energy levels have energies which are substantially equal. Then the contribution of these levels to the total energy will depend on the number $n_i G$ of them which have an electron in them. There are many ways of choosing $n_i G$ levels to be occupied, the remaining $(1 - n_i)G$ being empty. This number of ways is

$$G!/(n_i G)!(G - n_i G)!. \qquad \text{(IV.2)}$$

Since G is assumed large, we can replace the factorials by Stirling's approximation, which to a first approximation is

$$N! = (N/e)^N. \qquad \text{(IV.3)}$$

When we use this, the number of ways given in Eq. (IV.2) is

$$[1/n_i^{n_i}(1-n_i)^{1-n_i}]^G. \tag{IV.4}$$

To get the total number of arrangements for the system, we multiply quantities like (IV.4) for each group of G states in the whole system. Plainly this will give us something independent of the exact way we divide up the states into groups, or independent of G, and we find

$$W = \prod_i 1/n_i^{n_i}(1-n_i)^{1-n_i}. \tag{IV.5}$$

From Boltzmann's relation, Eq. (IV.1), we then have

$$S = -k \sum_i [n_i \ln n_i + (1-n_i)\ln(1-n_i)]. \tag{IV.6}$$

In Eq. (IV.6) we have the standard formula for the entropy of a Fermi gas.

We now use Eq. (IV.6) for the entropy, and find as the condition for thermal equilibrium

$$dA = d(U-TS) = \sum_i \left(\varepsilon_i + kT \ln \frac{n_i}{1-n_i}\right) dn_i, \tag{IV.7}$$

in which we have used Eq. (III.1) for dU. We must have Eq. (IV.7) satisfied, subject only to the condition

$$\sum_i dn_i = 0, \tag{IV.8}$$

expressing the fact that the changes of the n_i's are such that the total number of electrons remains fixed. The only way to satisfy Eq. (IV.7), subject to Eq. (IV.8), is to have

$$\varepsilon_i + kT \ln [n_i/(1-n_i)] = \varepsilon_F = \text{const} \tag{IV.9}$$

independent of i. For then the parenthesized term in Eq. (IV.7) can be taken outside the summation, and Eq. (IV.8) immediately makes the whole expression vanish. We then solve Eq. (IV.9) for n_i, and we obtain the Fermi distribution law,

$$n_i = [\exp(\varepsilon_i - \varepsilon_F)/kT + 1]^{-1}. \tag{IV.10}$$

Our aim in the present discussion is not to treat a system at temperatures above absolute zero, but to find the ground state. This will be the limit for $T = 0$, and we are familiar with the fact that the Fermi function of Eq. (IV.10) is unity for $\varepsilon_i < \varepsilon_F$, zero for $\varepsilon_i > \varepsilon_F$. It is possible, however, that we may have some states with ε_i exactly equal to ε_F. The value of the Fermi energy ε_F is of course to be determined in such a way that the total number of occupied levels will exactly equal the number of electrons in the system, and as a result of this, the n_i's for states for which $\varepsilon_i = \varepsilon_F$ might come out different than unity or zero. All of these states should have the same n_i, since Eq. (IV.10) tells us that all states of the same ε_i should have the same n_i. We arrive in this way at the possibility of having fractional occupation numbers, even at the absolute zero of temperature, for certain one-electron states whose energy is exactly ε_F. This will result in a nonvanishing entropy at $T = 0$; we note from Eq. (IV.6) that filled or empty spin-orbitals ($n_i = 1$ or $n_i = 0$) make no contributions to S, the only contributions coming from partly filled states.

This seems like an entirely academic problem until we begin to think of an actual physical case where it can be encountered: atoms, such as a 3d transition atom, with a partly filled electronic shell. Such problems are of great importance in cases like magnetism, ligand or crystal fields, and so on, and these are cases that we must think through with care. We shall now ask how we can apply straightforward determinantal methods to such a case, and this will give us a great deal of insight into the relationships between the one-electron approximation and the real many-electron problem. We cannot ordinarily treat such a problem by the Hartree–Fock method, since that implies that a single determinantal function adequately represents the system. Here, we are facing multiplet problems, and many determinantal functions, a situation very similar to that which we have just been discussing. We shall describe in the next section a method which was called the hyper-Hartree–Fock (HHF) method in a paper by the author and colleagues (Slater *et al.*, 1969b), and which furnishes the same sort of exact solution for an atom with a partially filled shell that the Hartree–Fock method does for a closed shell atom. It is this HHF method which agrees closely with the Xα method in a problem of atoms with partly filled outer shells.

V. The Hyper-Hartree–Fock Method

Let us think of an isolated atom with a partly filled outer shell of electrons. If the electrons are missing from a single shell, we have the familiar problem of multiplets, arising from the interactions between the electrons in this partly filled shell. For the atomic case, it is convenient to think of a shell of electrons of the same n and l values, but of different m_l and m_s values, which therefore would be capable of holding $2(2l+1)$

electrons if it were filled. Let this number be expressed as q_{i0} for the ith shell, and let the shell actually have q_i electrons in it, where q_i is less than or equal to q_{i0}. Then there will be $q_{i0}!/q_i!(q_{i0} - q_i)!$ determinantal functions which can be formed from the q_i electrons in the q_{i0} spin-orbitals, a number analogous to that of Eq. (IV.2). In the present case, with a small value of q_{i0}, we shall not make the approximation of replacing this number by its Stirling-formula approximation, as we did in Eqs. (IV.3)–(IV.5).

In the problem of atomic multiplets, we solve a secular equation with this number of rows and columns, and find the best approximations to solutions of Schrödinger's equation that we can build up from these determinantal functions. These lead to the various multiplets, though in an approximation which is known to be fairly inaccurate. There is no place in a one-electron approximation for the energy separations between these multiplet levels. The q_i electrons are supposed to be degenerate with each other, in a one-electron picture, corresponding to identical one-electron energies. They would be similarly degenerate in the Xα method, for an isolated atom, for a simple reason. As we have seen in the preceding section, they will have equal occupation numbers if they are degenerate. By Unsöld's theorem, the charge density will then be spherically symmetrical. The solution of Eq. (I.4) for a spherically symmetrical potential will lead to the familiar degeneracy found in the central-field case, which thus will be the self-consistent situation. With the degenerate one-electron energies, the best thing we can do, in setting up a one-electron picture, is to disregard the multiplet separations, and to assign all of these multiplet levels to the same many-electron energy, which we naturally choose as the average energy of all of them. The multiplet structure must be treated as a higher approximation, superposed on the one-electron picture given by the self-consistent field.

It is then reasonable to assume in a one-electron picture that the energy of an atom in our state with a partially filled shell is the average energy of these multiplet states. This problem has been discussed by the author (Slater, 1960) in connection with the theory of atomic multiplets. When it is carried through, the result is as has been stated in the reference just quoted, and in the paper of Slater *et al.* (1969b), Eq. (1), namely

$$\langle E_{\mathrm{HHF}} \rangle = \sum_i q_i I(i) + \tfrac{1}{2} q_i(q_i - 1)(i, i) + \sum_{\text{pairs } i,\, j, i \neq j} q_i\, q_j (i, j). \qquad \text{(V.1)}$$

Here the sums are over shells of electrons. The integrals $I(i)$, (i, i), (i, j) are expressed in the references just quoted in terms of the integrals appropriate for an atomic problem. However, we can state them in a more general form, which can be easily generalized to other cases. We have

$$I(i) = \int u_{ik}^{*}(1) f_1 u_{ik}(1)\, dv_1, \tag{V.2}$$

where u_{ik} is the kth basis function of the set of q_{i0} degenerate states associated with the ith shell, and f_1 is the one-electron operator of the first electron. Since this operator commutes with the group of symmetry operators characteristic of the system, the integrals $I(i)$ are independent of k.

The integrals (i, i) and (i, j) are defined by

$$(i, i) = \frac{\sum (k, l)[(ik, il|g|ik, il) - (ik, il|g|il, ik)]}{q_{i0}(q_{i0} - 1)}, \tag{V.3}$$

$$(i, j) = \frac{\sum (k, l)[(ik, jl|g|ik, jl) - (ik, jl|g|jl, ik)]}{q_{i0} q_{j0}}. \tag{V.4}$$

In these expressions, an integral, e.g., of the form of $(ik, jl|g|jl, ik)$ is an abbreviation for

$$(ik, jl|g|jl, ik) = \int u_{ik}^{*}(1) u_{jl}^{*}(2) g_{12} u_{jl}(1) u_{ik}(2)\, dv_1\, dv_2, \tag{V.5}$$

where g_{12} as previously is the Coulomb interaction between the first and second electrons, and where the integrations over dv_1 and dv_2 include summation over spins. The summations over k and l include all values corresponding to the various basis functions u_{ik}, etc. The special values taken on by these integrals for the case of the atom are

$$(i, i) = F^0(l_i, l_i) - \frac{1}{4l_i + 1} [c^2(l_i 0; l_i 0) F^2(l_i, l_i) + c^4(l_i 0; l_i 0) F^4(l_i, l_i) + \cdots],$$

$$(i, j) = F^0(l_i, l_j) - \tfrac{1}{2} [(2l_i + 1)(2l_j + 1)]^{-1/2} \sum_k c^\kappa(l_i 0; l_j 0) G^\kappa(l_i, l_j). \tag{V.6}$$

In these equations, the c's are the Gaunt coefficients, and the F's and G's are radial atomic integrals, described in detail in the text by the author just quoted (Slater, 1960). It is interesting to note that the quantities F^0, the leading terms in both formulas, are the spherically averaged self-interaction terms.

The energy of Eq. (V.1) is expressed in terms of contributions from pairs of shells. This is different from the formulation of Eq. (I.2), which includes a Coulomb term and an exchange term. The relation between the two is easily derived. In the first place, the charge density ρ is given by

$$\rho(1) = \sum_{ik} (q_i/q_{i0}) u_{ik}^*(1) u_{ik}(1), \tag{V.7}$$

where $n_i = q_i/q_{i0}$, the same for all k values. Thus we have

$$\tfrac{1}{2}\int \rho(1)\rho(2) g_{12}\, dv_1\, dv_2 = \tfrac{1}{2}\sum_{ik,jl} \frac{q_i q_j}{q_{i0} q_{j0}} (ik, jl|g|ik, jl). \tag{V.8}$$

We can then use Eq. (V.8) together with Eqs. (I.2) and (V.1) to find the final, exchange term equivalent to that of Eq. (I.2). It can be shown that

$$\begin{aligned}
&\tfrac{1}{2}\int [\rho\uparrow(1) U_{\mathrm{XHHF}\uparrow}(1) + \rho\downarrow(1) U_{\mathrm{XHHF}\downarrow}(1)]\, dv_1 \\
&\quad = -\tfrac{1}{2}\sum_i q_i \left[\frac{q_{i0} - q_i}{q_{i0}} \frac{\sum_{(k,l)}(ik, il|g|ik, il)}{q_{i0}(q_{i0} - 1)}\right. \\
&\qquad + (q_i - 1)\frac{\sum_{(k,l)}(ik, il|g|il, ik)}{q_{i0}(q_{i0} - 1)} \\
&\qquad \left. + \sum_{j \neq i} q_j \frac{\sum_{(k,l)}(ik, jl|g|jl, ik)}{q_{i0} q_{j0}}\right].
\end{aligned} \tag{V.9}$$

These potentials can be expressed as the sum of two parts: first, a self-interaction term, arising from the first two terms of Eq. (V.9), equivalent to the interaction, with an orbital in the ith shell, of an electron in a Fermi hole, averaged over the shells; secondly, characteristic exchange terms, coming from the second and third terms of Eq. (V.9). The self-interaction term is ordinarily the leading term in Eq. (V.9).

One can then take the total energy of the HHF method, and can vary the spin-orbitals to minimize the energy. In this way we find the equivalents of the Hartree–Fock equations for this case. We find an equation of the form of Eq. (I.4), with the exchange function $V_{\mathrm{XHHF}ik}(1)$ given by

$$\begin{aligned}
V_{\mathrm{XHHF}ik}(1) = &-\frac{q_{i0} - q_i}{q_{i0}(q_{i0} - 1)} \sum_l \int u_{il}^*(2) u_{il}(2) g_{12}\, dv_2 \\
&- \frac{q_i - 1}{q_{i0} - 1} \frac{\sum_l \int u_{ik}^*(1) u_{il}^*(2) g_{12} u_{il}(1) u_{ik}(2)\, dv_2}{u_{ik}^*(1) u_{ik}(1)} \\
&- \sum_{j \neq i} \frac{q_j}{q_{j0}} \frac{\sum_l \int u_{ik}^*(1) u_{jl}^*(2) g_{12} u_{jl}(1) u_{ik}(2)\, dv_2}{u_{ik}^*(1) u_{ik}(1)}.
\end{aligned} \tag{V.10}$$

This equation, for the case of the spherical atom, is discussed in the textbook by the author quoted earlier (Slater, 1960). As in that reference, we can show that the eigenvalue $\varepsilon_{i\mathrm{HHF}}$ is given by

$$\varepsilon_{i\mathrm{HHF}} = \langle E_{\mathrm{HHF}}(q_i)\rangle - \langle E_{\mathrm{HHF}}(q_i - 1)\rangle, \tag{V.11}$$

as in Eq. (III.2), and equivalent to the Hartree–Fock formula.

The exchange in the HHF method, as given in Eq. (V.10), is different for each spin-orbital u_{ik}. As in the treatment of the author, quoted in Section I (Slater, 1951a, b), we can get a single averaged exchange, by making a weighted mean of the exchange of Eq. (V.10). To do this, we weight each spin-orbital with the weight

$$(q_i/q_{i0})u_{ik}^*(1)u_{ik}(1)/\sum_{jl}(q_j/q_{j0})u_{jl}^*(1)u_{jl}(1)$$

and sum over i and k. When we do this, starting with Eq. (V.10), we find for the weighted exchange potential a quantity which, when multiplied by $\frac{1}{2}\rho(1)$, and integrated over dv_1, gives the quantity of Eq. (V.9). In other words, the exchange-correlation potential $U_{\mathrm{XHHF}}(1)$ of Eqs. (I.2) and (V.9), for the HHF method, is identical with the weighted mean of the various HHF potentials $V_{\mathrm{XHHF}ik}(1)$ met in the HHF equations. The special case of this relation for the Hartree–Fock method, in which each q_i equals the corresponding q_{i0}, was discussed by Slater and Wood (1971). It is to be noticed that in Eq. (V.10), since the integration over dr_2 also includes summation over the spin, the exchange potentials for orbitals of different spins are different. From Eq. (V.10) for the exchange-correlation potentials appearing in the HHF orbitals we can easily verify that these potentials all arise from a Fermi hole with a single electronic charge. They thus fit in with the general discussion that we have given in connection with Eqs. (II.1)–(II.6).

VI. Comparison of the Xα and HHF Methods

If the Xα and HHF methods are applied to the same problem, an atom with a partly filled shell of electrons such as the 3d shell, the results are very closely the same, in the following respects. First, the spin-orbitals of the inner, fully occupied shells and the partly occupied shells are very similar in the two methods. Consequently, the charge densities are very nearly the same, as well as the kinetic energies. For such an atom, the value of α is chosen to make the total energies agree by the two methods, as intimated in Section III. Hence the exchange-correlation energy, as well as the other terms, very approximately agree for the two cases. We have, in other words, the generalization of the discussion of Section III, in which we specifically considered the Hartree–Fock method, but hinted at a generalization for an open-shell case. Since the exchange-correlation energies as well as the charge densities approximately agree, the expression for $U_{\mathrm{XHHF}}(1)$ described in Eqs. (V.9) and (V.10) will agree closely with the Xα value for the same quantity. We have noted the close agreement of these quantities for Cu^+, a Hartree–Fock closed-shell case, as discussed by Slater and Wood (1971), but the agreement is equally good for open-shell atoms discussed by the HHF method.

As a result of these agreements, the various integrals, such as those given in Eq. (V.6), will have very nearly the same values whether computed from the HHF spin-orbitals, or from those derived from the Xα method. This fact can be easily verified from calculations made by readily available computer programs. Thus, Mann (1967) has solved the self-consistent problems of the HHF method for all the atoms of the periodic system, and his tables include not only the spin-orbitals, given in the form of tables of values, but also the various integrals met in Eq. (V.6). The Xα method has been programed by Herman and Skillman (1963), for the case $\alpha = 1$, but these computer programs have been extended by various workers to the case of arbitrary α, and programs for the computation of the various integrals of Eq. (V.6) from the Xα spin-orbitals have been added to the Herman–Skillman programs. Hence one can find all of these quantities by both methods, and can easily verify our statements regarding the good agreement of the results of the two methods. Both methods allow calculations to be made for arbitrary occupation numbers n_i, including fractional occupation numbers.

For isolated atoms and ions, in other words, one has good agreement between the two methods. This agreement can be checked in an overall way by computing from the Xα spin-orbitals the HHF expression for total energy, Eq. (V.1). Since the Xα spin-orbitals are not quite exact spin-orbitals of the HHF method, the resulting total energy is slightly greater than the exact HHF total energy. For instance, for Cu^+ the Hartree–Fock total energy is -3277.46 Ry, whereas if the Xα spin-orbitals are used for calculating the same energy expression, the result is -3277.367 Ry. The value of α chosen by Schwarz, as mentioned in Section III, is very nearly that which minimizes this energy computed from the Xα spin-orbitals, though not always precisely that value. Kmetko's (1970) calculation of α as a function of atomic number is based on an effort to choose the α that minimizes the Hartree–Fock total energy, but this varies so slowly with α that the determination of the precise minimum is very uncertain. For most purposes, we may treat the spin-orbitals of the Xα method as being practically indistinguishable from the HHF values, though one must take account of the differences in precise calculations.

While the two methods thus agree closely for isolated atoms and ions, for which the HHF method is adapted, the great advantage of the Xα method is that it can be applied as well to a case of a crystal, or a large molecule. Here we do not have equally good calculations by anything equivalent to the HHF method, but we may hope that the Xα method will be equally reliable here. The first comparison which we shall make is for the optical properties, and this leads us at once into the one respect in which there is striking disagreement between the Xα and the HHF methods. This is in the values of the one-electron eigenvalues ε_i, for which we have seen that the two methods lead to quite different values.

VII. Energy of an Atom as a Function of Occupation Numbers

We have seen in Eqs. (I.6), (III.2), and (V.11) that the eigenvalue of the Xα method is given by a partial derivative of the total energy with respect to an occupation number, whereas in the HF or HHF methods it is the difference of total energies between two states whose occupation numbers differ by unity. To exhibit the difference between these two types of eigenvalues, it is useful to consider the total energy of an atom as a function of the occupation numbers. Since we have just seen that these total energies are such similar quantities in the Xα and the HHF methods, we can use a power series expansion of the same type in either case. Such an expansion has been set up by Slater and Wood (1971).

In the paper just referred to, the power series expansion was set up in terms of $q_i\uparrow$, $q_i\downarrow$, the number of electrons with spin up and spin down in the shell, related through the equations

$$\begin{aligned} q_i &= q_i\uparrow + q_i\downarrow, & \mu_i &= q_i\uparrow - q_i\downarrow \\ q_i\uparrow &= \tfrac{1}{2}(q_i + \mu_i) & q_i\downarrow &= \tfrac{1}{2}(q_i - \mu_i). \end{aligned} \qquad \text{(VII.1)}$$

The energy $\langle E \rangle$ was expressed as a power series in $q_i - q_{i1}$, where q_{i1} is the occupation number in a standard state about which the expansion is made, and in μ_i, using as a standard state a non-spin-polarized one in which each $q_i\uparrow$ equals the corresponding $q_i\downarrow$. [In the reference above (Slater and Wood, 1971), the standard state was described as having occupation numbers q_{i0}, but we use q_{i1} so as not to cause confusion with our earlier use of q_{i0} to give the maximum value of q_i allowed by the exclusion principle.] There will be no terms in odd powers of the μ_i's, since the reference state corresponds to an unmagnetized state, and changing the sign of each μ cannot change the energy. We can then expand the energy in a series as follows:

$$\begin{aligned}\langle E\rangle = \langle E\rangle_0 &+ \sum_i (q_i - q_{i1}) \left.\frac{\partial\langle E\rangle}{\partial q_i}\right|_0 \\ &+ \frac{1}{2!}\sum_{i,j} (q_i - q_{i1})(q_j - q_{j1}) \left.\frac{\partial^2\langle E\rangle}{\partial q_i\,\partial q_j}\right|_0 \\ &+ \frac{1}{3!}\sum_{i,j,k} (q_i - q_{i1})(q_j - q_{j1})(q_k - q_{k1}) \left.\frac{\partial^3\langle E\rangle}{\partial q_i\,\partial q_j\,\partial q_k}\right|_0 \\ &+ \frac{1}{2!}\sum_{i,j} \mu_i\mu_j \left.\frac{\partial^2\langle E\rangle}{\partial \mu_i\,\partial \mu_j}\right|_0 \\ &+ \frac{1}{2!}\sum_{i,j,k} (q_i - q_{i1})\mu_j\mu_k \left.\frac{\partial^3\langle E\rangle}{\partial q_i\,\partial \mu_j\,\partial \mu_k}\right|_0 + \cdots.\end{aligned} \tag{VII.2}$$

For many purposes the third-power terms are as far as the series has to be carried to get sufficient accuracy. The subscripts 0 in Eq. (VII.2) indicate the standard state for which the partial derivatives are computed.

In the paper of Slater and Wood (1971) calculations of the various partial derivatives involved in Eq. (VII.2), for the non-spin-polarized case (all μ's equal to zero) are described for the chromium atom and ion. These numbers were obtained from a set of calculations of this atom, by the Xα method, for a number of different sets of occupation numbers, the resulting energies being fitted by a choice of derivatives $\partial\langle E\rangle/\partial q_i|_0$, $\partial^2\langle E\rangle/\partial q_i\,\partial q_j|_0$, and $\partial^3\langle E\rangle/\partial q_i\,\partial q_j\,\partial q_k|_0$. These calculations showed that the series rapidly converges, fast enough so that further terms are ordinarily not required. Unpublished calculations by the HHF method have indicated that the results of such a power-series expansion are very similar, whether the Xα or HHF method is used.

Let us now use Eq. (VII.2) to compute the eigenvalues of the Xα and HHF methods, so as to study the difference between these eigenvalues. We shall take the standard state with energy $\langle E\rangle_0$ to be the ground state of the atom, and we then find the energy of the ion in which an electron has been removed from the ith shell. Thus we assume that only $q_i - q_{i1}$ is different from zero, and equals -1. We then find

$$\langle E(q_i = q_{i1})\rangle - \langle E(q_i = q_{i1} - 1)\rangle$$
$$= \frac{\partial\langle E\rangle}{\partial q_i}\bigg|_0 - \frac{1}{2}\frac{\partial^2\langle E\rangle}{\partial q_i^2}\bigg|_0 + \frac{1}{6}\frac{\partial^3\langle E\rangle}{\partial q_i^3}\bigg|_0 - \cdots. \qquad \text{(VII.3)}$$

The expression on the left of Eq. (VII.3) is the value that would be found for the HHF eigenvalue, as we see from Eq. (V.11), provided the HHF method were used in computing the total energy. The first term on the right would be the Xα eigenvalue if the energy were $\langle E_{X\alpha}\rangle$. If we were using the HHF method, it would be the partial derivative of $\langle E_{\mathrm{HHF}}\rangle$ with respect to q_i, a quantity which plays the same role in the HHF method that $\varepsilon_{iX\alpha}$ does in the Xα method, and which is discussed at length by Slater *et al.* (1969b).

In either case, we see that the energy difference, on the left of Eq. (VII.3), differs from this partial derivative by terms in the second, third, and higher derivatives. When numerical values are used, we find that the quadratic term is the leading term in this energy difference, the cubic term being a small correction. Thus, in Table I, we give values of these three terms, from calculations of Slater and Wood, for the various orbitals of Cr in an Xα calculation, using the configuration 3d^{5}4s as the standard state. The first entries in Table I (such as −428.5459 for the 1s orbital) are the Xα eigenvalues $\varepsilon_{iX\alpha}$, while the last entries (such as −440.81) are

TABLE I

VALUES OF QUANTITY $\partial\langle E\rangle/\partial q_i|_0 - \frac{1}{2}\,\partial^2\langle E\rangle/\partial q_i^2|_0 + \frac{1}{6}\,\partial^3\langle E\rangle/\partial q_i^3|_0$ FOR CR IN THE 3d^{5}4s STATE[a]

	$\frac{\partial\langle E\rangle}{\partial q_i}\Big\vert_0 - \frac{1}{2}\frac{\partial^2\langle E\rangle}{\partial q_i^2}\Big\vert_0 + \frac{1}{6}\frac{\partial^3\langle E\rangle}{\partial q_i^3}\Big\vert_0$	Experimental	Koopmans	HHF
1s	−428.5459 − 10.1025 + 0.0378 = −438.6106	−437.4	−441.88	−440.81
2s	− 48.3468 − 1.3833 − 0.0766 = − 49.8067	− 51.0	− 51.29	− 52.54
2p	− 41.1868 − 1.6924 − 0.0858 = − 42.9650	− 42.9	− 44.57	− 44.40
3s	− 5.2691 − 0.4021 − 0.0618 = − 5.7330	− 5.9	− 6.23	− 6.66
3p	− 3.2758 − 0.3922 − 0.0588 = − 3.7268	− 3.6	− 4.19	− 4.19
3d	− 0.1895 − 0.3230 − 0.0552 = − 0.5677	− 0.75	− 0.82	− 0.64
4s	− 0.2533 − 0.2043 − 0.0084 = − 0.4660	− 0.57	− 0.49	− 0.42

[a] These represent binding energies for the Cr atom, according to Eq. (VII.3). "Experimental" values from Slater (1955), corrected to remove relativistic effect by Herman and Skillman (1963). "Koopmans," calculated from Eq. (VII.3), using second derivatives with nonrelaxed orbitals (described in Section VIII). HHF, hyper-Hartree-Fock eigenvalues, from Mann (1967). Energies in rydbergs.

the HHF eigenvalues $\varepsilon_{i\mathrm{HHF}}$. We observe the very considerable difference between these values. We even note that in some cases they come in a different order: $\varepsilon_{i\mathrm{X}\alpha}$ for the 3d orbital (-0.1895) lies above the value for 4s (-0.2533), while the order is reversed for the HHF eigenvalues, the 3d (-0.64) lying below the 4s (-0.42). Such inversions of order are discussed at length by Slater *et al.* (1969b), though at the time that paper was written it was not realized that $\varepsilon_{i\mathrm{X}\alpha}$ was rigorously given by $\partial\langle E_{\mathrm{X}\alpha}\rangle/\partial n_i$.

The sum of the three terms of Eq. (VII.3), given in Table I, agrees fairly well with the experimental values, given in the next column of the table. These experimental values are determined from X-ray data, corrected to remove the relativistic effect present in experiment by using corrections given by Herman and Skillman (1963). The calculated values we have just mentioned are found from separate self-consistent calculations by the Xα method for the ground state of the atom, and for the ion with an electron removed. Thus in the ionized state the orbitals are all modified, or relax, as compared with the orbitals of the ground state. On the other hand, in the HHF method, the orbitals appropriate for the ground state are used for the ionized state as well, so that relaxation is disregarded. Various writers, including Rosen and Lindgren (1968), Hedin and Johansson (1969), and Stukel *et al.* (1970b) have pointed out the importance of considering the relaxation of the orbitals.

It is difficult to attack the effect of this relaxation of the orbitals without making separate self-consistent calculations for the ions lacking inner electrons, as was done in the calculations of Slater and Wood leading to Table I. Hedin and Johansson (1969) have given a good discussion of the perturbation approach to the problem, but the modification of the orbitals is so great when an electron is removed that a perturbation approach is hardly adequate. We can get an idea of these modifications by considering the kinetic energy. We know that the total kinetic energy is the sum of the kinetic energies of the individual electrons, and that, since the virial theorem is satisfied, the change in total kinetic energy when an electron is removed is the negative of the change in total energy. If the orbitals were not modified when one electron was removed from the atom, the kinetic energies of the remaining orbitals would be unchanged, and the change of kinetic energy of the whole atom would simply equal the negative of the kinetic energy of the electron that has been removed.

This is far from the case. From the calculations of Slater and Wood on chromium used in preparing Table I, we can find the kinetic energy of each orbital, both in the atom and in the ion with any electron removed. In Table II, we show the change in kinetic energy when an electron is removed,

TABLE II

CHANGE OF KINETIC ENERGY OF CR WHEN ONE ELECTRON IS REMOVED[a]

Removed electron	−KE of removed electron	Change of KE of remaining electrons	Net change of KE
1s	−551.98	113.37	−438.61
2s	−98.57	48.76	−49.81
2p	−98.48	54.51	−42.97
3s	−20.85	15.12	−5.73
3p	−18.15	14.42	−3.73
3d	−9.60	9.03	−0.57
4s	−1.64	1.17	−0.47

[a] Made up from negative of removed electron and change of kinetic energy (KE) of remaining electrons. Energies in rydbergs.

made up of the negative of kinetic energy of the removed electron (as calculated for the neutral atom), plus the increase of kinetic energy of the remaining electrons. We see that, even for the removal of a 1s electron, the change of the kinetic energy of the remaining electrons cancels about 20% of the kinetic energy of the removed electron. As we go to the more loosely bound electrons, this fraction increases, until we see that for the 3d orbital nearly the whole of the kinetic energy of the removed electron is canceled by increase of kinetic energy of the remaining electrons. These changes of kinetic energy, of course, reflect very directly the changes in the orbitals, since an increase of kinetic energy represents a decrease of de Broglie wavelength, or a shrinkage of the dimensions of the orbital. These changes in dimensions result from the change of effective nuclear charge as a result of the removal of an inner electron, and are very clear if one looks at the changes of the actual wave functions of the electrons.

These changes in the orbitals and in the kinetic energy of the ion as compared to the atom are disregarded in the calculation of the ionization energy by the HHF method, or by the use of Koopmans' theorem. In that method, one uses the unrelaxed orbitals of the atom to represent those of the ion. Consequently, the calculated total energy of the ion will be too high, and the absolute value of the ionization energy will come out to be too large. This is illustrated in Table I, where the column marked HHF is the value computed from an exact HHF calculation, while that marked Koopmans is the value computed from the integrals defined as in the HHF calculation, but applied to the unrelaxed Xα spin-orbitals. We see that these two columns of Table I are in fairly close agreement, indicating the similarity between the Xα and HHF spin-orbitals. Furthermore, as we should expect, they are numerically larger than the values from Eq. (VII.3), computed with relaxation (except for the 4s case, which may be a result of numerical inaccuracies), and are numerically too large as compared with experiment.

One can ask where the difference between the results of Eq. (VII.3) and the Koopmans results arises. The first derivative terms in Eq. (VII.3) are the same, whether one considers relaxation of the orbitals or not. The reason is that the orbitals of either the Xα or the HHF method are determined by the variation method. The change in total energy when the occupation numbers are changed arises from two causes, the explicit dependence of energy on occupation numbers, and the change of energy on account of modification of the orbitals with occupation number. To the first order of small quantities, the second effect vanishes on account of the use of the variation method, and this leaves the same change in total energy, to the first order, whether or not relaxation is considered. However, the effect of modification of orbitals enters in the second derivative terms. These second derivatives come out about twice as large if relaxation is disregarded as if it is taken into account as is done in Table I. An illustration of this effect, for the Co atom as treated by the HHF method, was given by Slater *et al.* (1969b), Fig. 3. That figure showed the energy of the Co atom as a function of the number of 3d electrons, in a configuration $3d^q 4s^{9-q}$. One curve (the "envelope" in the figure) represented the use of relaxed orbitals. These other curves representing unrelaxed orbitals showed much larger curvature, or second derivatives. This is found to be a general situation, as we describe in the next section.

VIII. Computation of Unrelaxed Second Derivatives by the Xα and HHF Methods

It is easy to start with the general expressions for $\langle E_{X\alpha}\rangle$ or $\langle E_{\mathrm{HHF}}\rangle$ as a function of occupation numbers, as given in Eq. (I.2) and (I.3) or (V.1), respectively, and to find the second derivatives with respect to the q_i's, treating the spin-orbitals as being constant. These are the unrelaxed values which we have just been discussing. For the Xα method, as applied to a non-spin-polarized case for an isolated atom, which we are discussing at present, we can rewrite Eqs. (I.2) and (I.3) in the form

$$\langle E_{X\alpha}\rangle = \sum_i q_i I(i) + \tfrac{1}{2}\sum_{i,j} q_i q_j F^0(i,j) - (9\alpha/2)(3/8\pi)^{1/3} \int \left[\sum_j q_j \rho_j(1)\right]^{4/3} dv_1, \qquad \text{(VIII.1)}$$

in which $\rho_j(1)$ is the spherically averaged charge density arising from the jth spin-orbital, $I(i)$ is as in Eq. (V.1), and $F^0(i,j)$ is as in Eq. (V.6).

We next differentiate this expression with respect to q_i, treating the integrals $I(i)$, $F^0(i,j)$, and the charge density $\rho_i(1)$ as constants. We have

$$\left.\frac{\partial\langle E_{X\alpha}\rangle}{\partial q_i}\right|_{\text{unrelaxed}} = I(i) + \sum_j q_j F^0(i,j) - 6\alpha(3/8\pi)^{1/3}\int \rho_i(1)\left[\sum_j q_j \rho_j(1)\right]^{1/3} dv_1. \qquad \text{(VIII.2)}$$

We differentiate again to get the desired second derivatives. We have

$$\left.\frac{\partial^2\langle E_{X\alpha}\rangle}{\partial q_i\,\partial q_j}\right|_{\text{unrelaxed}} = F^0(i,j) - 2\alpha(3/8\pi)^{1/3}\int \frac{\rho_i(1)\rho_j(1)\,dv_1}{\left[\sum_k q_k \rho_k(1)\right]^{2/3}}. \qquad \text{(VIII.3)}$$

The expression for $\partial\langle E_{X\alpha}\rangle/\partial q_i$ from Eq. (VIII.2) equals the eigenvalue of the problem, from Eq. (I.6), when we express the various integrals in terms of atomic integrals. Thus we verify the fact that as far as the first derivatives are concerned, it is immaterial whether we differentiate keeping the integrals constant, as we are doing here, or not. As for the second derivatives, from Eq. (VIII.3) we observe that a new integral is involved, in addition to $F^0(i,j)$. Wood has made calculations of these new integrals for Cr, and they will be used in Table III, to be given shortly.

We next carry through a similar analysis of the case arising from the HHF method. The total energy is already given in terms of the integrals in Eq. (V.1), and we immediately find from that equation that we have

$$\begin{aligned} \left.\frac{\partial^2\langle E_{\text{HHF}}\rangle}{\partial {q_i}^2}\right|_{\text{unrelaxed}} &= (i,i), \\ \left.\frac{\partial^2\langle E_{\text{HHF}}\rangle}{\partial q_i\,\partial q_j}\right|_{\text{unrelaxed}} &= (i,j) \qquad \text{for} \quad i \neq j, \end{aligned} \qquad \text{(VIII.4)}$$

where (i,i) and (i,j) are given in Eq. (V.6). It is interesting to note that the leading term for both the Xα and the HHF cases is the spherically averaged self-interaction term $F^0(i,j)$, as we see by comparison of Eqs. (VIII.3) and (V.6).

In Table III, we give values of $\frac{1}{2}\,\partial^2\langle E_{X\alpha}\rangle/\partial {q_i}^2$ unrelaxed for the Xα method, as well as $\frac{1}{2}\,\partial^2\langle E_{\text{HHF}}\rangle/\partial {q_i}^2$ unrelaxed for the HHF method, compared with the relaxed Xα values already tabulated in Table I. We see that the Xα and HHF unrelaxed values agree with each other fairly closely, showing the approximate agreement between the orbitals determined by these two methods. On the contrary, the relaxed values given by the Xα method are in most cases only about half of the unrelaxed values. Values have also been computed for the cross derivatives, $i \neq j$, and they show the same type of behavior shown in Table III for the case $i = j$.

TABLE III

DIFFERENT ESTIMATES OF $\frac{1}{2}\,\partial^2\langle E\rangle/\partial q_i^2$ FOR CR

	Xα unrelaxed[a] (Ry)	HHF unrelaxed[b] (Ry)	Xα relaxed[c] (Ry)
1s	13.3335	14.6504	10.1025
2s	2.9376	3.0770	1.3833
2p	3.3790	3.3797	1.6924
3s	0.9597	0.9893	0.4021
3p	0.9082	0.8909	0.3922
3d	0.6321	0.6594	0.3230
4s	0.2375	0.2358	0.2043

[a] Calculation for Xα method, disregarding relaxation, from Eq. (VIII.3).

[b] Calculation by HHF method, unrelaxed, using Eq. (VIII.4), and Mann's (1967) integrals.

[c] Quantities of Table I, Xα method including relaxation.

Though we do not have HHF relaxed calculations for this atom, the indications from other cases are that relaxation has about the same effects in both Xα and HHF methods.

The calculations made so far in this section refer to the non-spin-polarized Xα and HHF methods. However, we wish to be able to take up magnetic problems, for which we make a distinction between the spin-up and spin-down cases. Our equation for energy, Eq. (VII.2), is set up for this general case, but we have been restricting ourselves to the case where the μ's are zero. In the spin-polarized case for the Xα method, Eq. (VIII.1) is replaced by

$$\langle E_{X\alpha}\rangle = \sum_i q_i I(i) + \tfrac{1}{2}\sum_{i,j} q_i q_j F^0(i,j) - (9\alpha/2)(3/4\pi)^{1/3}$$

$$\int\left\{\left[\sum \tfrac{1}{2}(q_j + \mu_j)\rho_j(1)\right]^{4/3} + \left[\sum_j \tfrac{1}{2}(q_j - \mu_j)\rho_j(1)\right]^{4/3}\right\} dv_1. \quad \text{(VIII.5)}$$

We differentiate with respect to the μ's, keeping the integrals and charge densities fixed. We find

$$\left.\frac{\partial^2\langle E_{X\alpha}\rangle}{\partial\mu_i\,\partial\mu_j}\right|_{\text{unrelaxed}} = -2\alpha(3/8\pi)^{1/3}\int\frac{\rho_i(1)\rho_j(1)\,dv_1}{\left[\sum_k q_k\rho_k(1)\right]^{2/3}}, \tag{VIII.6}$$

which shows by comparison with Eq. (VIII.3) that

$$\left.\frac{\partial^2\langle E_{X\alpha}\rangle}{\partial q_i\,\partial q_j}\right|_{\text{unrelaxed}} = F^0(i,j) + \left.\frac{\partial^2\langle E_{X\alpha}\rangle}{\partial\mu_i\,\partial\mu_j}\right|_{\text{unrelaxed}}. \tag{VIII.7}$$

From this result we see that the small deviation of the unrelaxed second derivative $\partial^2\langle EX\alpha\rangle/\partial q_i\,\partial q_j$ from $F^0(i,j)$, the self-interaction term, is just what we need to get the second derivatives $\partial^2\langle E_{X\alpha}\rangle/\partial\mu_i\,\partial\mu_j$ unrelaxed of Eq. (VIII.6).

In a similar way we can prove for the HHF method that

$$\left.\frac{\partial^2\langle E_{\text{HHF}}\rangle}{\partial q_i\,\partial q_j}\right|_{\text{unrelaxed}} = F^0(i,j) + \left.\frac{\partial^2\langle E_{\text{HHF}}\rangle}{\partial\mu_i\,\partial\mu_j}\right|_{\text{unrelaxed}}, \tag{VIII.8}$$

so that the second derivatives $\partial^2\langle E_{\text{HHF}}\rangle/\partial\mu_i\,\partial\mu_j$ unrelaxed can be determined from well-known atomic integrals. It is to be noted, however, as shown by Slater *et al.* (1969b), Sec. VII, that the values of the quantities (i,i) and (i,j), which equal the partial derivatives of Eq. (VIII.8), take slightly different forms for the spin-polarized case from what they do for the non-spin-polarized case given in Eqs. (V.6) of the present paper.

In connection with the work on chromium which has been discussed earlier, Slater and Wood (1971) have carried through relaxed calculations of the spin-polarized case. The results are not very complete, but they are enough to show that the differences between the unrelaxed and relaxed values of $\partial^2\langle E_{X\alpha}\rangle/\partial\mu_i\,\partial\mu_j$ are not nearly as great as the differences in $\partial^2\langle E_{X\alpha}\rangle/\partial {q_i}^2$ indicated in Table III. This is not surprising. The effect of relaxation comes because, when the occupation numbers are changed, the potential in which the electrons move is changed, and this makes a large change in the energy. If only the μ's change, however, and not the q's, the modification is only one in which the spins of electrons are changed, not the orbitals. Thus the only change in the potentials acting on other electrons comes in the exchange term, not in the much larger Coulomb term. Consequently, it is not very inaccurate to use the unrelaxed values of these second derivatives $\partial^2\langle E\rangle/\partial\mu_i\,\partial\mu_j$ in estimating the effect of spin polarization on the total energy. And since we may expect the HHF values of these derivatives, which can be found from atomic integrals, to be fairly reliable, we can attempt to estimate the effect of spin polarization by use of the HHF unrelaxed values of the second derivatives.

This method was used by the author (Slater, 1968c) in discussing the energy-band theory of magnetism, which we shall mention later. The results obtained by this quite simple method give reasonable numerical values. Similar methods were used (Slater, 1970) to estimate the values of the quantities $\partial\langle E_{\mathrm{HHF}}\rangle/\partial q_i\uparrow$, $\partial\langle E_{\mathrm{HHF}}\rangle/\partial q_i\downarrow$, the one-electron eigenvalues for spin-up and spin-down orbitals, in a HHF calculation of spin-polarized atoms. These quantities may be expected to agree approximately with the eigenvalues of the spin-polarized Xα method, and give us apparently reliable information regarding the occupation numbers of the transition atoms in their ground state. On account of Hund's rule, they lead to spin-polarized ground states. This is a result of the dependence of the total energy on the μ's, which results in a lower energy, either according to the Xα or the HHF method, if as many spin-orbitals as possible have spin up. In cases where spin-polarized Xα calculations have been made by Wood on 3d transition elements, they lead to results in good agreement with these consequences of the spin-polarized HHF method.

IX. Optical Absorption and the Transition State

In Sections VII and VIII we have been emphasizing the importance of calculating a properly self-consistent wave function both of the initial and the final state in a case of ionization. It is equally important to do this for excitation from one state to another. Instead of basing the calculations on the ground state, however, we shall show that there is a good deal to be said in favor of making a calculation for what we may call the transition state: a state in which the occupation numbers are half-way between those of the initial and final state. Thus let us calculate the energy difference between an initial state, and a final state in which q_i has decreased by one unit, q_j has increased by one unit, so that an electron has had a transition from the ith to the jth state. First, we carry the calculation through using the initial state as the standard state around which we make our power series expansion.

Thus we assume that in the initial state $q_i = q_{i1}$, $q_j = q_{j1}$, while in the final state $q_i = q_{i1} - 1$, $q_j = q_{j1} + 1$. Let us find the energies of initial and final states from Eq. (VII.2), and let us then find the difference between them, or the excitation energy. We have, assuming a non-spin-polarized case,

$$
\begin{aligned}
&\langle E(\text{initial})\rangle - \langle E(\text{final})\rangle \\
&\quad = \langle E(q_i = q_{i1}, q_j = q_{j1})\rangle - \langle E(q_i = q_{i1} - 1, q_j = q_{j1} + 1)\rangle, \\
&\quad = \left.\frac{\partial\langle E\rangle}{\partial q_i}\right|_0 - \left.\frac{\partial\langle E\rangle}{\partial q_j}\right|_0 \\
&\quad\quad + \frac{1}{2!}\left(-\left.\frac{\partial^2\langle E\rangle}{\partial q_i^2}\right|_0 + 2\left.\frac{\partial^2\langle E\rangle}{\partial q_i\partial q_j}\right|_0 - \left.\frac{\partial^2\langle E\rangle}{\partial q_j^2}\right|_0\right) \\
&\quad\quad + \frac{1}{3!}\left(\left.\frac{\partial^3\langle E\rangle}{\partial q_i^3}\right|_0 - 3\left.\frac{\partial^3\langle E\rangle}{\partial q_i^2\partial q_j}\right|_0 + 3\left.\frac{\partial^3\langle E\rangle}{\partial q_i\partial q_j^2}\right|_0 - \left.\frac{\partial^3\langle E\rangle}{\partial q_j^3}\right|_0\right) + \cdots.
\end{aligned}
\tag{IX.1}
$$

In other words, in addition to the difference of the two first derivatives, which would be the difference of Xα eigenvalues, we have second- and third-order correction terms.

This is the situation if the standard state is the ground state of the system. However, let us set up the case in which it is half-way between the initial and final states. In this case, the initial state has $q_i = q_{i1} + \frac{1}{2}$, $q_j = q_{j1} - \frac{1}{2}$, and the final state has $q_i = q_{i1} - \frac{1}{2}$, $q_j = q_{j1} + \frac{1}{2}$. We then find

$$
\begin{aligned}
&\langle E(\text{initial})\rangle - \langle E(\text{final})\rangle = \left.\frac{\partial\langle E\rangle}{\partial q_i}\right|_0 - \left.\frac{\partial\langle E\rangle}{\partial q_j}\right|_0 \\
&\quad + \frac{1}{24}\left(\left.\frac{\partial^3\langle E\rangle}{\partial q_i^3}\right|_0 - 3\left.\frac{\partial^3\langle E\rangle}{\partial q_i^2\partial q_j}\right|_0 + 3\left.\frac{\partial^3\langle E\rangle}{\partial q_i\partial q_j^2}\right|_0 - \left.\frac{\partial^3\langle E\rangle}{\partial q_j^3}\right|_0\right) + \cdots.
\end{aligned}
\tag{IX.2}
$$

In other words, with this choice of a state for which the self-consistent calculation is to be made, the second-order term, the principal correction term in Eq. (IX.1), has dropped out, and the third-order term has fallen to one-quarter of the value which it has in Eq. (IX.1).

These third-order terms have been computed by Slater and Wood from the calculations for Cr which we have been quoting earlier. The values are given in Table IV. We have included only those of these quantities which would come into play in an actual transition from the ground state of the Cr atom, in its configuration 3d^{5}4s, to an excited state containing no electrons beyond 3d and 4s. This demands that the final state *j*, which must add an electron, would be 3d or 4s. We see that with the exception of the K transition, in which the initial state is 1s, these correction terms are all less than 0.01 Ry in magnitude. In other words, we may safely say that the difference of Xα eigenvalues between initial state *i*

TABLE IV

QUANTITIES

$$\frac{1}{24}\left(\frac{\partial^3\langle E\rangle}{\partial q_i^3}\bigg|_0 - 3\frac{\partial^3\langle E\rangle}{\partial q_i^2\,\partial q_j}\bigg|_0 + 3\frac{\partial^3\langle E\rangle}{\partial q_i\,\partial q_j^2}\bigg|_0 - \frac{\partial^3\langle E\rangle}{\partial q_j^3}\bigg|_0\right)$$

OF EQ. (IX.2), FOR CR, USING TRANSITION STATE, FROM CALCULATIONS OF SLATER AND WOOD (1971)

ij	Quantity (Ry)	*ij*	Quantity (Ry)
1s3d	0.0302	3s3d	0.0002
1s4s	0.0232	3s4s	−0.0080
2s3d	0.0048	3p3d	0.0002
2s4s	−0.0044	3p4s	−0.0028
2p3d	0.0022	3d4s	−0.0050
2p4s	−0.0068		

and final state *j*, when calculated from a self-consistent transition state, is quite accurately equal to the difference between total self-consistent Xα energies of the atom in the initial and final states.

The use of this theorem is of advantage in calculating energy differences between initial and final states, particularly X-ray transitions. The available computer programs for carrying out self-consistent-field calculations are as convenient to use for fractional occupation numbers as for integral values, and they include the eigenvalues as part of their output. The single calculation of a transition state permits the evaluation of the energy difference between initial and final state, in terms of the eigenvalues of the Xα method. In addition to this convenience of the use of the transition state for isolated atoms, we shall next consider localized absorption in crystals, and we shall see that for that problem, the use of the transition state is of very considerable value.

X. Band Absorption versus Localized Absorption in Crystals

The Xα method can be applied to crystals without difficulty, as is shown from the many energy-band calculations that have been made by its use, included in the list of references at the end of this paper. For a perfect crystal, of course the spin-orbitals take the form of Bloch-type functions, which could be approximated as Bloch sums of localized orbitals. As we have seen in Section IV, the Fermi statistics will apply, and in the ground state all spin-orbitals up to the Fermi energy will have occupation numbers of unity, those above the Fermi energy being empty. Ordinarily for a crystal the number of spin-orbitals whose energies lie precisely at the Fermi energy will be small enough to be negligible.

One striking feature of the Xα method is that as the lattice spacing of the crystal is increased to infinity, the problem will go smoothly into that of the separated atoms. The reason for this is the localized nature of the exchange-correlation term: The total energy of Eqs. (I.2) and (I.3) depends only on the local charge density, and this will be the same whether we are dealing with a crystal formed of widely separated atoms, or with isolated atoms. Of course, it is well known in this limit that one can write the charge density either in terms of Bloch-type functions or in terms of localized orbitals determined from them by a unitary transformation. The net result of Eq. (I.1) will be the same in either case, since the charge density is invariant under a unitary transformation of the occupied spin-orbitals.

There is no complication about this statement in the case of an insulating crystal such as an inert gas crystal or an alkali halide; in such cases the localized functions are the well-known Wannier functions. For a metal, the situation is more complicated, and we shall not attempt a complete discussion in the present abbreviated report. We must set up the localized functions by making linear combinations of the occupied Bloch functions only, and this will include only the lower states of certain partially occupied energy bands, not the upper ones. As a result of this, the localized functions will appear to be made up out of fractional numbers of electrons in the various atomic orbitals. For isolated atoms, this situation has been discussed by Slater *et al.* (1969b) and by Slater (1970), particularly for the spin-polarized case, as is found in the 3d transition elements. Even in such a case, however, as the atoms are brought closer together, the discrete energy levels of the separated atoms, as given by the Xα method, will go smoothly into the energy bands of the crystal.

In considering an optical excitation of a crystal, we must consider not only the ground state, but also the excited state. This may consist of a state that would be represented in the Xα method by saying that an electron had been removed from a Bloch state whose eigenvalue was below the Fermi energy, to a Bloch state above the Fermi energy. The increase of energy of the crystal resulting from this transition would take the form discussed in Eqs. (VII.3), (IX.1), (IX.2), only now the occupation number would be that of a Bloch state, not of a localized atomic state. In such a case, the second and third derivative terms in Eq. (VII.2) are negligible. Let us inquire regarding the reason for this important statement.

We can see this reason more clearly if we write an equation for $\partial\langle E\rangle/\partial q_i$, by differentiating Eq. (VII.2). We consider the non-spin-polarized case, with $\mu_i = 0$. Then we have

$$\frac{\partial\langle E\rangle}{\partial q_i} = \left.\frac{\partial\langle E\rangle}{\partial q_i}\right|_0 + \sum_j (q_j - q_{j1}) \left.\frac{\partial^2\langle E\rangle}{\partial q_i\,\partial q_j}\right|_0 + \frac{1}{2!}\sum_{j,k} (q_j - q_{j1})(q_k - q_{k1}) \left.\frac{\partial^3\langle E\rangle}{\partial q_i\,\partial q_j\,\partial q_k}\right|_0 + \cdots. \tag{X.1}$$

In other words, the second derivative $\partial^2\langle E\rangle/\partial q_i\,\partial q_j|_0$ measures the change in the Xα eigenvalue $\varepsilon_{iX\alpha}$ when the occupation number of the jth spin-orbital increases by one unit, if we disregard the third-derivative term. Now in an atom this effect is large, as we saw in Table I. The reason is that if the occupation number of the jth atomic spin-orbital decreases by unity, a whole electron is removed from the jth shell of this atom; there is less screening of the nucleus by electrons, so that the eigenvalues all decrease (consistent with the positive nature of the second derivatives). The second derivative is in a sense a measure of the electrostatic interaction between electrons in the ith and jth atomic spin-orbitals, a relation which is very clear from the appearance of $F^0(i,j)$ as the leading term in the second derivatives in Eqs. (VIII.3) and (VIII.4).

If we are dealing with a Bloch state in a crystal, on the other hand, the charge density is distributed through all N atoms of the crystal. If we remove an electron from a Bloch state, only $1/N$ of an electronic charge is removed from each atom of the crystal. This will have a negligible effect on the eigenvalues of the electrons in this atom. In other words, the second derivatives in this case will be of the order of $1/N$ times as great as for an individual atom. It is as if we replaced $F^0(i,j)$ by the electrostatic interaction of an electron in a Bloch state with an electron in another Bloch state. On account of the spread-out nature of the Bloch states, the interaction energy would be negligible.

From such arguments we can conclude that if an electron is removed from one Bloch state to another, the change in total energy of the crystal, in the Xα approximation, is just the difference of the eigenvalues $\varepsilon_{iX\alpha}$ of the initial and final states. The second- and third-derivative terms are negligible, when multiplied by the values of unity which are the values of $q_j - q_{j1}$, etc., which one can encounter in the transfer of a single electron. One can use Eq. (III.1) for the energy change, even when dn_i is as great as unity, without the use of further terms.

Such a transfer of an electron from one Bloch state to another, however, is not the only sort which we can find in the optical absorption by a crystal. In the theory of the exciton, one encounters a localized excitation, in which an electron is excited from a low occupied state to a higher excited state in a single atom, as modified by its interactions with the neighboring atoms. The theory of the exciton is sketched by Slater and Wood (1971) in such a way as to apply to this problem. It is known that when one takes account of the electrostatic interactions between an excited electron and the positive hole which it has left behind, these interactions make possible excited states, in which the electron and hole remain tied to each other and result in discrete energy levels, having different energies from those arising from the energy-band theory. If these excitons are quite localized, transitions to the exciton states steal the larger part of the oscillator strength from the transitions of the energy-band type, so that they become of paramount importance in discussing the optical properties. This is particularly true in discussing a transition of the X-ray type, in which one of the inner electrons of an atom is excited to a higher bound state, or is ejected from the crystal as a photoelectron. The hole in the X-ray level is essentially completely localized in such a case, and the transition has a very close resemblance to what is found in an isolated atom.

For discussing the energy differences encountered in such transitions, one then wants to use a properly localized model for the excited state. The most graphic way to treat this is to use the concept of the transition state, which was introduced in Section IX. The transition state in such a case will have the properties of a crystal with a local perturbation at the site of the atom which is being excited. This atom will lack one-half of an electron from an inner shell, and will have an extra one-half electron in an excited but localized state. Thus the charge density and potential in its neighborhood will be quite different from what is found in an ordinary atom of the crystal. We must then solve the self-consistent-field problem for the transition state, with this localized perturbation, and must compute the transition as if it were from a lower to a higher orbital in such a problem.

It is well known, as is discussed in references quoted by Slater and Wood (1971), that if this perturbation is large enough, it will result in discrete levels separated from the continuum, and the transition that we must consider is from one of these discrete levels to another. The energy differences will then be very similar to those of an isolated atom, and the X-ray absorptions will come at quite different energies from those given by the Xα eigenvalues of the ground state. This is as shown in Table I, and it was reasonable in this table to compare energy differences of isolated atoms with observed X-ray levels.

We shall always find this situation unless we are considering absorption from a broad valence band to a conduction band, in which case we should not expect great localization. In such a case, it is found in the theory of the exciton that no discrete levels will be pushed out of the continuum, but the distribution of levels will be essentially as in an unperturbed crystal. It is in these cases that the familiar energy-band calculation of optical properties, from densities of states, is appropriate. Even in such a case, one can have an incipient discrete level, what Friedel (1954; see also references to Blandin and Daniel) refers to as a virtual excited state, which will modify the wave functions and transition probabilities profoundly.

We possess the mathematical machinery for studying perturbed crystals of the sort met with excitons, as well as those resulting from impurity atoms. Among these mathematical techniques are those of Koster and Slater (1954a, b), based on the expansion of the problem in terms of Wannier functions of the unperturbed problem, and the KKR cluster method of Johnson *et al.* (Johnson, 1966b, 1967, 1968a, b, 1971; Smith and Johnson, 1969). This latter method can handle the perturbation met in the exciton problem better than the earlier method of Koster and Slater, and probably will find great usefulness in the future in the study of excitons. It has already proved to be of great value in studying the energy levels of localized clusters of atoms in crystals, such as a 3d transition atom surrounded by its neighbors, producing a ligand or crystal field.

We have already mentioned that the transition state, in a case of localized excitation, has a localized perturbation. By use of the methods just described, one can solve the $X\alpha$ problem for such a localized perturbation, obtaining two types of spin-orbitals and eigenvalues. First, we have the localized spin-orbitals which we have been discussing, similar to those of an isolated atom, and falling off rapidly as we go away from this atom. Secondly, there are the continuum levels, with orbitals falling off in amplitude as we approach the perturbed atom. The general nature of these orbitals was described by the author (Slater, 1949) in a study of electrons in perturbed periodic lattices. We should now use these spin-orbitals as basis functions for studying the real behavior of the transition from the ground state to the excited state.

The most interesting feature which would be introduced by this further study would be the multiplet structure. Just as with an isolated atom, this comes in only when we make linear combinations of determinantal functions, to give better approximations to the actual wave functions of the states of the crystal. It is at this point that the crystal or ligand field comes into the theory. In a crystal containing 3d transition ions, for instance, the self-consistent field will automatically split the localized 3d levels of an excited ion in a cubic field into the familiar *dε* and *dγ* levels. Calculations which have already been made of such problems, such as those of Wilson (1968, 1969, 1970) on MnO, have shown that one gets the right order of magnitude for these splittings.

But beyond this point, one proceeds as in the conventional crystal or ligand field theory, to produce a theory of the multiplet levels. Such calculations have not yet been carried through in detail, but we must anticipate much activity of this type in the future. It is interesting to notice the way in which the concept of the localized transition state has been used to introduce the localized orbitals which are needed to lead to the multiplet levels met in crystal field theory. Here, however, in contrast to the semi-empirical crystal field which has prevailed up to the present, we should be able to get a priori calculation of the various parameters which go into the separations between the multiplets, rather than having to assume them from experiment, or to estimate them from the constants of the isolated atoms or ions.

XI. The Xα Method and Magnetic Problems

In earlier sections, we have presented the mathematical analysis involved in treating the Xα method as a spin-polarized method, but we have not so far made any use of it. The applications are, of course, to magnetism, and we find a number of such applications in papers included in the list of references. The applications are too extensive to treat in detail in a review article of the present length, and for this reason we shall limit ourselves in the present section to sketching the general types of approach which have been used, and those which can be looked forward to in the future.

The most straightforward application is to the band theory of ferromagnetism. Here a discussion has been given by the author (Slater, 1968c). The method is simple. One examines to see if a self-consistent Xα solution is possible, for such a crystal as iron, cobalt, or nickel, in which there are more electrons with spin up than spin down. This can be handled by starting with the assumption of some spin-polarization, which leads to two different sets of energy bands, for spin up and spin down. One finds the Fermi energy, which leads to a net magnetic moment, since the spin-up bands lie lower than the spin-down in such a case, so that more spin-up levels than spin-down lie below the Fermi energy, and are occupied. One finds the spin density as well as charge density from the resulting spin-orbitals and occupation numbers, and uses these as the starting point of the next stage in the iteration to produce self-consistency. Connolly (1967a, b, 1968), Wakoh and Yamashita (1966), Wakoh (1970), and Yamashita *et al.* (1966a,) have described such calculations, which show that in fact a self-consistent ferromagnetic solution can be achieved in iron, cobalt, and nickel, leading to magnetic results in fair agreement with experiment. These calculations were among the first which led to the conclusion that a value of α nearer two-thirds than unity had to be used: The agreement of the final energy bands with experiment was satisfactory for the smaller α, but not for $\alpha = 1$. The results agreed in general with much earlier calculations of the author (Slater, 1936), using the same ideas, but much cruder calculations of the energy bands.

In that early paper, it was indicated that it was likely that the lighter 3d transition elements would not be ferromagnetic, since their 3d energy bands were too broad. To test this idea, Hattox, in calculations so far unpublished (discussed at the 1971 Sanibel Symposium) has treated vanadium both at its normal lattice spacing, and at a larger spacing for which the 3d band would be narrower. At the normal spacing, he found, in agreement with experiment, that there was no ferromagnetism: If he started his iterations for self-consistency with some assumed magnetic moment, he found that each successive iteration resulted in a smaller moment, until finally it disappeared as he approached self-consistency. On the other hand, at 1.5 times the normal spacing, an assumed magnetic moment built up at each successive iteration, leading to the conclusion that ferromagnetism would be found at these larger spacings. This is the first time that real self-consistent calculation has verified the old idea that the tendency toward magnetism would be removed as the energy bands became broader.

Another approach to the question as to which elements should be ferromagnetic has been made by Yamashita *et al.* (1968b). They examined the question of the stability of the nonmagnetic state in 3d transition metals, using the general approach of Koster and Slater (1954a, b) for a localized perturbation in a crystal. They started by assuming a non-spin-polarized case, but then imposed a small ferromagnetic, or antiferromagnetic, perturbation in a restricted cluster of atoms. They were able to decide in this way whether the ferromagnetic or antiferromagnetic state was stable or unstable with respect to the non-spin-polarized case. The conclusion which they reached was in agreement with experiment: Iron, cobalt, and nickel should be ferromagnetic; the lighter elements up to vanadium should be nonmagnetic; and antiferromagnetism should be found in the intermediate elements, chromium and manganese.

Manganese is such a complicated element in its crystal structure that little progress has yet been made in interpreting its antiferrogmagnetic structure. Chromium, however, has been a very interesting case. It was at first thought by experimenters to be very simple. It is body-centered cubic, and it appeared that the atoms at the corners of the cube had spin up, those at the centers had spin down, the magnitude of these magnetic moments being of the order of magnitude of one-half Bohr magneton, rather than the five Bohr magnetons which would be found with a half-filled shell of 5d electrons. It was shown by Asano and Yamashita (1967) that a self-consistent spin-polarized Xα solution can be set up corresponding to approximately the experimental magnetic moment, a conclusion later verified by Connolly (1968).

This verified an earlier suggestion of Slater and Koster (1954), based on the following argument. If one has non-spin-polarized, body-centered cubic Cr, one can compute the energy bands by the Xα method. If then one superposes the different exchange-correlation terms for spin-up and spin-down atomic sites, suggested by the spin-polarized calculation, the crystal becomes simple cubic, since the centers and corners of the cube are no longer equivalent. The simple cubic unit cell is twice as large as the body-centered unit cell, and the Brillouin zone is half as large. When one draws the non-spin polarized energy bands in the simple cubic Brillouin zone, and then introduces the exchange-correlation characteristic of spin polarization, it seemed reasonable to Slater and Koster that gaps would be introduced at the surfaces of the Brillouin zone, in a way which had been suggested earlier by the author (Slater, 1951b,).

Arguments were brought out by Slater and Koster for thinking that these gaps might lie at the Fermi energy. Thus the levels slightly below the Fermi energy, which are occupied, would be pushed downward by the antiferromagnetic perturbation, while those above the Fermi energy, which are empty, would be pushed up. The net result would be a decrease of total energy. The much more accurate argument of Asano and Yamashita (1967) showed that this was essentially just what was happening. This is a rather exceptional situation, found only in chromium.

About 1960, however, it was found that the real situation in chromium was more complicated than this simple description indicated. The simple model which we have described would correspond to what is now called a spin-density wave, in which the spin orientation changed from spin up to spin down from one atomic layer to the next. It was found however by neutron diffraction that the true wavelength of this spin-density wave was not just two atomic distances, but somewhat different from this value. At about the same time it was discovered that a similar situation held in the magnetism of a number of rare-earth metals.

Lomer (1962), shortly after, showed on the basis of the chromium energy bands then available that this was a reasonable situation. If one has a perturbative potential, such as is produced by the antiferromagnetic exchange effect, with a wave vector q, then it can be shown that the condition which must be satisfied for a gap to open up at the Fermi surface is what is called the nesting of the energy surfaces. One energy surface displaced by an amount q in the reciprocal space must approximately coincide with another nondisplaced energy surface. Lomer showed that, with a reasonable assumption regarding the chromium energy surfaces, such nesting would occur with a wave vector q for the perturbative potential which was not commensurable with the periodicity of the crystal, but which instead was approximately equal to that found experimentally for the spin-density wave. Asano and Yamashita (1967) in their more accurate calculations showed that this was indeed the case.

Following this discovery, there was great activity in the study of similar phenomena in the rare-earth metals. Overhauser (1959, 1960a, b, 1962a, b, 1963, 1964, 1965) in a series of papers had proposed a theory of antiferromagnetism and its relation to spin-density waves which was essentially equivalent to the theory which we have been describing. He did not tie his theory closely to any accurate calculations of energy surfaces, however. More important for the study of actual cases was a series of augmented planewave Xα calculations of Fermi surfaces of rare-earth crystals by Andersen (1970; Andersen and Loucks, 1968), Dimmock *et al.* (1965; Dimmock and Freeman, 1964), Fleming *et al.* (1968, 1969), Freeman *et al.* (1966a, b, c), Gupta and Loucks (1968, 1969), Keeton and Loucks (1966a, b, 1968), Loucks (1965a, b, c, d, 1966a, b, 1967a, b, c, 1968), Mackintosh (1962a, b, 1963, 1966, 1967, 1968), Myron and Liu (1970), and Williams *et al.* (1966, Williams and Mackintosh, 1968). In many cases these energy surfaces were discussed in connection with the observed very complicated behavior of the magnetism, of the nature of spin-density waves, found for these elements. There seems to be no doubt but that the type of energy-band calculations which can now be made is capable of explaining these remarkable magnetic effects.

The Xα spin-polarized method can be used not only for discussing ferromagnetic and antiferromagnetic elements, but for compounds as well. In this connection we can cite the case of ferromagnetic EuS, discussed by Cho (1967, 1969, 1970), and antiferromagnetic MnO and NiO, discussed by Wilson (1968, 1969, 1970). In each of these cases we have crystals with the sodium chloride structure, of which the Xα spin-polarized method gives reasonable wave functions, eigenvalues, and occupation numbers for the type of magnetic structure which is found experimentally. In these cases, as in the metallic elements, the calculations which have been made come from a self-consistent solution of Eq. (I.4) with a readjustment of the occupation numbers at each stage of iteration so as to shift electrons from higher, occupied orbitals to lower, empty ones. But we have seen in Section I that this amounts to seeking the lowest possible value of the statistical energy of Eq. (I.2).

We might be interested in some cases in deciding whether a real crystal should be ferromagnetic or antiferromagnetic. Some crystals similar to EuS are known to be antiferromagnetic rather than ferromagnetic, as an illustration. To answer such a question theoretically, we should compute the value of the energy of Eq. (I.2) for both modifications, and should find which of these has the lower energy. It requires a very accurate calculation of the energies to determine this, since the energy difference between the modifications must be very small, and no such calculations have yet been made. With the accuracy which is now being attained in the calculation of total energy, however, it does not seem impossible that during the next years such calculations should prove to be practical.

The magnetic questions which we have been considering have been a determination of the ground state of a magnetic crystal. Once we come to consider the excited states, however, we meet new problems which have a certain analogy to the exciton problems which we have taken up in Section X. It is well known that the most successful treatments of the decrease of magnetic moment of a ferromagnetic crystal with temperature, and its disappearance at the Curie point, have made use of the Heisenberg Hamiltonian. This is a technique starting with a localized excitation. As a very simple case, suppose we have solved for the wave function and energy of the ground state of a ferromagnetic crystal, using a spin-polarized technique, and that we are next looking for the lowest excited states. These are known to be the spin wave states, in which we start with a crystal in which a single atom has its magnetic moment oriented opposite to the magnetic moment as a whole, and in which we then make a Bloch sum of such localized excited states. The author (Slater, 1937) has pointed out the close relation between such excited states and the theory of the exciton. The energy separation between the ground state and these spin wave states is directly proportional to the Heisenberg exchange integral.

It should now be possible to attack these spin-wave states by the same sort of localized treatment of a transition state which we have recommended for the exciton problem. It would be perfectly possible with existing techniques to find the energy of a state with such a localized magnetic state. The Heisenberg exchange integral, which up to the present has been treated as an empirically determined parameter, would come directly out of such a calculation. Calculations of this type have not yet been made, but the author believes that the next few years will see much activity in the direction of making such calculations.

To treat all of the problems which have been touched on in the present section would require a whole volume, since it would lead one into the whole theory of magnetism. The Xα method, however, provides a practical starting point for an a priori theory of such problems, a starting point which has not been practicable with earlier techniques. It is with such applications in mind that we have included in our list of references many papers dealing with localized states, defects, excitons, and magnetic excitations. It would not surprise the author to find that in a few years, the applications coming under these headings would far outnumber those in the categories devoted to perfectly periodic crystals.

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KEY TO THE REFERENCES

In the following list we give references to some of the papers dealing with energy bands, the application of self-consistent fields to solids, excited and magnetic states, impurity states, and related topics, mostly during the years since 1965. Extensive bibliographies of papers earlier than that time are contained in Volume 2 of *Quantum Theory of Molecules and Solids* (Slater, 1965a), and references to these earlier papers are in general omitted from the present listing. The author wishes to acknowledge valuable assistance from Dr. Karlheinz Schwarz in supplying numerous references for this tabulation

In order to make it easier to locate references dealing with specific crystals, we next give a key to the references, listing the authors and the date. Elements and compounds in this key are arranged in order of atomic number. Names of authors are italicized (as for example *Kenney*), if their papers have made some use of the statistical exchange method.

Li: Goodings (1965), *Kenney* (1964), *Lafon and Lin* (1966), Meyer and Young (1965), O'Keefe and Goddard (1969), Overhauser and de Graaf (1969), *Painter and Ellis* (1970b), *Rudge* (1969c).
LIH: *Kunz* (1969b).
LiF: Kunz *et al.* (1969), Mansikka and Bystrand (1966), Mansikka *et al.* (1967), Roessler and Walker (1967c, d).
LiCl: *Kunz* (1968).
LiI: *Kunz* (1969a).
Be: Shyu *et al.* (1966a), *Terrell* (1964, 1966), Tripp *et al.* (1967, 1969).
BeS: *Stukel* (1970c).
BeSe: *Stukel* (1970c).
BeTe: *Stukel* (1970c).
BN: *Keown* (1968), Phillips (1968e), *Wiff and Keown* (1967).
BP: *Stukel* (1970b).
BAs: *Stukel* (1970a).
C: Bassani and Parravicini (1967), Doggett (1965a), Dresselhaus and Dresselhaus (1965), Goroff and Kleinman (1967), *Herman et al.* (1967a), *Keown* (1966), Linderberg (1965), Linderberg and Mäkilä (1967), *Painter and Ellis* 1970a), Phillips (1965), Raccah, Euwema, Stukel, and Collins (1970), Roberts and Walker (1967), Saravia and Brust (1968), Saslow *et al.* (1966).
Ne: *Euwema et al.* (1971).
Na: *Boring* (1968), *Kenney* (1964), Shyu *et al.* (1967), Tong (1971), *Yamashita et al.* (1969).
NaF: Vallin *et al.* (1967).
NaCl: Fong *et al.* (1968), Hassan (1965), *Kunz* (1967a, b, 1968), Pettersson *et al.* (1967), Roessler and Walker (1968 a, b).
NaI: *Kunz* (1966, 1969a), Roessler (1966).
Mg: Falicov and Stachowiak (1966), Kimball *et al.* (1967), Shaw and Pynn (1969), Stark (1967).
MgO: Calais *et al.* (1967), Cohen *et al.* (1967), Fong, Saslow, and Cohen (1968), Roessler and Walker (1967a, c).
Mg_2Si: Au-Yang and Cohen (1969), Folland (1967), Lee (1964).
Mg_2Ge: Au-Yang and Cohen (1969), Lee (1964).
Mg_2Sn: Au-Yang and Cohen (1969).
Mg_2Pb: *Van Dyke and Herman* (1970).
Al: *Connolly* (1970), *Faulkner* (1969), Melz (1966), Raccah and Henrich (1969, 1970), Shyu, Das, and Gaspari (1966b), *Snow* (1967).

AlN: *Hejda* (1969).

AlP: *Stukel et al.* (1969).

AlAs: *Stukel et al.* (1969).

AlSb: Pollak *et al.* (1966).

Si: Alstrup and Johansen (1968), Brust (1964), Callaway and Hughes (1967b), Cardona and Pollak (1966), Dresselhaus and Dresselhaus (1967a, b), Harrison (1965b), *Herman et al.* (1966a, b, 1967a), Hughes (1968), Kane (1966), Raccah, Euwema, Stukel, and Collins (1970), *Stukel and Euwema* (1970), Williams (1970).

SiC: *Herman et al.* (1967a).

Ar: *Cowan et al.* (1966), *Euwema et al.* (1971), Gandelman (1965), *Mattheiss* (1964a) Ramirez and Falicov (1970).

K: Ashcroft (1965), Overhauser (1964), *Yamashita et al.* (1969).

KF: Roessler and Lempka (1966).

KCl: *De Cicco* (1967), *Kunz* (1968), Miyakawa and Oyama (1968), Oyama and Miyakawa (1965, 1966), Roessler and Walker (1968a, b), *Yamashita and Asano* (1967a).

$KNiF_3$: *Ellis, Freeman, and Ros* (1967, 1968), Rummer (1969), Sugano and Tanabe (1965).

KI: *Kunz* (1970), *Onodera et al.* (1966a, b), Roessler and Walker (1967b).

Ca: Animalu (1967a), Chatterjee and Chakraborty (1970), Vasvari *et al.* (1967).

Sc: *Fleming and Loucks* (1968).

ScC: *Schwarz et al.* (1969).

ScN: *Schwarz et al.* (1969).

Ti: Altmann and Bradley (1967), *Mattheiss* (1964b), *Snow and Waber* (1969).

TIC: *Conklin and Silversmith* (1968), *Ern and Switendick* (1965), Lye and Logothetis (1966), Ramqvist *et al.* (1969a, b).

TiN: *Ern and Switendick* (1965).

TiO: *Ern and Switendick* (1965), *Schoen and Denker* (1969).

Ti_2O_3: Honig (1968).

V: *Mattheiss* (1964b), *Snow and Waber* (1969).

VO: Hyland (1968a, b), *Norwood and Fry* (1970).

VO_2: Hyland (1968a, b).

V_3Al: *Mattheiss* (1965a).

V_3Si: *Mattheiss* (1965a).

V_3Co: *Mattheiss* (1965a).

V_3Ga: *Mattheiss* (1965a).

V_3Ge: *Mattheiss* (1965a).

V_3As: *Mattheiss* (1965a).

Cr: *Asano and Yamashita* (1967), *Connolly* (1968), Falicov and Penn (1967, 1968), Falicov and Zuckermann (1967), Falicov and Ruvalds (1968), *Gupta and Sinha* (1970), Kimball and Falicov (1968), Lomer (1962), *Loucks* (1965c) Mackintosh (1966), McWhan and Rice (1967), *Mattheiss* (1964b), Møller *et al.* (1965), Motizuki *et al.* (1968), Nagamiya *et al.* (1965), Overhauser and Arrott (1960, Rice *et al.* (1969), *Snow and Waber* (1969), Sokoloff (1969), Street *et al.* (1968), *Switendick* (1966), *Yamashita and Asano* (1967b).

Mn: Fletcher (1969), Freeman *et al.* (1970a). *Snow and Waber* (1969).

MnO: Nagai (1965, 1967), *Wilson* (1968, 1969).

Fe: Abate and Asdente (1965), Asdente and Delitala (1967, 1968), *Connolly* (1968), Cornwell *et al.* (1968), *De Cicco and Kitz* (1967), Gold (1968), Hubbard and Dalton (1968), Kaplan (1965), *Mattheiss* (1964b), Overhauser and Stearns (1964), Shimizu and Katsuki (1965), Shimizu and Terao (1967), *Snow and Waber* (1969), Thompson and Mook (1970), Tucker *et al.* (1965), *Wakoh and Yamashita* (1966, 1968), Wohlfarth (1965).

Fe_2Te_3: Manca and Mula (1969).

Co: *Connolly* (1968), *Mattheiss* (1964b), Wakoh (1970), Wohlfarth (1970).

CoO: Nagamiya *et al.* (1966).

CoFe: *Yamashita et al.* (1966 b).

Co: complexes: Thornley *et al.* (1965).

Ni: Allan *et al.* (1968a, b), Callaway and Zhang (1968, 1970), Callaway *et al.* (1971), *Connolly* (1967a, b, 1968), Ehrenreich and Philipp (1964), Gold (1968), Hayakawa (1967), Hodges and Ehrenreich (1965), Hodges *et al.* (1966a, b, 1967), Hubbard (1964b), Lang and Ehrenreich (1968), Lowde and Windsor (1968, 1969), *Mattheiss* (1964b), Mook *et al.* (1969), Mueller *et al.* (1970 b), Shimizu and Terao (1967), *Snow et al.* (1966), *Snow and Waber* (1969), Stark and Tsui (1968), Tsui (1967), *Wakoh* (1965), *Wakoh and Yamashita* (1964), Wohlfarth (1965, 1967), Zornberg (1970).

Ni-Be: Klein and Heeger (1966a, b).

NiAl: *Johnson and Connolly* (1970), *Johnson and Smith* (1970).

NiS: Tyler and Fry (1970), Tyler *et al.* (1970).

Cu: Abarenkov and Vedernikov (1966), Ballinger and Marshall (1967), Butler *et al.* (1969), *Davis et al.* (1968), Dresselhaus (1969), *Faulkner et al.* (1967), Fong and Cohen (1970), Goodings and Harris (1969a, b), Hagston (1968a), Hubbard and Dalton (1968), Hubbard and Jain (1968), *Koelling* (1970), *Mattheiss* (1964b), Mijnarends (1969), Mueller and Phillips (1967), *Slater et al.* (1969a), *Snow and Waber* (1967, 1969), *Snow* (1968a), Sokoloff (1967), *Wakoh* (1965), Zornberg and Mueller (1966).

Cu_2O: *Brahms et al.* (1966, 1967), *Dahl* (1967), *Dahl and Switendick* (1966).

CuCl: Song (1967a, b, c).

CuZn (Brass): *Amar et al.* (1966, 1967), *Arlinghaus* (1967a, b, 1969), *Johnson and Amar* (1965), *Pant and Joshi* (1969a).

CuBr: Song (1967a).

CuI: Song (1967a).

CuAu: Jones (1969b).

Cu_3Au: Gray and Brown (1967).

Zn: Harrison (1963), *Mattheiss* (1964b), Stark and Falicov (1967), *Van Dyke, McClure, and Doar* (1970).

ZnO: Rowe *et al.* (1968).

ZnS: Bergstresser and Cohen (1966, 1967), *Eckelt et al.* (1967), Stukel *et al.* (1969, 1970a, b).

Zn_3As_2: Lin (1969).

ZnSe: *Collins et al.* (1971), *Eckelt* (1967), Raccah *et al.* (1970), *Stukel et al.* (1969, 1970a, b).

ZnTe: *Eckelt* (1967).

Ga: Heine (1968), Reed (1969), *Wood* (1966).

GaP: Pollak, Higginbotham, and Cardona (1966).

GaS: Bassani and Parravicini (1967).

GaAs: Cardona *et al.* (1965), Chaves *et al.* (1966), *Collins et al.* (1970), *Herman and Spicer* (1968), Pollak and Cardona (1966), Saslow *et al.* (1967).

GaSe: Bassani and Parravicini (1967).

GaSb: Zhang and Callaway (1969).

Ge: Brust (1964), Cardona and Pollak (1966), Dresselhaus and Dresselhaus (1967a, b), *Herman et al.* (1966a, b, 1967a, 1968b), Morgan and Galloway (1967a), Pollak and Cardona (1966), Raccah *et al.* (1970), Shindo (1965).

GeTe: *Herman et al.* (1968a, b), Tung and Cohen (1969).

As: Golin (1965), Lin and Falicov (1966), Priestley *et al.* (1967)

Se: Gaspar (1965), Kramer and Thomas (1968), Olechna and Knox (1965), Sandrock (1968), Tutihasi and Chen (1967).

Kr: *Euwema et al.* (1971), *Stukel et al.* (1970b).

Rb: Ashcroft (1965), *Kenney* (1967).

RbI: *Kunz* (1970).

Sr: Animalu (1967a), Vasvari and Heine (1967).

$SrTiO_3$: Cardona (1965), Kahn and Leyendecker (1964), Kahn *et al.* (1964).

Y: Altmann and Bradley (1967), *Gupta and Loucks* (1968), *Loucks* (1966b).

Zr: Altmann and Bradley (1967), *Gupta and Loucks* (1968), *Loucks* (1967b).

$ZrZn_2$: Wohlfarth (1968b).

Nb: *Deegan and Twose* (1967), *Mattheiss* (1970).

Mo: Loucks (1965c).

Pd: Andersen (1970), Clogston (1967), *Freeman et al.* (1966a), Mueller *et al.* (1970a, b), Penn (1967), Thompson (1969).

Pd-Fe: Doniach and Wohlfarth (1967), Hicks *et al.* (1968).

Ag: Ballinger and Marshall (1969), *Bhatnagar* (1969), Chatterjee and Sen (1966, 1967), Cooper *et al.* (1971), Lewis and Lee (1968), *Snow* (1968b).

AgCl: *Scop* (1965).

AgBr: *Scop* (1965).

AgPd: Karlsson *et al.* (1967), Lee and Lewis (1969).

Cd: Katsuki and Tsuji (1965), Stark and Falicov (1967).

CdS: Bergstresser and Cohen (1967), *Euwema et al.* (1967), *Stuckel et al.* (1969).

Cd_3As_2: Lin (1969).

CdSe: Bergstresser and Cohen (1967), *Stukel et al.* (1969).

$CdIn_2S_4$: Meloni and Mula (1970), Rehwald (1967).

CdSb: Frei and Velicky (1965), Tauc and Abraham (1965).

CdTe: Bloom and Bergstresser (1968), Eckelt (1967), Segall (1966).

In: Gaspari and Das (1968).

InP: *James et al.* (1970), Pollak *et al.* (1966).

InSb: Bloom and Bergstresser (1968), Durkan and March (1968),

Sn: Bloom and Bergstresser (1968), Cardona (1967), Craven (1969), *Herman et al.* (1966a, b), Higginbotham *et al.* (1967), *Koelling* (1969), Pollak *et al.* (1970), Sherrington and Kohn (1968), Weisz (1966).

SnTe: *Herman and Spicer* (1968), Lin *et al.* (1967), *Rabii* (1969), Tung and Cohen (1969).

Sb: Falicov and Lin (1966), Lin and Phillips (1966).

Te: Beissner (1966), Kramer and Thomas (1968), Picard and Hulin (1967).

Xe: *Euwema and Stukel* (1971), Reilly (1967).

Cs: *Kenney* (1967), *Mahanti and Das* (1969).

CsI: *Onodera* (1968).

Ba: Animalu (1967a), *Johansen* (1969), Vasvari *et al.* (1967).

$BaTiO_3$: Cardona (1965).
La: *Fleming et al.* (1968), *Myron and Liu* (1970).
$LaCoO_3$: Raccah and Goodenough (1967).
$(La,Sr)CoO_3$: Raccah and Goodenough (1968).
Pr: *Fleming et al.* (1968, 1969), *Myron and Liu* (1970).
Nd: *Fleming et al.* (1968, 1969).
Eu: *Andersen and Loucks* (1968).
EuS: *Cho* (1967, 1969, 1970).
Gd: *Dimmock and Freeman* (1964),
Tb: Goodings (1968a, b), Jackson (1969), Mackintosh (1968), Møller and Houmann (1966).
Yb: *Johansen and Mackintosh* (1970), Piper *et al.* (1967), Thornley (1966).
Lu: *Keeton and Loucks* (1966a).
Ta: *Mattheiss* (1970).
W: *Loucks* (1965a, c, 1966a, 1967c), *Mattheiss and Watson* (1964), *Mattheiss* (1965b).
Tungsten bronze, M_xWO_3: Mackintosh (1963).
Re: *Mattheiss* (1966).
ReO_3: Honig *et al.* (1969), *Mattheiss* (1969).
$(IrX_6)^{2-}$ complexes: Thornley *et al.* (1968).
Pt: Mueller *et al.* (1970b).
Pt-Pd: Froidevaux *et al.* (1968b).
Pt-Ir: Froidevaux *et al.* (1968a).
Pt-Au: Froidevaux *et al.* (1965).
Au: Ballinger and Marshall (1969), Chatterjee and Chakraborty (1967), Chatterjee and Sen (1968), *Kupratakulu* (1970), *Kupratakulu and Fletcher* (1969), *Schlosser* (1970), *Sommers and Amar* (1969).
$AuAl_2$: *Switendick and Narath* (1969).
AuMn: Overhauser (1962b).
AuZn: *Johnson and Connolly* (1970),
$AuGa_2$: *Switendick and Narath* (1969).
AuPd: Karlsson *et al.* (1967),
$AuIn_2$: *Switendick and Narath* (1969).
Hg: Dishman and Rayne (1968), *Keeton and Loucks* (1966b), Mott (1966a).
HgTe: Gorzkowski (1965), Harman *et al.* (1964).
Tl: Mackintosh *et al.* (1963).
Pb: Harrison (1965a), *Loucks* (1965b).
PbS: Dimmock and Wright (1964), *Herman et al.* (1968a), Lin and Kleinman (1967), *Rabii* (1968).
PbSe: Dimmock and Wright (1964), *Herman et al.* (1968a), Lin and Kleinman (1967), *Rabii* (1968).
PbTe: *Buss and Parada* (1970), *Conklin et al.* (1965), Dimmock and Wright (1964), *Herman et al.* (1968a), Lin and Kleinman (1967), *Parada and Pratt* (1969), *Pratt and Ferreira* (1964), *Pratt and Parada* (1967), *Pratt et al.* (1971), Tung and Cohen (1969).
Bi: *Ferreira* (1967, 1968), Golin (1968).
Bi_2Se_3: Greenaway and Harbeke (1965).

Bi-Sb: Lerner *et al.* (1968).
Bi_2Te_3: Greenaway and Harbeke (1965).
Ac: *Keeton and Loucks* (1966a).
Th: *Gupta and Loucks* (1969), *Keeton and Loucks* (1966a).

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Aspects of the Localizability of Electrons in Atoms and Molecules: Loge Theory and Related Methods

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Introduction

When the principle of the indistinguishability of electrons is taken into account, it is not possible to associate particular electrons with atomic cores or molecular bonds. Therefore, it is necessary to establish a new bridge between chemical intuition and the pictures of atoms and molecules that result from wave-mechanical calculations.

If the wave function is computed by using simple techniques (e.g., self-consistent field functions made of molecular orbitals linear combinations of atomic orbitals (SCFLCAOMO) and extended on a minimal basis set) it is customary to associate "the most localized orbitals" with atomic cores and localized bonds.

But, since now it is possible to compute much more elaborate wave functions, there is a need for well-defined equivalent concepts for any kind of wave functions. The loge theory satisfies this need.

A loge is a part of the space (associated with an atom or a molecule) in which there is a high probability of finding a given number n of electrons (but not always the same) with a certain organization of their spins. The best decomposition of the space in loges is that one which gives the minimum amount of indetermination about the atom or the molecule.

In principle any kind of wave function (even a purely numerical one) makes it possible to calculate such a decomposition. It is automatically found that some loges represent the cores of the atoms and other loges correspond to localized or delocalized bonds. Therefore, *the loge theory provides a mathematical bridge between chemical intuition and wave mechanics, which may be considered as a theoretical justification of the main chemical ideas.*

This paper is concerned with the loge theory. It is divided into six sections. The origin of the concept is analyzed in the first. The mathematical definitions are given in the second section. Information theory is the starting point of that section. Simple examples of applications are immediately given.

As usual in wave mechanics, exact calculations are not possible. In Section III various methods are proposed to obtain an approximation of the best decomposition in loges, starting from wave functions in which the localizability of electrons is not introduced a priori. Relations with localized orbitals are discussed.

On the contrary, Section IV is written to show that the loge theory can be used to build new kinds of wave functions, or to improve approximate wave functions. Relations between loge functions and group functions are analyzed.

Section V is concerned with various applications of the loge theory for stationary states. It is shown that this theory leads to a criterion which make it possible to distinguish, from a mathematical viewpoint, between covalent and dative bonds. Furthermore, a theoretical justification of empirical molecular additivity is given. A very simple procedure to establish general relations between isomerization energies is derived. Section VI deals with the possibility of extending the localization concept to electronic excitation. It will be shown that under certain conditions the excitation energy may be localized in loges. More generally, excited-state properties may be expressed as contributions from loges.

I. Origin of the Concept of Loge

Following the discovery of the electron many attempts were made to build an electronic theory of the chemical bond, and the famous paper of Lewis (1916) was the best starting point. By taking account of the Perrin–Rutherford–Bohr planetary model it became customary to assume that the electrons of an atom follow various orbits and to speak of K, L, M, N,... electrons. This model is a projection on the microcosm of an astronomical structure. The extension of this theory to molecules led to the distinction of two kinds of electrons (core electrons and valence electrons) and, furthermore, to associate particular electrons with the various bonds of a molecule.

Wave mechanics gives a completely different picture of atoms and molecules, since it is not possible to know the trajectories (if they exist) of the electrons. It is only possible to calculate the probability of finding an electron at a given time in a small volume dv surrounding a given point.

Furthermore, the principle of indistinguishability of the electrons and the Pauli principle lead to the conclusion that the average value of any property associated with an electron in an atom or a molecule is the same for all the electrons of the system. For example, the mean value of the distance r of an electron from the nucleus of an atom does not depend on the electron considered. Therefore, it is forbidden to distinguish between K and L electrons. For the same reason, all the electrons of a molecule participate simultaneously in the interaction between two particular nuclei of the molecule and thus contribute the same amount of energy to the corresponding bond. It is not possible to distinguish now between core and valence electrons. It is not possible to associate particular electrons with a given bond.

We must add that in the framework of wave mechanics the notion of bond vanishes. In fact, the electrons of a given molecule participate in the interaction between any pair of nuclei. It is not possible to distinguish between bonded atoms and nonbonded atoms.

Finally, a large gap appeared between the old electronic theory of the chemical bond and the new one based on a purely wave-mechanical treatment, and it became difficult to establish a rigorous bridge between chemical intuition, based on a considerable amount of empirical observation, which leads to a partially localized picture of a molecule and wave mechanics which gives a complete blurred description of that same molecule.

The concept of orbital provided the first approach to build such a bridge. When the true independent electron model is used, i.e., when a system is represented by a product of orbitals, it is possible to associate an electron to each orbital and therefore to reintroduce a distinction between the electrons.

This is due to the fact that the corresponding wave function does not satisfy the Pauli principle. When antisymmetrization is introduced, a strong correlation between the electrons is also introduced and this possibility disappears. Let us consider, for example, the wave function

$$\Psi(\overbrace{M_1, \omega_1}^{1}, \overbrace{M_2, \omega_2}^{2}) = 2^{-1/2}[\varphi_{\mathrm{K}}(M_1)\varphi_{\mathrm{L}}(M_2) - \varphi_{\mathrm{L}}(M_1)\varphi_{\mathrm{K}}(M_2)]\alpha(\omega_1)\alpha(\omega_2)$$

associated with the first triplet state of the helium atom. The probability of finding electron 1 in a volume dv_{M_1} surrounding point M_1 is

$$\begin{aligned} dp &= dv_{M_1} \int d\omega_1 \, d\omega_2 \int |\Psi|^2 \, dv_{M_2} \\ &= \tfrac{1}{2}[|\varphi_{\mathrm{K}}(M_1)|^2 + |\varphi_{\mathrm{L}}(M_1)|^2] \end{aligned}$$

The probability of finding electron 2 in the same volume has exactly the same expression.

The probability of finding a *given electron* in dv depends on the value at point M_1 of *both orbitals* φ_{K} and φ_{L}. In this model it is allowed to distinguish between the K and the L orbitals, but contrary to the usual bad language, it remains impossible to distinguish between K and L electrons. Furthermore, it is well known that if we consider the functions χ_1 and χ_2 which obey the relations

$$\chi_i = \sum_j T_{ij} \varphi_j ,$$

where T is a unitary transform, the same function Ψ may be written as

$$\Psi(M_1, \omega_1, M_2, \omega_2) = 2^{-1/2}[\chi_1(M_1)\chi_2(M_2) - \chi_2(M_1)\,\chi_1(M_2)]\,\alpha(\omega_1)\,\alpha(\omega_2).$$

There are an infinite number of equivalent basis sets of orbitals to represent a given system. This is why, without change in the values of the total wave function, we can represent a molecule containing *localized bonds* with *localized* or *delocalized orbitals*. Therefore there is a certain arbitrariness in associating orbitals with bonds. Various criteria have been proposed to select the most localized orbitals among an infinity of equivalent basis sets or orbitals. In simple cases such criteria are helpful in associating localized orbitals with localized bonds.

But, with the development of electronic computers, it became possible to obtain very elaborate wave functions. When a large configuration interaction is introduced the correspondence between orbitals and bonds vanishes. This is also the case if the James and Coolidge wave function is used, since there is no orbital at all in such a wave function. It will also be the case when it becomes possible to compute purely numerical wave functions, and we are not far from this possibility.

Therefore, there is a need for a new concept which makes it possible to establish a bridge between chemical intuition and wave mechanics. More precisely, we need a concept which can be used for any kind of wave function. The concept of loge satisfies such a requirement (Daudel, 1953). Let us go back to our helium atom in its first triplet state. Let Ψ be any good space wave function associated with this state. Let us consider a sphere S of radius r (this value being absolutely arbitrary) with its center at the nucleus. The probability P of finding one electron, and one only, in this sphere is given by the expression

$$P = 2 \int_S dv_{M_1} \int_{\mathbb{R}^3 - S} |\Psi(M_1, M_2)|^2 \, dv_{M_2}$$

if $\mathbb{R}^3$ denotes the three-dimensional space. When r is very small, this probability is also very small because now the sphere is generally empty. When r is very large, P again is very small because now the sphere generally contains two electrons (and not only one). Thus, intuitively, we must anticipate that P will possess at least a maximum for a certain value of r. Figure 1 shows the result of the calculation when an Hylleraas wave function is used (Daudel *et al.*, 1955). The maximum is large as it corresponds to $P = 0.93$. The corresponding radius is $1.7\,a_0$. We shall say that the best division of the atomic space of the helium atom in its first triplet state corresponds to this sphere.

To establish a bridge between this result and the chemical language, we shall say that the sphere of radius $1.7a_0$ is the K loge and the remaining part of the space the L loge. Thus, when a helium atom is in its first triplet

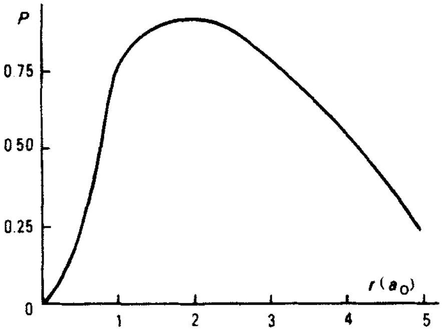

Fig. 1. P as a function of r.

state, there is a high probability (93%) of finding simultaneously one electron in the K loge and one electron in the L loge. It is important to point out that now there is no contradiction with respect to the principle of the indistinguishability of the electrons, because we do not distinguish between electrons, but only between certain parts of the space which are visited by the electrons.

II. Rigorous Definition of the Best Partition into Loges. Simple Applications

Loge theory has been formulated (Daudel, 1953, 1956; Daudel *et al.*, 1955; Odiot, 1957a, b) in the q representation of quantum mechanics in the Schrödinger picture. The purpose for such a representation is to give a quantal extension to traditional and useful chemical concepts without referring to any approximation; indeed, loge theory demands no more than the postulates of nonrelativistic quantum mechanics.

Let a pure ensemble be prepared in the eigenstate represented by $|\Psi\rangle$. For an n-fermion system, such a tensor belongs to a generalized Hilbert space (Guelfand and Vilenkin, 1967; Rosenbaum, 1969) $\mathscr{E}_n$, which is built as the tensorial product of n monoelectronic spaces, $\varepsilon_i^{(i)}$

$$\mathscr{E}_n = \varepsilon^{(1)} \otimes \varepsilon^{(2)} \otimes \cdots \otimes \varepsilon^{(n)}.$$

Each space ε is itself the product of a "continuous" space e (generated by $|q\rangle$ when q ranges over all $\mathbb{R}^3$) by a two-dimensional space σ (a basis of which is $\{|\omega\rangle\}_{\omega \in \{-1/2,\, +1/2\}}$); in the former, q denotes the three spatial coordinates of the point within the subspace pertaining to a fermion, in exists a macroscopic direction in the $\mathbb{R}^3$ physical space. Relative to the basis $\{|q_1\omega_1\rangle \otimes |q_2\omega_2\rangle \otimes \cdots \otimes |q_n\omega_n\rangle\}$, the state tensor can be written

$$\begin{aligned}|\Psi\rangle &= \sum_{\omega_1}\int_{q_1}\sum_{\omega_2}\int_{q_2}\cdots\sum_{\omega_n}\int_{q_n}|q_1\omega_1, \ldots, q_n, \omega_n\rangle\langle q_1\omega_1, \ldots, q_n\omega_n|\Psi\rangle \\ &\quad\times dq_1 dq_2 \cdots dq_n \\ &= \sum_{\{\omega\}_n}\int_{\{q\}_n}|\{q\}_n\rangle\langle\{q\}_n|\Psi\rangle\, d\{q\}_n,\end{aligned}$$

where $\{q\}_n$ is used for $q_1, q_2, \ldots, q_n$, $\langle\{q\}_n|\Psi\rangle \equiv \Psi(\{q\}_n)$ is the "wave function," which is antisymmetric with respect to any odd permutation of the symmetric group $\mathscr{S}_n$. If one is interested only in the "spatial part" of the wave function (Matsen, 1959), denoted as $|\Phi\rangle$, one can write

$$\begin{aligned}|\Phi\rangle &= \int_{q_1}\int_{q_2}\cdots\int_{q_n}|q_1q_2\cdots q_n\rangle\langle q_1q_2\cdots q_n|\phi\rangle\, dq_1dq_2\cdots dq_n, \\ &= \int_{\{q\}_n}|\{q\}_n\rangle\langle\{q\}_n|\phi\rangle\, d\{q\}_n,\end{aligned}$$

where $\{q\}_n$ generates the "orbital" space E_n when q_n ranges over all $\mathbb{R}^{3n}$. Now, $\Phi(\{q\}_n)$ no longer has in general the antisymmetric property; in other words, $\Phi(\{q\}_n)$ will not transform according to the one-dimensional antisymmetric representation of $\mathscr{S}_n$, unless either $n = 2$ [then Φ is symmetric (resp. antisymmetric) for $S = 0$ (resp. $S = 1$)] or, if $n > 2$, $S = S_{\max} = [\frac{1}{2}n(\frac{1}{2}n + 1)]^{1/2}\hbar$, then Φ is antisymmetric.

The principal aim of loge theory is to infer maximum information about the spatial distribution of the n fermions in physical space, when the total spin state is known. Indeed, one tries to define a partition of this space and calculates the probabilities of the resulting series of events with the hope that they will be particularly suitable for interpretation of the physical properties of the microsystem.

Let us define a partition of the physical space $\mathbb{R}^3$ in ν volumes V_λ (loges), the intersections of those having zero measure

$$\mathbb{R}^3 = \bigcup_{\lambda=1}^{\nu} V_\lambda, \qquad \mathrm{mes}(V_\lambda \cap V_{\lambda'}) = \tfrac{1}{2}\delta_{\lambda\lambda'}[\mathrm{mes}(V_\lambda) + \mathrm{mes}(V_{\lambda'})].$$

What are the different events resulting from that partition? In a physical way, we can see that analogy with the permutation modes in Bose–Einstein statistics: we have n fermions which must be distributed in ν loges, and the number of arrangements is of course equal to $(n + \nu - 1)!/n!(\nu - 1)! = l(n, \nu)$; in a more abstract manner, we can say that the partition in $\mathbb{R}^3$ (the order of which is ν) induces a partition in the orbital space E_n, the order of which is $l(n, \nu)$.

In any case, the probability of the event: finding n_λ fermions in the loge V_λ, $\forall \lambda \in [1, \nu] \subset \mathbb{N}$ is

$$P(\{n_\lambda \in V_\lambda\}_{\lambda \in [1, \nu]}) = \sum_\alpha \int_{V_1} \{dq\}_{n_1} \int_{V_2} \{dq\}_{n_2} \cdots \int_{V_\nu} \{dq\}_{n_\nu} \varpi_\alpha | \{q\}_n \rangle \langle \{q\}_n | \Phi \rangle,$$

where ϖ_α is one of the permutations belonging to the ensemble which is the complement in $\mathscr{S}_n$ of the subgroup $\mathscr{S}_{n_1} \times \mathscr{S}_{n_2} \times \cdots \times \mathscr{S}_{n_\nu}$. (If $\Phi(\{q\}_n)$ has the simple permutation property mentioned above, all integrals are equal and the factor $n!/\prod_{\lambda=1}^{\nu} (n_\lambda!)$ takes the place of the summation $\sum_\alpha$).

To summarize, we started with an infinite nondenumerable ensemble of events representing the presence of the n-fermion system at a point in the configuration space $\mathbb{R}^{3n}$, (the probability of such an event being given by the square of the modulus of the projection of $|\Phi\rangle$ on a certain direction in E_n) and we arrived at a finite ensemble of events related to the presence of groups of fermions in definite volumes in the $\mathbb{R}^3$ physical space. Clearly, we have transformed the information potentially contained in the state tensor in order to single out significant events.

Now the question is: How shall we make a choice among the different partitions of $\mathbb{R}^3$? Our problem is then to find a criterion that establishes a hierarchy of partitions; indeed, we must introduce a mathematical function whose numerical values will be representative of these partitions.

A first intuitive possibility is to focus our interest on *one* of the events and to characterize the partition by the probability of this event. Such a procedure appears incomplete for at least two reasons; first, the value of $\langle \Phi | \Phi \rangle$ reduced to a subspace of E_n does not imply a definite value for $\langle \Phi | \hat{\Omega}_{\text{op}} | \Phi \rangle$ taken in the same subspace, and we could lose our way to our aim; second, we would be unable to distinguish between two partitions corresponding to the same probability for that event, but differing for other probabilities.

We thus require a function which takes explicit account of the probabilities of *all* the events resulting from the partition of $\mathbb{R}^3$. If now we recall the essential pursued aim, we realize that a function has existed for a long time that possesses the desirable properties: This is the "missing information function," or "a priori indetermination function," I, defined in information theory (Hartley, 1928; Shannon, 1948; Wiener, 1948; Brillouin, 1959) as

$$I(\mathscr{P}) = \sum_{i=1}^{l} P_i \log_2 P_i^{-1},$$

where $\mathscr{P} = \{P_i\}_{i \in [1, l] \subset \mathbb{N}}$ is a probability distribution for a series of events. Among other remarkable properties of this function, we have

$$0 \le I(\mathscr{P}) \le \log_2 l$$

and

$$I(\mathscr{P}) = 0 \Leftrightarrow \exists\, i_0 \in [1, l], \forall i \in [1, l]\ P_i = \delta_{i, i_0}$$
$$I(\mathscr{P}) = \log_2 l \Leftrightarrow \forall i \in [1, l], P_i = 1/l$$

These two last propositions fully satisfy our intuition. According to the first one, there will always exist a partition which will give I its absolute lowest value, i.e., $I = 0$. This is the trivial partition arising from doing... nothing; since this does not lead to any progress, it is not considered further. In fact, we cannot hope to obtain a zero indetermination for a nontrivial partition $\mathscr{P}$, because strict localization in any finite domain can only occur if there exists infinitely high potential barriers, which is never the case in an atom or a molecule; but we may expect that the function I will possess minima and we conventionally define the best loges partitioning as the one which gives the lowest nonzero value, if it exists, to the missing information function.

It is important to realize the quite absolute meaning of the function I; this is clearly shown by considering its upper bound, $\log_2 l$, where l is the length of the series of probabilities: when there exists an equiprobability, the indetermination must increase if the number of events does. Such a feature is essential for a valuable comparison of partitions that depend either continuously or discretely of the loge parameters, or of partitions that do not introduce the same number of events.

We can now summarize the general procedure for obtaining the best partition into loges. Given an n-electron system, we consider all the divisions in v volumes; v being fixed, one examines all the physically relevant partitions and, for each of them, calculates the I function. Once v has ranged over its whole domain, we pick out the partition which gives rise to the lowest nonzero value for I.

Let us now consider two simple examples, related to the helium atom. For that atom, the only meaningful partitions will be achieved by planes containing the nucleus or by spheres centered at this nucleus. For a two-electron system, a partition into two loges introduces three events shown in Fig. 2. First, let us consider the terms 1 ^{3}P and 1 ^{1}P; the approximate corresponding spatial wave functions are obtained by symmetrization or antisymmetrization of a simple product of orbitals with screening constants. The probabilities for the partition by the plane are shown in Table I. For

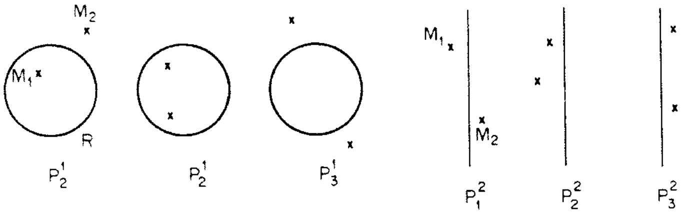

Fig. 2. Electronic events in helium.

TABLE I

S	$P_1{}^2$	$P_2{}^2$	$P_3{}^2$	I^2
0	0.480	0.260	0.260	1.519
1	0.520	0.240	0.240	1.479

the partition by the sphere, and in this approximation, the probabilities are independent of the total spin eigenvalue, because of a vanishing cross term. The variations of I^1 and $P_1{}^1$ with the parameter R/a_0 are plotted in Fig. 3 and summarized in Table II. We can thus conclude that, whatever the spin state, the best partition is defined by a sphere of radius $1.75a_0$, centered at the nucleus.

Let us now take the terms designated as 2^3P and 2^1P. Analogous calculations lead to the results of Tables III and IV and Fig. 4. For the singlet state, we see that the best partition does not exist; the partition by a plane introduces a greater indetermination than any spherical partition. So the lowest nonzero value cannot be associated with the planar division; we must now look at the best division among the partitions by the sphere; but in that case the lowest value for I is zero and corresponds to the trivial solution. For the triplet state, the indetermination given by the planar partition

TABLE II

	$P_1{}^1$	$P_2{}^1$	$P_3{}^1$	I^{1a}
$R = 1.75a_0$	0.920	0.052	0.028	0.478

[a] I minimum.

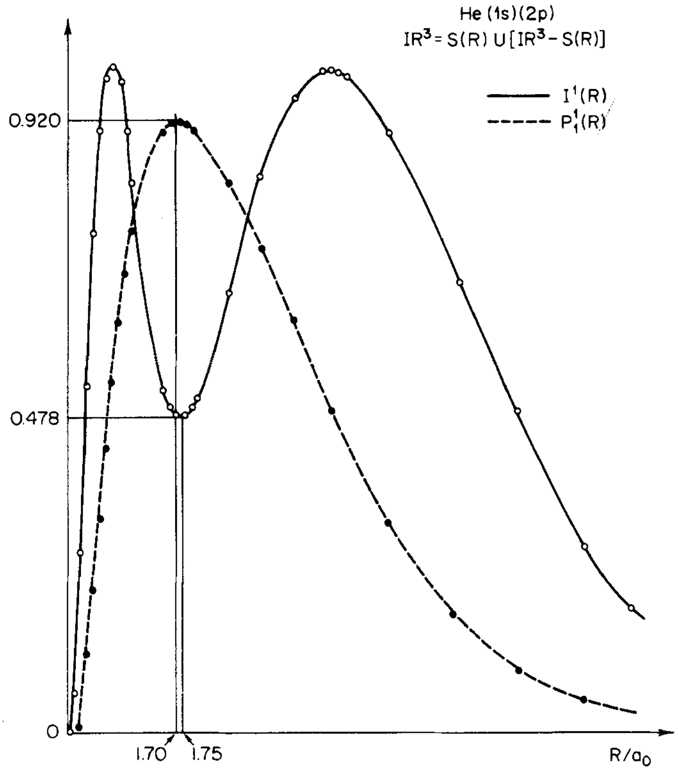

Fig. 3. The missing information function *I*.

is equal to 0.976 and we can conclude that the best partition in this state is given by a plane containing the nucleus.

With this simple example, we can realize how the *I* function seems suitable for characterizing a division into loges. In particular we see that, when the localization is "good," *I* possesses a minimum; if it is "bad" this function has none; but the qualification "good or bad" is now replaced by a mathematical condition, which gives an actual objective feature to our criterion; the answer is now: yes or no, and no more "perhaps." Another advantage of such a criterion stands in the bridge it establishes between two theories, quantum theory and information theory; drawing such a parallel can appear fruitful in the conceptual ground as well as in the technical one;

TABLE III

S	$P_1{}^2$	$P_2{}^2$	$P_3{}^2$	I^2
0	0.219	0.3905	0.3905	1.536
1	0.781	0.1095	0.1095	0.976

TABLE IV

	$P_1{}^1$	$P_2{}^1$	$P_3{}^1$	I^{1a}
$R = 3.20a_0$	0.521	0.244	0.235	1.477

[a] I maximum.

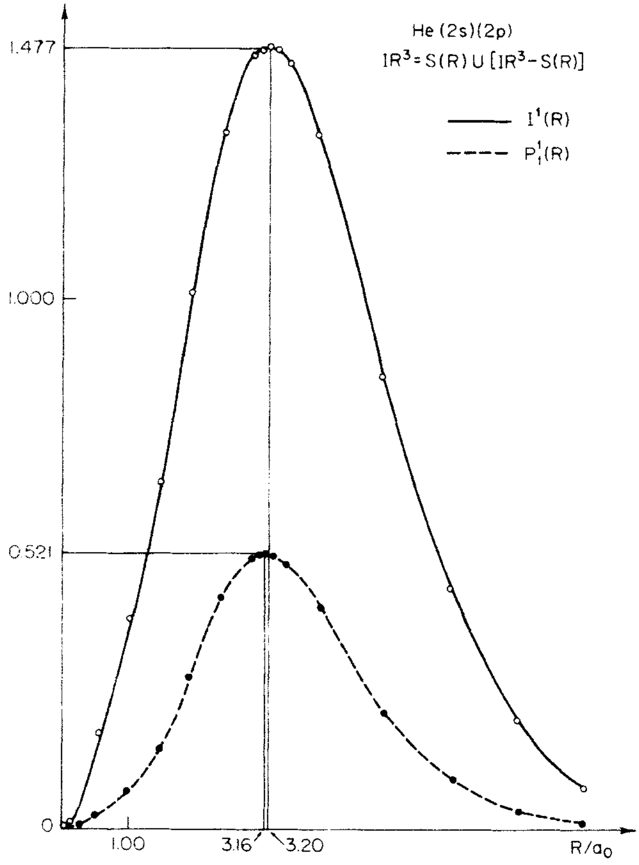

Fig. 4. The function *I* for He(2*s*)(2*p*).

for instance, one can see (Aslangul, 1971) that the usual loge notion is the realization in wave mechanics of a much more general concept, and we foresee applications of information theory to some fundamental problems of quantum mechanics. Lastly, our point of view (considering all the events resulting from the spatial partition), leads naturally to a new form of approximate wave function that could bring an improvement with regard to the group function method. This will be described in detail in Section IV.

III. From a Wave Function to the Corresponding Best Division into Loges

In Section II, the definition of the best division into loges has been given. In principle it is possible to determine that division for an atom or a molecule when a wave function is known, Obviously the division obtained will not depend on the way the wave function is written. It depends only on the total wave function. If, for example the wave function is built on a basis set made of orbitals, the best division into loges will be an invariant with respect to a unitary transform of the orbitals.

But, in wave mechanics, it is only possible to solve a problem rigorously for very small atoms and molecules. Therefore, it is not possible to determine rigorously the best division into loges for a large atom or a large molecule. Approximate approaches are needed. Some of them are described in this section.

Using Monoelectronic Localized Functions

A set of normalized functions f_i defined on a given space is localized with a precision ε in an ensemble of volumes V_i whose intersection has zero measure if:

$$\langle f_i | f_i \rangle_{V_i} \geq 1 - \varepsilon.$$

In other words, the normalized functions f_i are localized with precision ε if,

$$\exists\{V_1, V_2, \ldots, V_i, \ldots, V_n\}, \qquad \text{mes } V_i \cap V_j = 0, \qquad i \neq j,$$
$$\forall_i, \qquad \langle f_i | f_i \rangle_{V_i} \geq 1 - \varepsilon.$$

Let us assume that the space part of a wave function for a two-electron system is expressed as

$$\Phi = 2^{-1/2}[\varphi_1(M)\varphi_2(M') - \varphi_2(M)\varphi_1(M')]$$

φ_1 and φ_2 being, respectively, localized in V_1 and V_2 with precision ε.

The probability P_{12} of finding electron 1 in V_1 and electron 2 in V_2 is

$$\begin{aligned}P_{12} &= \int_{V_2} dv_M \int_{V_2} |\Phi|^2 \, dv_{M'} \\ &= \tfrac{1}{2}\langle\varphi_1|\varphi_1\rangle_{V_1}\langle\varphi_2|\varphi_2\rangle_{V_2} + \tfrac{1}{2}\langle\varphi_2|\varphi_2\rangle_{V_1}\langle\varphi_1|\varphi_1\rangle_{V_2} \\ &\quad - \langle\varphi_1|\varphi_2\rangle_{V_1}\langle\varphi_1|\varphi_2\rangle_{V_2},\end{aligned}$$

But since

$$\langle\varphi_1|\varphi_2\rangle = 0, \qquad \langle\varphi_1|\varphi_2\rangle_{V_1} = -\langle\varphi_1|\varphi_2\rangle_{V_2};$$

therefore

$$P_{12} = \tfrac{1}{2}\langle\varphi_1|\varphi_1\rangle_{V_1}\langle\varphi_2|\varphi_2\rangle_{V_2} + \tfrac{1}{2}\langle\varphi_2|\varphi_2\rangle_{V_1}\langle\varphi_1|\varphi_1\rangle_{V_2} + |\langle\varphi_1|\varphi_2\rangle_{V_1}|^2$$

The last two terms are positive. Then

$$P_{12} \geq \tfrac{1}{2}\langle\varphi_1|\varphi_1\rangle_{V_1}\langle\varphi_2|\varphi_2\rangle_{V_2}.$$

Since

$$\langle\varphi_1|\varphi_1\rangle_{V_1} \geq 1 - \varepsilon \qquad \text{and} \qquad \langle\varphi_2|\varphi_2\rangle_{V_2} \geq 1 - \varepsilon,$$

$P_{12} \geq \frac{1}{2}(1 - \varepsilon)^2$ and the probability P of finding simultaneously one electron in V_1 and one electron in V_2 obeys the relation

$$P = P_{12} + P_{21} \geq (1 - \varepsilon)^2.$$

It appears from what has been said in Section I that if ε is small, the volumes V_1 and V_2 will correspond approximately to the best division into loges.

When a wave function is expressed in terms of localized functions it is easy to obtain at least a good division in loges.

Let us apply this statement to atoms. It has been shown (Daudel, 1956; Odiot, 1957a, b) that the usual atomic orbitals corresponding to various shells are localized with good precision in various volumes of the atomic space limited by spheres centered at the nucleus. For example, if we consider the hydrogen atom

$$\int_0^R (1s)^2 r^2 \, dr \geq 0.92, \qquad \int_R^\infty (2s)^2 r^2 \, dr \geq 0.92,$$

if $R = 1.67$ Å.

Moreover, it has been observed empirically (Odiot, 1957a, b) that the radii of spheres between which the Hartree–Fock atomic orbitals are localized correspond approximately to the minima of the radial density. Therefore to obtain an approximation of the best division in loges of an atom for which a self-consistent-field wave function is known we can use the radii corresponding to the minima of the corresponding radial density. As an example, let us take the F^- ion in its ground state. The Hartree–Fock radial density has only one minimum for $R = 0.375a_0$. Furthermore,

$$\int_0^{0.375} (1s)^2 r^2\, dr \geq 0.94, \qquad \int_{0.375}^{\infty} (2s)^2 r^2\, dr \geq 0.94,$$

$$\int_{0.375}^{\infty} (2p)^2 r^2\, dr \geq 0.94.$$

Since the corresponding configuration is $(1s)^2\,(2s)^2\,(2p)^2$, it must be anticipated that the sphere with radius $R = 0.375a_0$ corresponds to a good division in loges of the atom, and that therefore there is a high probability of finding two electrons (with opposite spins) and *two only* in the sphere, the eight others being outside. The calculation shows that this probability is 0.81.

Table V shows the values of the radii corresponding to K, L, M, and N

TABLE V

ATOMIC LOGES RADII (ATOMIC UNITS)

Elements	Be	F^-	Al^{3+}	Ca^{2+}	Rb^+	Hg
R_K	1.12	0.37	0.22	0.13	0.06	0.025
R_L				0.64	0.26	0.10
R_M					1	0.28
R_N						0.93

loges calculated by following this procedure from SCF Hartree–Fock atomic wave functions.[1] If the volume of an atomic loge is divided by the number of electrons which are found in it with a high probability a certain volume v is obtained which gives an idea of the "space occupied" by an electron going through this loge. Now it is also possible to calculate the mean value p of the electric potential which acts on an electron when it is in the loge. The following relation is obtained:

$$p^{3/2} v = C,$$

where C is a constant, the same for all loges and all atoms. *There is a kind of Boyle–Mariotte law between the space which an electron tends to occupy*

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[1] G. Sperber (*Int. J. Quantum Chem.* 5, 189, 1971) has recently calculated analogous radii in other atoms.

in a loge and the mean "electric pressure" acting on the electron (Odiot and Daudel, 1954).

The most probable configuration of the electrons of an atom is the set of points $M_1, M_2, M_3, \ldots, M_n$ which give to the modulus of the wave function $|\Psi(M_1, M_2, M_3, \ldots, M_n)|$ its largest maximum. Figure 5 shows the most probable configuration of the electrons in Be (^{3}P), B (^{4}P), and C (^{5}S) with the trace of the sphere limiting the K loge (Linnet and Poe, 1951). It is seen that for that most probable configurations, there are two electrons with opposite spins in the K loges and, respectively, two, three, and four electrons with the same spin in the L loges. The angles formed by the electrons in the L loges with the nucleus are as large as possible: 180°, 120° and 109°28′, respectively.

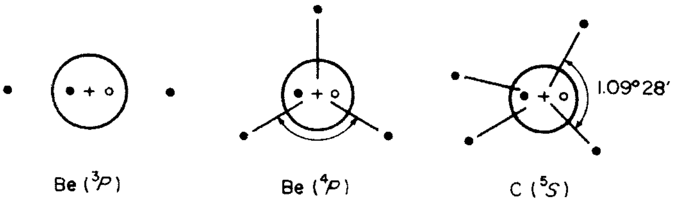

Fig. 5. Most probable electronic configurations.

The use of localized functions to obtain good divisions into loges of molecules is not so easy because the usual molecular orbitals are not so well localized. The molecular orbitals that diagonalize Roothaan matrices are usually built in such a way that they form a basis for irreducible representations of any group of operators which commute with the Hamiltonian (Roothaan, 1951). Let us consider a molecular orbital corresponding to a nondegenerate level (space viewpoint). It will be an eigenfunction of any symmetry operator of the molecule. If the molecule possesses, for example, a symmetry center and the orbital has a significant value at a point M near one end of the molecule it will have the same important value[2] at a point M' near the symmetrical end. Therefore that molecular orbital will be very delocalized. *There is no relation between loges and the usual molecular orbitals.*

To prepare a deeper discussion it is useful to present some good divisions in loges for small molecules. Let us take the Li_2 molecule described

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[2] Only the sign can be different.

with the Coulson and Duncanson wave function. Consider the division into loges formed by the two spheres of equal radius R, one concentric about each nucleus. The value of R corresponding to the highest probability of finding two electrons (with opposite spins) and two only in one of these spheres can be easily calculated. We find $R = 1.53a_0$ (Brion *et al.*, 1954). For that radius, the probability is 0.95. The probability for finding two electrons (with opposite spins) and two only outside of the two spheres is 0.90. The division into loges suggested in Fig. 6 is therefore very near to the best division into loges of the lithium molecules. Furthermore, it is observed that the two spheres are approximately identical with the K loge in a free lithium atom. They will be called the *core loge*; the remaining part of the space being the *bonding loge.*

It can be considered that electrons of the Li_2 molecule most frequently "occupy" positions conforming to Fig. 6; i.e., one electron of each spin in each core loge and one of each spin in the bonding loge. *This image derived by wave mechanics is the modern translation of Lewis ideas.*

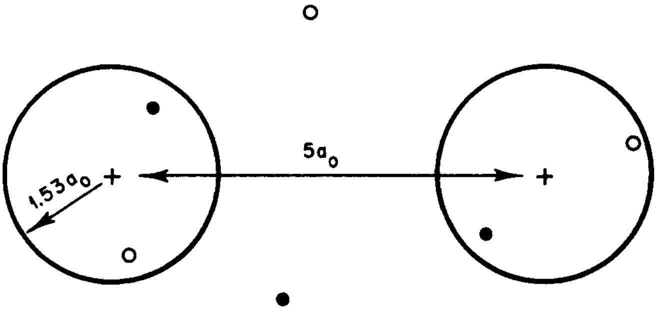

Fig. 6. Loges in Li_2.

Another useful notion that gives information on the nature of the chemical bond is the *density difference function* given by the equation

$$\delta(\mathrm{M}) = \rho(\mathrm{M}) - \rho^f(\mathrm{M})$$

where $\rho(M)$ is the actual electronic density at a given point M of a molecule, and $\rho^f(M)$ the electronic density which *would* occur at this point if the density in the molecule were the simple sum of the density in the free atoms. Therefore, at any point where $\delta(M)$ is positive, an increase of electronic density results from the binding. On the other hand, in any region where $\delta(M)$ is negative, the binding has led to a decrease in the electronic density. Figure 7 shows the variation of $\delta(M)$ along the line of the nuclei of the

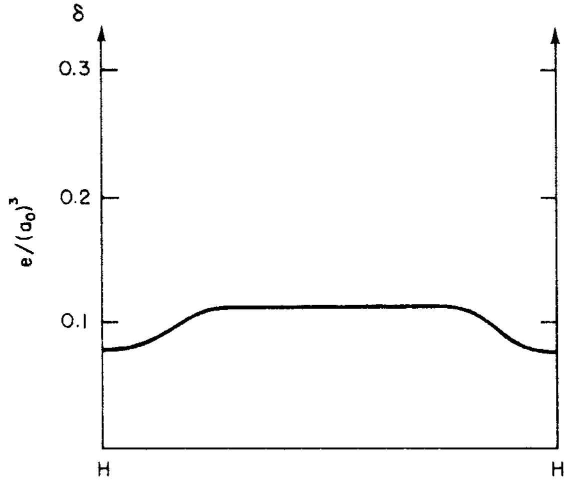

Fig. 7. The density difference function in H_2.

hydrogen molecule H_2 when a James and Coolidge wave function is used (Roux *et al.*, 1956). It is seen that the chemical binding produces a significant increase in the electronic density along that line between the nuclei.

Figure 8 corresponds to the O_2 molecules (Bratos *et al.*, 1960). There is no increase of electronic density between the nuclei but an annular region

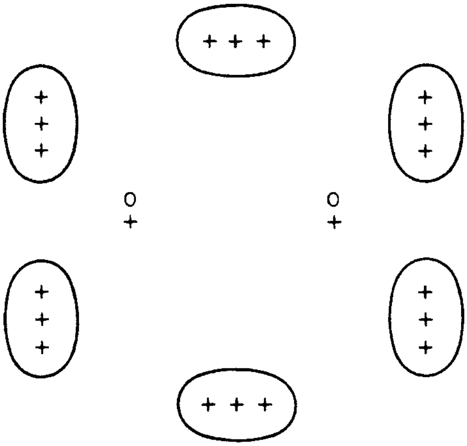

Fig. 8. The density difference function in O_2.

centered on the axis of the molecule where $\delta(M)$ is positive. The fact that there is no increase of electronic density along the nuclear axis is probably due to the presence of four electrons (two of each spin) in this vicinity. The strong repulsion between electrons possessing the same spin tends to place them outside the small space surrounding the bond axis. *Therefore, we can anticipate that between the cores of two small atoms near the bond axis there is only room for two electrons with opposite spins.*

Consider a molecule for which the number of electrons M found with a high probability outside of the core loges is exactly twice the number of pairs p of adjacent cores. It must be anticipated that a good division in loges will contain a two-electron loge between each pair of adjacent cores. *Such a loge will be called a two-electron localized bonding loge.* It corresponds mathematically to the classical chemical idea of single bond.

Methane is such a molecule. We can anticipate that Fig. 9 schematizes

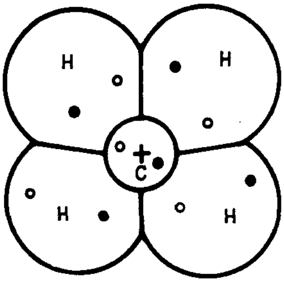

Fig. 9. Loges in methane.

a good division into loges. It contains a carbon K loge in which there is a high probability of finding two electrons. Eight electrons must be found outside.

Since the molecule contains four hydrogen nuclei adjacent to the carbon core loge, we can anticipate the presence of four two-electrons localized bonding loges, each of them surrounding one hydrogen nucleus and the core. Let us consider an SCF wave function associated with that molecule. Following Coulson (1950) a satisfactory approximate SCF function can be written

$$\Phi = N \det 1s\,(1)\ \overline{1s\,(2)}\ s\,(3)\,\overline{s\,(4)}\ t_x\,(5)\ \overline{t_x\,(6)}\ t_y\,(7)\ \overline{t_y\,(8)}\ t_z\,(9)\ \overline{t_z\,(10)}$$

where the s's and the t's are symmetry orbitals:

$$\begin{aligned} s &= 2s + \lambda(a + b + c + d), \\ t_x &= 2p_x + \mu(a + b - c - d), \\ t_y &= 2p_y + \mu(-a + b + c - d), \\ t_z &= 2p_z + \mu(-a + b - c + d). \end{aligned}$$

The notation is the following: a, b, c, d denote the various $1s$ hydrogen atomic orbitals; $1s$, $2s$, $2p_x$, $2p_y$, and $2p_z$ the carbon atomic orbitals; λ and μ some coefficients. As predicted, the molecular symmetry orbitals are completely delocalized over the carbon and the four hydrogen atoms.

But, as well known, if a new sets of orbitals f_i is derived from the symmetry orbitals with the help of a unitary transform the function:

$$\Phi = N \det[f_1(1)\ \overline{f_1(2)}\ f_2(3)\ \overline{f_2(4)}\ f_3(5)\ \overline{f_3(6)}\ f_4(7)\ \overline{f_4(8)} f_5(9)\ \overline{f_5(10)}$$

is identical to the previous one.

We can select the unitary transform that leads to the *equivalent orbitals*,

$$\begin{aligned} A &= s + t_x - t_y - t_z, \\ B &= s + t_x + t_y + t_z, \\ C &= s - t_x + t_y - t_z, \\ D &= s - t_x + t_y + t_z. \end{aligned}$$

The methane wave function Φ will be written

$$\Phi = \det 1s\,\bar{1}s\,A\bar{A}\,B\bar{B}\,C\bar{C}\,D\bar{D}$$

It is always the same function written in another way. Let us look more closely at the function B. We have

$$B = 2s + 2p_x + 2p_y + 2p_z + (\lambda + 3\mu)b + (\lambda - \mu)(a + c + d).$$

When the Roothaan equations are solved, it is found that $(\lambda - \mu)$ is much smaller than $\lambda + 3\mu$. Since the first four terms in B represent the tetrahedral hybrid, te, pointing in the direction of the nucleus b, the equivalent orbital B may be written as

$$B \simeq te + (\lambda + 3\mu)b.$$

Therefore it is localized between the carbon core loge and one hydrogen nucleus. The other equivalent orbitals are, respectively, localized between the core and another hydrogen nucleus.

We can conclude that if there is no relation between molecular symmetry orbitals and the loges, there is a fair agreement between the loges and the equivalent orbitals. Therefore, an approximate way of finding a good division into loges of a molecule must be to search for *the most localized orbitals*. From the loge viewpoint the most appropriate criterion to define the most localized orbitals will be to minimize the product of the various $\langle |f_i| |f_j| \rangle$ because it is possible to show that if all $\langle |f_i| |f_j| \rangle$ are small

$$\exists\{V_i\}, \qquad V_i \cap V_j = \emptyset, \qquad i \neq j, \qquad \forall i, \langle f_i | f_i \rangle \simeq 1$$

(Daudel, 1956).

Unfortunately, this criterion has not been used. Brion and Daudel (1953) suggested minimization of the exchange energy, a criterion commonly applied [see, e.g., Edmiston and Ruedenberg, (1963)]. Foster and Boys (1960) proposed maximization of the distances between the gravity centers of the various orbitals. An example of application of this criterion is given in Section V.

But it is easy to predict that it is not possible to divide the bonding region of all molecules into only two-electron localized loges. This fact appears particularly when $n \neq 2p$.

It is easy to see that in certain cases it is not possible to localize, between only two cores, a region where three is a high probability of finding n electrons with a precise organization of spins. This is the case with diborane B_2H_6. This molecule contains 16 electrons. Four of them can be associated with the two K loges of boron. Twelve electrons remain for binding purposes. Diborane consists of eight pairs of neighboring cores. Therefore, it is not possible to associate a two-electron localized bond with each pair of neighboring cores. From the experimental viewpoint the four outer B–H bonds have the same behavior as normal localized two-electron bonds. Then, we are led to try a division into loges similar to the one described in Fig. 10a, since only four electrons remain for the four central pairs of neighboring cores. But obviously, Fig. 10b corresponds to another situation, which for symmetry reasons possesses the same probability as the one shown in Fig. 10a. Therefore, the probability of the electronic configuration being symbolized by one of these two figures cannot be higher than one-half, which does not correspond to a good division into loges.

If now, the space of the central B–H is divided between two three-center loges, as in Fig. 11, this difficulty disappears. There are no a priori reasons to exclude the possibility of finding such good loges. Since they are now extended over more than two cores, we shall say that they correspond to delocalized bonds; more precisely to two-electron bonds delocalized over

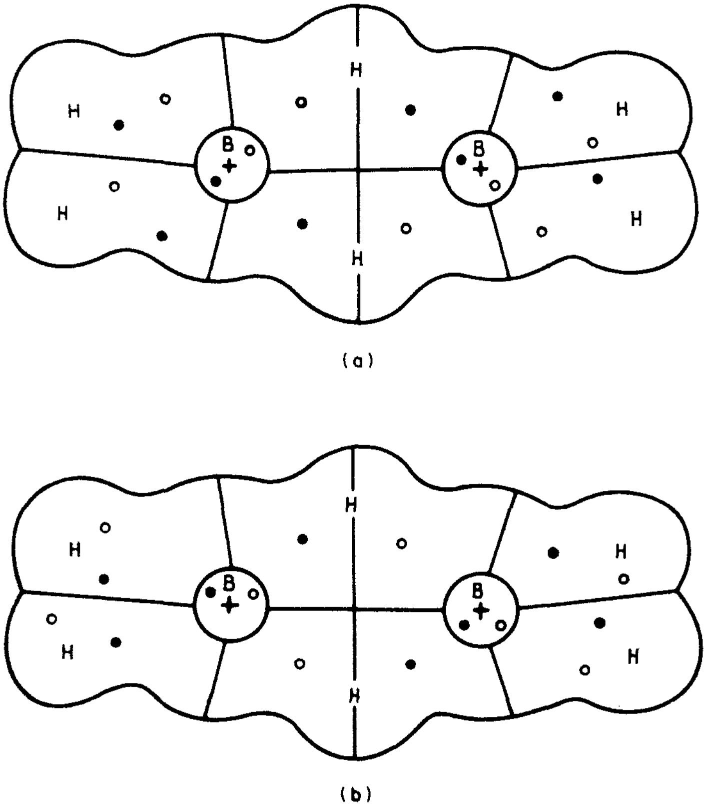

Fig. 10. Decompositions in loges of diborane.

three centers. In conclusion, when it is not possible to find a good loge between two cores, the loge will be extended over a greater number of cores and an n-electron bond delocalized over p centers will be considered.

Finally, Fig. 12 shows a division into loges where all main kinds of loges are present. Between the two core loges A and B there is a two-electron loge. It corresponds to a localized single bond. Surrounding the three core loges B, C, and D, a four-electron loge delocalized over those three centers is found. It corresponds to a delocalized bond. In the bonding region there is a two-electron loge adjacent to only one core (the core A). It corresponds to a lone pair.

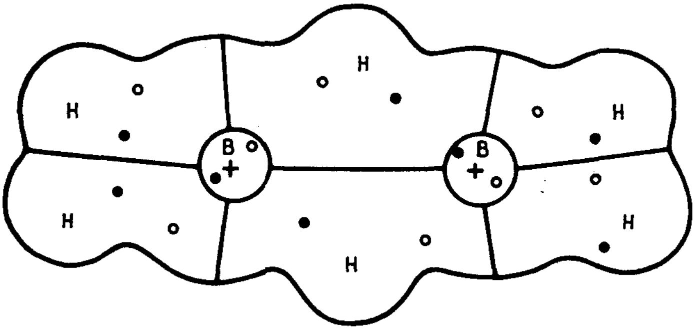

Fig. 11. Loges in diborane.

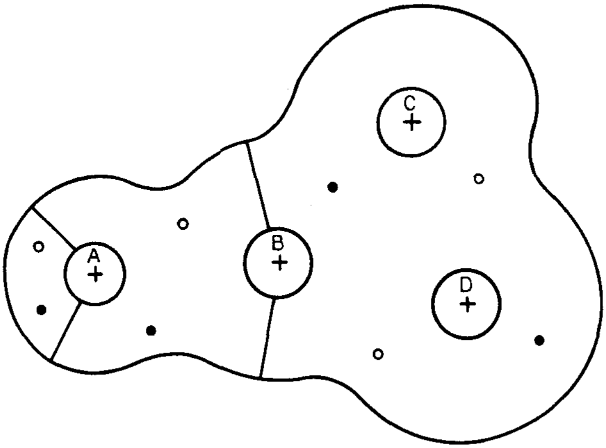

Fig. 12. A typical division into loges.

IV. Using a Division into Loges as a Starting Point to Calculate Elaborate Wave Functions

A. The Formalism of the Loge Functions

Section III has been devoted to showing how the concept of loge can be used to extract from a wave function some information about the localizability of the electrons of a given system. The concept of loge was used as a procedure of analysis of a wave function already known. It has been proved that the main interest in the loge concept from this viewpoint is to lead to the best division of the system space into loges that give a rigorous mathematical definition of core, localized, delocalized bonds, lone pairs, and so on.

All these concepts, which were present in chemical intuition in a rather vague manner, have now a very precise definition in the framework of wave mechanics. Furthermore, the new mathematical concepts are defined in a unique way for all kinds of wave functions. The expansion of the wave function in terms of orbitals is not a necessary condition to obtain the loges.

A purely numerical function, a James and Coolidge one, or an Hylleraas wave function can be used. If the wave function is expanded in terms of orbitals, the loges are invariant with respect to a unitary transform of the orbitals.

But these very important results are not the only ones. The concept of loge can be used to build wave functions. This fact is, a priori, rather surprising. This section is devoted to showing how it is possible to proceed.

Let us assume that for any reason we already have an idea about the topology of a good division into loges of an atom or a molecule. Such information may result from the knowledge of an approximate wave function already computed. Also such a topology can be anticipated for a large molecule by analogy, taking account of previous results concerning smaller molecules of the same family.

Furthermore, many experimental measurements can be interpreted in terms of loges. For example, some interatomic distances can be associated with the presence of a simple localized bond, i.e., of a two-electron localized loge.

Let us assume, for example, that the expected topology of a good division into loges of a molecule is that one represented by the last figure (Fig. 12). It is not necessary to know the actual limit of the loges but only a rough idea of their topology. The figure suggests associating with the molecule the following generating function if all the cores are two electron loges:

$$\Upsilon = A(1, 2)\, B(3, 4)\, C(5, 6)\, D(7, 8)\, P(9, 10)\, L_{AB}(11, 12)\, L_{BCD}(13, 14, 15, 16).$$

The various functions $A, B, \ldots, L$ are called *loge functions* because they are assumed to be at least partially localized in loges.

If σ is the spin function that represents the state of the molecule under consideration, the wave function will be written as

$$\Psi = \sum_P (-1)^P P \Upsilon \sigma,$$

and the loge functions will be computed following a classical variational procedure,

$$\delta \langle \Psi | H - E | \Psi \rangle = 0.$$

This is the formalism of the loge functions proposed by Daudel (1956).

Obviously, when all loges are two electron loges, this formalism reduces to the geminal one if the total spin function σ is conveniently introduced (Fock, 1950; Hurley *et al.*, 1953; Kapuy, 1958). If no additional requirement is introduced, the geminals are said to be free geminals (Bopp, 1959; Kroner, 1960; McWeeny and Sutcliffe, 1963). Usually the geminals are calculated in order to satisfy the usual *orthogonality condition*, such as,

$$\int G_k(1,2)G_{k'}(1,2)\,dv_1\,dv_2 = 0$$

or a strong *orthogonality condition*,

$$\int G_k(1,2)G_{k'}(1,3)\,dv_1 = 0.$$

The strong orthogonality condition may follow well the spirit of the loge theory because very often the corresponding geminals are more or less localized in the various loges of the atom or the molecule considered. For this reason, the corresponding procedure is often called the separated pair model.

From the practical viewpoint, it is useful to expand the various loge functions in terms of monoelectronic functions, χ (as atomic orbitals or Gaussian functions). In this way we shall write, for example,

$$L_{BCD} = \sum_i \sum_j \sum_k \sum_l C_{ijkl}\chi_i(13)\chi_j(14)\chi_k(15)\chi_l(16),$$

and the variational procedure will furnish the c's. Many more specific methods have been proposed to solve those problems that can be considered particular cases of the loge theory.

B. The Atomic Case. Geminals and Completely Localized Loge Functions

Consider the beryllium atom in its ground-state. The best division into loges is made of two-electron K loge and the remaining part of the space, a two-electron L loge. The corresponding wave function is

$$\Psi = \sum_P (-1)^P PK(1,2)\,L(3,4).$$

This kind of wave function has been used to compute the energy of the ground state of beryllium. It is found to be -14.6575 (a.u.) (experimental, 14.6673) (Miller and Ruedenberg, 1965).

The K and L geminals are rather well localized in two loges. But the localization is not complete. Only an important part of the norm of the function is found in the corresponding loge. This is normal because there is, for example, a small probability of finding the four electrons in the K loge.

However, since that probability is small, it can be neglected in a first approximation. This is why Ludeña and Amzel (1970) have introduced the new concept of *completely localized loge functions* [See also Ludeña (1971)].

Let V_r the volume in which the loge function $\mathcal{L}_r$ is completely localized. The Ludeña and Amzel hypothesis may be written as

$$\exists\{V_1, \ldots, V_r, \ldots, V_n\} \in R^3, \qquad V_r \cap V_{r'} = \emptyset, \qquad r \neq r',$$
$$\forall M \notin V_r \Rightarrow \mathcal{L}_r(\cdots M \cdots) = 0.$$

The authors have applied that formalism to the ground state of beryllium. The K loge has been chosen as a sphere centered at the nucleus. Its radius has been calculated from a Hartree–Fock wave function. The loge localized functions used correspond to a projected single Slater determinant. In comparison to a Hartree–Fock wave function leading to an energy of -14.56, the corresponding completely localized loge function leads to -14.58. This result shows that completely localized loge functions can be considered as a better starting point than the SCF wave function from the energy viewpoint. It turns out that when completely localized loge functions are used, spin localized properties appear. For example, the first triplet state of beryllium atom appears to be made of a singlet K loge and a triplet L loge. *That is to say that in the central sphere corresponding to the K loge the density of the probability of finding two electrons at the same point is not zero. But this probability is zero at any point outside of that sphere (Daudel and Sandorfy 1971).*

C. Representation of Cores and Lone Pairs

We saw that it is easy to obtain a good idea of the topology of the best division into loges of atoms. Therefore there is no problem in writing the part of the generating function associated with the cores of a molecule. A K loge is usually represented by a geminal. In some rough wave function we can replace the geminal by the first term in the expansion in terms of monoelectronic functions. The loge function reduces to

$$K(1, 2) = 1s\,(1)\;\; 1s\,(2).$$

A lone pair is also usually represented by a geminal. If we want to take into account only the first term of its expansion we must use hybrid orbitals.

If, for example, the NH_3 molecule is considered, the loge function P associated with the lone pair can be approximated as

$$P = te\,(1)\;\; te\,(2)$$

if te represents the appropriate tetrahedral hybrid.

D. Representation of Localized Bonds

A two-electron localized bond loge is usually represented by a geminal. Therefore molecules for which a good division into loges is made of K loges, two-electron localized bond loges and lone pair loges are conveniently represented by a wave function built on orthogonalized geminals. This is why Ahlrichs and Kutzelnigg (1968, 1969) have used such a procedure to study LiH, BeH_2, BH_3, and CH_4. In the case of LiH the results are highly accurate. In the other cases the results are not so spectacular, but the method does appear to offer a significant improvement over the independent-particle model, at little extra cost in item and effort, both as an end in itself, and as a starting point for more accurate calculations.

From the loge theory viewpoint, the McWeeny group functions method (1959, 1960) is a nice particular procedure to calculate loge functions. The geminals are usually expressed by following a particular way to ensure their localization. Let us consider the case of methane, a loge function associated with the CH two-electron loge will be written as

$$L_{\mathrm{CH}} = \{ah(1)\ h(2) + b(te(1)\ h(2) + h(1)\ te(2) + c\, te(1)\ te(2)\}.$$

This is a selection of the terms which appear in the expansion of the loge function on an atomic orbitals basis. Here *te* is a tetrahedral hybrid pointing in the direction of the hydrogen nucleus and *h* is the corresponding 1*s* hydrogen orbital. The variational calculation leads to an energy of −53.48 eV (Klessinger and McWeeny, 1965). The procedure is faster than the corresponding SCF calculation which leads to −53.44 eV. In some rough procedures the two-electron bond loge function expansion is reduced to one term,

$$L(1,2) = b(1)\,b(2).$$

In such a case *b* is called a *bond orbital.*

With Misses Valdemoro and Le Guen we have written a program which result from the fusion of a McWeeny group function program with IBM ØL program. The program makes it possible to calculate a wave function for a molecule for which a good division in two-electron loges is convenient. With an IBM 360–75 electronic computer the time required to compute the methane wave function is less than one minute.

E. Representation of *n*-Electron Bonds and Delocalized Bonds

We are extending the program to include *n*-electron loge functions (with $n > 2$). There is no difficulty in principle. The loge function has to be extended over all the gaussian functions which may be important in the corresponding loge. The four-electron delocalized bond loge of butadiene, for example, can be represented by

$$L_{c_1c_2c_3c_4} = \sum_{ijkl} c_{ijkl} 2pz_i(1)\ 2pz_j(2)\ 2pz_k(3)\ 2pz_l(4).$$

It corresponds to a complete π configuration interaction.

F. Improvement of Loge Function Formalism

The loge functions that have been considered as of now correspond to the most probable event associated with the best partition into loges. More elaborate wave functions can be built if the other events are taken into account. Consider the first triplet states of the helium atom. We know that the best partition of the space into loges correspond to a certain sphere centered at the nucleus; the part of the space inside the sphere is called the K loge and the other part the L loge. There is a high probability to find one electron in the K loge and the other in the L loge. This event suggests the function $L_K(1)\,L_L(2)$. But there is also a certain probability of finding the two electrons in the K loge suggesting the function $L_K'(1, 2)$. Finally, there is a probability of finding the two electrons in the L loge which suggests to consider the function $L_L'(1, 2)$.

Therefore we are led to approximate the total wave function with an expression like

$$\Psi = \sum_P (-1)^P P[aL_K(1)\,L_L(2) + bL_K'(1, 2) + cL_L'(1, 2)]\sigma, \tag{1}$$

where a, b. c, L_K, L_K', L_L, L_L' are, respectively, variational coefficients and variational functions. Their values and shapes will be determined by solving the usual equation

$$\delta\langle\Psi|H - E|\Psi\rangle = 0.$$

For practical reasons, the L's will usually be expanded on a basis of monoelectronic functions (gaussian functions, Slater functions, ...). The procedure has many similarities with the multiconfigurational method. That general procedure can be applied by following different techniques.

A first one is to start from an approximate wave function (e,g., Hartree–Fock) to calculate a good partition into loges; we know empirically (Odiot, 1957a, b) that only small fluctuations can occur if we take a better wave function, with regard to the exact best partition. The square root of the probabilities P_i of the various events can be chosen as a good approach of the coefficients *a*, *b*, *c*, and one can take for the functions *L trial strictly localized functions* and minimizes the mean value of the exact Hamiltonian. This procedure seems advantageous for several reasons: The strong orthogonality condition has no obscure meaning when considering strictly localized functions; on the contrary, it corresponds to a clear physical situation. The wave function can be written as

$$\Psi = \sum_{i=1}^{l(n,\,v)} \varepsilon_i (P_i)^{1/2} F_i$$

if

$$F_1 = AL_\mathrm{K}(1)L_\mathrm{L}(2)\sigma, \qquad F_2 = AL_\mathrm{K}'(1,2)\sigma, \qquad F_3 = AL_\mathrm{L}'(1,2)\sigma,$$

with $\varepsilon_i = \pm 1$, A being the antisymmetrizer. Therefore the mean value of any observable Ω will have the simple expression

$$\begin{aligned}\langle \Omega_\mathrm{op} \rangle &\equiv \langle \Psi | \Omega_\mathrm{op} | \Psi \rangle,\\ &= \sum_{i=1}^{l(n,v)} P_i \langle F_i | \Omega_\mathrm{op} | F_i \rangle.\end{aligned}$$

Furthermore, the antisymmetrization between two loge functions in the same E_i is no longer necessary (since there is no special overlap between them) and there results a considerable simplification in the formalism, as we can realize on consideration of $\langle \Omega_\mathrm{op} \rangle$. Finally, the interloge correlation is taken into account, at least partly.

From the point of view of the loge theory the perturbative configuration interaction using localized orbitals (PCILO) technique may be considered as another procedure to obtain a wave function like that given in Eq. (1). The main idea in this technique is to start from a function suggested by "chemical intuition," which corresponds here to the most probable event, and to introduce the least-probable events by following a perturbation method. This is why the technique is described as a perturbative configuration interaction using localized orbitals (Claverie *et al.*, 1967; Diner *et al.*, 1969a, b; Malrieu *et al.*, 1969; Jordan *et al.*, 1969). Usually the various space loge functions are approximated by a simple product of orbitals; e.g., a two-electron localized bond loge is represented with a product of two bond orbitals. These orbitals are usually expressed as a linear combination of hybrid orbitals associated with the two atoms,

$$b = \lambda t_1 + \mu t_2 .$$

In the zero-order function (or leading configuration) the bond loge functions are simple products of bonding bond orbitals. If, for example, a two two-electron localized-bond loge is considered (two interacting hydrogen molecules) the zero-order function is written as

$$\Psi = A\, L_1(1,2)\, L_2(3,4)\sigma$$

with $L_1(1,2) = b_1(1)b_1(2)$ and $L_2(3,4) = b_2(3)b_2(4)$ if b_1 and b_2 are bonding orbitals. But to improve the representation of the most-probable event, configurations are introduced in which antibonding orbitals $b_1{}^*$ anx $b_2{}^*$ are used, like those corresponding to

$$L_1{}^*(1,2)\,L_2(3,4), \qquad L_1(1,2)\,L_2{}^*(3,4), \qquad \text{and } L_1{}^{**}(1,2)\,L_2(3,4), \ldots$$

if $L_1{}^* = b_1b_1{}^*$, $L_2{}^* = b_2b_2{}^*$, and $L_1{}^{**} = b_1{}^*b_1{}^*$.

Now to take account of the least-probable events, functions like

$$\Psi' = A\, L_1{}''(1,2,3)\ L_2{}'(4)\sigma,$$
$$\Psi'' = A\, L_1{}'(1)\ L_2{}''(2,3,4)\sigma,$$

with

$$L_1{}'(1) = b_1(1), \qquad L_1{}''(1,2,3) = b_1(1)\, b_1\, (2)\, b_1{}^*(3),$$
$$b_2{}'(4) = b_2(4), \qquad L_2{}''(2,3,4) = b_2(2)\, b_2(3)\, b_2{}^*(4),$$

and so on are introduced. The effective calculation is made following the Rayleigh–Schrödinger perturbation expansion, but the partition of the Hamiltonian between unperturbed and perturbed parts is made by following the Epstein (1926) and Nesbet (1955) proposals. Introduced in a semiempirical framework this algorithm is very powerful. B. Pullman (1971) by following this way determined the most stable conformations of a great number of biomolecules.

When only geminals are concerned, the improvement of loge function formalism can be achieved by using the natural orbitals introduced by Löwdin (1955). Scarzafara (1969) has used the separated pair model to determine the electronic wave function associated with the ground state of the water molecule. Then a configuration interaction calculation is made, employing the natural orbitals of the separated-pair wave function as a basis with that separated-pair wave function as the leading configuration. The corresponding configuration energy is partitioned into various intrageminal and intergeminal components. From this analysis this author concludes that for the water molecule the separated-pair model yields approximately 50 % of the correlation energy.

The use of natural geminals (Löwdin, 1955) in the separated-pair model may also lead to a description in the schema of the theory of loges, where one obtains a series of two-electron loges.

Let us take a four-electron system for which a good partition into two loges V_1, V_2, is supposed known, and consider two geminals L_1 and L_2 which are well localized in V_1 and V_2, respectively. Such functions can be written as previously; indeed,

$$L_l = b_1(1)b_1(2), \qquad L_2 = b_2(3)\, b_2(4),$$

and are easily shown to be eigenfunctions of the two-body density operator, ρ_2, the kernel of which being $\rho_2(1, 2; 1', 2')$,

$$\rho_2(1, 2; 1', 2') = [4(4-1)/2] \iint \Psi(1, 2, 3, 4)\Psi^*(1', 2', 3, 4)\, d\tau_3\, d\tau_4,$$

Ψ being the wave function built from L_l and L_2 as before, Other eigenfunctions for ρ_2 are

$$L_3 = 2^{-1/2}\, [b_1(1)\, b_2(2) \pm b_1(2)\, b_2(1)],$$

and we realize that each L refers to an event of our reduced two-body problem: $L_j\, (j \in \{1, 2\})$ describes the situation where two electrons are expected to be inside the loge V_j, L_3 is related to the event defined by the presence of one electron in each loge V_1 and V_2. Finally, the total energy E is $E = \mathrm{Tr}\ K\rho_2$, where K is the two-body Hamiltonian

$$K(1, 2) = \tfrac{1}{3}[H_1(1) + H_1(2)] + H_2(1, 2),$$

since $L_i\, (i \in \{1, 2, 3\})$ is an eigenfunction of ρ_2, $E = \sum_i \langle L_i | K | L_i \rangle$; and the total energy appears as the sum of contributions associated which some events of the reduced problem.

Such a procedure can be improved by a configuration interaction. For this, we develop Ψ on a basis of functions Ψ_M, each of them being built from a set of natural geminals $L_{M,\, i}$

$$\Psi = \sum_M C_M \Psi_M .$$

The total energy is now

$$E = \sum_M \sum_N C_M C_N^* \mathrm{Tr}\ K\rho_2^{MN},$$

where

$$\rho_2^{M,N}(1, 2, 1', 2',) = 6 \iint \Psi_M(1, 2, 3, 4)\Psi_N^*(1', 2', 3, 4)\, d\tau_3\, d\tau_4,$$

and appears to be the sum of intra- $(\langle L_{M,i}|K|L_{N,i}\rangle)$ and intergeminal $(\langle L_{M,i}|K|L_{N,j}\rangle)$ contributions.

The configuration interaction procedure gives an improvement in two different ways; first, it introduces contributions related to events which were neglected before (for instance, three electrons in the same loge V_i) and which are now directly connected with the four-body problem. Secondly, it provides a better description of events yet considered in the first step.

V. Applications

A. A Criterion to Distinguish between Covalent and Dative Bonds

The classical criterion that permits one to distinguish between a covalent and a dative bond is related to a possible mechanism of the formation of the bond. It is said, for example, that a two-electron bond is dative when it results from a lone pair shared by two atoms. Such a mechanism may be normally assumed in the case of borazene:

$$H_3B + :NH_3 \longrightarrow H_3B \leftarrow NH_3.$$

But in some cases several mechanisms may be admitted for the same bond that lead to different conclusions concerning the nature of the bond. Furthermore, the relation between the nature of a bond and the mechanism of its formation is not necessarily direct, because a certain reorganization of the electronic density can follow the establishment of the bond. It is not sure that a bond possesses a good rememberance of its history.

Consider the $NH_4{}^+$ ion. Let us write the equation

$$H^+ + :NH_3 \longrightarrow [H \leftarrow NH_3]^+.$$

This equation suggests that one of the four bonds of $NH_4{}^+$ is dative, the others being covalent. This is certainly not true, because $NH_4{}^+$ has tetrahedral symmetry. An electronic reorganization must occur during the formation of the fourth bond.

For all these reasons it is better to search for a criterion based directly on the structure of the molecules. The concept of loge has been used by Daudel and Veillard (1970) to propose such a criterion.

This criterion is based on the notion of most-probable charge of a loge, which is the total charge contained in the loge (including electrons and nuclei) when there is in it the number of electrons which is found with a high probability.

A two-electron bond loge is a covalent bond if it is established between *two groups of loges having the same most probable charge +e. The loge is a dative bond if it is established between a group of loges with a most probable charge +2e and another one having a null most probable charge.* It is easy to see (Fig. 13) that from that viewpoint the BN loge in borazane is dative, the BN loge in the hypothetical molecule H_2BNH_2 being covalent.[3]

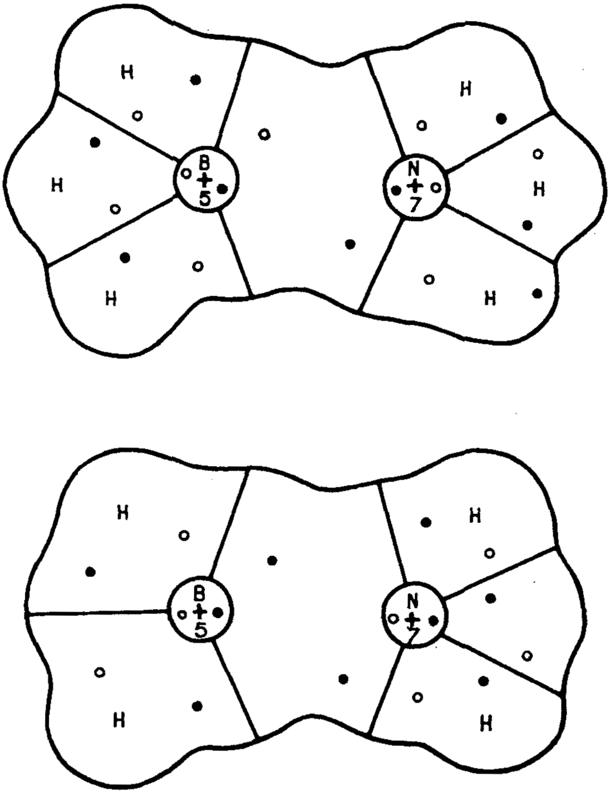

Fig. 13. Loges in borazane and in H_2BHN_2.

Aslangul *et al.* (1971) have determined good divisions into loges for these by calculating SCF wave functions and searching for the best localized orbitals. They found that the actual charges of the groups surrounding

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[3] To simplify the discussion the delocalization of the nitrogen lone pair is neglected.

the BN loge are very similar to their most probable charges. More precisely, if in H_3BNH_3 the BN loge is taken out, the charge of the remaining H_3B group is $-0.1e$ and the charge of the remaining H_3N group is $+2.1e$ In $H_2B\ NH_2$ the corresponding charges are $0.8e$ and $1.2e$. This result shows that the criterion proposed is not artificial.

Furthermore, the gravity center of the electronic density in the two BN bond loges have been calculated. In the two cases it is between the middle of the bond and the nitrogen nucleus. The dipole moment associated with the bond may be written as $:B \rightarrow N$. Therefore, there is no relation between the polarity of a dative bond and its classical notation $B \leftarrow N$ which, as we said, only refers to a possible mechanism. The distance between the gravity center of the loge and the nitrogen has been found to be smaller in the borazane molecule than in the aminoborane. This result is satisfactory because, if in the two molecules the fact that the nitrogen core is more positive than the boron one introduces a certain polarity in the bond, this polarity is enhanced in the borazane because, as we saw, the BN loge lies between two groups of loges which do not have the same charge, the NH_3 group being the more positive one.

B. General Theory of Molecular Additivity Rules

The loge theory provides an elegant framework for understanding the origin of molecular additivity rules. Using completely localized loge functions is an approximation appropriate for such an analysis. If $\mathscr{L}_i$ denotes the function localized in the volume V_i, it is readily seen that the wave function reduces to

$$\begin{aligned}\Psi &= \prod_i \sum_P (-1)^p P \mathscr{L}_i \sigma_i,\\ &= \prod_i \mathscr{L}_{Ti},\end{aligned}$$

if

$$\mathscr{L}_{Ti} = \sum_P (-1)^p P \mathscr{L}_i\, \sigma_i$$

is a normalized function, and σ_i is an appropriate spin function.

Consider the mean value A of a certain molecular property represented by the operator A

$$\bar{A} = \langle \Psi | A | \Psi \rangle = \left\langle \prod_\lambda \mathscr{L}_{T\lambda} \middle| A \middle| \prod_\mu \mathscr{L}_{T\mu} \middle| \right\rangle.$$

Let us assume that the operator is a sum of mono- and bielectronic operators:

$$A = \sum_k A_k + \tfrac{1}{2} \sum_{\substack{kk' \\ k \neq k'}} A_{kk'}.$$

It is easy to see that

$$\begin{aligned} \sum_k \left\langle \prod_\lambda \mathscr{L}_{T\lambda} | A_k | \prod_\mu \mathscr{L}_{T\mu} \right\rangle &= \sum_\lambda l_\lambda \langle \mathscr{L}_{T\lambda} | A_{k_\lambda} | \mathscr{L}_{T\lambda} \rangle, \\ &= \sum_\lambda l_\lambda \langle \mathscr{L}_{T\lambda} | A^{\lambda}_{k_\lambda} \, | \mathscr{L}_{T\lambda} \rangle \\ &\quad + \sum_\lambda l_\lambda \sum_{\mu \neq \lambda} \langle \mathscr{L}_{T\lambda} | A^{\mu}_{k_\lambda} | \mathscr{L}_{T\lambda} \rangle \end{aligned}$$

if l_λ is the number of electrons found in volume V_λ, k_λ refer to a point in this volume, $A^{\mu}_{k_\lambda}$ refer to an operator acting in V_λ but connected with V_μ, for example, the potential operator due to a nucleus in V_μ. Furthermore, for analogous reasons

$$\begin{aligned} \sum_{k,k'} \left\langle \prod_\lambda \mathscr{L}_{T\lambda} | A_{kk'} | \prod_\mu \mathscr{L}_{T\mu} \right\rangle &= \sum_\lambda m_{\lambda\lambda} \langle \mathscr{L}_{T\lambda} | A_{k_\lambda k_\lambda'} | \mathscr{L}_{T\lambda} \rangle \\ &\quad + \sum_{\lambda \neq \mu} m_{\lambda\mu} \langle \mathscr{L}_{T\lambda} \mathscr{L}_{T\mu} | A_{k_\lambda k_\mu} | \mathscr{L}_{T\lambda} \mathscr{L}_{T\mu} \rangle. \end{aligned}$$

where $m_{\lambda\mu}$ is related to l_λ and l_μ, k_λ and k_λ' to points in $\mathscr{L}_{T\lambda}$, k_λ and k_μ to points in $\mathscr{L}_{T\lambda}$ and $\mathscr{L}_{T\mu}$.

Therefore, if we write

$$\begin{aligned} \gamma_\lambda &= l_\lambda \langle \mathscr{L}_{T\lambda} | A^{\lambda}_{k_\lambda} | \mathscr{L}_{T\lambda} \rangle + m_{\lambda\lambda} \langle \mathscr{L}_{T\lambda} | A_{k_\lambda k_\lambda'} | \mathscr{L}_{T\lambda} \rangle, \\ \gamma_{\lambda\mu} &= m_{\lambda\mu} \langle \mathscr{L}_{T\lambda} \mathscr{L}_{T\mu} | A_{k_\lambda k_\mu} | \mathscr{L}_{T\lambda} \mathscr{L}_{T\mu} \rangle + l_\lambda \langle \mathscr{L}_{T\lambda} | A^{\mu}_{k_\lambda} | \mathscr{L}_{T\lambda} \rangle \\ &\quad + l_\mu \langle \mathscr{L}_{T\mu} | A^{\lambda}_{k_\mu} | \mathscr{L}_{T\mu} \rangle, \end{aligned}$$

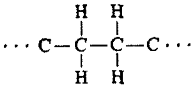
we obtain

$$\bar{A} = \sum_\lambda \gamma_\lambda + \sum_{\lambda < \mu} \gamma_{\lambda\mu}.$$

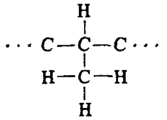
The mean value of the molecular property appears to be the sum of the moduli associated with each loge plus the sum of terms representing interaction between the loges. In the case of a monoelectronic operator the mean value reduces to the sum of the loge moduli. If the modulus associated with a given kind of loge remains approximately constant in a family of molecules, an additivity rule is found. This is why Daudel *et al.* (1967) were able to explain the additive properties of the Faraday effect in terms of the loge theory

For a bielectronic operator the situation is more involved. The additivity can appear when the loges have similar surroundings. This is why it has been possible to derive additive bond energies. However, for a bielectronic property, as the energy, the additivity must be only approximate. The interacting terms $\sum_{\lambda<\mu} \gamma_{\mu\nu}$ yield deviations to the additivity.

This term has been used (Daudel, 1970) to calculate the isomerization energies of satured hydrocarbons by using a very simple semiempirical procedure. Let us consider a normal molecule and its isoderivative. To evaluate the isomerization energy ΔE it is sufficient to consider the two parts of the paraffins which differ, i.e.,



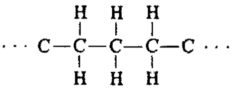
$\cdots C-CH_2-CH_2-C\cdots$



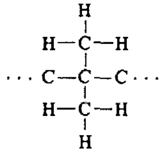
To simplify the discussion we shall only take into account the interacting terms between the two electron loges starting from the same core loge. Therefore no calculations are necessary; it is only necessary to look at the structure of the molecule to find

$$\begin{aligned}\Delta E &= [3\gamma_{CC,CC} + 3\gamma_{CH,CH} + 6\gamma_{CC,CH}] - [2\gamma_{CC,CC} + 2\gamma_{CH,CH} + 8\gamma_{CC,CH}],\\ &= \gamma_{CC,CC} + \gamma_{CH,CH} - 2\gamma_{CC,CH}.\end{aligned}$$

In the same way it is readily found that the isomerization energy $\Delta E'$ between a normal molecule and its 2,2-dimethyl derivative



$\cdots C-CH_2-CH_2-CH_2-C\cdots$



is $\Delta E' = 3(\gamma_{CC,CC} + \gamma_{CC,CH} - 2\gamma_{CC,CH}) = 3\Delta E$. The experimental findings support this result as

$$\Delta E = 1.7\ \text{kcal/mole} \qquad \text{and} \qquad \Delta E' = 4.7\ \text{kcal/mole}.$$

These results were previously obtained (Brown, 1953). But the method used was a rough LCBO method based on monoelectronic orbitals and on the simplified picture in which the total energy is obtained as the sum of the orbital energies.

The interest of the new derivation is that it is much more directly concerned with the localization of the electrons and therefore with the topology of the molecule. It is established with polyelectronic loge functions, and therefore intraloge correlation is taken into account. It is valid not only for single-bond but for all kinds of loges (core loges, localized-bond loges, delocalized bond loges, lone-pair loges). In particular, the lone pairs must not be forgotten. It couls be objected that completely localized functions have been introduced. This is certainly an approximation. But it may be anticipated that the same kind of formalism remains valid for a good division into loges. Compensations must occur between some new terms which appear, and other terms can be included in the empirical parameters associated with the loges and with the interaction among them.

VI. Localized Excitons and Loges in Large Molecules or in Molecular Aggregates

A. Introductory Remarks

In this section we want to indicate tentatively how localized excitons may also be described as loges when we consider the states of a large molecule or a molecular aggregate coupled to a thermal bath and to the radiation field.

The aggregates are formed by van der Waals force couplings W_{ij} and by resonance force couplings U_{ij} which appear between the identical subsystems (the molecules) in the excited states of the aggregate. The couplings W_{ij} and U_{ij} between the subsystems M_i and M_j are called coherent couplings; their couplings to the thermal bath Λ_i and Λ_j are called incoherent couplings. According to the respective importance of U_{ij} and Λ_i, Λ_j, the observed excited states will be stationary states of the aggregate or nonstationary states of the subsystems M_i, M_j (Kottis, 1970b). Let us consider the first case, where the coupling of the aggregate to the radiation field leads to one of its electronic excited stationary states $|i\rangle$, the thermal bath being ignored for the moment. Two situations may occur concerning the reorganization of the electronic distribution $|\Psi|^2$: (1) the topology of the best decomposition in loges of that excited stationary state $|i\rangle$ is the same as the one associated with the ground state $|0\rangle$. (2) The topology in the state $|i\rangle$ is different. We shall analyze case (1) because it is of practical importance for the use of the loge theory. This situation often occurs; we will cite two examples: (a) the aggregate made of weakly interacting molecules (The system is a supermolecule and the part of physical space associated with each molecule are very good loges for certain excited states.) (b) in a molecule, like the 6,3-dihydropentacene for instance, when properties of delocalized π-systems are considered. In such a molecule, there are two separated ten-electron delocalized bonds, one in each double aromatic ring. In the first excited state, the interaction between the aromatic double-rings is very small (Lemaistre, 1970). They correspond to two ten-electron loges which possess approximately the same geometry for the ground state and for the low-lying excited states.

We shall consider a two-electron loges problem: a supermolecule A–B. Let V_A and V_B be the two loges which, in such a case, correspond to spaces associated with each molecule, a specific case being that of two interacting hydrogen molecules H_2–H_2. The spin independent Hamiltonian for the system will be denoted as

$$\mathrm{H} = \mathrm{H}^{\mathrm{A}} + \mathrm{H}^{\mathrm{B}} + \mathrm{H}^{\mathrm{AB}}, \tag{1}$$

with H^{A} and H^{B} describing the intraloge interactions and H^{AB} describing the interloges interactions (see Section V).

The completely localized loge functions are appropriate to describe such a system in its ground singlet state. If $\mathscr{L}_{\mathrm{A}}{}^0$ and $\mathscr{L}_{\mathrm{B}}{}^0$ are the ground state loge functions, the ground state of A–B can be written as

$$\Psi_0(1, 2, 3, 4) = \mathscr{L}_{\mathrm{A}}{}^0(1, 2)\sigma_{\mathrm{A}}{}^0(1 ,2)\mathscr{L}_{\mathrm{B}}{}^0(3, 4)\sigma_{\mathrm{B}}{}^0(3, 4) \tag{2}$$

As seen in Section V, the energy of the state (2) is,

$$E_0 = E_A{}^0 + E_B{}^0 + E_{\mathrm{AB}}^0 \tag{3}$$

with

$$E_A{}^0 = \langle \mathscr{L}_{\mathrm{A}}{}^0 | \mathrm{H}^{\mathrm{A}} | \mathscr{L}_{\mathrm{A}}{}^0 \rangle, \qquad E_{\mathrm{B}}{}^0 = \langle \mathscr{L}_{\mathrm{B}}{}^0 | H^{\mathrm{B}} | \mathscr{L}_{\mathrm{B}}{}^0 \rangle,$$
$$E_{\mathrm{AB}}^0 = \langle \mathscr{L}_A{}^0 \mathscr{L}_B{}^0 | H^{\mathrm{AB}} | \mathscr{L}_{\mathrm{A}}{}^0 \mathscr{L}_{\mathrm{B}}{}^0 \rangle. \tag{4}$$

To describe the excited states of A–B, we use perturbation methods. Let us consider the isolated molecules A and B and assume that their first excited electronic levels $E_{\mathrm{A}}{}^*$ and $E_B{}^*$ have about the same energy, their other excited electronic levels being very distant. If A and B were alone, they would be represented in that state with functions $\varphi_{\mathrm{A}}{}^*$ and $\varphi_{\mathrm{B}}{}^*$. If the overlap between the two molecules is negligible, $\varphi_{\mathrm{A}}{}^*$ and $\varphi_{\mathrm{B}}{}^*$ (the isolated molecules functions) are, respectively, almost completely localized in V_{A} and V_{B} (the loges in the A–B system) and can be used as excited loge functions, i.e.,

$$\mathscr{L}_{\mathrm{A}}{}^* = \varphi_{\mathrm{A}}{}^*, \qquad \mathscr{L}_{\mathrm{B}}{}^* = \varphi_{\mathrm{B}}{}^*.$$

Therefore, the resonance, or quasi resonance ($a \neq b$), excited state is given by

$$\Psi_{(1,2,3,4)} = \mathscr{A}[a\Phi_{\mathrm{A}}{}^*\Phi_{\mathrm{B}}{}^0 + b\Phi_{\mathrm{A}}{}^0\Phi_{\mathrm{B}}{}^*], \tag{5}$$

where Φ_A and $\Phi_A{}^*$ are spin electronic molecular eigenfunctions, and is expressed in loge and excited loge functions as

$$\Psi_{(1,2,3,4)} = \mathscr{A}[a\mathscr{L}^*_{T_A}\mathscr{L}^0_{T_B} + b\mathscr{L}^0_{T_A}\mathscr{L}^*_{T_B}], \tag{6}$$

following the notation of Section V for $\mathscr{L}_{T_A}$ and $\mathscr{L}_{T_B}$. $\mathscr{A}$ is an antisymmetrizer which generates, from $a\Phi_A{}^*\Phi_B{}^0 + b\Phi_A{}^0\Phi_B{}^*$, the proper antisymmetrized function with regards to the full permutation group. The operator $\mathscr{A}$ may be ignored when the functions $\Phi_A{}^*$ and $\Phi_B{}^*$ are completely localized, cf. Section V. The coefficients a and b are easily calculated from the 2×2 secular system.

B. Properties of the Collective Excitation States

Let us consider an assembly of identical molecules in thermal equilibrium, which might show resonance, coherent, and incoherent phenomena, i.e., collective excitation states and excitation transfer between such states.

A localization of the excitation of the assembly in certain loges, coinciding with individual molecule volumes, is not a physical description of the excitation. Indeed, the indistinguishability for interacting electrons implies that of the excitation in one loge, i.e., we cannot observe localized excitation states for interacting molecules forming aggregates, as it is seen in (6).

The same restriction holds in the exciton theory (Davydov, 1962) where a localized exciton or a running excitation wave is not considered to represent an excitation state of the crystal at very low temperature (Craig, and Walmsley, 1968) or of an aggregate (Kottis, 1969a, 1970b), i.e., a localized exciton cannot be physically observed.[4]

In effect, in an assembly of interacting molecules collective excitation (CE) stationary states[5] show up in which, from the quantum point of view the individual molecules participating in these states are not distinguishable. This means that the probability that a measure reveals an observable of an individual molecule is strictly zero. The classical example put forward in order to describe this situation is that of a system of two identical

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[4] Note, however, that a phase destroying perturbation or a coherent preparation of an excitation packet may create quasi localized excitons (hopping excitons) or an excitation coherent waves, respectively (Kottis, 1970b, 1972).

[5] Excited stationary states do not exist. By stationary we mean that this state has a long life time so that we can measure the spectroscopic properties characterizing this state. We use here the name "collective excitation states" in order to emphasize the fact that many molecules are involved in this excitation, although none of them is in one of its eigenstates as would suggest the independent particle model.

coupled oscillators. In none of the two modes states can we isolate the properties (time dependent or not) of one of the components.

To make these concepts clear, we study excited states of a system of identical molecules—say two naphthalene molecules A and B—in which the concept of localized exciton representation might be linked to that of loges, when considering electronic transitions and excited states properties: electronic reorganization following an electronic transition, energies, spin densities, and spin polarizations.

It would be of practical importance to be able to express the observables of a CE state $\Psi(2n)$ in terms of weighted localized exciton properties. In the language of loges, this means to express, as contributions from loges V_A and V_B, the properties of CE state $\Psi(2n)$, n being the number of electrons associated with each molecule. In this way, we join the chemical intuition of localizations, although we know from theory that no physical experiment will allow us to "see" these localizations, as we anticipated just above. In the last sub-section, we introduce a phase destroying process—the perturbation of the two-molecule system by a thermal bath—and show that loges become experimental observables.

C. The Excited States of an Aggregate in a Thermal Bath

We consider the excited states of a dimer embedded in a solvent, which corresponds to the weak-coupling limit (Witkowski and Moffitt, 1960) and which is characterized by weak local interactions between the solvent and the monomers A and B. These two local interactions are time dependent[6] and uncorrelated. The latter allows us to introduce a perturbation process which gradually, with increasing temperature T, destroys the phase between the two subsystems A and B. Thus, we can go from a CE state to a state to two distinguishable subsystems in thermal equilibrium. The incoherent couplings to the bath Λ_A and Λ_B are compared to the coherent coupling U_{AB} between A and B, i.e.,

$$U_{AB} = \langle \mathscr{A} \mathscr{L}^*_{T_A} \mathscr{L}^0_{T_B} | H^{AB} | \mathscr{A} \mathscr{L}^0_{T_A} \mathscr{L}^*_{T_B} \rangle. \tag{7}$$

It is this coherent coupling that ensures the indistinguishability of the exciton and the stationary character of the excited dimer state. The comparison between Λ and U_{AB} will show us up to which limit we can describe

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[6] In order to calculate macroscopic properties of the dimers, the properties of the cell, the dimer plus the environment, are averaged over the sample. In thermal equilibrium, the phases of the cells state Ψ_c are randomly distributed, and the averages over the sample are time independent.

the excited dimer with stationary states. Beyond this limit, the dimer excitation will be described by two loges V_A and V_B into which the excitation stochastically relaxes under the perturbation of the thermal bath (thermal fluctuations). The theory of the temperature-induced localization of the triplet exciton in aggregates and of its stochastic transfer rates, was recently given by one of us (Kottis, 1969a, 1970b; Lemaistre and Kottis 1971). We will summarize this theory here, insisting on the localizability aspects—explicit (observable) and implicit (nonobservable)—of the excitation.

The time dependent Hamiltonian H^D for a dimer coupled to the solvent will be written explicitly as follows

$$H^D(t) = H^A(q^A, Q^A, \omega^A) + H^B(q^B, Q^B, \omega^B) + H^{AB}(q^A, q^B, L^{AB}) + H^{SA}(t) + H^{SB}(t) \qquad (8)$$

with $H(q^A, Q^A, \omega^A) = H(q^A, Q^A) + H(q^A, \omega^A)$. $H(q^A, Q^A)$ is the electronic–nuclear Hamiltonian of subsystem A. $H(q^A, \omega^A)$ denotes the electron spin interactions operator. A spin–Hamiltonian for the phosphorescent state is derived by first order perturbation theory.

$$\langle \Psi_1 | H(q^A, \omega^A) + H(q^B, \omega^B) | \Psi_1 \rangle_q$$

where Ψ_1 is the phosphorescent state of the spinless Hamiltonian in (8). The spin–Hamiltonian contains the Zeeman interaction and the anisotropic dipolar interaction. The latter is expressed with a tensor $\mathbf{T}$ whose principle values are the so-called zero-field splittings (zfs), i.e., X, Y and Z. H^{AB} is the operator for the coulombic time-independent interactions between A and B. In the usual approximation H^{AB} depends only on the electronic variables q^A and q^B and on the distance L^{AB}. $H^{SA}(t)$ is the adiabatic local interaction between the molecule A and the bath, i.e., $H^{SA}(t)$ randomly modulates the energies of A, but does not induce intramolecular transitions. The same holds for $H^{SB}(t)$. The Hamiltonian of the dimer, (8), will be written as usual in terms of a secular (time-independent) part H^0 and a perturbing (time-dependent) part $H^P(t)$ which induces transitions, if any, among the states of H^0

$$H^D(t) = H^0 + H^P(t). \qquad (9)$$

The secular and perturbing parts take the forms, respectively,

$$H^0 = \langle H^D(t) \rangle_{\tau_0} = H^A + H^B + \hat{H}^{AB} + \hat{H}^{SA} + \hat{H}^{SB}, \qquad (10)$$

with

$$\hat{H}^{AB} = \langle H^{AB} \rangle_{\tau_0} \qquad \hat{H}^{SA} = \langle H^{SA}(t) \rangle_{\tau_0} \qquad \hat{H}^{SB} = \langle H^{SB}(t) \rangle_{\tau_0}$$

and

$$H^{\mathrm{P}}(t) = H^{\mathrm{D}}(t) - H^{0}, \tag{11}$$

with $\langle H^{\mathrm{P}}(t)\rangle_{\tau_0} = 0$. In what follows, we contract

$$H^{S}(t) = H^{\mathrm{SA}}(t) + H^{\mathrm{SB}}(t).$$

τ_0 is the minimum time necessary to make a measure of the dimer in a CE state; τ_0 is the coherent period of the exciton and is of the order of U_{AB}^{-1} (Holstein, 1959).

If we define a coherence time τ in the coupling $H^{\mathrm{SA}}(t)$, τ is of the order of $\Lambda_{\mathrm{A}}^{-1}$ and may be the lifetime of a local vibration in a solid solvent or the time between two phase-destroying collisions in a liquid solvent (Sewell, 1963; Kottis, 1970b) we will have a completely different description of the excited dimer according to the value of the ratio $\tau_0/\tau = \rho$. $\rho \ll 1$ defines coherent coupling states (coherent excitons), $\rho > 1$ defines incoherent coupling states (hopping excitons).

D. Coherent Coupling States

The matrix elements of $\dot{H}^{\mathrm{AB}}$ and $H^{\mathrm{P}}(t)$, cf. (10) and (11), are crucial for the determination of the nature of the excited dimer states. Indeed, H^{AB} does not commute with $H^{S}(t)$; therefore, it will be affected by changes in $H^{S}(t)$. The time dependence of H^{AB} is then obtained in the Heisenberg representation.

$$\dot{H}^{\mathrm{AB}} = (i/\hbar)[H^{\mathrm{D}}(t), H^{\mathrm{AB}}], \tag{12}$$

which gives in a straightforward manner the time evolution of the matrix element U_{AB}, cf. (7),

$$U_{\mathrm{AB}}(t) = U_{\mathrm{AB}} \exp\left[-(i/\hbar) \int_0^t \Delta E(t')\, dt'\right] \tag{13}$$

with $\Delta E(t') = E_{\mathrm{A}}^{*}(t') - E_{\mathrm{B}}^{*}(t)$. $E_{\mathrm{A}}^{*}(t)$ and $E_{\mathrm{B}}^{*}(t)$ are the diagonal matrix elements (14) and (15) respectively; therefore, they will be called localized exciton energies at the instant t':

$$E_{\mathrm{A}}^{*}(t') = \langle \mathscr{L}_{T_{\mathrm{A}}}^{*} \mathscr{L}_{T_{\mathrm{B}}}^{0} | H^{0} + H^{\mathrm{P}}(t') | \mathscr{L}_{T_{\mathrm{A}}}^{*} \mathscr{L}_{T_{\mathrm{B}}}^{0} \rangle, \tag{14}$$

$$E_{\mathrm{B}}^{*}(t') = \langle \mathscr{L}_{T_{\mathrm{A}}}^{0} \mathscr{L}_{T_{\mathrm{B}}}^{*} | H^{0} + H^{\mathrm{P}}(t') | \mathscr{L}_{T_{\mathrm{A}}}^{0} \mathscr{L}_{T_{\mathrm{B}}}^{*} \rangle. \tag{15}$$

Neglecting solvent-monomer van der Waals force couplings in the ground state and taking the ground-state energy as the origin ($E_A{}^0 = E_B{}^0 = 0$), (14) and (15) may be expressed in the following detailed form

$$E_A{}^*(t') = E_A{}^* + W_{A^*B^0} + \Delta E_A{}^* + \delta E_A{}^*(t'), \qquad (14')$$

$$E_B{}^*(t') = E_B{}^* + W_{A^0B^*} + \Delta E_B{}^* + \delta E_B{}^*(t'), \qquad (15')$$

with

$$E_A{}^* = \langle \mathscr{L}^*_{T_A} | H^A | \mathscr{L}^*_{T_A} \rangle; \qquad E_B{}^* = \langle \mathscr{L}^*_{T_B} | H^B | \mathscr{L}^*_{T_B} \rangle,$$

$$W_{A^*B^0} = \langle \mathscr{L}^*_{T_A} \mathscr{L}^0_{T_B} | H^{AB} | \mathscr{L}^*_{T_A} \mathscr{L}^0_{T_B} \rangle,$$

$$W_{A^0B^*} = \langle \mathscr{L}^0_{T_A} \mathscr{L}^*_{T_B} | H^{AB} | \mathscr{L}^0_{T_A} \mathscr{L}^*_{T_B} \rangle.$$

$\Delta E_A{}^*$ is the average solvent-excited molecule A interaction energy and $\delta E_A{}^*(t)$ is the fluctuating part of this interaction determining an energy distribution $E_A{}^*(t')$ of width Λ_A. $\Delta E_A{}^*$ and Λ_A will be expressed as parameters although we could calculate them, in principle, as exciton local modes average interactions ($\Delta E_A{}^*$) and local modes average lifetime (Λ^{-1}) (Holstein, 1959; Kottis, 1970b).

In the absence of solvent, the localized exciton energies are degenerate at any time ($\Delta E(t') = 0$) and U_{AB} is time independent. The dimer excited states are CE stationary states and correspond to symmetric and antisymmetric combinations of localized excitons functions.

In the presence of solvent, the phase of $U_{AB}(t)$ is determined by

$$\Delta E(t') = \Delta E_A{}^* - \Delta E_B{}^* + \delta E_A{}^*(t) - \delta E_B{}^*(t). \qquad (16)$$

In (16), the degeneracy of the localized excitons is lifted by two factors: (1) the static terms, if $\Delta E_A{}^* \neq \Delta E_B{}^*$; (2) The uncorrelated couplings Λ_A and Λ_B, which by definition introduce a random phase between the localized excitons functions, i.e.,

$$\delta E_A{}^*(t') - \delta E_B{}^*(t') = \delta E(t'),$$

$\delta E(t')$ being a random function. The first term introduces a periodic variation in $U_{AB}(t)$. This does not destroy the stationary character of the CE state, since the energy of the state involves $|U_{AB}(t)|^2$, but changes the contributions of $\mathscr{L}^*_{T_A} \mathscr{L}^0_{T_B}$ and $\mathscr{L}^0_{T_A} \mathscr{L}^*_{T_B}$ in the CE state, cf. (6), and diminishes the coherent period of the exciton between the loges V_A and V_B. The solvent random perturbation term $\delta E(t)$ may average out the coherent coupling (13) and localize the excitation in one of the loges, V_A or V_B, [for this coherent motion, see example given in (24)].

At low temperature, the thermal fluctuations become negligible ($\Lambda_A = \Lambda_B = 0$), the general form of the excited state is then

$$\begin{aligned}\Psi_1 &= \mathscr{A}[a(\Delta\Lambda)\mathscr{L}^*_{T_A}\mathscr{L}^0_{T_B} + b(\Delta\Lambda)\mathscr{L}^0_{T_A}\mathscr{L}^*_{T_B}],\\ \Psi_2 &= \mathscr{A}[b(\Delta\Lambda)\mathscr{L}^*_{T_A}\mathscr{L}^0_{T_B} - a(\Delta\Lambda)\mathscr{L}^0_{T_A}\mathscr{L}^*_{T_B}],\end{aligned} \tag{17}$$

with

$$a^2(\Delta\Lambda) = \frac{(E^1 - E^2) + \Delta\Lambda}{2(E^1 - E^2)}, \qquad b^2(\Delta\Lambda) = \frac{(E^1 - E^2) - \Delta\Lambda}{2(E^1 - E^2)},$$

and $\Delta\Lambda = \Delta E_A^* - \Delta E_B^*$. E^1 and E^2 are the energies of the stationary states (17).

Having in mind the localizability aspects of the electronic excitation, we consider three particular forms of (17)

(1) $\Delta\Lambda = 0$, the molecules have the same environmental average perturbation. The loges V_A and V_B have the same contributions ($a = \pm b$) in (17). In the latter, the coherent period of the exciton is

$$\tau_0 = [U_{AB}]^{-1}.$$

(2) $\Delta\Lambda \neq 0$, with $|\Delta\Lambda| > |U_{AB}|$. The loges have different contributions to the CE state ($|a| \neq |b|$). In the latter, the coherent period of the exciton becomes larger, i.e.,

$$\tau_0 = \left[\frac{|U_{AB}|^2}{\Delta\Lambda}\right]^{-1}.$$

(3) $|\Delta\Lambda| \gg |U_{AB}|$. The excited states are localized stationary states[7]

$$\begin{aligned}\Psi_1 &= \mathscr{L}^*_{T_A}\mathscr{L}^0_{T_B}, \qquad & E_A^* + \Delta E_A^*,\\ \Psi_2 &= \mathscr{L}^0_{T_A}\mathscr{L}^*_{T_B}, \qquad & E_B^* + \Delta E_B^*.\end{aligned} \tag{18}$$

This discussion on the state (17) comes out in a straightforward manner when we consider the Hamiltonian (9) in coherent coupling case, i.e., $\rho = \tau_0/\tau \ll 1$. The latter condition implies that $\langle U_{AB}(t)\rangle_{\tau_0} = U_{AB}$, i.e., the coherent coupling is not affected by the random variation of its phase, cf. (13).

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[7] In fact this implies a very slow coherent motion of the exciton between V_A and V_B. Therefore, the slightest incoherent perturbation of the environment will localize the exciton and will induce transitions between loges in a mean time shorter than τ_0 (cf. last subsection).

Then, the states in the subspace $\{\Phi_A{}^*\Phi_B, \Phi_A{}^0\Phi_B{}^*\}$ can be obtained as solutions of a secular Hamiltonian

$$H = H^A + H^B + H^{AB} + \hat{H}^{SA} + \hat{H}^{SB} \tag{19}$$

whose eigenstates are (17). The perturbing Hamiltonian in this subspace reduces to

$$H^P(t) = H^S(t) - \langle H^S(t)\rangle \tau_0 . \tag{20}$$

$H^P(t)$ does not couple the states of (19). Therefore, the excited states (17) of the dimer corresponding to $\tau_0 \ll \tau$ are CE stationary states.

The practical problem will be to express the properties of an excited system (the dimer) as contributions from independent parts of the physical space, the loges V_A and V_B, with possibly adiabatic interactions between them.

(a) The spin densities on the carbon atoms of the excited triplet dimer. The spin densities of the two triplet excited states, say (17), ρ^{D_1} and ρ^{D_2} may be expressed as contributions from the loges V_A and V_B:

$$\begin{array}{ll} \rho^{D_1}(i) = a^2\rho^A(i), & \rho^{D_1}(i) = b^2\rho^B(i), \\ \rho^{D_2}(i) = b^2\rho^A(i), & \rho^{D2}(i) = a^2\rho^B(i), \\ \text{for } i \in V_A & \text{for } i \in V_B . \end{array} \tag{21}$$

This is also an example of additivity when the considered property corresponds to a monoelectronic operator, cf. Section V.

(b) The components of the electron spin–spin interaction tensor $T(X^D, Y^D, Z^D)$. When the two naphthalene molecules are parallel, these components for the two triplet excited states of the dimer have the form

$$\begin{aligned} X^{D_1} &= a^2X^A + b^2X^B + 2ab\varepsilon(S_{AB}), \\ X^{D_2} &= b^2X^A + a^2X^B - 2ab\varepsilon(S_{AB}), \end{aligned} \tag{22}$$

X^A and X^B are the components associated, respectively, with the excited A and B isolated molecules. The additivity is conserved in (22) for a bielectronic operator if we disregard the third term which is practically negligible $(a^2X^A/2ab\varepsilon(S_{AB}) \sim S_{AB}$; S_{AB} is the overlap molecules functions and is of the order of 10^{-3}).

(c) The energies of the excited states of the dimer

$$\begin{aligned} E^1 &= a^2\overline{E_A{}^*} + b^2\overline{E_B{}^*} + 2abU_{AB}, \\ E^2 &= b^2\overline{E_A{}^*} + a^2\overline{E_B{}^*} - 2abU_{AB}, \end{aligned} \tag{23}$$

$\overline{E_A{}^*}$ and $\overline{E_B{}^*}$ are the average energies of the excited loges, cf. (14) and (15).

Compared to these energies, U_{AB} may be neglected. Then, in the two states (23), the energy is stored in the two loges. For instance, in the state Ψ_1, the a^2 part of the energy is stored in the loge V_A and the b^2 part in V_B, although $a^2\overline{E_A}{}^*$ and $b^2\overline{E_B}{}^*$ are not eigenenergies of the molecules A and B, respectively.

In order to visualize the situation that a molecule can be thought of in a dynamical state which never can be observed, and chemists quite often think in this manner, let us write a stationary state with its phase factor

$$\Psi_1(t) = 2^{-1/2}[\mathscr{L}^*_{T_A}\mathscr{L}^0_{T_B} + \mathscr{L}^0_{T_A}\mathscr{L}^*_{T_B}]\exp(-iE^1t), \tag{24}$$

with $E^1 = E^0 + U_{AB}$ and $\hbar = 1$. We consider here the resonance state with $|a| = |b|$ and $E^0 = \frac{1}{2}(E_A{}^* + E_B{}^*) = E_A{}^*(\text{or } E_B{}^*)$, (24) may also be written

$$\begin{aligned}\Psi_1(t) = {} & 2^{-1/2}[\mathscr{L}^*_{T_A}\mathscr{L}^0_{T_B}\cos U_{AB}t - i\mathscr{L}^0_{T_A}\mathscr{L}^*_{T_B}\sin U_{AB}t]\exp(-iE^0t),\\ & + 2^{-1/2}[-i\mathscr{L}^*_{T_A}\mathscr{L}^0_{T_B}\sin U_{AB}t + \mathscr{L}^0_{T_A}\mathscr{L}^*_{T_B}\cos U_{AB}t]\exp(-iE^0t).\end{aligned} \tag{24'}$$

Apart from a phase factor, the stationary state (24) appears as an interference between two excitation waves, the one running from V_A to V_B, the other one from V_B to V_A. The stationary state is the result of an interference of the two waves. At each instant, this interference maintains an amount of energy $\frac{1}{2}E_A{}^*$ in V_A and $\frac{1}{2}E_B{}^*$ in V_B. We cannot observe this sharing of the total energy unless we destroy the interference by a phase-destroying perturbation.

E. Incoherent Coupling States

For $\tau \ll \tau_0\,(\rho > 1)$ the matrix element $U_{AB}(t)$ undergoes random changes in a time less than a coherent period. The possibility of interference between excitation waves (24′) disappears, the average of $U_{AB}(t)$ in a period τ_0 is zero,

$$\langle U_{AB}(t)\rangle_{\tau_0} = U_{AB}\left\langle \exp\left(-i\int_0^t \Delta E(t')\,dt'\right)\right\rangle_{\tau_0} = 0. \tag{25}$$

The excitation in the subspace $\{\Phi_A{}^*\Phi_B{}^0, \Phi_A{}^0\Phi_B{}^*\}$ can be described by the two operators

$$H^0 = H^A + \hat{H}^{SA} + H^B + \hat{H}^{SB} \tag{26}$$

$$H^P(t) = H^{AB}(t) + H^S(t) - \langle H^S(t)\rangle\tau_0. \tag{27}$$

The states of (26) are localized states

$$\begin{aligned} \Psi_1 &= \mathscr{L}^*_{T_A} \mathscr{L}^0_{T_B}, & E^1 &= \overline{E_A^*} \\ \Psi_2 &= \mathscr{L}^0_{T_A} \mathscr{L}^*_{T_B}, & E^2 &= \overline{E_B^*}. \end{aligned} \tag{28}$$

Contrary to the preceding subsection, these localized states are not stationary, they are coupled by $H^P(t)$. During the lifetime of the excited dimer, each perturbation by $H^P(t)$ will show up a state of H^0, i.e., a localized state. $H^P(t)$ is a stochastic perturbation, then we may define a rate k of excitation transfer from one loge to the other (Gamurar *et al.*, 1969; Le Falher *et al.* 1970; Lemaistre and Kottis 1971).

$$k_{V_A \to V_B} = \frac{2\pi}{\hbar} \frac{U_{AB}^2 \Lambda(T)}{(E_A^* - E_B^*)^2 + \Lambda^2(T)} \tag{29}$$

with $\Lambda^{-1}(T) = \tau$. The loges are in thermal equilibrium and their statistical weights obey the usual relation

$$\frac{W(V_A)}{W(V_B)} = \exp\left[- \frac{(\overline{E_A^*} - \overline{E_B^*})}{KT} \right]. \tag{30}$$

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Magnetic Circular Dichroism and Diamagnetic Molecules

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The role of the Faraday effect in structure determination has not yet been fully delineated. Since all substances display this phenomenon in a magnetic field, there is little hope that it will become as sensitive a conformational tool as natural optical activity, as has proved the case. At the very least we are provided with additional matrix elements with which to test the precision of wave functions. Theoretically the insensitivity to subtle molecular variations is one of the strong points of the Faraday effect in that the basic shape of the wave function is predominant in determining its quantitative features.

Unlike ordinary absorption and natural optical activity, the Faraday effect cannot be evaluated by one or two matrix elements, since the magnetic field provides a static perturbation which mixes all other states with the one being studied. In many instances excited states are classed into groups where it is equally tractable to construct a wave function for one as for another. In this case it may often happen that the greater part of the magnetic circular dichroism (MCD) will come from the mixing of these states. In other cases it will be generally possible to employ an approximate summation or variation technique, particularly at this stage of development where a qualitative understanding of the observed behavior is still to be gained.

Among the general factors which appear to play an interesting role in MCD research are vibronic, degeneracy, and spin phenomena. Closely coupled to this behavior is the strength of the transition with the categories, strong, weak, and forbidden often providing qualitatively distinct types. In circular dichroism (CD) spectra we are quite used to weakly allowed transitions giving large effects, when they are magnetically allowed; however, there are still no well-established reasons for spin-forbidden transitions to play any more important role than they do in ordinary absorption.

The situation is somewhat different in MCD. The largest magnetic rotational strengths are invariably associated with strong absorption. There has been a certain amount of evidence that spin-forbidden transitions play a more important role in the Faraday effect, but many of the observed peaks have later proved to be artifacts. More experimental work is clearly indicated. The behavior to MCD and CD in degenerate transitions is markedly different. When there is symmetry degeneracy, the splitting caused by the magnetic field leads to a sinusoidal MCD curve. On the other hand, if the state is truly degenerate and not merely approximately so, a simple CD curve results; it is only when the degeneracy is split by substitution that opposite-signed components are observed. In the case of group degeneracy one expects a reversal in behavior. The coupling of the identical groups, which leads to a sinusoidal CD behavior, has a negligible effect on the MCD, which is essentially the same as that of the individual groups.

A particularly promising aspect of the Faraday effect is in the realm of vibronic interactions. There are many forbidden transitions whose MCD curves display a rich fine structure often with alternating signs. As will be shown below, this situation can occur when different vibrational modes of the same symmetry cause comparable perturbations of opposite phase; it can also occur with nearly degenerate forbidden transitions under the right combination of circumstances. The combination of weak vicinal and strong vibronic perturbations on a forbidden transition can also lead to very interesting effects. This is potentially a sensitive way in which to study systems where such perturbations are believed to be comparable. The appearance of an alternating-signed MCD spectrum is invariably an indication that vibrations are playing an important role.

In semiclassical radiation theory the perturbation to the molecular Hamiltonian is given by

$$H' = -(e/mc) \sum_i \mathbf{A}_i \cdot \mathbf{p}_i, \tag{1}$$

where for the Faraday effect $\mathbf{A}_i$ is the sum of the radiation field and constant magnetic field vector potentials. The most general form for the latter quantity is

$$\mathbf{A}_0 = \tfrac{1}{2}\mathbf{H}_0 \times \mathbf{r} + \nabla\phi, \tag{2}$$

where ϕ is any scalar function of the fixed laboratory coordinates.

A lengthy calculation using second-order time-dependent perturbation theory gives a result which is independent of ϕ. Since the problem of gauge dependence is central to the Faraday effect, it is worthwhile to present a brief heuristic argument on how this occurs. The substitution of the first-order time-independent wave functions in the presence of the magnetic field into the standard first-order expression of radiation theory gives for the average induced dipole moment

$$\begin{aligned}
\langle\boldsymbol{\mu}\rangle_{00} = \boldsymbol{\mu}_{00} &+ \frac{2}{\hbar}\sum_{n\neq 0}\frac{1}{\omega_{0n}^2-\omega^2} \\
&\times\biggl\{\omega_{0n}\langle\boldsymbol{\mu}_{0n}\boldsymbol{\mu}_{n0}\cdot\mathbf{E}\rangle_{\mathrm{av}} + \sum_{s\neq n}\frac{1}{E_s-E_n} \\
&\times \mathrm{Im}\,\biggl\langle\boldsymbol{\mu}_{0s}\biggl[\mathbf{H}_0\cdot\mathbf{m}_{sn}+\frac{e}{mc}(\nabla\phi)\cdot\mathbf{p}_{sn}\biggr] \\
&\times(\boldsymbol{\mu}_{n0}\cdot\dot{\mathbf{E}}) + \boldsymbol{\mu}_{0n}\biggl[\mathbf{H}_0\cdot\mathbf{m}_{ns}+\frac{e}{mc}(\nabla\phi)\mathbf{p}_{sn}\biggr](\boldsymbol{\mu}_{s0}\cdot\dot{\mathbf{E}})\biggr\rangle_{\mathrm{av}} \\
&+\sum_{t\neq 0}\frac{1}{E_t-E_0}\,\mathrm{Im}\biggl\langle\boldsymbol{\mu}_{tn}\biggl[\mathbf{H}_0\cdot\mathbf{m}_{0t}+\frac{e}{mc}(\nabla\phi)\cdot\mathbf{p}_{0t}\biggr](\boldsymbol{\mu}_{n0}\cdot\dot{\mathbf{E}}) \\
&+\boldsymbol{\mu}_{0n}\biggl[\mathbf{H}_0\cdot\mathbf{m}_{t0}+\frac{e}{mc}(\nabla\phi)\cdot\mathbf{p}_{t0}\biggr](\boldsymbol{\mu}_{nt}\cdot\dot{\mathbf{E}})\biggr\rangle_{\mathrm{av}}\biggr\}.
\end{aligned}\tag{3}$$

The standard formula for averaging vectors is

$$\langle\mathbf{a}(\mathbf{b}\cdot\mathbf{B})(\mathbf{c}\cdot\mathbf{C})\rangle_{\mathrm{av}} = \tfrac{1}{6}(\mathbf{a}\cdot\mathbf{b}\times\mathbf{c})(\mathbf{B}\times\mathbf{C}),$$

where **a**, **b**, **c** are vectors with a fixed relative orientation, and **B**, **C** determine the fixed laboratory frame of reference. The coefficient of $(\nabla\phi)\times\mathbf{E}$ vanishes, since

$$\sum_{s\neq n}\frac{1}{E_s-E_n}\,\boldsymbol{\mu}_{0s}\times\mathbf{p}_{sn}\cdot\boldsymbol{\mu}_{n0} = \frac{im}{e\hbar}\sum_{s}[\boldsymbol{\mu}_{0s}\times\boldsymbol{\mu}_{sn}-\boldsymbol{\mu}_{0n}\times\boldsymbol{\mu}_{nn}]\cdot\boldsymbol{\mu}_{n0} = 0. \tag{4}$$

Equation (3) then becomes

$$\begin{aligned}
\langle\boldsymbol{\mu}\rangle_{00} = \boldsymbol{\mu}_{00} &+ \frac{2}{3\hbar}\sum_{n}\frac{\omega_{0n}}{\omega_{0n}^2-\omega^2}\,|\boldsymbol{\mu}_{0n}|^2\,\mathbf{E} \\
&\times\biggl\{\frac{2}{3\hbar}\sum_{n}\frac{1}{\omega_{0n}^2-\omega^2}\,\mathrm{Im}\,\biggl[\sum_{s\neq n}\frac{1}{E_s-E_n}\,\boldsymbol{\mu}_{0n}\cdot\mathbf{m}_{ns}\times\boldsymbol{\mu}_{s0} \\
&+\sum_{t\neq 0}\frac{1}{E_t-E_0}\,\boldsymbol{\mu}_{0n}\cdot\mathbf{m}_{t0}\times\boldsymbol{\mu}_{nt}\biggr]\biggr\}\mathbf{H}_0\times\dot{\mathbf{E}}.
\end{aligned}\tag{5}$$

From this it follows that the quantity corresponding to $\boldsymbol{\mu}_{0n} \cdot \mathbf{m}_{n0}$ in natural optical activity which measures MCD is

$$f_{0n} = \boldsymbol{\mu}_{0n} \cdot \mathrm{Im}\left[\sum_{s \neq n} \frac{1}{E_s - E_n} \mathbf{m}_{ns} \times \boldsymbol{\mu}_{s0} + \sum_{t \neq 0} \frac{1}{E_t - E_0} \mathbf{m}_{t0} \times \boldsymbol{\mu}_{nt}\right]. \qquad (6)$$

This expression is unwieldy for two reasons: first, the magnetic rotational strength for a given transition depends on all the states of the molecule, and second, the individual terms in the summation depend on the choice of origin. It is only the sum which is invariant. This undesirable feature has led to search for a gauge-invariant theory, whose terms are independent of origin.

Since the magnetic field necessarily causes a mixing of states, we cannot expect to find an exact finite expression for f_{0n} that depends only on the ground and excited states; nor should the origin dependence of the individual terms in an origin independent sum be considered suitable grounds for rejection. It happens that this is a gauge-invariant theory only for an exact solution to the problem; in its present form the theory is not particularly suitable for approximate methods.

It is not surprising that this problem should arise when it is recognized that the conventional wave-mechanical formulation of electromagnetic perturbations introduces an origin dependence in the Hamiltonian. Classically the origin independent Newtonian equations of motion are reproduced by a Lagrangian,

$$L = (m/2)(\dot{\mathbf{r}})^2 + (e/c)\dot{\mathbf{r}} \cdot \mathbf{A} - e\phi,$$

where $\mathbf{A}$ and ϕ are the vector and scalar potentials of the field. For a constant magnetic field $\mathbf{A} = \frac{1}{2}\mathbf{H}_0 \times \mathbf{r}$, and the generalized momentum is $\mathbf{p} = \partial L/\partial\dot{\mathbf{r}} = m\dot{\mathbf{r}} + (e/c)\mathbf{A}$. The Hamiltonian becomes $H = \mathbf{p} \cdot \dot{\mathbf{r}} - L = (m/2)\dot{\mathbf{r}}^2 + e\phi$, which is independent of origin. The origin independence is preserved when H is written in the form, $H = (1/2m)(\mathbf{p} - (e/c)\mathbf{A})^2 + e\phi$; however, $\mathbf{p}$ must be understood to be the generalized momentum, not the quantity $m\dot{\mathbf{r}}$.

In order to preserve the relation between classical and quantum Poisson brackets, $\{A, H\} = (1/i\hbar)(\hat{A}\hat{H} - \hat{H}\hat{A})$, it is necessary that the operator $-i\hbar\nabla$ correspond to the generalized momentum, even though one replaces an origin-dependent quantity with one not dependent on origin. The Hamiltonian operator,

$$= H\frac{1}{2m}\left(-\hbar^2\nabla^2 + 2i\hbar\frac{e}{c}\mathbf{A} \cdot \nabla + \frac{e^2}{c^2}|\mathbf{A}|^2\right) + V \qquad (7)$$

depends on origin through **A**. The solutions to $H\Psi = i\hbar\,\partial\Psi/\partial t$ will also depend on origin, but expectation values of observables must be invariant.

If careful attention is paid to the inclusion of all terms to a given order, the expectation value of any operator $\hat{Q}_{nn}$ will be gauge invariant, i.e., independent of origin. For example, the expectation value of H for a diamagnetic molecule is to second order

$$H_{nn} = \frac{e^2}{2mc^2}[|\mathbf{A}|^2]_{nn} + \frac{e^2}{m^2c^2}\sum_{s\neq n}\frac{(\mathbf{A}\cdot\mathbf{p})_{ns}(\mathbf{A}\cdot\mathbf{p})_{sn}}{E_n - E_s}. \tag{8}$$

For a constant magnetic field, the vector potential is generally taken to be $\mathbf{A} = \frac{1}{2}\mathbf{H}_0 \times \mathbf{r}$. Averaging over all molecular orientations gives

$$H_{nn} = \left[\frac{e^2}{8mc^2}\frac{2}{3}(r^2)_{nn} + \frac{1}{3}\sum_{s\neq n}\frac{|\mathbf{m}_{ns}|^2}{E_n - E_s}\right]|\mathbf{H}_0|^2. \tag{9}$$

This quantity is a sum of origin dependent terms; however, the total is independent of origin, as can be seen by making the transformation, $\mathbf{r}' = \mathbf{r} + \mathbf{R}$, and using the relation $e\mathbf{p}_{ns}/(E_n - E_s) = (im/\hbar)\boldsymbol{\mu}_{ns}$ in the second term. For the ground state, all the terms in the summation over s will be negative, while $(r^2)_{nn}$ is positive. The evaluation of (9) will most readily be accomplished by choosing the origin which minimizes the absolute values of the two terms, namely the center of charge of the ground state. Furthermore, this choice allows the most convenient estimate of the ratio between the two terms.

Now for any choice of origin it follows that

$$\sum_{s\neq n}\frac{(\mathbf{m}_{0s})^2}{E_s - E_0} < \frac{(\mathbf{m}^2)_{00}}{E_I - E_0},$$

where E_I is the first ionization energy. It then follows that the ratio of the second term to the first term is quite small for the choice of origin which minimizes the absolute values of the two terms; otherwise this ratio approaches unity. Thus one may write

$$H_{00} = \frac{1}{12mc^2}[(\boldsymbol{\mu} - \boldsymbol{\mu}_{00})^2]_{00}|\mathbf{H}_0|^2. \tag{10}$$

For excited states, the procedure is a bit more complex, but the result is essentially the same.

Since $-i\hbar\nabla$ corresponds to the generalized momentum, not the classical quantity $m\mathbf{v}$, it will be necessary to modify the current density expression. For the most general choice of gauge, the term $(i\hbar e/mc)\nabla\cdot\mathbf{A}$ must be added to (7). Since $m\hat{\mathbf{v}} = \hat{\mathbf{p}} - (e/c)\mathbf{A}$, we are led to expect that the current density must be written in the form

$$\mathbf{J} = (\hbar/2mi)[\Psi^*\nabla\Psi - \Psi\nabla\Psi^*] - (e/mc)\Psi^*\mathbf{A}\Psi. \tag{11}$$

The continuity equation, $\nabla \cdot \mathbf{J} + \partial\Psi^*\Psi/\partial t = 0$, will be satisfied for this choice of $\mathbf{J}$, as can be seen by considering the equation,

$$\left[\frac{1}{2m}\left(-i\hbar\nabla - \frac{e}{c}\mathbf{A}\right)^2 + e\phi\right]\Psi = i\hbar\frac{\partial\Psi}{\partial t};$$

and its complex conjugate.

Radiation problems may then be solved either by computing the average value of $\langle\mathbf{r}\rangle_{nn}$ or the average value of $\langle\dot{\mathbf{r}}\rangle_{nn}$ (i.e., $\langle J\rangle_{nn}$) in the perturbed state Ψ_n. The dynamical equations require that these two procedures give the same result. It then follows that a calculation which includes all terms to the required order will lead to a result that is independent of gauge and hence origin.

When an incomplete set of basis functions is used, expectation values of observables are dependent on origin; however, this is only an apparent anomaly. Just as the energies of eigenstates are subject to a variation principle, so are the wave functions in a dynamical problem. For example, if a finite number of terms are used in the evaluation of the sum in Eq. (9), the variation principle requires that the energy be a minimum. In this simple case it is immaterial how many terms are evaluated, since the total is negligible compared with the first term for the origin where $\boldsymbol{\mu}_{nn} = 0$.

In a dynamical problem we must implement the variation method by means of the Lagrangian density. The equation, $H\Psi = i\hbar\,\partial\Psi/\partial t$, with H expressed by (7) may be derived by finding the extremum of the integral, $\int_{t_1}^{t_2}\int L\,d\tau\,dt$, where

$$L = \Psi^* H_0 \Psi + \frac{e^2}{2mc^2}\Psi^*\Psi|\mathbf{A}|^2 - \frac{e}{mc}(\Psi^*\mathbf{A}\cdot\mathbf{p}\Psi - \Psi\mathbf{A}\cdot\mathbf{p}\Psi^*) - i\hbar(\Psi^*\dot{\Psi} - \Psi\dot{\Psi}^*). \tag{12}$$

If one uses for a trial function the sum,

$$\Psi_0' = \psi_0 e^{-iE_0t/\hbar} + \sum c_n \psi_n e^{-iE_nt/\hbar}, \tag{13}$$

the familiar results of perturbation theory are obtained; however, expectation values will depend on origin for any finite sum. In this case the best origin is obtained by substituting (13) into (12) with the c_n's determined to the appropriate order and finding the extremum of $\iint L\,d\tau\,dt$ with respect to the origin.

Unfortunately, it is necessary to calculate $L = \int L d\tau$ to fourth order with a rather unwieldy result. This follows from the fact that, when averaged over molecular orientation, quantities such as $\langle(\mathbf{H}_0 \cdot \mathbf{m}_{0n})(\mathbf{E} \cdot \mathbf{p}_{n0})\rangle_{\text{av}} = \frac{1}{3}(\mathbf{H}_0 \cdot \mathbf{E})(\mathbf{m}_{0n} \cdot \mathbf{p}_{n0})$ and $\langle(\mathbf{H}_0 \cdot \mathbf{m}_{0n})(\mathbf{E} \cdot \mathbf{p}_{ns})(\mathbf{E} \cdot \mathbf{p}_{s0})\rangle_{\text{av}} = \frac{1}{6}(\mathbf{H}_0 \cdot \mathbf{E} \times \mathbf{E}) \times (\mathbf{m}_{0n} \cdot \mathbf{p}_{ns} \times \mathbf{p}_{s0})$ vanish, since $\mathbf{H}_0$ is perpendicular to $\mathbf{E}$ and $\mathbf{H}_0 \cdot \mathbf{E} \times \mathbf{E} \equiv 0$. Furthermore, third order terms like $\langle(\mathbf{H}_0 \cdot \mathbf{m}_{0n})(\mathbf{E} \cdot \mathbf{p}_{ns})(\nabla \times \mathbf{E} \cdot \mathbf{m}_{s0})\rangle_{\text{av}} = \frac{1}{6}[\mathbf{H}_0 \times \mathbf{E} \cdot (\nabla \times \mathbf{E})](\mathbf{m}_{0n} \cdot \mathbf{p}_{ns} \times \mathbf{m}_{s0})$ will only make a small correction to the parameters of optically active molecules.

If the ψ_n in (13) are replaced by an arbitrary set χ_n', one must first make H_0 locally diagonal by solving the secular determinant. This will lead to a set of χ_n's with $\varepsilon_n = \int \chi_n H_0 \chi_n \, d\tau$ and $\int \psi_m H_0 \psi_n \, d\tau = 0$. Formally the variation of L will proceed just as before with $\psi_n \to \chi_n$, $E_n \to \varepsilon_n$; f_{0n} will be given by Eq. (6) with the appropriate changes in notation. The final step will consist in minimizing the fourth-order expression for L with respect to origin.

The evaluation of (6) may also be approached from a purely mathematical point of view. For example, if all the terms have been evaluated except $(E_q - E_n)^{-1}\mathbf{m}_{nq} \times \boldsymbol{\mu}_{q0}$, an origin may be chosen which makes $\mathbf{m}_{nq}$ vanish. On the other hand, it is possible to choose an origin for which the sum of all the terms except this one vanishes. The most practicable procedure is to construct a reasonable set of variation functions which approximate the behavior of all excited states that could make a significant contribution, and use an approximate technique to find the origin which makes the remaining terms vanish. If an insufficient number of terms is used, the result will be an origin far removed from the center of the molecule, indicating that the approximation is particularly susceptible to error.

It will generally be convenient to evaluate the two summations in Eq. (6) for separate origins. If $\chi_0, \ldots, \chi_N$ is a set of basis functions, we may suppose that they have been obtained from the variation procedure with the result that $\langle \chi_i | H_0 | \chi_j \rangle = \delta_{ij} \varepsilon_i$. In general the χ_i will be eigenfunctions of different Hamiltonians, but it will always be possible to find a complimentary set of functions $\chi_{N+1}, \ldots$, which are orthogonal to $\chi_0, \ldots, \chi_N$ and together with them comprise a complete set. There are in general an infinite number of such sets. It will then be necessary to find the origins for which

$$\boldsymbol{\mu}_{0n} \cdot \left[\sum_{s=N+1}^{\infty} \frac{\mathbf{m}_{ns} \times \boldsymbol{\mu}_{s0}}{\varepsilon_s - \varepsilon_n} \right] = 0, \tag{14a}$$

$$\boldsymbol{\mu}_{0n} \cdot \left[\sum_{s=N+1}^{\infty} \frac{\boldsymbol{\mu}_{ns} \times \mathbf{m}_{s0}}{\varepsilon_s - \varepsilon_0} \right] = 0. \tag{14b}$$

As ε_s approaches its asymptotic value, the denominators in the summations vary slightly and (14) becomes

$$\boldsymbol{\mu}_{0n} \cdot \left[(\mathbf{m} \times \boldsymbol{\mu})_{n0} - \sum_{s=0}^{N} \mathbf{m}_{ns} \times \boldsymbol{\mu}_{s0} \right] = 0, \tag{15a}$$

$$\boldsymbol{\mu}_{0n} \cdot \left[(\boldsymbol{\mu} \times \mathbf{m})_{n0} - \sum_{s=0}^{N} \boldsymbol{\mu}_{ns} \times \mathbf{m}_{s0} \right] = 0. \tag{15b}$$

If, as often happens, ψ_n is the lowest excited state which enters into the evaluation of (6), the first approximation is to seek origins for which

$$\boldsymbol{\mu}_{0n} \cdot [(\mathbf{m} \times \boldsymbol{\mu})_{n0} - \mathbf{m}_{n0} \times \boldsymbol{\mu}_{00}] = 0,$$
$$\boldsymbol{\mu}_{0n} \cdot [(\boldsymbol{\mu} \times \mathbf{m})_{n0} - \boldsymbol{\mu}_{nn} \times \mathbf{m}_{n0}] = 0.$$

It is most convenient to start with origins at $\boldsymbol{\mu}_{00} = 0$ and $\boldsymbol{\mu}_{nn} = 0$, respectively. The necessary shifts required to make the expressions vanish are found to be

$$\boldsymbol{\mu}_{0n} \cdot \left\{ (\mathbf{m} \times \mathbf{r})_{n0} + \frac{e}{2mc} (\mathbf{p} \cdot \mathbf{r})_{n0} \mathbf{R} - \frac{1}{2} \mathbf{R} \times \mathbf{m}_{n0} + \frac{1}{2} \frac{e}{2ich} (E_n - E_0)(\mathbf{rr})_{n0} \cdot \mathbf{R} \right\} = 0, \tag{16a}$$

$$\boldsymbol{\mu}_{0n} \cdot \left\{ (\mathbf{r} \times \mathbf{m})_{n0} + \frac{e}{2mc} (\mathbf{r} \cdot \mathbf{p})_{n0} \mathbf{R} + \frac{1}{2} \mathbf{R} \times \mathbf{m}_{n0} + \frac{1}{2} \frac{e}{2ich} (E_n - E_0)(\mathbf{rr})_{n0} \cdot \mathbf{R} \right\} = 0, \tag{16b}$$

where the matrix elements in the first equation are evaluated at $\boldsymbol{\mu}_{00} = 0$ and those of the second at $\boldsymbol{\mu}_{nn} = 0$.

These equations can be put in the form, $\mathbf{a} \cdot \mathbf{R} = a^2$, $\mathbf{b} \cdot \mathbf{R} = b^2$, where $a = |\mathbf{a}|$, $b = |\mathbf{b}|$. This represents two planes whose normal vectors from the origin are **a** and **b**. The point of closest approach to the origin can be shown to be given by

$$\mathbf{R}_0 = \left[\frac{1 - (\mathbf{a} \cdot \mathbf{b})^2}{a^2 b^2} \right]^{-1} \left[\left(1 - \frac{\mathbf{a} \cdot \mathbf{b}}{a^2} \right) \mathbf{a} + \left(1 - \frac{\mathbf{a} \cdot \mathbf{b}}{b^2} \right) \mathbf{b} \right]. \tag{17}$$

This method will only be useful when **a** and **b** are not nearly parallel, for the closest approach of the line to the center of the group will be small, and hence the approximations used have some hope of being valid. It is quite possible that an origin not far from the center of the group may be found for cases of rather low symmetry for which

$$\boldsymbol{\mu}_{0n} \cdot \mathbf{m}_{n0} \times (\boldsymbol{\mu}_{nn} - \boldsymbol{\mu}_{00})/(E_n - E_0)$$

represents a first approximation to f_{0n}.

In most cases of interest more terms are required. If a rather precise variation program is being employed, Eq. (15) will lead to an origin not too far removed from the center of charge and from the center prescribed by the Lagrangian variation method. For an extensive basis set, it is anticipated that there will be little difference between the two origins. It is worth emphasizing that any finite sum of terms linearly dependent on origin will be constant over an entire plane; thus, although an approximation technique may initially determine a particular origin that is best for the calculation, in effect this will determine a particular plane passing through that origin. The parameter f_{0n} will be of the form $f_{0n} = a + \mathbf{b} \cdot \mathbf{R}$, and the task is to find the best plane in which to perform a summation over a particular finite basis set. As a more complete set of trial functions is used, the value of $|\mathbf{b}|$ will become progressively smaller and origin dependence will become less critical.

By use of the magnetic moment operator it is possible to generate a set of functions which have all the symmetry properties of any of the terms in (6). This will assure an origin close to the one prescribed by the more precise variational procedure. First, it will be instructive to consider the behavior of molecules in the centric groups, D_{nh}, D_{nd}, O, etc. For these groups, the individual terms in the summation are independent of origin; for example, if $\boldsymbol{\mu}_{0n} \neq 0$ and $\boldsymbol{\mu}_{0s} \neq 0$, then $\mathbf{p}_{ns} = 0$ and $\mathbf{m}_{ns} \neq 0$; hence, the term $\mathbf{m}_{ns} \times \boldsymbol{\mu}_{s0}$ is independent of origin. Consider a nondegenerate electric dipole allowed transition. There is no loss in generality by supposing the transition to be polarized along the z axis. The product $\psi_0 \psi_n$ transforms like z; the products $m_x \mu_y$ and $m_y \mu_x$ also transform like z. There will be two terms of the type $\mathbf{m}_{ns} \times \boldsymbol{\mu}_{s0}$. A transition polarized along z will have two companion transitions polarized along x and y. Since the angular momentum operator tends to create functions whose charge distributions are rotated about the appropriate axis, the energy expectation values of the functions, $S_1^{(n)} m_x \psi_n$ and $S_2^{(n)} m_y \psi_n$ will probably lie close to E_n. Furthermore, these functions are orthogonal to each other and to ψ_0 and ψ_n. Similarly, the functions, $S_1^{(0)} m_x \psi_0$ and $S_2^{(0)} m_y \psi_0$ will have appropriate symmetry and energy expectation values to be suitable variation functions for the $\boldsymbol{\mu}_{nt} \times \mathbf{m}_{t0}$ terms. Not only are these functions orthogonal, but they are already diagonal with respect to H, since matrix elements such as $\langle m_x \psi_n | H | m_y \psi_n \rangle$ vanish by symmetry.

Provided that the energies differ sufficiently from E_n, the individual terms in the variation expression will be formally identical to the sum in Eq. (6):

$$f_{0n} = (\mu_z)_{0n} \operatorname{Im}\left\{\left[\frac{(m_x \mu_y)_{n0}}{\varepsilon_1^{(n)} - E_n} - \frac{(m_y \mu_x)_{n0}}{\varepsilon_2^{(n)} - E_n}\right] - \left[\frac{(\mu_x m_y)_{n0}}{\varepsilon_2^{(0)} - E_0} - \frac{(\mu_y m_x)_{n0}}{\varepsilon_1^{(0)} - E_0}\right]\right. . \tag{18}$$

Transitions which are strongly allowed tend to give simpler CD curves than weakly allowed ones, where the effects of vibrations can be observed. If the transition is purely vibronic, (18) will require additional refinements, since all the zeroth-order terms vanish. This expression will also be suitable for estimating the contribution of so-called C terms to degenerate allowed transitions. It should be remembered that not all vibrational modes of a centric molecule lead to conformations with centric symmetry.

For noncentric groups, the orthogonality assumptions in the derivation of the preceding equation require modification. In general neither $(m_x m_y)_{nn}$ nor $(m_x)_{0n}$ and $(m_y)_{0n}$ vanish; however, it is possible to choose an origin for which

$$(m_x m_y)_{nn} = \left(\frac{e\hbar}{2mc}\right)^2 \left(-xy \frac{\partial^2}{\partial z^2} + yz \frac{\partial^2}{\partial x \partial z} - z^2 \frac{\partial^2}{\partial x \partial y} + xz \frac{\partial^2}{\partial y \partial z}\right)_{nn}$$

vanishes. In general the exact location will be dependent on the orientation of the axes, which is not always automatically prescribed in problems of low symmetry. If the charge distribution ψ_n were spherically symmetrical, $(m_x m_y)_{nn}$ would vanish for any orientation of axes about its center; furthermore, it would vanish for any origin provided one of the axes points toward its center. This will be approximately true for any ψ_n which is not too irregular in shape.

For simplicity, let an origin consistent with $(m_x m_y)_{nn} = 0$ be chosen such that $\mathbf{m}_{n0}$ is parallel to the x axis. Let the following definitions be made:

$$\begin{aligned} \phi_1 &= N_1 m_x \psi_n, & \phi_2 &= N_2 m_y \psi_n, \\ \chi_1 &= \frac{\phi_1 - S\psi_0}{(1 - S^2)^{1/2}}, & \chi_2 &= \phi_2, \end{aligned} \tag{19}$$

where $S = \int \psi_0 \phi_1 \, d\tau$. It then follows that ψ_0, ψ_n, χ_1, χ_2 is a mutually orthogonal set of basis functions. Although a variation procedure will prescribe the correct linear combination of χ_1 and χ_2, it will be more instructive to consider them to be suitable approximations to excited states of the system.

The summation $\sum_{s \neq n} (\mathbf{m}_{ns} \times \boldsymbol{\mu}_{s0})/(E_s - E_n)$ is over the three states χ_1, χ_2, and ψ_0. The result is

$$\boldsymbol{\mu}_{0n} \cdot \left[\sum_{s=0,1,2} \frac{\mathbf{m}_{ns} \times \boldsymbol{\mu}_{s0}}{E_s - E_n}\right] = (\mu_z)_{0n}\left\{\frac{[(m_x \mu_y)_{n0} - (m_x)_{n0}(\mu_y)_{00}]}{\varepsilon_1^{(n)} - E_n} - \frac{[(m_y \mu_x)_{n0}]}{\varepsilon_2^{(n)} - E_n} + \frac{[(m_x)_{n0}(\mu_y)_{00}]}{E_0 - E_n}\right\}. \tag{20}$$

The sum of the numerators is equal to $\boldsymbol{\mu}_{0n} \cdot (\mathbf{m} \times \boldsymbol{\mu})_{n0}$, which indicates that this choice of origin tends to minimize the remainder terms. It should be remembered that the energies $\varepsilon_1^{(n)}$ and $\varepsilon_2^{(n)}$ are dependent on origin.

A similar procedure may be carried out on the $\boldsymbol{\mu}_{ns} \times \mathbf{m}_{s0}$ terms resulting in an equation similar to (20). The locus of points for which $(m_x m_y)_{00}$ and $(m_x m_y)_{nn}$ are both zero is approximately a circle passing through both centers of charge with diameter $|\mathbf{r}_{nn} - \mathbf{r}_{00}|$. As a final simplification one may average the values of f_{0n} for all such points and evaluate the expression at the midpoint of the centers of charge:

$$f_{0n} = (\boldsymbol{\mu}_z)_{0n} \operatorname{Im}\left\{\frac{[(m_x \mu_y)_{n0} - (m_x)_{n0}(\mu_y)_{00}]}{\varepsilon_1^{(n)} - E_n} - \frac{[(m_y \mu_x)_{n0}]}{\varepsilon_2^{(n)} - E_n} + \frac{[(m_x)_{n0}(\mu_y)_{00}]}{E_0 - E_n} - \frac{[(\mu_x m_y)_{n0}]}{\varepsilon_2^{(0)} - E_0} + \frac{[(\boldsymbol{\mu}_y m_x)_{n0} - (\mu_y)_{nn}(m_x)_{n0}]}{\varepsilon_1^{(0)} - E} + \frac{(\mu_y)_{nn}(m_x)_{n0}}{E_n - E_0}\right\}, \tag{21}$$

where $\boldsymbol{\mu}_{0n}$ is along z, $\mathbf{m}_{n0}$ is along x, and $\varepsilon_1^{(n)} = (N_1^{(n)})^2 \int (m_x \psi_n) H (m_x \psi_n) d\tau$, etc. When $(m_x)_{n0}$ or $(\boldsymbol{\mu}_y)_{00}$ and $(\boldsymbol{\mu}_y)_{nn}$ vanish, this expression reduces to (18) for centric groups.

For vibronic transitions Eq. (18) and (21) are still not in their most useful form, since it is desirable to have an expression that is dependent on both zeroth and first-order vibrational perturbation terms. In order to prevent the omission of certain terms it will be advisable to begin with Eq. (6). The complete second order version f_{0n} may be obtained by substituting ψ_0', ψ_n', and ψ_s' into (6), where $\psi_s' = \psi_s - \sum_i (V_{is}\psi_i/(E_i - E_s)$, etc.:

$$f_{0n} = -\boldsymbol{\mu}_{0n}' \cdot \operatorname{Im}\left\{\sum_{s,t \neq n} \frac{[\mathbf{m}_{ns} V_{st} \times \boldsymbol{\mu}_{t0} + V_{ns}\mathbf{m}_{st} \times \boldsymbol{\mu}_{t0}]}{(E_s - E_n)(E_t - E_n)} + \sum_{\substack{s \neq n \\ t \neq 0}} \frac{[\mathbf{m}_{ns} \times \boldsymbol{\mu}_{st} V_{t0} - V_{ns}\boldsymbol{\mu}_{st} \times \mathbf{m}_{t0}]}{(E_s - E_n)(E_t - E_0)} - \sum_{s,t \neq 0} \frac{[\boldsymbol{\mu}_{ns} \times V_{st}\mathbf{m}_{t0} + \boldsymbol{\mu}_{ns} \times \mathbf{m}_{st} V_{t0}]}{(E_s - E_0)(E_t - E_0)}\right\}. \tag{22}$$

The same variational method as in the derivation of Eq. (18) may be used to sum this expression. This will require a consideration of the general summation

$$\sum_{s,t} \frac{A_{ns} B_{st} C_{t0}}{(E_s - E_n)(E_t - E_0)},$$

where A, B, and C are operators. The procedure will be greatly simplified by first considering only centric groups. In this case only the product $\psi_n ABC\psi_0$ will have total symmetry. Others such as $\psi_n AB\psi_n$, $\psi_n ABC\psi_n$, etc. will vanish upon integration over the electronic coordinates. The appropriate pairs of ψ_s and ψ_t functions which give terms proportional to $(ABC)_{n0}$ or permutations thereof are seen to be

	ψ_s	ψ_t
I	$A\psi_n$	$AB\psi_n$
II	$A\psi_n$	$BA\psi_n$
III	$A\psi_n$	$C\psi_0$
IV	$BC\psi_0$	$C\psi_0$
V	$CB\psi_0$	$C\psi_0$.

The pairs $A\psi_n$, $BC\psi_0$ and $AB\psi_n$, $C\psi_0$, are not orthogonal. A thorough variational treatment would tend to obscure the essential features of the method without adding anything of substantial importance. It will be assumed that E_s is the average of the energies for the $A\psi_n$, $BC\psi_0$, and $CB\psi_0$ states. One may then write

$$\sum_{s,t} \frac{A_{ns} B_{st} C_{t0}}{(E_s - E_n)(E_t - E_0)} \cong \frac{(ABC)_{n0}}{(\varepsilon_1 - E_n)(\varepsilon_2 - E_0)}, \tag{23}$$

where

$$\varepsilon_1 = \frac{1}{3}\left\{\frac{\int \psi_n AHA\psi_n \, d\tau}{\int \psi_n A^2 \psi_n \, d\tau} + \frac{\int \psi_0 CBHBC\psi_0 \, d\tau}{\int \psi_0 CB^2 C\psi_0 \, d\tau} + \frac{\int \psi_0 BCHCB\psi_0 \, d\tau}{\int \psi_0 BC^2 B\psi_0 \, d\tau}\right\},$$

$$\varepsilon_2 = \frac{1}{3}\left\{\frac{\int \psi_0 CHC\psi_0 \, d\tau}{\int \psi_0 C^2 \psi_0 \, dt} + \frac{\int \psi_n BAHAB\psi_n \, d\tau}{\int \psi_n BA^2 B\psi_n \, d\tau} + \frac{\int \psi_n ABHBA\psi_n \, d\tau}{\int \psi_n AB^2 A\psi_n \, d\tau}\right\}.$$

Equation (22) becomes

$$f_{0n} = (\mu_z V)_{0n}\left[\frac{1}{\varepsilon_1 - E_0} + \frac{1}{\varepsilon_2 - E_n}\right]$$

$$\times \operatorname{Im}\left\{\left[\frac{(m_x V \mu_y)_{n0}}{(\varepsilon^{(1)}_{m_x V \mu_y} - E_n)(\varepsilon^{(2)}_{m_x V \mu_y} - E_n)} - \frac{(m_y V \mu_x)_{n0}}{(\varepsilon^{(1)}_{m_y V \mu_x} - E_n)(\varepsilon^{(2)}_{m_y V \mu_x} - E_n)}\right]\right.$$

$$
\begin{aligned}
&+\left[\frac{(Vm_x\mu_y)_{n0}}{(\varepsilon^{(1)}_{Vm_x\mu_y}-E_n)(\varepsilon^{(2)}_{Vm_x\mu_y}-E_n)}-\frac{(Vm_y\mu_x)_{n0}}{(\varepsilon^{(1)}_{Vm_y\mu_x}-E_n)(\varepsilon^{(2)}_{Vm_y\mu_x}-E_n)}\right]\\
&+\left[\frac{(m_x\mu_y V)_{n0}}{(\varepsilon^{(1)}_{m_x\mu_yV}-E_n)(\varepsilon^{(2)}_{m_x\mu_yV}-E_0)}-\frac{(m_y\mu_x V)_{n0}}{(\varepsilon^{(1)}_{m_y\mu_xV}-E_n)(\varepsilon^{(2)}_{m_y\mu_xV}-E_0)}\right]\\
&-\left[\frac{(V\mu_x m_y)_{n0}}{(\varepsilon^{(1)}_{V\mu_xm_y}-E_n)(\varepsilon^{(2)}_{V\mu_xm_y}-E_0)}-\frac{(V\mu_y m_x)_{n0}}{(\varepsilon^{(1)}_{V\mu_ym_x}-E_n)(\varepsilon^{(2)}_{V\mu_ym_x}-E_0)}\right]\\
&-\left[\frac{(\mu_x Vm_y)_{n0}}{(\varepsilon^{(1)}_{\mu_xVm_y}-E_0)(\varepsilon^{(2)}_{\mu_xVm_y}-E_0)}-\frac{(\mu_y Vm_x)_{n0}}{(\varepsilon^{(1)}_{\mu_yVm_x}-E_0)(\varepsilon^{(2)}_{\mu_yVm_x}-E_0)}\right]\\
&-\left.\left[\frac{(\mu_x m_y V)_{n0}}{(\varepsilon^{(1)}_{\mu_xm_yV}-E_0)(\varepsilon^{(1)}_{\mu_xm_yV}-E_0)}-\frac{(\mu_y m_x V)_{n0}}{(\varepsilon^{(1)}_{\mu_ym_xV}-E_0)(\varepsilon^{(2)}_{\mu_ym_xV}-E_0)}\right]\right\}. \qquad (24)
\end{aligned}
$$

The development will be somewhat more complex for noncentric groups, but in analogy to Eq. (21) one would expect that

$$
\begin{aligned}
(Vm_x\mu_y)_{n0} &\to (Vm_x\mu_y)_{n0}-(Vm_x)_{n0}(\mu_y)_{00},\\
(V\mu_y m_x)_{n0} &\to (V\mu_y m_x)_{n0}-(V\mu_y)_{nn}(m_x)_{n0},
\end{aligned}
$$

etc. Since the energy of $m_x\psi_n$ or $m_y\psi_n$ is often close to E_n, it may happen that the behavior of the transition is described by the leading terms

$$f_{0n}=(\mu_z V)_{0n}[A(m_x V\mu_y)_{n0}+B(m_y V\mu_x)_{n0}]. \qquad (25)$$

For purely vibronic transitions the perturbing potential will have the form

$$V=\sum_i Q_i\Gamma_i^{(1)}(r_{el})+\sum_{i,j} Q_iQ_j\Gamma^{(2)}(\mathbf{r}_{el})+\cdots, \qquad (26)$$

where the Q_i are the normal vibrational coordinates and the Γ_i's are functions of the electronic coordinates having the same symmetry as the coordinates Q_i. Most phenomena appear to have a satisfactory interpretation in the lowest-order nonvanishing terms; thus, only the first summation will be employed. The case of two separate vibrations is of particular interest; the potential will then have the form $V=Q_1\Gamma_1+Q_2\Gamma_2$.

First, let Q_1 and Q_2 be the components of a degenerate mode with ψ_n nondegenerate; if $Q\Gamma$ is the perturbation for an arbitrary choice of normal coordinate and R is one of the group's operations, an orthogonal pair of normal coordinates may be chosen such that

$$\Gamma_1=\frac{(R+R^{-1})\Gamma}{2\cos t\theta},\qquad \Gamma_2=\frac{(R-R^{-1})\Gamma}{2\sin t\theta}, \qquad (27)$$

where t is the order of the representation.

If the ground and excited vibrational states are given by the functions, $\chi_0(Q_1)$, $\chi_0(Q_2)$, $\chi_{n_1}(Q_1)$, $\chi_{n_2}(Q_2)$ for a z axis perpendicular to the degeneracy plane, Eq. (25) leads to a relation of the form

$$\begin{aligned} f_{0n} = A\{&(Q_1)^2_{0n_1}\langle\chi_0|\chi_{n_2}\rangle^2[(\boldsymbol{\mu}\Gamma_1)_{0n}\cdot(\mathbf{m}\times\Gamma_1\boldsymbol{\mu})_{n0}] \\ &+(Q_2)^2_{0n_2}\langle\chi_0|\chi_{n_1}\rangle^2[(\boldsymbol{\mu}\Gamma_2)_{0n}\cdot(\mathbf{m}\times\Gamma_2\boldsymbol{\mu})_{n0}] \\ &+(Q_1)_{0n_1}(Q_2)_{0n_2}\langle\chi_0|\chi_{n_1}\rangle\langle\chi_0|\chi_{n_2}\rangle \\ &\times[(\boldsymbol{\mu}\Gamma_1)_{0n}\cdot(\mathbf{m}\times\Gamma_2\boldsymbol{\mu})_{n0}+(\boldsymbol{\mu}\Gamma_2)_{0n}\cdot(\mathbf{m}\times\Gamma_1\boldsymbol{\mu})_{n0}]\}. \end{aligned} \tag{28}$$

By a rotation of axes in the integration one may show with the aid of (27) that

$$(\boldsymbol{\mu}\Gamma_1)_{0n}\cdot(\mathbf{m}\times\boldsymbol{\mu}\Gamma_1)_{n0}=(\boldsymbol{\mu}\Gamma_2)_{0n}\cdot(\mathbf{m}\times\boldsymbol{\mu}\Gamma_2)_{n0} \tag{29a}$$

$$(\boldsymbol{\mu}\Gamma_1)_{0n}\cdot(\boldsymbol{\mu}\Gamma_2)_{0n}=0 \tag{29b}$$

$$(\mathbf{m}\times\boldsymbol{\mu}\Gamma_1)_{n0}\cdot(\mathbf{m}\times\boldsymbol{\mu}\Gamma_2)_{n}=0 \tag{29c}$$

$$(\boldsymbol{\mu}\Gamma_1)_{0n}\cdot(\mathbf{m}\times\boldsymbol{\mu}\Gamma_2)=(\boldsymbol{\mu}\Gamma_2)_{0n}\cdot(\mathbf{m}\times\boldsymbol{\mu}\Gamma_1)_{n0}. \tag{29d}$$

It is possible without loss of generality to choose the coordinate system so that $(\mu_x\Gamma_1)_{0n}\neq 0$, $(\mu_y\Gamma_1)_{0n}=0$. Since $\mathbf{m}\times\boldsymbol{\mu}$ has exactly the same symmetry properties as $\boldsymbol{\mu}$, this choice of axes will also require that $[(\mathbf{m}\times\boldsymbol{\mu})_x\Gamma_1]_{n0}\neq 0$, $[(\mathbf{m}\times\boldsymbol{\mu})_y\Gamma_1]_{n0}=0$. From the above equation it then follows that

$$(\boldsymbol{\mu}\Gamma_1)_{0n}\cdot(\mathbf{m}\times\boldsymbol{\mu}\Gamma_2)_{n0}=(\boldsymbol{\mu}\Gamma_2)_{0n}\cdot(\mathbf{m}\times\boldsymbol{\mu}\Gamma_1)_{n0}=0.$$

A typical term in the evaluation of integrals is

$$\begin{aligned} &(\chi\Gamma_1)_{0n}[(\mathbf{m}\times\boldsymbol{\mu})_x\Gamma_1]_{n0} \\ &\quad=\frac{1}{4\cos 2t\,\theta}[\langle 0|x(R+R^{-1})\Gamma|n\rangle\langle n|(\mathbf{m}\times\boldsymbol{\mu})_x(R+R^{-1})\Gamma|0\rangle], \\ &\quad=\frac{\cos^2\theta}{4\cos^2 t\,\theta}(x\Gamma_1)_{0n}[(\mathbf{m}\times\boldsymbol{\mu})_x\Gamma_1]_{n0}\,. \end{aligned}$$

One obtains the result,

$$\left[\frac{\cos^2\theta}{\cos^2 t\theta}-\frac{\sin^2\theta}{\sin^2 t\theta}\right][(\boldsymbol{\mu}\Gamma)_{0n}\cdot(\mathbf{m}\times\boldsymbol{\mu}\Gamma)_{n0}]=0. \tag{30}$$

Since Γ is arbitrary the second term does not vanish in general; therefore $\cos^2\theta/\cos^2 t\theta=\sin^2\theta/\sin^2 t\theta$ and Eq. (29a) follows.

Strictly speaking the excited state is vibrationally degenerate; however, the degeneracy is only lifted by the magnetic field to the degree that the Born–Oppenheimer approximation breaks down. Accordingly, one will more than likely have to seek elsewhere for the cause of sign changes within an electronic absorption band.

There are essentially two ways in which sign changes may occur. First, the two vibrations may carry the excited state wave function into regions of lower and higher energy, respectively. If the sign of the $(\boldsymbol{\mu}\Gamma)_{0n} \cdot (\mathbf{m} \times \boldsymbol{\mu}\Gamma)_{n0}$ terms is the same in both cases, the two modes will make opposite-signed contributions. It may also happen that the energy terms have the same sign with the numerators of opposite sign.

A particularly interesting situation occurs in molecules of high symmetry where different vibrational modes with the same symmetry may occur. The vibronic fine structure of the B_{2u} band in benzene exhibits a particularly regular sinusoidal CD curve with several maxima and minima. It is very tempting to propose a mechanism governed by the E_{2g} in-plane vibrations. There are four such degenerate pairs describing C–C and C–H bending and stretching modes. To the first approximation attention may be concentrated on the C–C vibrations. The appropriate modes are shown in Fig. 1.

(a) (b)

Fig. 1. (a) stretching; (b) bending.

The behavior of the two modes may be studied by considering the term, $(x\Gamma)_{OB_{2u}}(m_z y\Gamma)_{B_{2u}O}$. The function, $\chi_{B_{1u}} = Nm_z\psi_{B_{1u}}$, will have B_{1u} symmetry and will be closely related to the exact $\psi_{B_{2u}}$ wave function. Bearing in mind that the B_{2u} state has nodes at the vertices and the B_{1u} has nodes at the midpoints of the bonds, we are led to conclude that the products, $\psi_0 x\psi_{B_{2u}}$ and $\psi_0 y\chi_{B_{1u}}$, will have the form shown in Fig. 2.

(a) (b)

Fig. 2. (a) $\psi_0 x\psi_{B_{2u}}$ (b) $\psi_0 y\chi_{B_{1u}}$.

The integrals will be of the form,

$$\int \phi_1 \phi_2 \boldsymbol{\sigma} \cdot \mathbf{r}_1 \, d\tau = \boldsymbol{\sigma} \cdot \mathbf{b}_{12} \int \phi_1 \phi_2 x_1 \, d\tau,$$

where $\mathbf{b}_{12}$ is the unit vector from atom 1 to atom 2 and

$$x\psi_{B_{2u}} = \text{const}\,[-\phi_1\phi_2 + 2\phi_1\phi_3 - \phi_3\phi_4 - \phi_4\phi_5 + 2\phi_5\phi_6 - \phi_6\phi_1] \quad (31a)$$

$$y\chi_{B_{2u}} = \text{const}\,[2\phi_1{}^2 - \phi_2{}^2 - \phi_3{}^2 + 2\phi_4{}^2 - \phi_5{}^2 - \phi_6{}^2\,]. \quad (31b)$$

It happens that $(m_z \mu_y \Gamma)_{B_{2u}O}$ is negative for both modes; while $(\boldsymbol{\mu}\Gamma)_{OB_{2u}}$ is positive for pure stretching and zero for pure bending. Since the actual vibrations are a composite of stretching and bending, it follows that appropriate linear combinations of Γ_1 and Γ_2 may well lead to opposite signs for the products $(x\Gamma)_{OB_{2u}}(m_z y\Gamma)_{B_{2u}O}$.

This rudimentary analysis by no means proves that sign changes in the B_{2u} band are brought about by the E_{2g} stretching and bending modes, but rather shows the plausibility of an hypothesis, which can be strengthened only by a more detailed calculation. A rather critical interplay of vibrations is indicated in order to display so regular a curve as in benzene; the corresponding band in the D_{6h} compound, coronene, does not display nearly so regular an alternation of extrema.

It is evident that properly interpreted, the Faraday effect has great potential as a subtle tool in the analysis of vibronic spectra and in the structure determination of molecular excited states.

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Collective Electron Oscillation in Pi-Electron Systems

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I. Introduction

Most of the dynamical systems we deal with in the application of quantum mechanics consist of a large number of particles. Thus, the many-particle problem is an important problem common to different branches of physics. As is well known, there is no mathematical procedure that can be generally used in the treatment of many-particle problems. We know from our day-to-day experience that a fairly large class of dynamical system consisting of many particles have a common feature—the constituent particles can perform collective motion. We know that liquids and gases, for example, can perform uniform flow or wave motion. In these classical systems the collective motions are known to be described by rather simple equations of hydrodynamics, notwithstanding the fact that the motion of individual molecules is so complicated that it is impossible to describe in a simple way.

This situation in classical dynamics suggests that there will be a fairly large class of quantum mechanical systems that also should be capable of collective motions, and the latter motions should be expressible in terms of some simple equations. Landau (1941) was the first to point out this possibility and discuss the peculiar properties of liquid helium from the viewpoint of quantized collective motion.

There are two methods of approach in the treatment of quantum-mechanical collective motions. The one is to quantize directly the hydrodynamical equations without giving any justification to this procedure (Kronig and Thellung, 1952, 1953), and the second approach is to give justification to this procedure and to establish what relation the equations for collective motion have to the Schrödinger equation of the many-particle system (Tomonaga, 1955).

Tomonaga (1955) has developed a theory of collective motion that is applicable to a large class of dynamical systems, provided the system is actually capable of performing collective motions, not only longitudinal oscillation but also surface oscillations similar to that of an incompressible fluid. This theory is a natural generalization of the use of center-of-mass coordinates to describe translational motions and to separate them for the internal relative motions of the system.

II. Tomonaga Gas Model

The fundamental idea of the theory may be illustrated by taking an example of surface oscillation of an incompressible system of particles. Suppose a dynamical system consisting of N particles interacting with each other by a force of such a nature that it strongly resists compression of the system. (A collection of free electrons, i.e., an electron gas, is one such system.) The particles will move in this system in such a way that the density undergoes no change, because in this motion the change of potential energy will be the smallest.

In order to avoid unnecessary complications we shall, for the present, investigate the two-dimensional case and take up only one mode of oscillation. We further assume that the motion is irrotational. As is well known, an irrotational displacement of a particle in an incompressible fluid is described by a displacement potential which satisfies $\Delta\phi = 0$. The infinitesimal displacement of a particle at the position (x, y) is then given by ε times the gradient of ϕ, where ε is an infinitesimal quantity. Let the coordinates of the nth particle be denoted by (x_n, y_n). Then its displacement is given by

$$\delta x_n = \varepsilon\, \partial\phi(x_n, y_n)/\partial x_n, \qquad \delta y_n = \varepsilon\, \partial\phi(x_n, y_n)/\partial y_n. \tag{II.1}$$

There are many ϕ's which satisfy $\Delta\phi = 0$; but as mentioned above we just consider one of them, the simplest nontrivial ϕ of the form

$$\phi = \tfrac{1}{2}x^2 - \tfrac{1}{2}y^2. \tag{II.2}$$

The displacement of the nth particle is given by

$$\delta x_n = \varepsilon x_n, \qquad \delta y_n = -\varepsilon y_n \tag{II.3}$$

so that each particle is displaced along a hyperbola whose asymptotes are the x and y axes, the original circular boundary being deformed into an elliptical one.

We now introduce an operator

$$\begin{aligned} \Pi &= -i\hbar \sum_n (\nabla_n \phi(x_n, y_n) \cdot \nabla_n) \\ &= -i\hbar \sum_n (x_n\, \partial/\partial x_n - y_n\, \partial/\partial y_n) \end{aligned} \tag{II.4}$$

Then we have

$$[1 + i\varepsilon\Pi/\hbar, f(x_1, y_1, \ldots, x_N, y_N)] = f(x_1 + \varepsilon x_1, y_1 - \varepsilon y_1, \ldots, x_N + \varepsilon x_N, y_N - \varepsilon y_N) \tag{II.5}$$

The last relation means that our $\Pi/\hbar$ is the operator that generates simultaneous displacement of particles, each displacement being specified by (II.3). Now the operator $-i\hbar \sum_n \partial/\partial x_n$, which generates the simultaneous displacements of particles in the x direction, is the momentum that describes the translation in the x direction; a translation is the most elementary form of collective motion; the coordinates that describe it are the well-known center-of-mass coordinates. The natural generalization of this fact associates the operator Π with the collective momentum that describes the incompressible deformation.

Having found the momentum, our next task is to find the corresponding coordinate that describes the collective motion. As can be easily verified, the quantity

$$\xi' = (1/N) \sum_n (\log x_n - \log y_n) \tag{II.4a}$$

satisfies the canonical commutation relation with

$$[\Pi, \xi'] = -i\hbar \tag{II.6}$$

so that it seems at first sight that this ξ' is to be used as the coordinate for our collective motion. But this ξ' is not a proper quantity for the present purpose, as will become evident from the following considerations. In order to give a full description of the motion of the system, we must use, besides the collective coordinate, a coordinate which describes the internal motion. The internal coordinates must have the property that they undergo no change when the particles are displaced simultaneously according to (II.3).

Let an internal coordinate be denoted by $\zeta = \zeta(x_1, y_1, \ldots, x_N, y_N)$. Then this requires

$$(x_n\, \partial\zeta/\partial x_n - y_n\, \partial\zeta/\partial y_n) = 0$$

i.e.,

$$[\Pi, \zeta] = 0 \tag{II.7}$$

the trivial requirement of commutability of ζ and Π. On the other hand, in order that the collective motion can be separated, from the internal motion the internal coordinate must be orthogonal in the sense that the surfaces

$$\zeta(x_1, y_1, \ldots, x_N, y_N) = \text{const}$$

and

$$\xi'(x_1, y_1, \ldots, x_N, y_N) = \text{const.}$$

in the configuration space must be orthogonal to each other. Otherwise, the kinetic energy operator would contain cross-product terms of the internal and collective momenta; the internal and collective motion then becomes entangled in a complicated manner.

This difficulty can be avoided by the fact that there exists a useful quantity $\xi(x_1, y_1, \ldots, x_N, y_N)$ which satisfies the orthogonality condition and, at the same time, the canonical relation with Π (not exactly) with sufficient accuracy. Let us define ξ by

$$\begin{aligned}\xi &= 2/NR_0^2 \sum_n \phi(x_n, y_n) \\ &= 2/NR_0^2 \sum_n (\tfrac{1}{2}x_n^2 - \tfrac{1}{2}y_n^2)\end{aligned} \tag{II.8a}$$

where R_0 is a constant which will be determined later. Then the orthogonality condition is

$$\sum_n \left(\frac{\partial\xi}{\partial x_n}\frac{\partial\zeta}{\partial x_n} + \frac{\partial\xi}{\partial y_n}\frac{\partial\zeta}{\partial y_n}\right) = 0$$

or

$$\frac{2}{NR_0^2}\sum_n \left(x_n \frac{\partial\zeta}{\partial x_n} - y_n \frac{\partial\zeta}{\partial y_n}\right) = 0 \tag{II.8}$$

The commutation relation of ξ with Π is

$$[\Pi, \xi] = -i\hbar(2/NR_0^2) \sum_n (x_n^2 + y_n^2), \tag{II.9}$$

which is not of a canonical form. But here we must notice the fact that when the number of particles is very large the quantity $\sum_n (x_n{}^2 + y_n{}^2)$ can be replaced by its mean value

$$\sum_n (\langle x_n{}^2\rangle + \langle y_n{}^2\rangle) = \sum_n \langle r_n{}^2\rangle = N\langle r^2\rangle \tag{II.10}$$

because the mean deviation is $[N(\langle r^4\rangle - \langle r^2\rangle^2)]^{1/2}$ and therefore, of the order of $N^{1/2}\langle r^2\rangle$, i.e., $N^{-1/2}$ times smaller than the mean value itself. Geometrically this follows from the fact that the region of the configuration space in which the quantity $\sum_n (x_n{}^2 + y_n{}^2)$ deviates appreciably from its mean value is negligibly small when the space is of very high dimension. Denoting $\langle r^2\rangle = R_0{}^2/2$ we find $[\Pi, \xi] = -i\hbar$.

In the preceding section we obtained the collective coordinate that satisfies the requirement of orthogonality to the internal coordinates, ζ. Then it must be possible to separate the kinetic energy of the collective motion from the kinetic energy of internal motion. The total kinetic energy of the system is given by

$$T = -\frac{\hbar^2}{2m}\sum_n \left(\frac{\partial^2}{\partial x_n{}^2} + \frac{\partial^2}{\partial y_n{}^2}\right) \tag{II.11}$$

and we separate this into internal and collective parts

$$T = T_{\text{in}} + T_{\text{c}} \tag{II.12}$$

It is to be anticipated that T_{c} will have the form

$$T_{\text{c}} = \Pi^2/2I \tag{II.13}$$

where I represents the inertia of collective degrees of freedom. This I is determined by the requirement that

$$T_{\text{in}} = T - (\Pi^2/2I) \tag{II.14}$$

should represent the kinetic energy of internal motion alone, i.e., T_{in} should not contain Π. This requires that

$$[T - (\Pi^2/2I), \xi] = 0 \tag{II.15}$$

and the relations

$$\begin{aligned}[T, \xi] &= -\frac{2\hbar^2}{NR_0{}^2m}\sum_n \left(x_n\frac{\partial}{\partial x_n} - y_n\frac{\partial}{\partial y_n}\right)\\ &= -(2i\hbar/NR_0{}^2m)\Pi \qquad\qquad \text{(II.16)}\\ [\Pi^2, \xi] &= -2i\hbar\Pi\end{aligned}$$

determine I if we chose

$$I = NR_0{}^2m/2$$

$$T_{\text{in}} = -\frac{\hbar^2}{2m}\sum_n\left(\frac{\partial^2}{\partial x_n{}^2}+\frac{\partial^2}{\partial y_n{}^2}\right)+\frac{\hbar^2}{NR_0{}^2m}\left(\sum_n\left\{x_n\frac{\partial}{\partial x_n}-y_n\frac{\partial}{\partial y_n}\right\}\right)^2 \qquad \text{(II.17)}$$

and

$$T_c = \Pi^2/NR_0{}^2m$$

i.e., T_{in} actually becomes the kinetic energy of the internal motion alone.

In order to obtain the potential energy for the collective motion it is necessary to know how the energy depends on the collective coordinate ξ. Let the potential energy of the system be denoted by $V = V(x_1, y_1, \ldots, x_N, y_N)$. Our task is to find how V changes when we change the collective coordinate, keeping the internal coordinate unaltered. In practical applications the amplitudes of the collective motion will be so small that it is sufficient to know this ξ dependence in the form of a power series, in which terms of power higher than the second are neglected.

Suppose that V is expressed as a function of ξ and ζ.

$$V = V(\zeta, \xi) \qquad \text{(II.18)}$$

Then expanding in a power series we get

$$\begin{aligned} V &= V(\zeta, 0) + \xi V'(\zeta, 0) + \tfrac{1}{2}\xi^2 V''(\zeta, 0) \\ &= V_0 + \xi V_1 + \tfrac{1}{2}\xi^2 V_2 \end{aligned} \qquad \text{(II.19)}$$

It should be noticed that all these V's depend only on the internal coordinates in the accuracy of our approximation and are not affected by the collective deformation of the system.

The Schrödinger equation for collective motions becomes

$$[(\Pi^2/2I) + V_0 + V_1\xi + \tfrac{1}{2}V_2\xi^2 - E]U(\xi) = 0. \qquad \text{(II.20)}$$

This expression still depends on internal coordinates through V_1 and V_2. In order to determine V_1 and V_2 we must first determine the wave function for the internal motion. That is, the collective motion cannot be studied independently of internal motion, unless V_1 and V_2 are either zero or constant.

Let us introduce the system into an electric field of strength F. The Hamiltonian for our system then becomes

$$H' = H - eNF\xi.$$

In order to obtain the Schrödinger equation for Ψ_{in} and $U(\xi)$, we use the variational equation

$$\delta\langle\Phi|H - eNF\xi - E|\Phi\rangle = 0$$

where $\Phi = \Psi_{\text{in}}(\zeta_1\zeta_2\ldots\ldots)U(\xi)$. We have

$$\begin{aligned}\langle\Phi|H - eNF\xi - E|\Phi\rangle = &\iint(\Psi^*_{\text{in}} H_{\text{in}} \Psi_{\text{in}})(U^* U)\, d\zeta\, d\xi\\ &-eNF \iint (\Psi^*_{\text{in}} \Psi_{\text{in}})(U^* \xi U)\, d\zeta\, d\xi\\ &+(1/2I) \iint (\Psi^*_{\text{in}} \Psi_{\text{in}})(U^* \Pi^2 U)\, d\zeta\, d\xi\\ &-E \iint (\Psi^*_{\text{in}} \Psi_{\text{in}})(U^* U)\, d\zeta\, d\xi \qquad \text{(II.21)}\end{aligned}$$

since Ψ_{in} is practically independent of ξ. By variation of Eq. (II.21) with respect to Ψ^*_{in} we get

$$H_{\text{in}}\Psi_{\text{in}} - eNF\xi\Psi_{\text{in}} + (U^*\Pi^2 U/2IU^*U)\Psi_{\text{in}} - E\Psi_{\text{in}} = 0 \qquad \text{(II.22)}$$

From Eq. (II.20) we obtain

$$(1/2I)(U^*\Pi^2 U/U^*U) = -(V_1\xi + \tfrac{1}{2}V_2\xi^2 - eNF\xi) + E_c$$

where $E_c = E - V_0$. Inserting this relation into (II.21) we get

$$\{H_{\text{in}} - (V_0 + V_1\xi + \tfrac{1}{2}V_2\xi^2)\}\Psi_{\text{in}} = 0$$

In this equation $V_0 + V_1\xi + \frac{1}{2}\xi^2 V_2$ appears in place of an eigenvalue, hence

$$\langle\Psi_{\text{in}}|H_{\text{in}}|\Psi_{\text{in}}\rangle = V_0 + V_1\xi + \tfrac{1}{2}V_2\xi^2 \qquad \text{(II.23)}$$

It may be observed that Eq. (II.23) does not contain $eNF\xi$ term, hence the internal motion is completely independent of F.

Now the variation of Eq. (II.21) with respect to U gives us

$$(\Pi^2/2I + \langle\Psi_{\text{in}}|H_{\text{in}}|\Psi_{\text{in}}\rangle - eNF\xi - E)U = 0 \qquad \text{(II.24)}$$

In absence of F our system is symmetrical; thus, $\langle\Psi_{\text{in}}|H_{\text{in}}|\Psi_{\text{in}}\rangle$, which is a function of ξ, must be an even function of ξ. This is satisfied if and only if V_1 is zero in (II.23) in absence of F. But since the internal motion does not depend on F, V_1 is zero even in the presence of F. Equation (II.23) also means that both V_0 and V_2 must also be independent of F.

The Schrödinger equation for collective motion in presence of F is then given by

$$[(\Pi^2/2I) + \tfrac{1}{2}V_2\xi^2 - eNF\xi - E_c']U' = 0 \qquad \text{(II.25)}$$

where $U' = u(\xi - \frac{1}{2}eNF)$

$$E_c' = E_c - \tfrac{1}{2}(e^2N^2F^2/V_2)$$

The total energy then becomes

$$\begin{aligned} E' &= E_{\mathrm{in}} + E_{\mathrm{c}} - \tfrac{1}{2}(e^2N^2/V^2)F^2 \qquad \text{(II.26)} \\ &= E - \tfrac{1}{2}(e^2N^2/V_2)F^2 \end{aligned}$$

Thus we find that when we introduce the system into the electric field F, the center of mass ξ is displaced by the amount

$$\Delta\xi = (eN/V_2)F \qquad \text{(II.27)}$$

in the direction of F and the dipole moment thus induced is

$$\mu = eN\,\Delta\xi = (e^2N^2/V_2)F \qquad \text{(II.28)}$$

The polarizability α of the system is given by

$$\alpha = \mu/F = e^2N^2/V_2 \qquad \text{or} \qquad V_2 = e^2N^2/\alpha. \qquad \text{(II.29)}$$

Since all the terms appearing in (II.29) are constant, V_2 must be constant. The Schrödinger equation for collective motion then becomes

$$[(\Pi^2/2I) + (e^2N^2/2\alpha)\xi^2 - E_{\mathrm{c}}]U = 0$$

which is basically an equation for the harmonic oscillator, and we get a frequency for collective motion, i.e., oscillation, as

$$\omega = (Ne^2 2/R_0{}^2 m\alpha)^{1/2} \qquad \text{(II.30)}$$

III. Collective Oscillation in Pi-Electron System in Aromatic Hydrocarbons

In the free-electron model for the pi-electrons in aromatic hydrocarbons (Platt, 1949) the electrons are assumed to move freely along the circumference of a circle in a zero potential field. The pi-electrons in effect form a two-dimensional electron gas. Because of the electrostatic repulsion between the electrons, a dynamical system consisting of N electrons will strongly resist compression of the system. The electrons will move in such a way that the density undergoes no change because in this motion the change of potential energy will be smallest. The motion which is most likely to occur in this system is a two-dimensional collective oscillation. It is surmised, therefore, that the quantum-mechanical collective motion proposed by Tomonaga will be applicable to the pi-electron system in aromatic hydrocarbons if we assume that when a molecule is excited, the centers of mass of the electrons and nuclei perform a two-dimensional dipolar oscillation.

So if we can estimate α, the pi-electron polarizability, either experimentally or theoretically, then relation (II.30) enables us to calculate the collective frequency associated with a one-electron transition. It has been shown that pi-electron polarizability of a series of aromatic hydrocarbons can be calculated using a free-electron model (Sen and Basu, 1966). Since the first singlet excitation gives rise to several bands in aromatic hydrocarbons, the question now arises as to which one is likely to be associated with collective oscillation. The oscillator strength for collective oscillation is given by that of a harmonic oscillator, i.e.,

$$f = N/3 \tag{III.1}$$

Moffitt (1954) observed that theoretical oscillator strength for catacondensed hydrocarbons must be multiplied by 0.3 to get agreement with experimental results. This suggests that the f value for collective oscillation should be

$$f = 0.1N \tag{III.2}$$

consequently, the band with highest oscillator strength should be associated with collective frequency. In Table I are summarized relevant experimental and theoretical data. The constant R_0 was estimated by matching the spectra of a four-ring compound and was found to be 4.02.

TABLE I

CALCULATED AND EXPERIMENTAL FREQUENCY FOR SINGLE TRANSITION

Number of rings	N	α(calc)[a]	λ ($m\mu$)		f	
			Calc.[b]	Exp.[c]	Calc.[b]	Exp.[c]
1	6	31×10^{-25}	194.2	183	0.60	0.69
2	10	72	229.7	220	1.00	1.70
3	14	136	270.7	256	1.40	2.28
4	18	180	274.0	274	1.80	1.85
5	20	250	293.0	309	2.00	2.20

[a] Sen and Basu (1966).
[b] Basu (1967).
[c] Platt (1949).

It may be observed that the calculated and experimental frequency and oscillator strength are in excellent agreement. The maximum deviation occurs for three-ring systems where the transition has rather high oscillator strength. The formulation is, however, not expected to hold good for this type of system, since the commutation relation

$$[\Pi, \xi] = -i\hbar$$

is valid if N is so large that $N^{-1/2}$ can be neglected against unity. This condition is not satisfied by the aromatic hydrocarbons.

The agreement between the experimental and theoretical results in the present case may be purely accidental, or there may be a more fundamental reason for the agreement, which will become evident in a later section.

IV. Collective Oscillation in Linear Conjugated Molecules

When we deal with the color of organic dyes which contain a chain of conjugated double bonds, we usually assume that in the lower electronic excitation of the molecule, the excitation occurs only for the pi-electron in the chain and remaining σ-electrons play no role in the excitation. Lewis and Calvin (1939) proposed a theory for the spectra of these dyes in which they assumed the chain molecule to behave as a dipole oscillator. In essence this is a collective description of the excitation of pi-electrons in the conjugated chain. We consider the pi-electrons in the conjugated chain to be confined in a long spheroid, and we assume that these pi-electrons form an electron gas in a one-dimensional box, and, when the molecule is excited, the center of mass of pi-electrons oscillates along the long axis of the spheroid, hence a dipole oscillation will be generated. The method of collective oscillation proposed by Tomonaga will be applicable to this problem if the collective coordinate ξ and the collective momenta Π are expressed as

$$\xi = (1/N) \sum_i x_i \tag{IV.1}$$

$$\Pi = -i\hbar \sum_i (\partial/\partial x_i) \tag{IV.2}$$

The frequency of collective oscillation will be given by the expression

$$\omega = (Ne^2/m\alpha)^{1/2} \tag{IV.3}$$

The polarizability α for the π-electrons in a conjugated chain may be calculated using a free-electron model, i.e., assuming the electrons as trapped in a one-dimensional potential well of length equal to the length of the conjugated carbon chain. This enables us to connect the frequency of collective oscillation with chain length. Murai has deduced an expression for α as

$$\alpha = (256/\pi^6)d^4n^3a_0{}^3 \tag{IV.4}$$

where $n = N/2$, $d = C{-}C$ bond length $= 1.39$ Å and a_0 is the Bohr radius $= \hbar^2/me^2 = 0.5292$ Å.

The frequency of collective oscillation calculated by the relations (IV.3) and (IV.4) are tabulated for a number of cyanines in Table II (Araki and Murai, 1952).

TABLE II

FREQUENCY OF COLLECTIVE OSCILLATION FOR CYANINES

Number of electrons N	Number of double bonds n	$\alpha_{\text{ind}}(10^{-25}\ \text{cm}^3)$	$\lambda_{\max}$ ($m\mu$) Calculated	Observed
2	1	18.8	115	235
4	2	150.4	230	270
6	3	507.6	345	423
8	4	1203.2	460	558
10	5	2350.0	575	650
12	6	4060.8	690	758

The polarizability calculated by the free-electron model is effectively an independent particle approximation. This is evidently too crude since it neglects completely the effect of the electron correlation. The classical treatment of polarizability of a dielectric spheroid embedded in a homogeneous medium of dielectric constant ε partially takes into account this correlation effect. The classical polarizability is given by

$$\alpha_c = \frac{\alpha_{\text{ind}}}{1 + (4\pi A(x)/\varepsilon V)\alpha_{\text{ind}}} \tag{IV.5}$$

where $A(x) = (\log x)/x^2$, x being equal to a/b, the ratio of the long-to-short axis of the spheroid. Calculating α_c in this way and introducing it in the expression (IV.5) Murai (1962) obtained very good agreement between the frequency of collective oscillation and the longest wavelength electron transition in a number of carotenoids. The experimental and calculated results are shown in Fig. 1.

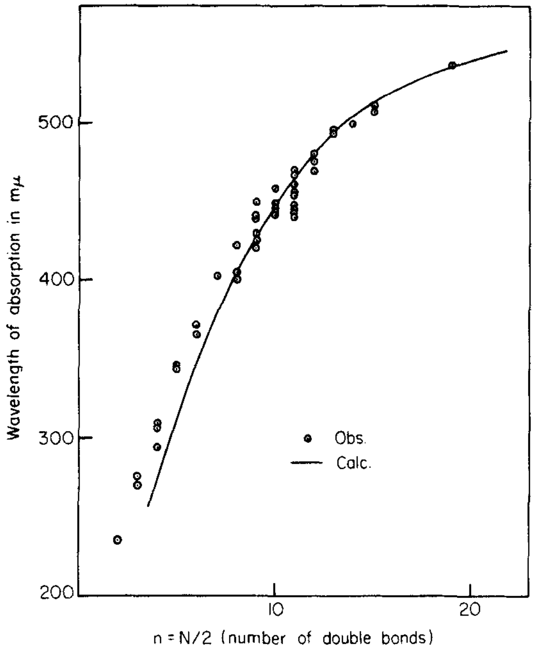

Fig. 1. Wavelength of absorption of carotenoids.

V. Collective Oscillation and Configuration Interaction

It appears that the collective frequency estimated from polarizability calculated by the independent particle approximation does not agree with the experimental transition frequency, while that estimated from polarizability calculated classically does. Let us look into the matter more closely to find a reason for this (Murai, 1962). The Schrödinger equation for the collective motion is given as

$$[(1/2I)\Pi^2 + \tfrac{1}{2}V_2\xi^2 - E_c]U(\xi) = 0 \qquad \text{(V.1)}$$

where $V_2 = N^2e^2/\alpha_{\text{ind}}$ in one case and as

$$[(1/2I)\Pi^2 + \tfrac{1}{2}V_2'\xi^2 - E_c']U'(\xi) = 0 \qquad \text{(V.2)}$$

where $V_2' = N^2e^2/\alpha_c$ in the other.

Since the potential energies in the two cases differ by only a numerical factor, Eq. (V.2) may be derived from Eq. (V.1) by a simple canonical transformation:

$$\xi \rightarrow (V_2'/V_2)^{1/4}\xi \tag{V.3}$$

$$\Pi \rightarrow (V_2/V_2')^{1/4}\Pi \tag{V.4}$$

Now it can be immediately shown that this canonical transformation is generated by the unitary transformation

$$\xi \rightarrow U\xi U^{-1} \tag{V.5}$$

$$\Pi \rightarrow U\Pi U^{-1} \tag{V.6}$$

with the unitary operator

$$U = \exp\{(i/8\hbar)\log(V_2'/V_2)(\Pi\xi + \xi\Pi)\} \tag{V.7}$$

so that

$$U'(\xi) = \exp\{(i/8\hbar)\log(V_2'/V_2)(\Pi\xi + \xi\Pi)\}U(\xi) \tag{V.8}$$

$(\Pi\xi + \xi\Pi)$ may be written as $(1/N)\sum_{i,j}(p_i x_j + x_i p_j)$, where $U(\xi)$ must be replaced by Ψ_0, a single Slater determinantal wave function in independent-particle approximations. The operator $(p_i x_j + x_j p_i)$ brings two electrons from levels i and j to the levels i' and j', hence $(p_i x_j + x_j p_i)\Psi_0$ describes an excited configuration. Accordingly U' represents a wave function which includes the mixing of configurations, since α_c takes into account, at least partly, the electron correlation effect. It was the finding of Tomonaga (1950) that configurational mixing can be properly described in terms of the zero-point amplitude of the collective sound oscillation. In the present treatment, on the other hand, the collective motion is a dipole oscillation, but as far as the oscillation in the lowest mode is concerned, the fact that we are dealing with a long-range interaction of a Coulomb type, makes this difference insignificant. Since collective description takes into account configurational mixing, the calculation gives good results for conjugated organic molecules, although the number of electrons is not large enough for the formulation to hold good exactly.

VI. One-Dimensional Collective Oscillation and Plasma Oscillation

It may be asked as to how collective oscillation takes into account the effect of interaction between electrons and, when the interaction is Coulomb, how does it correlate with plasma oscillation.

Let us consider a system of particles with no boundary; though we imagine it to be enclosed in a box of finite volume, this is done just for the sake of mathematical simplicity. We assume that the total number of particles is N per unit volume.

To avoid unnecessary complications, we shall consider just two modes of oscillation, whose displacement potentials are given by

$$\phi^+(xyz) = e^{ikx}, \qquad \phi^-(xyz) = e^{-ikx}, \qquad k > 0 \tag{VI.1}$$

The use of complex potentials is often more convenient than that of real ones. Then according to our general prescription we introduce the operators which generate our displacements. They are

$$(i/2)\{(\nabla_n \phi^\pm(x_n, y_n, z_n) \cdot \nabla_n) + \nabla_n \cdot \nabla_n \phi^\pm(x_n, y_n, z_n)\}$$
$$= \pm ik e^{\pm ikx_n}\{(-i\partial/\partial x_n) \pm k/2\}$$

Here the symmetrization with respect to the noncommuting operators $\nabla\phi$ and ∇ is performed in order to make these two operators adjoint to each other. We then define two momenta that describe our collective oscillations:

$$\begin{aligned} \Pi^+ &= -(i\hbar/k) \sum_n e^{-ikx_n}\{(-i\partial/\partial x_n) - k/2\} \\ \Pi^- &= (i\hbar/k) \sum_n e^{ikx_n}\{(-i\partial/\partial x_n) + k/2\} \end{aligned} \tag{VI.2}$$

Here we notice $\Pi^- = (\Pi^+)^\dagger$, which is the result of the symmetrization. The collective coordinates are now defined by

$$\begin{aligned} \xi^+ &= (1/N) \sum_n \phi^+(x_n, y_n, z_n) = (1/N) \sum_n e^{ikx_n} \\ \xi^- &= (1/N) \sum_n \phi^-(x_n, y_n, z_n) = (1/N) \sum_n e^{-ikx_n} \end{aligned} \tag{VI.3}$$

the expressions on the right-hand side can be replaced by their mean values, which obviously vanish. The mean deviation of the expressions from the mean value is of the order of $\hbar/N^{1/2}$, and this can be neglected. We now proceed to the separation of the kinetic energy into internal and collective parts. Namely, assuming that the collective kinetic energy be of the form

$$T_c = (1/2I)\Pi^+\Pi^- \tag{VI.4}$$

we determine the value of I in such a way that $T - (\Pi^+\Pi^-/2I)$ commutes with both ξ^+ and ξ^-. As can be shown we have

$$[\Pi^+\Pi^-, \xi^+] = i\hbar\Pi^-, \qquad [\Pi^+\Pi^-, \xi^-] = -i\hbar\Pi^+ \tag{VI.5}$$

and

$$[T, \xi^+] = -(i\hbar k^2/Nm)\Pi^-, \qquad [T, \xi^-] = -(i\hbar k^2/Nm)\Pi^+ \tag{VI.5'}$$

so that the choice

$$i/2I = k^2/Nm \tag{VI.6}$$

is the required one:

$$[T - (k^2/Nm)\Pi^+\Pi^-, \xi^\pm] = 0 \tag{VI.7}$$

In this way we get

$$T = T_{\text{in}} + T_{\text{c}} \tag{VI.8}$$

with

$$\begin{aligned} T_{\text{in}} = {} & -\frac{\hbar^2}{2m}\sum_n \left(\frac{\partial^2}{\partial x_n{}^2} + \frac{\partial^2}{\partial y_n{}^2} + \frac{\partial^2}{\partial z_n{}^2}\right) \\ & -\frac{\hbar^2}{Nm}\left[\sum_n e^{-ikx_n}\left\{\left(-i\frac{\partial}{\partial_{x_n}}\right) - \frac{k}{2}\right\}\right]\left[\sum_n e^{ikx_n}\left\{\left(-i\frac{\partial}{\partial_{x_n}}\right) + \frac{k}{2}\right\}\right] \end{aligned} \tag{VI.9}$$

$$T_{\text{c}} = (k^2/Nm)\Pi^+\Pi^- \tag{VI.10}$$

Let the interaction potential between the nth and n'th particles be denoted by

$$V(\mathbf{x}_n - \mathbf{x}_n') \tag{VI.11}$$

Then the total potential energy is given by

$$V = \tfrac{1}{2}\sum_{n,n'} V(\mathbf{x}_n - \mathbf{x}_n'). \tag{VI.12}$$

It is convenient to express $V(\mathbf{x}_n - \mathbf{x}_n')$ in the form

$$V(\mathbf{x}_n - \mathbf{x}_n') = \sum_{\mathbf{K}} f(K)\, e^{ik(x_n - x_n')}, \tag{VI.13}$$

$f(K)$ being the matrix element of the interaction energy corresponding to the momentum transfer of $\mathbf{K}$. When $V(\mathbf{x}_n - \mathbf{x}_n')$ is spherically symmetric, $f(\mathbf{K})$ will be a function of $\mathbf{K}$ only: $f(K)$, K being $|\mathbf{K}|$.

In the Fourier representation of $V(\mathbf{x}_n - \mathbf{x}_n')$, those terms which have wave number equal to the wave number of the collective waves are subtracted out. In our calculation we took into account only two modes of collective waves, but if we introduce all modes having wave numbers up to k_c, then all Fourier terms up to this wave number will be dropped. Then we shall have

$$V_0(\mathbf{x}_n - \mathbf{x}_n') = \sum_{|\mathbf{K}| > k_c} f(K)\, e^{iK(x_n - x_n')} \tag{VI.14}$$

In the Coulomb case we just have

$$f(K) = 4\pi e^2/K^2 \qquad \text{(VI.15)}$$

The Hamiltonian for our collective oscillation is

$$\begin{aligned} H_c &= (1/2I)\Pi^+\Pi^- + N^2 f(k)\xi^+\xi^- \\ &= (k^2/Nm)\Pi^+\Pi^- + N^2 f(k)\xi^+\xi^- \qquad \text{(VI.16)} \end{aligned}$$

from which we find the frequency. In the special case of Coulomb interaction

$$v = (Ne^2/\pi m)^{1/2}. \qquad \text{(VI.17)}$$

This is just the well-known plasma frequency.

It is well-known that the wave-length of the absorption maxima of carotenoids increases with increasing length of the conjugated chain, but ultimately converges to a limit, i.e., when the observed wave length is plotted against the number of conjugated double bonds one obtains a monotone increase with a downward curvature. It has been shown in Araki (1956) that if the pi-electrons in a linear polyene are assumed to move in a parallelopiped of length L and rectangular cross section A and the electron interaction potential is taken into account, then the convergence limit corresponds to the frequency of plasma oscillation of the pi-electrons in the polyene. For long chain molecules containing 15 to 20 double bonds, the main cause of absorption is a one-dimensional plasma oscillation of pi-electrons. Although there are some doubtful assumptions in Araki's calculation, his analysis brings out the role of electron interaction effect, in determining the convergence limit of linear polyenes.

VII. Concluding Remarks

The electrostatic or Coulomb force between two electrons, each of charge $-e$ and a distance r apart is e^2/r^2. In addition, moving electrons exert a magnetic force upon each other. For small electronic velocities, this magnetic force is negligible compared with the Coulomb force. A conjugated organic molecule consists essentially of atomic nuclei and electrons. However, it is convenient for theoretical purposes to divide the electrons into three groups: the ion-core electrons, which are assumed to remain tightly bound to the nuclei; then σ-electrons, which form bonding orbitals symmetric to the plane of the molecule, and pi-electrons, which form pi-orbitals antisymmetric to the plane of the molecule. It is these pi-electrons which are more or less free to travel throughout the molecule and are responsible for most of the characteristic properties of conjugated organic molecules. There are about 10^{22} pi-electrons per unit volume in an organic molecule like benzene. The electrons, therefore, are close together and the Coulomb force between any pair of them can be very large. What is perhaps more important is that the Coulomb force is of a long-range type so that the motions of all the electrons are coupled. The electronic interactions would therefore be expected to have a profound effect on the properties of conjugated organic molecules in spite of the successful calculations in which such interactions are neglected. Unfortunately, owing to mathematical difficulties, quantum-mechanical problems involving large numbers of interacting particles cannot be solved directly and even the standard perturbation methods give unsatisfactory results. It is here that the theory of collective motion may come to our rescue.

In fact it has been shown by Herzenberg, Sherrington, and Suveges (1964) that the singlet excited states of small molecules with singlet ground states should be affected by cooperative effects arising from the long-range part of the Coulomb potential and involving several electrons. The major points arising from these effects should be collective states and a systematic transfer of oscillator strength from the individual levels to the collective state.

The analysis set forth in this article refers to free-electron gases and its analogy to actual cases is rather too remote. It is desirable that the theory of collective motion should be developed for electronic motions which are constrained. Then probably a better analogy may be drawn between theoretical results and the actual situation obtained in the pi-electron system of conjugated organic molecules.

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Molecular Orbital Theory of Chemical Reactions

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I. Introduction

The molecular orbital (MO) theories of chemical reactivity can be divided into three groups: the static, the localization, and the delocalization approaches. Some of the theories are based on the "isolated molecule approximation." Several theories have been proposed along the static (Ri and Eyring, 1940; Pullman and Pullman, 1946; Dewar, 1946; Coulson and Longuet–Higgins, 1947a, b) and the localization (Wheland, 1942; Dewar, 1952) approaches. Chemical reactivity indices, frontier electron density, and superdelocalizability have been put forth on the basis of the delocalization model (Fukui *et al.*, 1952, 1954a, b, 1957; Fukui, 1964, 1965a, 1970a, b). Brown's Z value was also derived from the delocalization picture (Brown, 1959). In recent years, MO theory has achieved a great success in the field of stereochemistry. The selection rules for pericyclic reactions, which were first proposed by Woodward and Hoffmann (Woodward and

Hoffmann, 1965, 1969a, b; Hoffmann and Woodward, 1965, 1968), seem now to be well established, with a number of examples observed (Gill, 1968; Anh, 1970) and with several theoretical works developed later (Longuet-Higgins and Abrahamson, 1965; Fukui, 1965b, 1966; Zimmerman, 1966; Dewar, 1966, 1969; Fukui and Fujimoto, 1966a, 1967; Salem, 1968). These works are interesting since they have shown the correlation between the course of chemical reaction and the symmetry property of the wave function. Extensions to other systems have been made along this line (Mango and Schachtschneider, 1967; Goldstein, 1967; Simmons and Fukunaga, 1967; Hoffmann *et al.*, 1967).

Although the Woodward–Hoffmann selection rules and chemical reactivity indices mentioned above have been obtained from simplified interaction models, some more comprehensive treatments of chemical interaction have been proposed (Rein and Pollak, 1967; Klopman and Hudson, 1967; Klopman, 1968; Salem, 1968; Fukui and Fujimoto, 1968; Devaquet and Salem, 1969; Devaquet, 1970). These theoretical approaches intend to make possible the comparison of various factors that govern chemical reactions.

Recent progress in the methods of MO calculation has resulted in some knowledge on reaction intermediates and activated complexes (Hoffmann, 1963, 1964; Pople *et al.*, 1965; Yonezawa *et al.*, 1967; Baird and Dewar, 1969a, b; Baird *et al.*, 1969). Such an approach may be, no doubt, promising for the understanding of the nature of chemical reactions, as well as the theoretical treatments mentioned above. In the following, however, we limit ourselves to the theory of chemical reactions based upon the electronic structures of the isolated reactant and reagent molecules.

II. Chemical Interaction Energy between Two Systems

Let us consider the interaction energy between two systems A and B. We try to represent the wave function of the system composed of two mutually interacting species A and B by a configuration interaction procedure among various electronic states,

$$\Psi = C_0\Psi_0 + \left(\sum_p^{\text{monotr}} + \sum_p^{\text{monoex}} + \sum_p^{\text{ditr}} + \sum_p^{\text{diex}} + \cdots \right) C_p\Psi_p, \qquad (1)$$

where monotr, diex, etc., imply monotransferred, diexcited configurations, etc., with respect to the initial configuration, 0. The electronic configurations are schematically shown in Fig. 1 in regard to the initial, the monotransferred, and the monoexcited configurations.

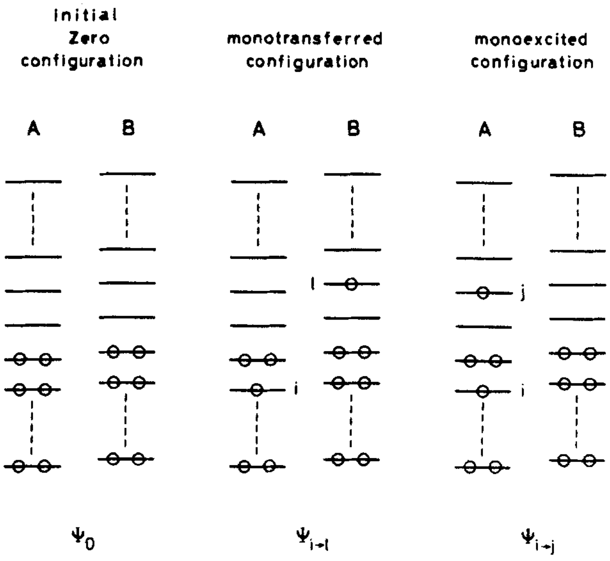


Fig. 1. Electron configurations of the combined system AB.

The energy of interaction between two systems, in which, tentatively, no nuclear configuration change is considered, is defined by

$$\Delta W = W - (W_{A0} + W_{B0}),$$

where ΔW is the interaction energy, W is the lowest total energy of the system composed of the two mutually interacting systems A and B, and W_{A0} and W_{B0} are the energies of the initial stationary states of two isolated systems A and B. The energies of all the systems are calculated in the frame of the Born–Oppenheimer approximation (Born and Oppenheimer, 1927).

The Hamiltonian operator of the system composed of A and B is (in atomic units)

$$\begin{aligned} H &= \sum_{\lambda} H(\lambda) + \sum_{\lambda<\lambda'} 1/r_{\lambda\lambda'} + \sum_{\gamma<\gamma'} Z_\gamma Z_{\gamma'}/R_{\gamma\gamma'}, \\ H(\lambda) &= -\tfrac{1}{2}\Delta(\lambda) + V(\lambda), \\ V(\lambda) &= V_A(\lambda) + V_B(\lambda), \\ V_A(\lambda) &= -\sum_{\alpha} Z_\alpha/r_{\lambda\alpha}, \qquad V_B(\lambda) = -\sum_{\beta} Z_\beta/r_{\lambda\beta}, \end{aligned} \tag{2}$$

where $H(\lambda)$ is the one-electron Hamiltonian operator of the electron λ;

Z_α, Z_β and Z_γ are the positive charges of the nuclei α, β, and γ, belonging to the system A, the system B, and the combined system AB, respectively; $r_{\lambda\lambda'}$ is the distance between the two electrons λ and λ', $r_{\lambda\alpha}$ is the distance of the electron λ from the nucleus α; and $R_{\alpha\beta}$ is the distance between the two nuclei α and β.

The normalized wave functions of A and B are assumed to be represented by means of Slater determinants which are composed of orthonormal spin orbitals with LCAO–MO spatial functions. The MO's of each system are made SCF with respect to the isolated ground-state molecule by the usual procedure, introduced by Roothaan (Roothaan, 1951). The excited and charge-transferred configurations may be written by the use of unoccupied MO's corresponding to the nonrealistic roots of the Fock–Roothaan equations for the ground state.

The spatial parts of LCAO–MO's are given by

$$a(1) = \sum_t C_t t(1) \qquad \text{for the system A}$$

and (3)

$$b(1) = \sum_u C_u u(1) \qquad \text{for the system B,}$$

where t and u are the AO's belonging to the nuclei of A and B, respectively. Here all functions can be taken real.

The occupied and unoccupied MO's in the ground state are distinguished as shown in Fig. 2. The wave function for ${}^1\Psi_{i\to l}$, for instance, is represented by

$$\begin{aligned}2^{-1/2}\{&\mathscr{N}\mathscr{A}[a_1\bar{a}_1a_2\bar{a}_2\cdots a_{i-1}\bar{a}_{i-1}a_i\,a_{i+1}\bar{a}_{i+1}\cdots a_n\bar{a}_n b_1\bar{b}_1\cdots b_m\bar{b}_m\bar{b}_l]\\ &-\mathscr{N}\mathscr{A}[a_1\bar{a}_1a_2\bar{a}_2\cdots a_{i-1}\bar{a}_{i-1}\bar{a}_i\,a_{i+1}\bar{a}_{i+1}\cdots a_n\bar{a}_n b_1\bar{b}_1\cdots b_m\bar{b}_m b_l]\},\end{aligned} \tag{4}$$

where $\mathscr{N}\mathscr{A}$ signifies the normalization–antisymmetrization operator and the nonbarred and barred MO's represent the spin orbitals with spin function of α and β, respectively. The number of doubly occupied MO's of A and B in Ψ_0 state are denoted by n and m, respectively.

The ground-state energy of the combined system of A and B is given by the lowest root of the secular equation

$$\begin{vmatrix} H_{0,0}-E & H_{0,p}-S_{0,p}E & \cdots \\ H_{p,0}-S_{p,0}E & H_{p,p}-E & \cdots \\ \vdots & \vdots & \vdots \end{vmatrix} = 0, \tag{5}$$

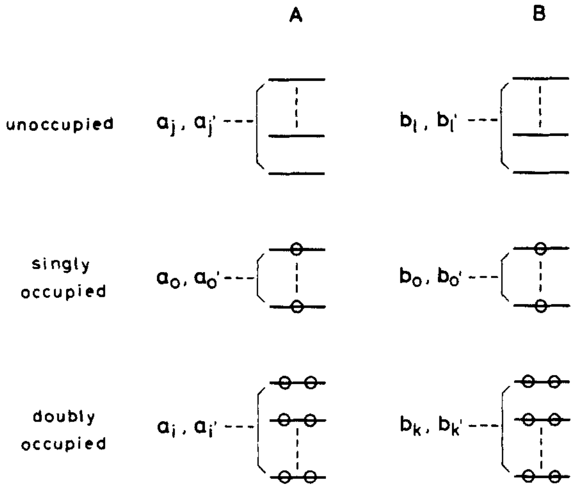


Fig. 2. MO's of the isolated systems A and B.

where

$$H_{p,p'} = \int \Psi_p^* H \Psi_{p'} \, d\tau, \qquad S_{p,p'} = \int \Psi_p^* \Psi_{p'} \, d\tau.$$

If the integrals $S_{p,p'}$ and $H_{p,p'}$ $(p \neq p')$ are small, W can be approximately expanded in the form:

$$W = H_{0,0} - \left(\sum_{p}^{\text{monotr}} + \sum_{p}^{\text{monoex}} + \sum_{p}^{\text{ditr}} + \sum_{p}^{\text{diex}} + \cdots \right) \times \frac{|H_{0,p} - S_{0,p} H_{0,0}|^2}{H_{p,p} - H_{0,0}} + \cdots. \qquad (6)$$

On the basis of an assumption that the interaction between A and B is not yet very strong, we employ only monotransferred and monoexcited electron configurations.

Then, the singlet interaction energy, ΔW between two closed-shell systems is given by

$$\Delta W \cong \varepsilon_0 - D - \pi, \qquad (7)$$

where

$$\varepsilon_0 = H_{0,0} - (W_{A0} + W_{B0}), \qquad (8)$$

$$D = \sum_{i}^{\text{occ}} \sum_{l}^{\text{uno}} \frac{|H_{0,i\to l} - S_{0,i\to l} H_{0,0}|^2}{H_{i\to l,i\to l} - H_{0,0}} + \sum_{k}^{\text{occ}} \sum_{j}^{\text{uno}} \frac{|H_{0,k\to j} - S_{0,k\to j} H_{0,0}|^2}{H_{k\to j,k\to j} - H_{0,0}}, \tag{9}$$

and

$$\pi = \sum_{i}^{\text{occ}} \sum_{j}^{\text{uno}} \frac{|H_{0,i\to j} - S_{0,i\to j} H_{0,0}|^2}{H_{i\to j,i\to j} - H_{0,0}} + \sum_{k}^{\text{occ}} \sum_{l}^{\text{uno}} \frac{|H_{0,k\to l} - S_{0,k\to l} H_{0,0}|^2}{H_{k\to l,k\to l} - H_{0,0}}. \tag{10}$$

The first-order interaction energy ε_0 can be divided into two terms, the Coulomb interaction energy ε_Q, and the exchange interaction energy ε_K:

$$\varepsilon_0 = \varepsilon_Q + \varepsilon_K \tag{11}$$

in which

$$\varepsilon_Q \cong 2 \sum_i V_{\mathrm{B}ii} + 2 \sum_k V_{\mathrm{A}kk} + 4 \sum_i \sum_k (ii|kk) + \sum_\alpha \sum_\beta Z_\alpha Z_\beta / R_{\alpha\beta} \tag{12}$$

and

$$\begin{aligned} \varepsilon_K \cong {} & -2 \sum_i \sum_k [(ik|ki) + s_{ik} V_{ik} + \sum_{i'} s_{ik}\{2(ik|i'i') - (ii'|i'k)\} \\ & + \sum_{k'} s_{ik}\{2(ik|k'k') - (ik'|k'k)\}], \end{aligned} \tag{13}$$

where

$$\begin{aligned} V_{\mathrm{B}ii} &= \int a_i(1) V_{\mathrm{B}}(1) a_i(1)\, dv(1) \\ V_{ik} &= \int a_i(1) V(1) b_k(1)\, dv(1) \\ (ij|kl) &= \iint a_i(1) b_k(2) r_{12}^{-1} a_j(1) b_l(2)\, dv(1)\, dv(2) \\ s_{ik} &= \int a_i(1) b_k(1)\, dv(1), \end{aligned}$$

If we employ the Mulliken approximation (Mulliken, 1949), we have

$$\varepsilon_Q \cong \sum_t N_{\mathrm{A}t} v_{\mathrm{B}tt} + \sum_u N_{\mathrm{B}u} v_{\mathrm{A}uu} + \sum_t \sum_u N_{\mathrm{A}t} N_{\mathrm{B}u} (tt|uu) + \sum_\alpha \sum_\beta Z_\alpha Z_\beta / R_{\alpha\beta}, \tag{14}$$

where

$$N_{At} = 2\sum_{i}^{\text{occ}}\sum_{t'} C_t^{(i)}C_{t'}^{(i)}\, s_{tt'},$$

$$v_{Btt} = \int t(1)V_B(1)t(1)\, dv(1) = \sum_{\beta} v_{\beta tt},$$

$$s_{tt'} = \int t(1)t'(1)\, dv(1),$$

$$v_{\beta tt} = -\int t(1)\,\frac{Z_\beta}{r_{1\beta}}\,t(1)\, dv(1),$$

$$(tt\,|\,uu) = \iint t(1)u(2)r_{12}^{-1}t(1)u(2)\, dv(1)\, dv(2).$$

Further approximations which put

$$v_{\beta tt} \cong -Z_\beta/R_{\alpha\beta}, \qquad (tt\,|\,uu) \cong 1/R_{\alpha\beta},$$

lead to a succinct expression of ε_Q

$$\varepsilon_Q \cong \sum_\alpha\sum_\beta \frac{(Z_\alpha - N_\alpha)(Z_\beta - N_\beta)}{R_{\alpha\beta}}, \tag{15}$$

where

$$N_\alpha = \sum_t^{(\alpha)} N_{At}.$$

Equation (15) is convenient to interpret the physical meaning of the Coulomb interaction energy. The Coulomb term is important at the initial stage of interaction in polar reactions, while not in neutral, nonpolar systems.

The exchange interaction term ε_K is usually positive in the ground-state interaction except for the singlet interaction between two ground-state odd electron systems.

The polarization energy π is not usually important, since the Brillouin theorem (Brillouin, 1933, 1934) makes the $H_{0,p}$ values for monoexcited configurations small. If it is assumed that $H_{0,p}$ is almost linear with $S_{0,p}$, the numerator of the delocalization energy D will possess magnitudes of the order of s_{ab}^2 (s_{ab} implies the overlap integral between an MO of A and an MO of B) for monotransferred configurations, while that of the polarization energy π will have the order of s_{ab}^4 for monoexcited configurations.

The denominator of D can usually be sufficiently small for monotransferred terms, in comparison with that of π for monoexcited terms, so that the delocalization energy is supposed to be more important than the polarization energy in determining the favorable position and spatial direction of mutual approach of reagent and reactant in the majority of chemical reactions.

Murrell and collaborators (1965) extended the theory of long-range forces to the region of small orbital overlap and represented the interaction energy as the combined sum of the five energy terms: Coulomb, exchange, induction, dispersion, and charge-transfer interaction energies.

III. Charge-Transfer Interaction in Chemical Reactions

Let us consider the delocalization energy D in some detail. The denominator of D is given by

$$H_{i\to l,\, i\to l} - H_{0,0} \cong -(E_{\mathrm{B}l} + \Delta E_{\mathrm{B}l}) + (I_{\mathrm{A}i} + \Delta I_{\mathrm{A}i}) + a_{il} \tag{16}$$

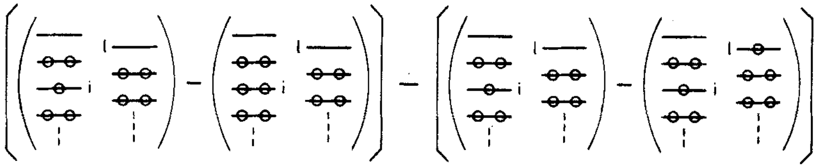
in which

$$\begin{aligned}
E_{\mathrm{B}l} &= -\left[H_{\mathrm{B}ll} + \sum_k \{2(ll\,|\,kk) - (lk\,|\,kl)\}\right] \\
\Delta E_{\mathrm{B}l} &= -\left\{V_{\mathrm{A}ll} + 2\sum_{i'} (ll\,|\,i'i')\right\} + \sum_{i'} \{V_{li'} s_{li'} + (li'\,|\,i'l)\} \\
I_{\mathrm{A}i} &= -\left[H_{\mathrm{A}ii} + \sum_{i'} \{2(ii\,|\,i'i') - (ii'\,|\,i'i)\}\right] \\
\Delta I_{\mathrm{A}i} &= -\left\{V_{\mathrm{B}ii} + 2\sum_k (ii\,|\,kk)\right\} + \sum_k \{V_{\mathrm{i}k} s_{ik} + (ik\,|\,ki)\} \\
a_{il} &= -(ii\,|\,ll) + 2\{V_{il} s_{il} + (il\,|\,li)\} \\
H_{\mathrm{A}ii} &= \int a_i(1) H_{\mathrm{A}}(1) a_i(1)\, dv(1) \\
H_{\mathrm{A}}(1) &= -\tfrac{1}{2}\Delta(1) + V_{\mathrm{A}}(1)
\end{aligned}$$

$I_{\mathrm{A}i}$ is the vertical ionization potential of the isolated system A with respect to the electron in the ith MO and $E_{\mathrm{B}l}$ is the vertical electron affinity of the isolated system B with respect to the lth MO (Koopmans, 1933). By the aid of the schematic diagrams given in the equations, the denominator of D can be written in the following form:

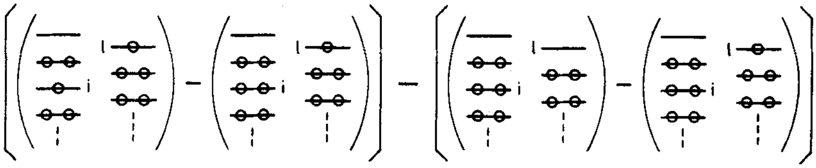
$$H_{i\to l,\, i\to l} - H_{0,0}$$

$=$



$$= I_{Ai}^{(B)} - E_{Bl}^{(A-i)}$$

$=$



$$= I_{Ai}^{(B+l)} - E_{Bl}^{(A)}$$

where $I_{Ai}^{(B+l)}$ is the value of I_{Ai} in the case of the approach of the system B with an additional electron occupying the lth originally unoccupied MO, and where $E_{Bl}^{(A-i)}$ is the value of E_{Bl} in the case of the approach of the system A in which one electron occupying the ith MO is subtracted.

Now we consider the case in which two neutral systems interact with each other. As mentioned above, $I_{Ai}^{(B)}$ represents the ionization potential of the ith MO of the reactant A in the neutral field of the reactant B. Therefore, $I_{Ai}^{(B)}$ may not differ so much from I_{Ai}. $E_{Bl}^{(A-i)}$ is the electron affinity of the lth MO of the reactant B under the influence of the cationic species A of which the electron in the ith MO is subtracted. Thus, $E_{Bl}^{(A-i)}$ may be much greater than E_{Bl}. This implies that the denominator of D can be small in comparison with $I_{Ai} - E_{Bl}$.

Next we take the case in which one of the reactants is an ionic system. When the reactant A is an anion, $E_{Bl}^{(A-i)}$ may be close to E_{Bl}, since the system A of which an electron in the ith MO is subtracted is electronically neutral, while $I_{Ai}^{(B)}$ may be much smaller than that of a neutral system. If the reactant B is a cationic species, $E_{Bl}^{(A)}$ may be greater than that in a neutral system, although $I_{Ai}^{(B+l)}$ is supposed to be close to I_{Ai}.

In any event the denominator of the delocalization term D is considered to be small enough in comparison with the values of $I_{Ai} - E_{Bl}$ of neutral systems. This indicates that the denominator corresponding to the term of

D in which i is the highest occupied (HO) MO of electron donating system and l is the lowest unoccupied (LU) MO of electron accepting system could be considerably small in comparison with the denominators of other terms. In some cases, like ones where the reactant A is an anion and the reagent B is a cation, the quantity, $I_{Ai}^{(B)} - E_{Bl}^{(A-i)}$, happens to be zero. In such an event, the delocalization interaction energy D can be approximated by the first-order equation

$$D \cong |H_{0,\mathrm{HO}\to\mathrm{LU}} - S_{0,\mathrm{HO}\to\mathrm{LU}} H_{0,0}|. \tag{17}$$

Even in not exactly degenerate cases, the HOMO–LUMO interaction term is usually sufficiently large, so that the one-term approximation as given in the following equation is valid:

$$D \cong \frac{|H_{0,\mathrm{HO}\to\mathrm{LU}} - S_{0,\mathrm{HO}\to\mathrm{LU}} H_{0,0}|^2}{H_{\mathrm{HO}\to\mathrm{LU},\mathrm{HO}\to\mathrm{LU}} - H_{0,0}}. \tag{18}$$

IV. Charge-Transfer Interaction and Molecular Deformation

As reaction proceeds, the geometries of reactant and reagent will change. The molecular deformation is usually conspicuous in the neighborhood of the reaction center, while the residual part of the molecule stays almost unchanged. How the direction of molecular deformation is determined is most easily understood by the following simple consideration. When we employ the simple Hückel MO method (Hückel, 1931) for hydrocarbon systems, the following relation holds with respect to the rth AO (Fukui and Fujimoto, 1969b)

$$\sum_{s}^{\mathrm{nei}} C_r^{(i)} C_s^{(i)} = \frac{\alpha - \varepsilon_i}{(-\beta)} (C_r^{(i)})^2, \tag{19}$$

where α is the Coulomb integral, β is the resonance integral and $\sum_s^{\mathrm{nei}}$ implies the summation over all the neighboring AO's of the rth AO. As usual, the energies of the occupied orbitals are lower than α, while those of the unoccupied orbitals are higher than α. Therefore, $\sum_s^{\mathrm{nei}} C_r^{(i)} C_s^{(i)}$ is positive for occupied MO's and is negative for unoccupied MO's. This implies that the electron donation from the ith occupied MO and the electron acceptance in the jth MO will cause the bond weakening of the AO r with the neighboring AO's. Equation (19) also indicates that the weakening of the bond with the neighboring AO's due to the charge-transfer interaction is parallel to the magnitudes of $(C_r^{(i)})^2$ and $(C_r^{(j)})^2$. In general, the HOMO and

LUMO have maximum partial electron density at the atom where reaction takes place dominantly. In other words, the position that has the largest value of $(C_r^{(HO)})^2$ or $(C_r^{(LU)})^2$ is at the same time the position where weakening of the bonds with the neighboring AO's is most striking. The decrease in bond order will be the source of bond loosening, which is represented in terms of the decrease in the magnitude of the resonance integral β. The increase in the absolute value of the resonance integral will cause the lowering of bonding levels and the elevation of antibonding levels. On the other hand, the decrease in the absolute value of the resonance integral will bring the elevation of bonding levels and the lowering of antibonding levels. A typical example is given in the Diels–Alder addition of a diene and a dienophile (Fig. 3). As is clear from Fig. 4, the contribution of terms

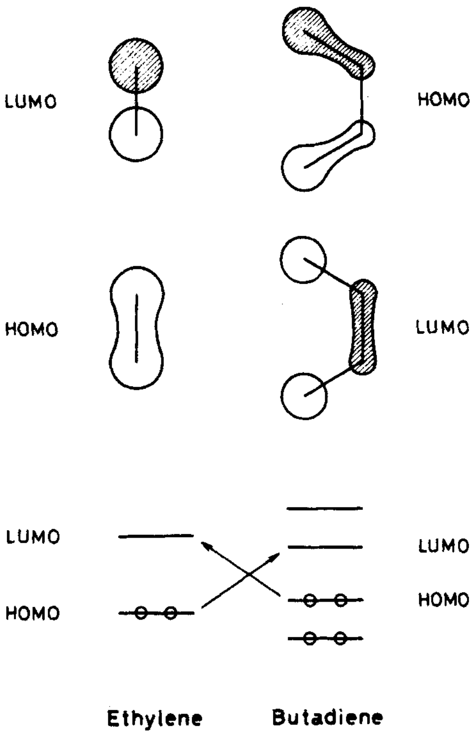


Fig. 3. Mode of orbital interaction between ethylene and butadiene (hatched and non-hatched areas indicate the plus and minus parts of a real MO).

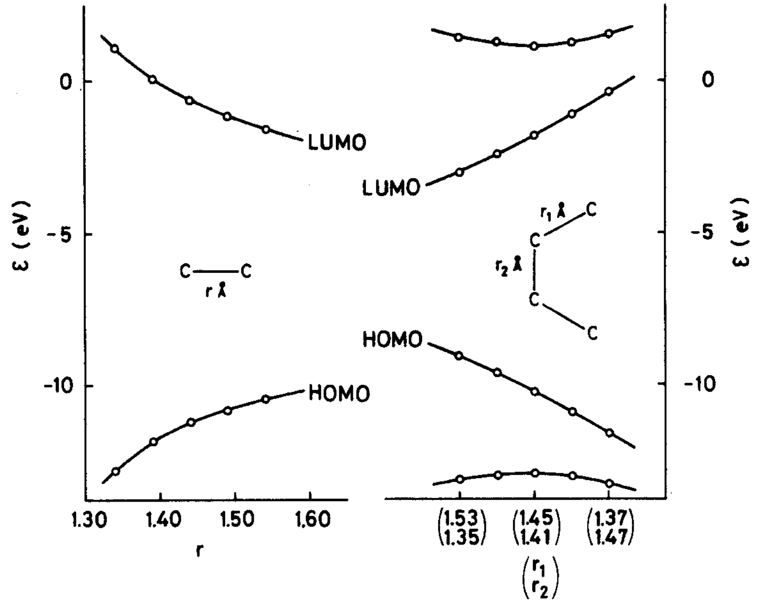


Fig. 4. Changes in MO energies due to deformation (calculated by Pariser–Parr–Pople method).

corresponding to the charge-transfer interaction between HOMO of diene and LUMO of dienophile and that between HOMO of dienophile and LUMO of diene will be enhanced by the molecular deformation with the progress of the reaction. Such changes in MO levels due to the molecular deformation with mutual charge-transfer are supposed to be a general feature of chemical reactions, and may be even more conspicuous in aliphatic systems. In Fig. 5 is shown the case of LUMO of methyl chloride due to the loosening of the C–Cl bond in S_N2 reaction.

Here we may say a general conclusion of chemical interaction that charge-transfer will cause the bond interchange which brings the lowering of LUMO and the elevation of HOMO, in turn, promoting further charge-transfer interaction. This relation is easily understood by Eq. (18). Thus, the role of the charge-transfer between HOMO and LUMO will be more and more dominant over other terms with the progress of reaction.

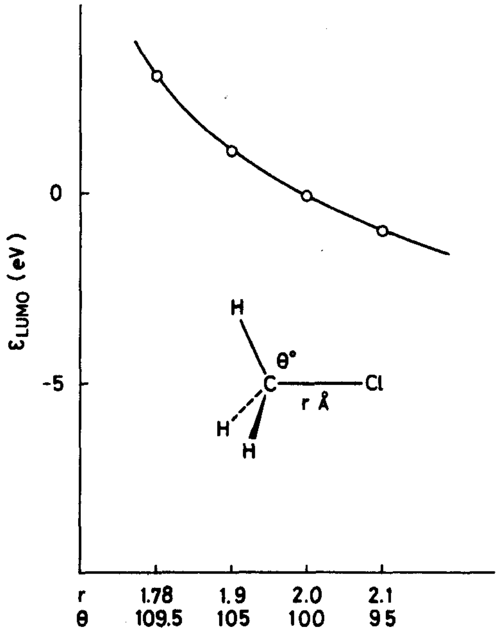


Fig. 5. Change in LUMO energy due to deformation (calculated by a semiempirical SCF MO method).

V. Charge-Transfer Interaction and Orientation

A. Singlet Interaction between Two Closed-Shell Systems

The numerator of Eq. (9) is given by

$$H_{0,i\to l} - S_{0,i\to l}H_{0,0} \cong 2^{1/2}\Big[V_{Bil} + 2\sum_k (il|kk) - s_{il}\Big\{V_{Bii} + 2\sum_k (ii|kk)\Big\} - \sum_k \{(ik|kl) - s_{il}(ik|ki)\}\Big], \tag{20}$$

which is approximately rewritten in the following form for multicentric interactions through paired orbital overlappings of the *r*th AO of A and the *r*′th AO of B

$$H_{0,i\to l} - S_{0,i\to l}H_{0,0} \cong 2^{1/2}\sum_r C_r^{(i)}C_{r'}^{(l)}\gamma_{rr'}^{(i)}, \tag{21}$$

where

$$\begin{aligned}\gamma_{rr'}^{(i)} &\cong s_{rr'}\Biggl[\tfrac{1}{2}(v_{\mathrm{B}rr}+v_{\mathrm{B}r'r'})+\tfrac{1}{2}\sum_{u}N_{\mathrm{B}u}\{(rr\,|\,uu)\\&\qquad+(r'r'\,|\,uu)\}+\sum_{\alpha}\sum_{\beta}\frac{n_{\alpha}^{(ii)}(Z_{\beta}-N_{\beta})}{R_{\alpha\beta}}\Biggr],\\&\cong-\int r(1)\Biggl(\sum_{\beta}\frac{Z_{\beta}-N_{\beta}}{r_{1\beta}}\Biggr)r'(1)\,dv(1)\\&\qquad+s_{rr'}\sum_{\alpha}\sum_{\beta}\frac{n_{\alpha}^{(ii)}(Z_{\beta}-N_{\beta})}{R_{\alpha\beta}},\end{aligned}$$

in which

$$n_{\alpha}^{(ii)}=\sum_{t}^{(\alpha)}\sum_{t'}C_{t}^{(i)}C_{t'}^{(i)}s_{tt'}\,.$$

Thus, we obtain an approximate expression for D

$$D\cong 2\left\{\sum_{i}^{\mathrm{occ}}\sum_{l}^{\mathrm{uno}}\frac{(\sum_{r}C_{r}^{(i)}C_{r'}^{(l)}\gamma_{rr'}^{(i)})^{2}}{I_{\mathrm{A}i}^{(\mathrm{B})}-E_{\mathrm{B}l}^{(\mathrm{A}-i)}}+\sum_{k}^{\mathrm{occ}}\sum_{j}^{\mathrm{uno}}\frac{(\sum_{r}C_{r}^{(j)}C_{r'}^{(k)}\gamma_{rr'}^{(k)})^{2}}{I_{\mathrm{B}k}^{(\mathrm{A})}-E_{\mathrm{A}j}^{(\mathrm{B}-k)}}\right\}. \tag{22}$$

1. Single-Centric Interactions

We consider the case of a single-centric interaction between the rth AO of the reactant A and the r'th AO of a reagent B. If we assume that the reagent B has only one AO, we have, when the reagent orbital is unoccupied,

$$D\cong 2\sum_{i}^{\mathrm{occ}}\frac{(C_{r}^{(i)})^{2}}{\varepsilon_{\mathrm{B}}-\varepsilon_{\mathrm{A}i}}\,{\gamma_{r}}^{2},$$

$$\gamma_{r}=C_{r'}^{(l)}\gamma_{rr'}^{(i)},\qquad \varepsilon_{\mathrm{A}i}=-I_{\mathrm{A}i}^{(\mathrm{B})},\qquad \varepsilon_{\mathrm{B}}=-E_{\mathrm{B}}^{(\mathrm{A}-i)}; \tag{23}$$

and, when the reagent orbital is occupied,

$$D\cong 2\sum_{j}^{\mathrm{uno}}\frac{(C_{r}^{(j)})^{2}}{\varepsilon_{\mathrm{A}j}-\varepsilon_{\mathrm{B}}}\,\gamma_{r}'^{2},$$

$$\gamma_{r}'=C_{r'}^{(k)}\gamma_{rr'}^{(k)},\qquad \varepsilon_{\mathrm{A}j}=-E_{\mathrm{A}j}^{(\mathrm{B}-k)},\qquad \varepsilon_{\mathrm{B}}=-I_{\mathrm{B}}^{(\mathrm{A})}.$$

The quantities in Eq. (23) lead to the reactivity indices, superdelocalizability (Fukui *et al.*, 1954b, 1957), and delocalizability (Fukui *et al.*, 1961) defined for unsaturated compounds, and saturated compounds respectively. A good correlation between calculated reactivity indices and experimental observations can be found in a number of articles (Fukui, 1964, 1965a, 1970a, b; Streitwieser, 1961).

If we employ the one-term approximation as Eq. (17), we can compare the chemical reactivity of each AO only by $(C_r^{(i)})^2$, provided the integral $\gamma_{rr}^{(i)}$ is almost constant with respect to any r. The chemical reactivity index, frontier electron density, f_r, is defined under such a condition (Fukui *et al.*, 1952, 1954a):

$$\begin{aligned} f_r^{(\mathrm{E})} &= 2(C_r^{(\mathrm{HO})})^2 \quad \text{for electrophilic reactions,} \\ f_r^{(\mathrm{N})} &= 2(C_r^{(\mathrm{LU})})^2 \quad \text{for nucleophilic reactions.} \end{aligned} \tag{24}$$

A good parallelism has been found between this index and experimental results (see Fig. 6).

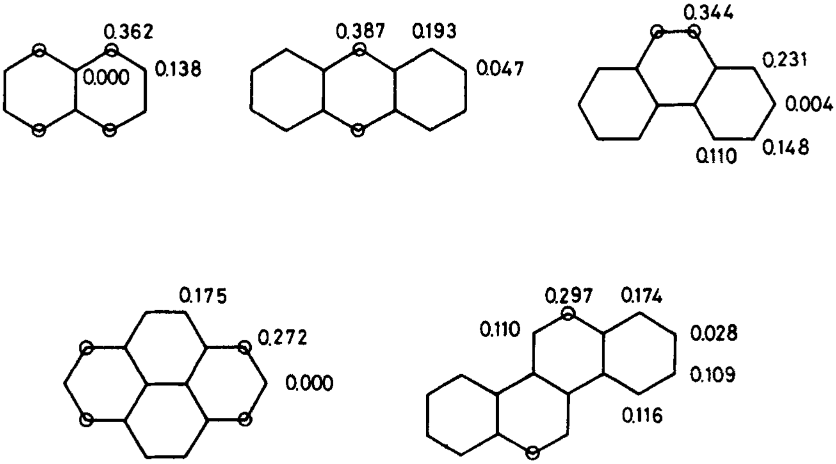


Fig. 6. Frontier electron densities in some aromatics (calculated by simple Hückel method; circles indicate the positions of electrophilic reactions.)

Further we show some results applied for aliphatic compounds. One of typical reactions of aliphatic systems is the abstraction of hydrogen by nucleophiles. In Fig. 7 are shown the frontier electron densities of hydrogens toward a nucleophile (Fukui and Fujimoto, 1965).

In ethyl chloride and 2-chlorobutane, the β-hydrogen which is trans to the leaving nucleophile has the largest value of reactivity index among various hydrogens. According to the well-known Saytzeff rule, *trans-β*-hydrogen should be more reactive toward an attacking nucleophile than *trans-β'*-hydrogen (Saytzeff, 1875). The calculated result is in accordance with experiments. In case of 2-exo-bromonorbornane, exo-cis elimination has been reported to take place (Kwart *et al.*, 1964). The indices show a fair

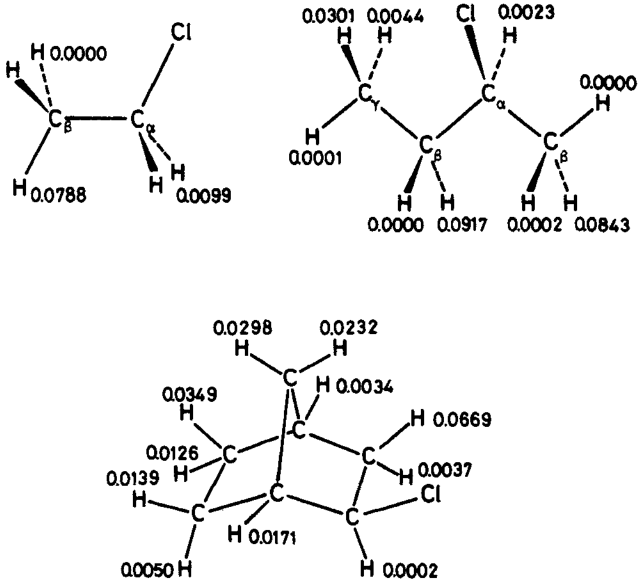


Fig. 7. Frontier electron densities of hydrogens in some chlorinated hydrocarbons for nucleophilic attack (calculated by extended Hückel method).

success. Thus, we may say that the reactivity indices, frontier electron density, and, of course, superdelocalizability, can be measures in discussing the favorable position of chemical reactions in the frame of the isolated molecule approximation.

The frontier electron density f_r of the most reactive position often becomes larger as it becomes isolated from the neighboring AO's. Therefore, the one-term approximation of D as given by Eq. (18) becomes more and more valid with the progress of reaction.

2. *Multicentric Interactions*

The most familiar of multicentric interactions is the two-centric case. In this case, we have

$$D \cong 2^{1/2} | C_r^{(\mathrm{HO})} C_{r'}^{(\mathrm{LU})} \gamma_{rr'} + C_s^{(\mathrm{HO})} C_{s'}^{(\mathrm{LU})} \gamma_{ss'} |,$$

or

$$D \cong 2^{1/2} | C_r^{(\mathrm{LU})} C_{r'}^{(\mathrm{HO})} \gamma'_{rr'} + C_s^{(\mathrm{LU})} C_{s'}^{(\mathrm{HO})} \gamma'_{ss'} |. \qquad (25)$$

Each spatial function has an arbitrary factor +1 or −1. Therefore, the signs of $C_r^{(i)}$ and $C_{r'}^{(l)}$ are not definite. However, once, we assign +1 or −1 to $C_r^{(i)}$ and $C_{r'}^{(l)}$, the values of $C_s^{(i)}$ and $C_{s'}^{(l)}$ are uniquely determined. Here we may have two cases. The one is the case where $C_r^{(i)}C_{r'}^{(l)}$ and $C_s^{(i)}C_{s'}^{(l)}$ have the same sign, and the other is the case in which the two quantities have different signs. In order to make the energy stabilization D large, we have the following relations (see Fig. 8):

number of electrons forming a cycle	favorable reaction path
$4n$	$\text{sign}(\gamma_{rr'}) = -\text{sign}(\gamma_{ss'})$
$4n+2$	$\text{sign}(\gamma_{rr'}) = \text{sign}(\gamma_{ss'})$

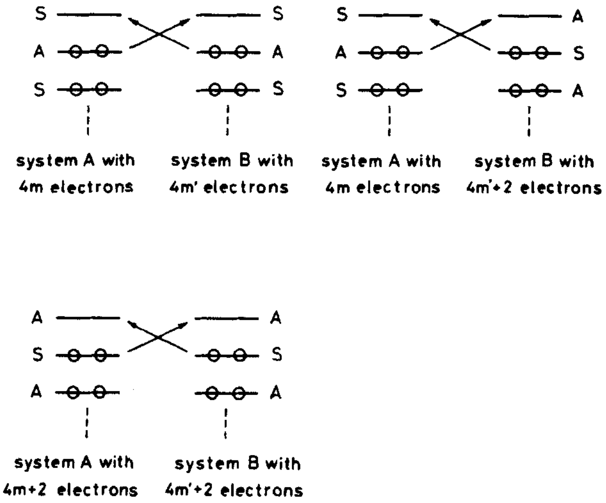


Fig. 8 Mode of orbital interaction in thermal reactions of two open chains (S and A denote symmetric and antisymmetric MO's).

The case $\text{sign}(\gamma_{rr'}) = \text{sign}(\gamma_{ss'})$ corresponds to the Hückel cycle, and the case $\text{sign}(\gamma_{rr'}) = -\text{sign}(\gamma_{ss'})$ to the anti-Hückel cycle. The latter is often referred as the Möbius strip conjugation (Heilbronner, 1964; Zimmerman, 1966). Various examples of pericyclic interactions can be found in many articles (Gill, 1968; Anh, 1970). A most typical example may be found in Diels–Alder reactions. Figure 3 shows that the HOMO–LUMO interaction favors Hückel interaction. Hoffmann and Woodward discussed the exo–endo selectivity in this reaction regarding the interaction between a diene and a dienophile three-centric with respect to both of the two (Hoffmann and Woodward, 1965). Herndon and Hall (Herndon and Hall, 1967) treated this problem from a different viewpoint.

B. Doublet Interaction between a Closed-Shell System and an Open-Shell System

When one of the two interacting species, say B, is an odd electron system, having a singly occupied (SO) MO b_o, we have the following equation instead of Eq. (22)

$$D \cong 2\left\{\sum_i^{\text{occ}}\sum_l^{\text{uno}} \frac{(\sum_r C_r^{(i)}C_{r'}^{(l)}\gamma_{rr'}^{(i)})^2}{I_{\mathrm{A}i}^{(\mathrm{B})} - E_{\mathrm{B}l}^{(\mathrm{A}-i)}} + \sum_k^{\text{occ}}\sum_j^{\text{uno}} \frac{(\sum_r C_r^{(j)}C_{r'}^{(k)}\gamma_{rr'}^{(k)})^2}{I_{\mathrm{B}k}^{(\mathrm{A})} - E_{\mathrm{A}j}^{(\mathrm{B}-k)}}\right\}$$
$$+ \left\{\sum_i^{\text{occ}} \frac{(\sum_r C_r^{(i)}C_{r'}^{(o)}\gamma_{rr'}^{(i)})^2}{I_{\mathrm{A}i}^{(\mathrm{B})} - E_{\mathrm{B}o}^{(\mathrm{A}-i)}} + \sum_j^{\text{uno}} \frac{(\sum_r C_r^{(j)}C_{r'}^{(o)}\gamma_{rr'}^{(o)})^2}{I_{\mathrm{B}o}^{(\mathrm{A})} - E_{\mathrm{A}j}^{(\mathrm{B}-o)}}\right\} \tag{26}$$

This equation is represented in terms of the restricted open-shell MO's with respect to the reagent B. If the reagent B has only one AO r', we have

$$D \cong \sum_i^{\text{occ}} \frac{(C_r^{(i)})^2}{\varepsilon_\mathrm{B} - \varepsilon_{\mathrm{A}i}} \gamma_r{}^2 + \sum_j^{\text{uno}} \frac{(C_r^{(j)})^2}{\varepsilon_{\mathrm{A}j} - \varepsilon_\mathrm{B}'} \gamma_r'^2 \tag{27}$$

in which ε_B is $(-E_{\mathrm{B}o}^{(\mathrm{A}-i)})$ and ε_B' is equal to $(-I_{\mathrm{B}o}^{(\mathrm{A})})$. This equation is interesting because it implies that, even in the interaction of a neutral molecule with a neutral radical, the magnitude of D depends on the local charge of atoms through γ_r and γ_r'. The frontier electron density for radical attack is defined by (Fukui *et al.*, 1954a)

$$f_r^{(\mathrm{R})} = (C_r^{(\mathrm{HO})})^2 + (C_r^{(\mathrm{LU})})^2. \tag{28}$$

In Fig. 9 are shown $f_r^{(\mathrm{R})}$ values of hydrogens of 2-methyl butane. The calculated results indicate that the tertiary hydrogen is the most reactive and the secondary hydrogens are next reactive, in agreement with experimental results.

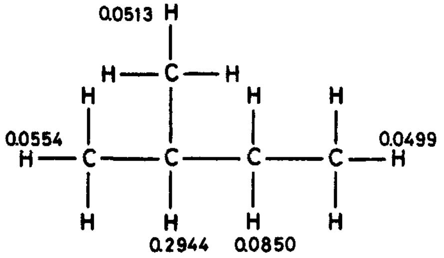


Fig. 9. Frontier electron densities of hydrogens in 2-methyl butane for radical attack (calculated by CNDO/2 method).

C. Singlet Interaction between a Closed-Shell System and an Open-Shell System

In photoinduced reactions, one or both of two reactants have excited open-shell configurations. We suppose here that the lowest excited electronic state is concerned in the reaction. Although some modifications will be necessary, the essential feature of the interaction energy will be not different from thermal reactions. We must employ monoexcited or diexcited electron configuration as Ψ_0. Therefore, the summation over monotransferred and monoexcited configurations should be made with respect to Ψ_0 with an excited configuration. In the case of interaction between a closed-shell system and a singlet-excited system, the most contributing term among the various orbital overlapping interaction terms will be as

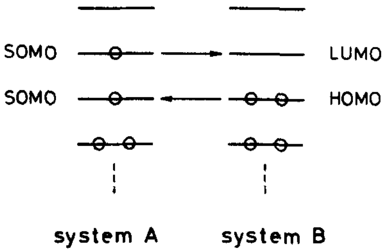


Fig. 10. Mode of orbital interaction in photochemical reactions.

shown in Fig. 10. In this case the delocalization interaction energy D may be given in the first-order form

$$D \cong \left\{ \left(\sum_r C_r^{(\mathrm{SO})} C_{r'}^{(\mathrm{HO})} \gamma_{rr'} \right)^2 + \left(\sum_r C_r^{(\mathrm{SO'})} C_{r'}^{(\mathrm{LU})} \gamma'_{rr'} \right)^2 \right\}^{1/2}. \tag{29}$$

Frequently, one of these two has a greater importance than the other

$$D \cong \left| \sum_r C_r^{(\mathrm{SO})} C_{r'}^{(\mathrm{HO})} \gamma_{rr'} \right| \quad \text{or} \quad D \cong \left| \sum_r C_r^{(\mathrm{SO'})} C_{r'}^{(\mathrm{LU})} \gamma'_{rr'} \right|. \tag{30}$$

If we apply the above discussion to two-centric interactions, we have a different selection rule for pericyclic interactions from that for thermal reactions:

number of electrons forming a cycle	favorable reaction path
$4n$	sign $(\gamma_{rr'})$ = sign $(\gamma_{ss'})$
$4n+2$	sign $(\gamma_{rr'}) = -$sign $(\gamma_{ss'})$

Application of this rule to pericyclic interactions, such as photochemical ring-closure of open-chain systems, ring-opening of cyclic conjugated systems, cycloaddition of two conjugated systems, etc., gives the same result as was proposed by Woodward and Hoffmann (Woodward and Hoffmann, 1965).

Photochemical cycloaddition of carbonyl compounds with olefins was discussed by Herndon and Giles (Herndon and Giles 1970), using simple Hückel perturbational MO method.

D. Singlet Interaction between Two Open-Shell Systems

Another class of chemical interaction is that between two odd electron systems. One of the most important characteristics is that the singlet interaction between two doublet systems is facilitated by the negative exchange interaction energy ε_K. The most typical example is the interaction between two hydrogen atoms to form a hydrogen molecule. The well-known result indicates that the exchange interaction energy ε_K is responsible for the multiplet separation, making the singlet interaction stabilized. In usual interaction between two radicals, however, the delocalization interaction is also important. The transition state of the Cope rearrangement of 1,5-hexadiene may be regarded as a cyclic interaction between two allyls (Hoffmann and Woodward, 1965; Fukui and Fujimoto, 1966b; Simonetta *et al.*, 1968). The interaction between two SO levels will make such a cyclic transition state possible, while the interaction between HOMO and LUMO makes the chair-form transition state more favorable than the boat-form one (see Fig. 11).

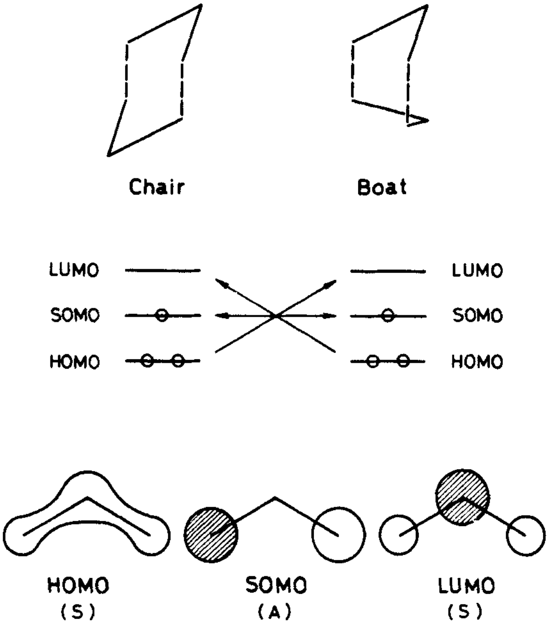


Fig. 11. Mode of orbital interaction in Cope rearrangement.

VI. Intramolecular Reactions

Recently, some theoretical approaches to unimolecular reactions have been developed (Bader, 1960, 1962; Pearson, 1969, 1970; Salem, 1969a,b; Trindle and Sinanoğlu, 1969; Trindle, 1970). Salem made an elegant generalization, connecting the symmetry of an excited electronic state with that of the nuclear configuration change along the reaction path. Trindle devised a general procedure to correlate the wave functions of the initial and the final systems of unimolecular reactions.

If we employ a localized bond orbital model instead of MO's we may apply the theory of chemical interaction developed in the preceding sections to unimolecular reactions (Fukui and Fujimoto, 1969a; Fukui, 1971). Namely, if each orbital is completely localized to each particular bond, we can regard an intramolecular bond interchange as if it were an intermolecular interaction between two fragments of a molecule. The validity of the theory may be evident from Fig. 12.

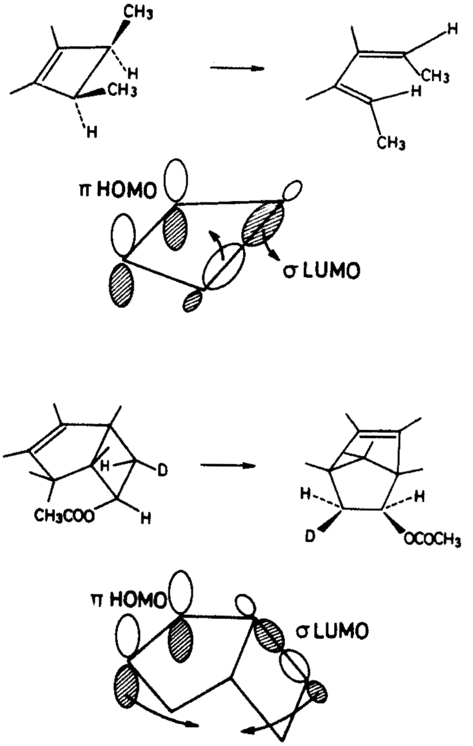


Fig. 12. Mode of HOMO–LUMO interaction in cyclobutene rearrangement (Winter, 1965) and in bicycloheptene rearrangement (Berson, 1968).

VII. Charge-Transfer Interaction and Bond Interchange

As has been discussed in the preceding sections, donation of an electron from HOMO and acceptance of an electron into LUMO cause the change in bond populations which usually conforms to the nuclear configuration change along reaction. The Diels–Alder reaction is an example. The charge-transfer from HOMO and that into LUMO will be responsible for the double bond shift of a diene from 1,2 and 3,4 bond regions to 2,3 bond region, to make possible forming a cyclohexene with a dienophile.

The change in the electron distribution due to the chemical interaction is obtainable from the wave function given by Eq. (1). Density matrix expression may be convenient for this purpose. Mixing of charge-transferred configurations into Ψ_0 can express the bond interchanges in each of two molecules in case of chemical interaction as mentioned above. Further, we have the relation

$$\begin{aligned} M \int \Psi_0{}^*(1, 2, \ldots, M)\, \Psi_{i\to l}(1, 2, \ldots, M)\, d\xi_1 d\tau_2 \cdots d\tau_M \\ \cong 2^{1/2} s_{il} \left\{ 2 \sum_{i'}^{\text{occ}} a_{i'}(1) a_{i'}(1) + 2 \sum_{k}^{\text{occ}} b_k(1) b_k(1) \right\} \\ - 2^{1/2} \left\{ \sum_{i'}^{\text{occ}} a_i(1) a_{i'}(1) s_{i'l} + \sum_{k}^{\text{occ}} b_k(1) b_l(1) s_{ik} - a_i(1) b_l(1) \right\} \end{aligned} \tag{31}$$

and

$$\int a_i(1) b_l(1) dv(1) = s_{il} = \sum_{t}^{\text{A}} \sum_{u}^{\text{B}} C_t^{(i)} C_u^{(l)} s_{tu}. \tag{32}$$

These equations represent that the possibility of finding an electron in the intermolecular region is parallel to the orbital overlapping between the occupied MO's of one molecule and the unoccupied MO's of the other. The quantity $C_0 C_{i\to l} \int \Psi_0{}^* \Psi_{i\to l}\, d\tau$ is positive for the lowest energy state (C_0, $C_{i\to l}$; taken real). The fraction of electrons that is influent into the intermolecular region through the orbital overlapping between the ith occupied MO of A and the lth unoccupied MO of B is supplied from the ith MO of A.

As has been mentioned in the preceding sections, the interaction energy between two systems is partitioned into the Coulomb, exchange, delocalization, and polarization interaction energy terms. In some cases, one of these four, say the Coulomb interaction term, is important (Klopman, 1968; Devaquet and Salem, 1969) and, in some other cases, another term predominates. Our present discussion is directed to the "frontier-controlled" (Klopman, 1968) cases where the delocalization interaction term plays the most dominant role. The mixing of charge-transferred states is of significance not only as a source of stabilization but also as the major origin of the bond interchange in chemical reactions. Of the various charge-transferred configurations, the one in which an electron is transferred from HOMO of one molecule into LUMO of the other molecule is almost solely important. In the reactants that possess SOMO's, these play the part of HOMO or of LUMO, or of both. These particular MO's, HOMO, LUMO, and SOMO may be termed "generalized frontier orbitals" in chemical reactions. When the discussion is applied to the molecular complex formation between an electron donor and an acceptor, our conclusion is in conformity with the "overlap and orientation" principle of Mulliken (Mulliken, 1956). Numerical calculations could supply an interesting result (Fujimoto *et al.*, 1971).

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Unified Treatment of van der Waals Forces between Two Molecules of Arbitrary Sizes and Electron Delocalizations

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I. Introduction

Although several new methods have been advanced in the last decade for treating long-range intermolecular forces, the emphasis has been almost exclusively on the interaction between small molecules for which the electron distribution can be considered localized. The standard formulation for the van der Waals forces is based on two mathematical approximations, a perturbation expansion and a multipole expansion. For small molecules at moderate to large separations, each series may be approximated by the first nonzero term. For nonpolar molecules, that term can be expressed as a function of spatially independent polarizabilities.

The description of the interaction between large molecules is considerably more complicated. If the electrons in the molecules are fairly delocalized, the series expansion may converge too slowly (or not at all) even at large separations, and the interaction cannot be formulated in terms of molecular polarizabilities. For, a perturbation at one point in the molecule causes a response at another point, and the response must be characterized by a spatially dependent susceptibility: The interaction energy will depend on the correlative contributions from different parts of the molecule. On the other hand, if the charge distribution is localized in small units, the dipolar approximation may be reasonable for distances large compared to the unit size, and the intermolecular force could then be formulated in terms of the attraction between individual units in different molecules. Early studies of the forces between large molecules have focused on molecules that fall in the latter category. Pairwise additivity was assumed and the overall attraction was obtained from the ordinary London dispersion formula (London, 1937). For some recent papers (and criticisms) see, e.g. Salem (1962), Zwanzig (1963), and Yasuda (1969). In more recent years several studies were made of the attraction between large molecules containing delocalized electrons (Coulson and Davies, 1952; Haugh and Hirschfelder, 1955; Longuet-Higgins, 1956; Longuet-Higgins and Salem, 1960–1961; Sternlicht, 1964). Most of these dealt with long-chain polyenes. The dipolar approximation was avoided by the use of various devices [e.g., the Tomonaga method (Tomonaga, 1950), the London monopole technique (London, 1942), the Longuet-Higgins charge density formulation (Longuet-Higgins, 1956) or by direct numerical calculation]; all treatments were based on second-order perturbation theory. For a general review of these methods the reader is referred to the treatise on intermolecular forces by Margenau and Kestner (1969).

One of the difficulties in formulating a theory for the attraction between large molecules lies in the fact that the molecules are many-body systems of smaller units (electrons, nuclei, etc.) and thus the intermolecular force has many-body character even when only two molecules are present. Many-body theories, developed over the past two decades, have made it possible to treat realistically a variety of problems in different fields, including intermolecular forces. For a general discussion of some of the methods applied specifically to the interaction between molecules, the reader is referred to the volume "Intermolecular Forces" (1967) of the Advances in Chemical Physics, and also the discussion on "Intermolecular Forces" (1965) of the Faraday Society.

Three general approaches have been adopted to treat the van der Waals forces. In one class, the interaction is formulated in terms of the properties of the individual molecules by considering their charge fluctuations (e.g., Jehle, 1965; Linder, 1964; McLachlan, 1963a,b). In the second class are those theories which treat the material bodies in terms of their collective properties (e.g., Linderberg, 1964; McLachlan *et al.*, 1963–1964; Lundqvist and Sjölander, 1964; Mahan, 1965; Lucas, 1967). These formulations bear close resemblance to the electron gas theories of Nozières and Pines (1958) and Englert and Brout (1960). Like the electron gas theories, they are generally based on a self-consistent-field approximation (e.g., the random phase approximation in the theory of Nozières and Pines; the time-dependent Hartree approximation in the formalism of McLachlan *et al.*). The third class of theories begin by treating parts of the material collectively, and deduce in the limit of very dilute matter an intermolecular force (e.g., Lifshitz, 1956; Dzyaloshinski *et al.*, 1961; Linder, 1962; McLachlan, 1965; Langbein, 1970).

In this paper we present a unified treatment for the interaction between two non-overlapping molecular systems of arbitrary sizes and electron delocalizations. The theory is formulated on the basis of a generalization of the reaction-field technique developed earlier (for a general review, see Linder, 1967) and results are expressed in terms of spatially dependent susceptibilities. The present approach is, in essence, an infinite-order perturbative method which, in the absence of resonance interaction, yields an expression for the interaction (free) energy in terms of the properties of the noninteracting system. A rigorous expression is derived for the second-order free energy at finite temperatures and an approximate closed-form expression is obtained for the perturbation series by invoking the decorrelation approximation (Rhodes and Chase, 1967) which neglects correlations between virtual excitations within each molecule. Special forms are derived for the dipolar approximation and the results are found to agree with previously derived results obtained by other methods. The connection between the reaction-field approach and those formulations based on collective behavior is discussed.

II. Generalized Susceptibility Theory

In this section we review briefly those aspects of generalized susceptibility theory that are pertinent to the present work (for extensive reviews see, e.g., Bernard and Callen, 1959; Kubo, 1966). Generalized susceptibility theory (also called response theory), is a form of time dependent perturbation theory. The generalized susceptibility of a system characterizes its response to a particular kind of disturbance. The response is defined as the difference between the average value of an observable with and without the perturbation. The average value of the observable in the presence of a perturbation is obtained as an expansion in powers of the external force. In this review, we consider only the term linear in the force—the linear response.

In order to obtain an expression for the generalized susceptibility it is necessary to determine the response of some dynamical variable to the perturbation, i.e., obtain the expectation value of an operator $\hat{O}$ representing the dynamical variable. (The operator $\hat{O}$ is assumed to have no explicit time dependence.) Upon applying the perturbation the system changes with time and the expectation value therefore changes with time.

The time-evolution of the state of a system can be approximated by well-established techniques (Löwdin, 1967). The Kubo formalism (Kubo, 1957), based on the evolution of the density matrix, is particularly useful inasmuch as it provides a quantum-statistical description applicable to any temperature. In essence it is a procedure for relating the nonequilibrium density matrix to the equilibrium one by successive approximations. The term linear in the probe produces

$$\langle \hat{O}^{(1)}(t)\rangle = \langle \hat{O}^{0}(t)\rangle + (i/\hbar)\int_{-\infty}^{t} dt' \langle [\hat{V}^{0}(t'), \hat{O}^{0}(t)]_{-}\rangle, \tag{1}$$

where $\hat{V}(t)$ is the interaction part of the Hamiltonian $\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$ and the superscript ^{0} indicates operators in an unperturbed Heisenberg picture. The brackets denote an ensemble average where the ensemble is made up of an incoherent weighted superposition of eigenstates of the unperturbed Hamiltonian, the weighting factor being a Boltzmann factor.

If we let $\hat{\rho}$ be the charge density,

$$\hat{\rho}(\mathbf{r}) = e\sum_{\nu} Z_{\nu}\delta(\mathbf{r} - \mathbf{r}_{\nu}) - e\sum_{j}\delta(\mathbf{r} - \mathbf{r}_j), \tag{2}$$

where e is the absolute magnitude of the electronic charge, Z_ν the atomic number of the νth atom and $\mathbf{r}_j$ the position vector of the jth electron then

$$\hat{V}(t) = \int d\mathbf{r}\, \hat{\rho}(\mathbf{r})\, \hat{\phi}(\mathbf{r}, t), \tag{3}$$

where $\hat{\phi}(\mathbf{r}, t)$ is the scalar potential. The operators here (without superscripts) are in the Schrödinger picture. The linear response is

$$\langle \hat{\rho}^{(1)}(\mathbf{r}, t)\rangle = \langle \hat{\rho}^{0}(\mathbf{r}, t)\rangle + (i/\hbar)\int d\mathbf{r}' \int_{-\infty}^{t} dt' \langle [\hat{\rho}^{0}(\mathbf{r}', t')\hat{\phi}^{0}(\mathbf{r}', t'), \hat{\rho}^{0}(\mathbf{r}, t)]_{-}\rangle \tag{4}$$

The expectation value is over the noninteracting system consisting of the radiation field and matter. The scalar potential operator commutes with the matter variables and so

$$\langle\hat{\rho}^{(1)}(\mathbf{r},t)\rangle = \langle\hat{\rho}^{0}(\mathbf{r},t)\rangle + (i/\hbar)\int d\mathbf{r}'\int_{-\infty}^{t} dt'\,\langle[\hat{\rho}^{0}(\mathbf{r}',t'),\hat{\rho}^{0}(\mathbf{r},t)]_{-}\rangle \times\langle\hat{\phi}^{0}(\mathbf{r}',t')\rangle. \quad (5)$$

We shall concern ourselves only with classical fields and henceforth replace $\langle\hat{\phi}^{0}(\mathbf{r}',t')\rangle$ by its classical value $\phi(\mathbf{r}',t')$. The quantity

$$(i/\hbar)\langle[\hat{\rho}^{0}(\mathbf{r}',t'),\hat{\rho}^{0}(\mathbf{r},t)]_{-}\rangle = \chi(\mathbf{r},\mathbf{r}',t,t') \quad (6)$$

is the linear response function and $\langle\hat{\rho}^{(1)}(\mathbf{r},t)\rangle - \langle\hat{\rho}^{0}(\mathbf{r},t)\rangle$ the linear response. The response at position $\mathbf{r}$ and time t depends on the cumulative effect of the perturbation at all past times and space points. In this sense the response function is a memory function. Since the expectation value of the charge-density operator obeys (5), we have

$$\hat{\rho}^{(1)}(\mathbf{r},t) - \hat{\rho}^{0}(\mathbf{r},t) = \int d\mathbf{r}'\int_{-\infty}^{t} dt'\,\hat{\chi}(\mathbf{r},\mathbf{r}',t,t')\,\phi(\mathbf{r}',t') \quad (7)$$

where $\hat{\chi}(\mathbf{r},\mathbf{r}',t,t')$ is the operator for the charge-density linear response function.

The linear response function $\chi(\mathbf{r},\mathbf{r}',t,t')$ characterizes the equilibrium system in the absence of perturbation and it determines the linear response as affected by the perturbation. If the response function is to characterize an attribute of the equilibrium state of the system, it is necessary that in obtaining $\chi(\mathbf{r},\mathbf{r}',t,t')$ the perturbation not cause real transitions which would change the system. Therefore, the perturbation is limited to one that vanishes sufficiently as $t\to-\infty$. To ensure the adiabatic turning on of the perturbation we replace $V(t)$ by $V(t)\exp(\varepsilon t)$ where ε is greater than zero, but infinitesimally small. The calculations are performed with the adiabatic potential, whereafter the limit as $\varepsilon\to 0$ is taken. The charge-density response function reduces to

$$\chi(\mathbf{r},\mathbf{r}',t,t') = (i/\hbar)\sum_{m,n}\sigma^{0}_{mm}\,\{\rho_{mn}(\mathbf{r}')\rho_{nm}(\mathbf{r})\exp\{(i/\hbar)(E_n-E_m)(t-t')\} - \rho_{mn}(\mathbf{r})\rho_{nm}(\mathbf{r}')\exp\{-(i/\hbar)(E_n-E_m)(t-t')\}\}, \quad (8)$$

where E_n and E_m are energies of the unperturbed states and σ^{0}_{mm} is an element of the statistical operator

$$\hat{\sigma}_0 = \exp(-\hat{H}_0/k_{\mathrm{B}}T)/\mathrm{tr}\,\exp(-\hat{H}_0/k_{\mathrm{B}}T).$$

With $t - t' = \tau$ the response function takes the form $\chi(\mathbf{r}, \mathbf{r}', \tau)$. Introducing the transformation $\tau \to -\tau$ yields $\chi(-\tau) = -\chi(\tau)$. This follows since the operators are assumed to be hermitian and the wave functions real.

If we Fourier decompose the right-hand side of (7) we get

$$\begin{aligned}\Delta\langle\rho(\mathbf{r}, t)\rangle &= \int d\mathbf{r}' \int_{-\infty}^{\infty} d\omega \int_{0}^{\infty} d\tau\, \chi(\mathbf{r}, \mathbf{r}', \tau)\phi(\mathbf{r}', \omega)\exp\{i\omega t - i\omega\tau + \varepsilon t - \varepsilon\tau\} \\ &= \int d\mathbf{r}' \int_{-\infty}^{\infty} d\omega\, \chi(\mathbf{r}, \mathbf{r}', \omega)\phi(\mathbf{r}', \omega)\exp(i\omega t) \qquad (9)\end{aligned}$$

where $\chi(\mathbf{r}, \mathbf{r}', \omega)$ is the charge-density susceptibility defined by

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \lim_{\varepsilon\to 0} \int_{0}^{\infty} d\tau\, \chi(\mathbf{r}, \mathbf{r}', \tau)\exp\{-i\omega\tau - \varepsilon\tau\}. \qquad (10)$$

Substitution of (8) yields

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \lim_{\varepsilon\to 0} \frac{1}{\hbar} \sum_{m,n} \sigma^{0}_{mm} \left\{ \frac{-\rho_{mn}(\mathbf{r})\rho_{nm}(\mathbf{r}')}{\omega + \omega_{nm} - i\varepsilon} + \frac{\rho_{mn}(\mathbf{r}')\rho_{nm}(\mathbf{r})}{\omega - \omega_{nm} - i\varepsilon} \right\}. \qquad (11)$$

Using the identity

$$\lim_{\varepsilon\to 0} \frac{1}{\omega \pm i\varepsilon} = \frac{\mathscr{P}}{\omega} \mp i\pi\delta(\omega), \qquad (12)$$

where $\mathscr{P}$ is the principal value operator, produces

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \chi'(\mathbf{r}, \mathbf{r}', \omega) - i\chi''(\mathbf{r}, \mathbf{r}', \omega), \qquad (13)$$

where

$$\chi'(\mathbf{r}, \mathbf{r}', \omega) = \mathscr{P} \frac{1}{\pi} \sum_{m,n} \sigma^{0}_{mm} \left\{ \frac{-\rho_{mn}(\mathbf{r})\rho_{nm}(\mathbf{r}')}{\omega + \omega_{nm}} + \frac{\rho_{mn}(\mathbf{r}')\rho_{nm}(\mathbf{r})}{\omega - \omega_{nm}} \right\} \qquad (14)$$

and

$$\begin{aligned}\chi''(\mathbf{r}, \mathbf{r}', \omega) = \frac{\pi}{\hbar} \sum_{m,n} \sigma^{0}_{mm} \{ &-\rho_{mn}(\mathbf{r}')\rho_{nm}(\mathbf{r})\delta(\omega - \omega_{nm}) \\ &+ \rho_{mn}(\mathbf{r})\rho_{nm}(\mathbf{r}')\delta(\omega + \omega_{nm})\}. \end{aligned} \qquad (15)$$

It should be noted that $\chi'(\omega) = \chi'(-\omega)$, $\chi''(-\omega) = -\chi''(\omega)$ and $\chi(\mathbf{r}, \mathbf{r}') = \chi(\mathbf{r}', \mathbf{r})$.

It is also useful to define susceptibilities that are spatially Fourier transformed. If we write

$$\hat{\rho}(\mathbf{r}) = \Omega^{-1} \sum_{\mathbf{k}} \hat{\rho}_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}) \qquad (16)$$

where Ω is the volume of the container, we can take

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \Omega^{-2} \sum_{\mathbf{k}, \mathbf{k}'} \chi_{\mathbf{k}\mathbf{k}'}(\omega) \exp(i\mathbf{k} \cdot \mathbf{r} - i\mathbf{k}' \cdot \mathbf{r}') \tag{17}$$

and

$$\chi_{\mathbf{k},\mathbf{k}'}(\omega) = \int d\mathbf{r} \int d\mathbf{r}' \, \chi(\mathbf{r}, \mathbf{r}', \omega) \exp(-i\mathbf{k} \cdot \mathbf{r} + i\mathbf{k}' \cdot \mathbf{r}') \tag{18}$$

or, in matrix form

$$\chi_{\mathbf{k},\mathbf{k}'}(\omega) = \lim_{\varepsilon \to 0} \frac{1}{\hbar} \sum_{mn} \sigma_{mm}^{0} \left\{ \frac{-\rho_{mn}(\mathbf{k})\rho_{nm}(-\mathbf{k}')}{\omega + \omega_{nm} - i\varepsilon} + \frac{\rho_{mn}(-\mathbf{k}')\rho_{nm}(\mathbf{k})}{\omega - \omega_{nm} - i\varepsilon} \right\}. \tag{19}$$

For real wave functions and hermitian operators $\chi_{\mathbf{k},\mathbf{k}'}(\omega) = \chi_{-\mathbf{k}',\,-\mathbf{k}}(\omega)$. If the system has translational symmetry along an axis say the Z axis then $\chi(z, z', \omega) = \chi(z - z', \omega)$. For this to be so, the summand in (17) must have the nature of a delta function, i.e.,

$$\chi_{k_z,k_z'}(\omega) = \Omega^{1/3} \chi_{k_z}(\omega) \, \delta_{k_z,k_z'}$$

or

$$\chi(z - z', \omega) = \Omega^{-1/3} \sum_{k_z} \chi_{k_z}(\omega) \exp\{ik_z(z - z')\}. \tag{20}$$

Similar expressions can be derived for different probes. Thus, more general results are obtained if we let $\hat{O}$ represent the current-charge-density four vector $\hat{\mathbf{J}}(\hat{j}_0, \hat{j}_1, \hat{j}_2, \hat{j}_3)$, and $\mathscr{A} = (A_0, A_1, A_2, A_3)$ the four-vector potential; then

$$\hat{V}(t) = -(1/c) \int d\mathbf{r} \, \hat{\mathbf{J}}(\mathbf{r}) \cdot \mathscr{A}(\mathbf{r}, t). \tag{21}$$

Here, $\hat{j}_0 = c\hat{\rho}$ and $A_0 = -\phi$. The linear response equation is

$$\Delta j_\mu(\mathbf{r}, t) = (i/c\hbar) \sum_{\nu} \int_{-\infty}^{t} dt' \int d\mathbf{r}' \langle [\hat{j}_\mu{}^0(\mathbf{r}, t), \hat{j}_\nu{}^0(\mathbf{r}', t')]_- \rangle A_\nu(\mathbf{r}', t') \tag{22}$$

and the corresponding susceptibility

$$\chi_{\mu\nu}(\mathbf{r}, \mathbf{r}', \omega) = (1/c\hbar) \lim_{\varepsilon \to 0} \int_0^\infty d\tau \langle [\hat{j}_\mu{}^0(\mathbf{r}, t), \hat{j}_\nu{}^0(\mathbf{r}', t - \tau)]_- \rangle \exp\{-\tau(i\omega + \varepsilon)\}. \tag{23}$$

If the probe is a field constant over the extent of the system, then $\hat{V}(t) = -\hat{\mathbf{m}} \cdot \mathbf{E}(t)$ where $\mathbf{m}$ is the dipole moment and $\mathbf{E}$ the external field. The linear response yields the polarizability

$$\boldsymbol{\alpha}(\omega) = \lim_{\varepsilon \to 0} (i/\hbar) \int_0^\infty d\tau \langle [\hat{\mathbf{m}}^0(t), \hat{\mathbf{m}}^0(t')]_- \rangle \exp\{-\tau(i\omega + \varepsilon)\}. \tag{24}$$

From the definition of the dipole moment $\mathbf{m} = \int \mathbf{r}\rho(\mathbf{r})\, d\mathbf{r}$ and (6) and (10) it follows that

$$\boldsymbol{\alpha}(\omega) = -\int d\mathbf{r} \int d\mathbf{r}'\, \mathbf{r}\chi(\mathbf{r}, \mathbf{r}', \omega)\mathbf{r}'. \tag{25}$$

For harmonic oscillators,

$$\begin{aligned} \boldsymbol{\alpha}'(\omega) &= \boldsymbol{\alpha}(0)\omega_0{}^2/(\omega_0{}^2 - \omega^2), \\ \boldsymbol{\alpha}''(\omega) &= (\pi/2)\boldsymbol{\alpha}(0)\omega_0[\delta(\omega - \omega_0) - \delta(\omega + \omega_0)], \end{aligned} \tag{26}$$

where $\boldsymbol{\alpha}(0)$ is the static polarizability and ω_0 the natural frequency.

An important relation, first developed by Callen and Welton (1951) and known as the fluctuation–dissipation theorem, exists between the dissipative process caused by the system interacting linearly with a probe and the appropriate equilibrium fluctuation. For a system of fluctuating charges, this relation is

$$\begin{aligned} &(1/2\pi) \int_{-\infty}^{\infty} d(t - t') \exp\{-i\omega(t - t')\} \langle [\hat{\rho}(\mathbf{r}', t'), \hat{\rho}(\mathbf{r}, t)]_+ \rangle \\ &\qquad = (\hbar/\pi)\chi''(\mathbf{r}, \mathbf{r}', \omega) \coth(\hbar\omega/2k_{\mathrm{B}}T). \end{aligned} \tag{27}$$

It has been tacitly assumed that the frequencies ω are real. For many purposes it is more convenient to extend the definition of the susceptibility to complex frequency in the lower half of the frequency plane, $f = \omega - iy$ where the function is analytic; i.e., we define

$$\chi(f) = \int_0^\infty d\tau\, \chi(\tau) \exp(-if\tau). \tag{28}$$

Along the real axis

$$\lim_{y \to 0} \chi(f) \equiv \chi(\omega) = \chi'(\omega) - i\chi''(\omega).$$

Along the imaginary axis the suceptibility is real and can be related to $\chi''(\omega)$ by a generalization of the Kramers–Kronig transform, (Landau and Lifshitz, 1958)

$$\lim_{\omega\to 0} \chi(f) \equiv \chi(-iy) = (2/\pi) \int_0^\infty dy\, \omega\chi''(\omega)/(\omega^2 + y^2). \tag{29}$$

III. The Free Energy of Interaction

The free energy of a system of interacting particles can generally be developed in a perturbation series of the interaction Hamiltonian. For two nonoverlapping neutral atoms at fixed internuclear separation, the first nonvanishing term in the free energy shift is of second order in the perturbation. In the dipolar approximation this term reduces to the London dispersion formula at absolute zero and moderate separations and to the Casimir–Polder (Casimir and Polder, 1948) expression at $T = O$ and large separations.

In this section we develop a general expression for the free energy for two arbitrary nonoverlapping neutral charge distributions with fixed positions of centers of gravity. The charge distributions are assumed to fluctuate (i.e., oscillate, rotate etc.) freely in the absence of perturbation: Permanent multipole moments (if present) have no preferred orientation in space.

The method to be employed is based on a generalization of the reaction-field technique developed earlier (Linder, 1962, 1964, 1965, 1966, 1967; Linder and Hoernschemeyer, 1964; Linder and Kromhout, 1968; Kromhout and Linder, 1968; Rosenkrans *et al.* 1968). The reaction-field of a moment $\mathbf{m}_i$ is the field at i produced by the surroundings which were polarized by $\mathbf{m}_i$. In the present context the emphasis is on the charge distributions and potentials. We define the reaction scalar potential of a charge density ρ_i as the scalar potential at the site i produced by the surroundings which were polarized by ρ_i. The free energy of interaction is obtained from the coupling of the reaction potential with ρ_i. This leads directly to a description of the free energy shift in terms of the dynamic charge-density susceptibilities of the isolated charge distributions. These susceptibilities contain not only high-frequency components due to electronic transitions but include also low frequency transitions associated with the rotation of the charge distribution as a whole. In short, the interaction includes besides dispersion forces also induction, and orientation forces. However, since the centers of gravity of the charge distributions are assumed fixed, the effects related to acoustical properties are excluded.

In Section III, A we develop an expression for the second-order free energy. In III, B the formalism is extended to include all higher-order terms in the perturbation expansion. These entail multiple transitions among the states, which are intractable, except for harmonic oscillators and without approximations the results remain formal. By employing the decorrelation approximation, the general formulation can be reduced to simple form. The higher-order potentials so obtained do therefore not have the same degree of accuracy as the second-order one.

A. Second-Order Free Energy

Let us consider molecule 1 to be the "central" molecule and the radiation field plus molecule 2 to be the surroundings s. As a result of the charge fluctuations in 1 the radiation field is acted upon causing a scalar potential to propagate to 2 which then polarizes (causes a response in) 2. The scalar potential which acts back on 1 is the reaction (scalar) potential. The latter can be written in operator form

$$\hat{\Phi}^{(2)}(\mathbf{r}_1, t) = \int d\mathbf{r}_1' \int_{-\infty}^{t} dt' \, \hat{K}^{(2)}(\mathbf{r}_1, \mathbf{r}_1', t, t')\hat{\rho}^0(\mathbf{r}_1', t'). \tag{30}$$

Here, $\hat{\rho}^0(\mathbf{r}_1', t')$ is an unperturbed Heisenberg operator representing the charge density of 1, $\hat{K}^{(2)}(\mathbf{r}_1, \mathbf{r}_1', t, t')$ the operator for the reaction potential response function and $\hat{\Phi}^{(2)}(\mathbf{r}_1, t)$ is the reaction potential operator. Accordingly, the reaction potential which acts back on 1 at a time t and position $\mathbf{r}_1$ is a function not only of the charge density of 1 at time t and position $\mathbf{r}_1$ but also of all preceding times $t' \leqslant t$ and neighboring positions $\mathbf{r}_1'$. The superscript on $\hat{\Phi}^{(2)}(\mathbf{r}_1, t)$ serves to denote that the field has been allowed to propagate twice between the two charge distributions. Multiple scatterings will be considered in Section III, B.

In order to obtain an expression for $\hat{K}^{(2)}$, we first determine the potential at 2 arising from the charge distribution at 1. The potential can be gotten from Maxwell's classical equations which, when written in terms of the scalar and vector potentials in the Lorentz gauge, yield the uncoupled equations

$$\begin{aligned} \nabla^2\phi(\mathbf{r}, t) - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\phi(\mathbf{r}, t) &= -4\pi\rho(\mathbf{r}, t), \\ \nabla^2\mathbf{A}(\mathbf{r}, t) - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{A}(\mathbf{r}, t) &= -\frac{4\pi}{c}\mathbf{j}(\mathbf{r}, t), \end{aligned} \tag{31}$$

with the subsidiary condition

$$\nabla \cdot \mathbf{A}(\mathbf{r}, t) + \frac{1}{c}\frac{\partial\phi(\mathbf{r}, t)}{\partial t} = 0. \tag{32}$$

The solution for ϕ is

$$\phi(\mathbf{r}, t) = \int d\mathbf{r}' \int dt' \, v_{\mathrm{R}}(\mathbf{r}, \mathbf{r}', t, t')\rho(\mathbf{r}', t'), \tag{33}$$

where v_{R} is the retarded Green's function for the inhomogeneous differential equation (31), i.e.

$$v_{\mathrm{R}} = \delta\left(t - t' - \frac{|\mathbf{r} - \mathbf{r}'|}{c}\right) \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \tag{34}$$

We shall treat only the charge distributions quantum mechanically; the field will be assumed to behave classically. For the present, we confine our attention to static potentials:

$$v = 1/|\mathbf{r} - \mathbf{r}'|. \tag{35}$$

Using these relations we obtain for the scalar potential at 2 arising from the unperturbed charge distribution at 1.

$$\hat{\Phi}^{(1)}(\mathbf{r}_2', t') = \int d\mathbf{r}_1' \, v(\mathbf{r}_2', \mathbf{r}_1')\hat{\rho}^0(\mathbf{r}_1', t'). \tag{36}$$

The scalar potential gives rise to a response in 2 which, to first order, is

$$\hat{\rho}^{(1)}(\mathbf{r}_2, t) = \hat{\rho}^0(\mathbf{r}_2, t) + \int d\mathbf{r}_2' \int_{-\infty}^{t} dt' \, \hat{\chi}(\mathbf{r}_2, \mathbf{r}_2', t, t')\hat{\Phi}^{(1)}(\mathbf{r}_2', t'), \tag{37}$$

where $\hat{\chi}(\mathbf{r}_2, \mathbf{r}_2', t, t')$ is the linear response function. The polarized charge distribution produces, in turn, a potential in 1 which consists of two terms

$$\hat{\Phi}^{(1)}(\mathbf{r}_1, t) = \int d\mathbf{r}_2 \, v(\mathbf{r}_1, \mathbf{r}_2)\hat{\rho}^0(\mathbf{r}_2, t) \tag{38}$$

and

$$\hat{\Phi}^{(2)}(\mathbf{r}_1, t) = \int d\mathbf{r}_2 \int d\mathbf{r}_2' \int d\mathbf{r}_1' \int_{-\infty}^{t} dt' \times v(\mathbf{r}_1, \mathbf{r}_2)\hat{\chi}(\mathbf{r}_2, \mathbf{r}_2', t, t')v(\mathbf{r}_2', \mathbf{r}_1')\hat{\rho}^0(\mathbf{r}_1', t'). \tag{39}$$

The latter is the reaction potential. Equating (39) with (30) defines $\hat{K}^{(2)}$

$$\hat{K}^{(2)}(\mathbf{r}_1, \mathbf{r}_1', t, t') = \int d\mathbf{r}_2 \int d\mathbf{r}_2' \, v(\mathbf{r}_1, \mathbf{r}_2)\hat{\chi}(\mathbf{r}_2, \mathbf{r}_2', t, t')v(\mathbf{r}_2', \mathbf{r}_1'). \tag{40}$$

The second-order free energy is obtained from the coupling of $\hat{\rho}^0$ and $\hat{\Phi}^{(2)}$. The potential $\hat{\Phi}^{(1)}$ would give rise to a first-order perturbation free energy. The first-order free energy is zero if there are no permanent multipole moments. It is also zero if the charge distributions have permanent moments but the molecules are tumbling freely in the absence of perturbation.

The work of polarization can be calculated by considering a hypothetical process whereby the charges on 1 are increased reversibly from zero to their full value by means of a parameter which runs from 0 to 1. Since $\hat{\rho}^0$ is linearly dependent on the charges we have $d\hat{\rho}^0(\lambda) = d(\hat{\rho}^0\lambda) = \hat{\rho}^0(\lambda = 1)\,d\lambda$. The work of polarization of the "surroundings" by the electrical fluctuations in 1, is then

$$W^{(2)}_{s\leftarrow 1} = \tfrac{1}{2}\int_0^1 d\lambda \int d\mathbf{r}_1 \langle [\hat{\rho}^0(\mathbf{r}_1, t, \lambda = 1), \hat{\Phi}^{(2)}(\mathbf{r}_1, t, \lambda)]_+ \rangle, \tag{41}$$

where the brackets denote quantum-statistical average over the *unperturbed states.* The symmetrical form is used because $\hat{\rho}^0$ and $\hat{\Phi}^{(2)}$ do not commute. Since $\hat{\Phi}^{(2)}$ is linearly dependent on $\hat{\rho}^0$ and therefore also on λ it is clear that the λ-integration produces a factor of one-half. Alternatively, we can write

$$W^{(2)}_{s\leftarrow 1} = \tfrac{1}{2}\int_0^1 \frac{d\lambda}{\lambda} \int d\mathbf{r}_1 \langle [\hat{\rho}^0(\mathbf{r}_1, t, \lambda), \hat{\Phi}^{(2)}(\mathbf{r}_1, t, \lambda)]_+ \rangle \tag{42}$$

which will prove useful in later development. To reduce (42) we substitute (39), Fourier decompose the integrand and apply the fluctuation-dissipation theorem (Eq. 27). The result is

$$W^{(2)}_{s\leftarrow 1} = -(\hbar/4\pi)\int d\mathbf{r}_1 \int d\mathbf{r}_1{}' \int_{-\infty}^{\infty} d\omega\, \chi''(\mathbf{r}_1{}', \mathbf{r}_1, \omega) K^{(2)\prime}(\mathbf{r}_1, \mathbf{r}'_1, \omega) \times \coth(\hbar\omega/2k_{\mathrm{B}}T) \tag{43}$$

where $K^{(2)\prime}$ is the real part of the reaction potential susceptibility

$$K^{(2)}(\mathbf{r}_1, \mathbf{r}_1{}', \omega) = \int d\mathbf{r}_2 \int d\mathbf{r}_2{}'\, v(\mathbf{r}_1, \mathbf{r}_2)\chi(\mathbf{r}_2, \mathbf{r}_2{}', \omega) v(\mathbf{r}_2{}', \mathbf{r}_1{}') \tag{44}$$

and the χ's are given in (13)–(15).

A similar expression with the prime and double prime interchanged represents the work of polarization of 1 by the electrical fluctuations in the surroundings, $W^{(2)}_{1\leftarrow s}$. The second-order free energy, $F^{(2)}(T)$, is the sum of $W^{(2)}_{s\leftarrow 1}$ and $W^{(2)}_{1\leftarrow s}$,

$$F^{(2)}(T) = -(\hbar/4\pi)\,\mathrm{Re}\, i \int d\mathbf{r}_1 \int d\mathbf{r}_1{}' \int_{-\infty}^{\infty} d\omega\, \chi(\mathbf{r}_1{}', \mathbf{r}_1, \omega) K^{(2)}(\mathbf{r}_1, \mathbf{r}_1{}', \omega) \times \coth(\hbar\omega/2k_{\mathrm{B}}T). \tag{45}$$

An expression like this for $T = 0$ was obtained by McLachlan (1963a,b; McLachlan *et al.*, 1963–1964) and Longuet-Higgins (1965) by different methods. It expresses, as pointed out by Longuet-Higgins, that in general the interaction depends on the correlative contributions from different parts of each molecule as is evident from the double spatial dependence of each of the χ's.

Equation (45) can also be expressed in terms of the **k**-dependent susceptibilities. To do so, we Fourier decompose χ and $K^{(2)}$ in accordance with (17) and write

$$F^{(2)}(T) = -(\hbar/4\pi)\,\mathrm{Re}\, i \int d\mathbf{r}_1 \int d\mathbf{r}_1{}' \int_{-\infty}^{\infty} d\omega\, \Omega^{-2} \sum_{\mathbf{k},\mathbf{k}',\mathbf{k}'',\mathbf{k}'''} \chi_{\mathbf{k}',\mathbf{k}}(\omega) K^{(2)}_{\mathbf{k}'',\mathbf{k}'''}(\omega)$$
$$\times [\exp i\{\mathbf{k}'\cdot\mathbf{r}_1{}' - \mathbf{k}\cdot\mathbf{r}_1 + \mathbf{k}''\cdot\mathbf{r}_1 - \mathbf{k}'''\cdot\mathbf{r}_1{}'\}] \coth(\hbar\omega/2k_\mathrm{B}T). \tag{46}$$

Integrating out the spatial variables produces the Kronecker deltas $\delta_{\mathbf{k},\mathbf{k}''}$ and $\delta_{\mathbf{k}',\mathbf{k}'''}$, and yields

$$F^{(2)}(T) = -(\hbar/4\pi)\,\mathrm{Re}\, i \int_{-\infty}^{\infty} d\omega \sum_{\mathbf{k},\mathbf{k}'} \chi_{\mathbf{k}',\mathbf{k}}(\omega) K^{(2)}_{\mathbf{k},\mathbf{k}'}(\omega) \coth(\hbar\omega/2k_\mathrm{B}T). \tag{47}$$

To express $K^{(2)}_{\mathbf{k},\mathbf{k}'}(\omega)$ in terms of the Fourier components of $\chi(\mathbf{r}_2, \mathbf{r}_2{}', \omega)$ and $v(\mathbf{r}_1, \mathbf{r}_2)$, we first note that since $v(\mathbf{r}_1, \mathbf{r}_2)$ depends only on $|\mathbf{r}_2 - \mathbf{r}_1|$ we can write

$$v(\mathbf{r}_1, \mathbf{r}_2) = v|\mathbf{r}_1 - \mathbf{r}_2| = \sum_{\mathbf{k}} v_{\mathbf{k}} \exp[i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)]. \tag{48}$$

Here, the usual volume normalization has been absorbed in $v_{\mathbf{k}}$. Decomposition of (40) then yields

$$K^{(2)}_{\mathbf{k},\mathbf{k}'}(\omega) = v_{\mathbf{k}} \chi^{(2)}_{\mathbf{k},\mathbf{k}'}(\omega) v_{\mathbf{k}'}. \tag{49}$$

Effects of Retardation

In order to take account of the finite speed of light one must consider fluctuations in both current and charge densities. The contributions from the vector potential must then be included and the theory has to be formulated in terms of the current–charge density response functions [Eqs. (22) and (23)] and the retarded Coulomb potential v_R defined by (34). An expression like (45) but with the χ replaced by $\chi_{\mu\nu}$ was obtained by McLachlan (1963a) and others (for a critical review see, e.g., Power, 1967). Unfortunately, there is no simple way to reduce the general equation to practical form except under special limited conditions.[1] A detailed discussion of retardation is postponed till the treatment of the dipolar approximation in Section IV.

B. Free Energy to Infinite Order

The procedure for generating the second-order free energy can readily be extended to include higher-order terms. Instead of the single reflection considered before, the reaction potential is now obtained by allowing all possible reflections, i.e.,

$$\hat{\Phi}(\mathbf{r}_1, t) = \sum_{n\text{ even}}^{\infty} \hat{\Phi}^{(n)}(\mathbf{r}_1, t) \tag{50}$$

where n is the number of times the field propagates between 1 and 2. For $n = 4$, we readily find

$$\begin{aligned}\hat{\Phi}^{(4)}(\mathbf{r}_1, t) = \int d\mathbf{r}_2 \int d\mathbf{r}_2' \int d\mathbf{r}_1' \int d\mathbf{r}_1'' \int d\mathbf{r}_2'' \int d\mathbf{r}_2''' \int d\mathbf{r}_1''' \\ \times \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \int_{-\infty}^{t''} dt''' v(\mathbf{r}_1, \mathbf{r}_2)\hat{\chi}(\mathbf{r}_2, \mathbf{r}_2', t, t')v(\mathbf{r}_2', \mathbf{r}_1') \\ \times \hat{\chi}(\mathbf{r}_1', \mathbf{r}_1'', t', t'')v(\mathbf{r}_1'', \mathbf{r}_2'')\hat{\chi}(\mathbf{r}_2'', \mathbf{r}_2''', t'', t''')v(\mathbf{r}_2''', \mathbf{r}_1''') \\ \times \hat{\rho}^0(\mathbf{r}_1''', t'''),\end{aligned} \tag{51}$$

or, symbolically

$$\hat{\Phi}^{(4)} = v\hat{\chi}_2 v\hat{\chi}_1 v\hat{\chi}_2 v\hat{\rho}_1{}^0. \tag{52}$$

(The times are so arranged that the later time is always to the left, i.e., $t \geqslant t' \geqslant t'' \geqslant t'''$.) This expression can be written also as

$$\hat{\Phi}^{(4)} = \hat{K}^{(2)}\hat{\chi}_1\hat{\Phi}^{(2)}, \tag{53}$$

which has a simple physical interpretation: The reaction potential $\hat{\Phi}^{(2)}$ generated in a single reflection polarizes 1 which then produces the new potential $\hat{\Phi}^{(4)}$ through another reflection. This result is readily generalized to potentials of arbitrary order

$$\hat{\Phi}^{(n)} = \hat{K}^{(2)}\hat{\chi}_1\hat{\Phi}^{(n-2)}. \tag{54}$$

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[1] Meath and Hirschfelder (1966), among others, have made extensive calculations of the effects of retardation using a multipole expansion. Langbein (1970) has computed the retarded dispersion energies for macroscopic bodies without the recourse of a multipolar expansion by the use of macroscopic dielectric constants.

(We shall henceforth suppress the index on $\hat{\chi}_1$; it will be understood that $\hat{\chi}$ refers to 1 unless stated otherwise.)

The work of polarization can be obtained by the same charging process as outlined in Section III, A. For the general case it yields

$$W_{s\leftarrow 1} = \sum_n W^{(n)}_{s\leftarrow 1} = \tfrac{1}{2}\sum_n \int_0^1 d\lambda(1/\lambda) \int d\mathbf{r}_1 \langle[\hat{\rho}^0(\mathbf{r}_1, t; \lambda)\hat{\Phi}^{(n)}(\mathbf{r}_1, t; \lambda)]_+\rangle, \quad (55)$$

where each $\hat{\rho}_1{}^0$ introduces a factor of λ. Since $\hat{\Phi}^{(n)}$ contains $(n-1)$ products of $\hat{\rho}_1$'s, the anticommutator introduces a factor of λ^n in the integrand. The exponent of λ is the same as the number of times the field propagates between the molecules and can be determined by counting the factors v in $\hat{\Phi}^{(n)}$. The terms in (55), other than the leading one, involve correlations between multiple excitations within the molecules. They give rise to (hyper) susceptibilities which in general depend on more than one frequency and are difficult to reduce to simpler forms. To avoid these difficulties, we invoke the decorrelation approximation which replaces the matrix elements of the products by the products of the expectation values. For example, the quantity

$$\langle\hat{\rho}_1{}^0 v\hat{\chi}_2 v\hat{\chi}_1 v\hat{\chi}_2 v\hat{\rho}_1{}^0\rangle = \langle\hat{\rho}_1{}^0\hat{\rho}_1{}^0 v\hat{\chi}_2 v\hat{\chi}_1 v\hat{\chi}_2 v\rangle,$$

which is one of the terms in $W^{(4)}_{s\leftarrow 1}$, is replaced by $\langle\hat{\rho}_1{}^0\hat{\rho}_1{}^0 v\hat{\chi}_2 v\rangle\langle\hat{\chi}_1 v\hat{\chi}_2 v\rangle$. If we make this approximation, $W^{(4)}_{s\leftarrow 1}$ can be Fourier decomposed in the same manner as $W^{(2)}_{s\leftarrow 1}$ and yields, upon addition of $W^{(4)}_{1\leftarrow s}$

$$\begin{aligned} F^{(4)}(T) = -(\hbar/8\pi)\,\mathrm{Re}\, i \int d\mathbf{r}_1 \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_1''' \int_{-\infty}^{\infty} d\omega \chi_1(\mathbf{r}_1''', \mathbf{r}_1, \omega) \\ \times v(\mathbf{r}_1, \mathbf{r}_2)\chi_2(\mathbf{r}_2, \mathbf{r}_2', \omega)v(\mathbf{r}_2', \mathbf{r}_1')\chi_1(\mathbf{r}_1', \mathbf{r}_1'', \omega)v(\mathbf{r}_1'', \mathbf{r}_2'') \quad (56) \\ \times \chi_2(\mathbf{r}_2'', \mathbf{r}_2''', \omega)v(\mathbf{r}_2''', \mathbf{r}_1''')\coth(\hbar\omega/2k_{\mathrm{B}}T). \end{aligned}$$

Integrating out the variables $\mathbf{r}_2$, $\mathbf{r}_2'$, $\mathbf{r}_2''$, $\mathbf{r}_2'''$ and using (44), gives

$$\begin{aligned} F^{(4)}(T) = -(\hbar/8\pi)\,\mathrm{Re}\, i \int d\mathbf{r}_1''' \int d\mathbf{r}_1 \int d\mathbf{r}_1' \int d\mathbf{r}_1'' \int_{-\infty}^{\infty} d\omega \\ \times \chi(\mathbf{r}_1''', \mathbf{r}_1, \omega)K^{(2)}(\mathbf{r}_1, \mathbf{r}_1', \omega)\chi(\mathbf{r}_1', \mathbf{r}_1'', \omega) \quad (57) \\ \times K^{(2)}(\mathbf{r}_1'', \mathbf{r}_1''', \omega)\coth(\hbar\omega/2k_{\mathrm{B}}T), \end{aligned}$$

or, in **k** space

$$\begin{aligned} F^{(4)}(T) = -(\hbar/8\pi)\,\mathrm{Re}\, i \sum_{\mathbf{k}''', \mathbf{k}', \mathbf{k}'', \mathbf{k}} \int_{-\infty}^{\infty} d\omega \chi_{\mathbf{k}''', \mathbf{k}}(\omega)K^{(2)}_{\mathbf{k}, \mathbf{k}'}(\omega) \\ \times \chi_{\mathbf{k}', \mathbf{k}''}(\omega)K^{(2)}_{\mathbf{k}'', \mathbf{k}'''}(\omega)\coth(\hbar\omega/2k_{\mathrm{B}}T). \quad (58) \end{aligned}$$

We next define a quantity

$$K^{(4)}_{\mathbf{k},\mathbf{k}'''}(\omega) = \sum_{\mathbf{k}',\mathbf{k}''} K^{(2)}_{\mathbf{k},\mathbf{k}'}(\omega)\chi_{\mathbf{k}',\mathbf{k}''}(\omega)K^{(2)}_{\mathbf{k}'',\mathbf{k}'''}(\omega), \tag{59}$$

and obtain, after relabeling the dummy indices

$$F^{(4)}(T) = -(\hbar/8\pi)\,\mathrm{Re}\, i \sum_{\mathbf{k},\mathbf{k}'} \int_{-\infty}^{\infty} d\omega \chi_{\mathbf{k},\mathbf{k}'}(\omega)K^{(4)}_{\mathbf{k}',\mathbf{k}}(\omega)\coth(\hbar\omega/2k_{\mathrm{B}}T). \tag{60}$$

The higher-order perturbation terms are generated in a similar fashion.

The free energy shift can now be written

$$\begin{aligned} \Delta F(T) &= F(T) - F_0(T) \\ &= -(\hbar/2\pi)\int_0^1 d\lambda(1/\lambda)\,\mathrm{Re}\, i\sum_{\mathbf{k},\mathbf{k}'}\int_{-\infty}^{\infty} d\omega\chi_{\mathbf{k},\mathbf{k}'}(\omega;\lambda) \\ &\qquad \times G_{\mathbf{k}',\mathbf{k}}(\omega;\lambda)\coth(\hbar\omega/2k_{\mathrm{B}}T), \end{aligned} \tag{61}$$

where $G_{\mathbf{k},\mathbf{k}'}(\omega;\lambda)$ is the infinite-order reaction scalar potential susceptibility defined by

$$G_{\mathbf{k},\mathbf{k}'}(\omega;\lambda) = K^{(2)}_{\mathbf{k},\mathbf{k}'}(\omega) + \lambda^2 K^{(4)}_{\mathbf{k},\mathbf{k}'}(\omega) + \cdots + \lambda^{(n-2)}K^{(n)}_{\mathbf{k},\mathbf{k}'}(\omega) \tag{62}$$

in which $K^{(n)} = K^{(2)}\chi K^{(n-2)}$ and $\chi_{\mathbf{k},\mathbf{k}'}(\omega;\lambda) = \lambda^2\chi_{\mathbf{k},\mathbf{k}'}(\omega)$.

Although the theory is formally complete it is often more convenient to express the results in terms of frequencies along the negative axis of the complex frequency plane, since there the susceptibilities are real (see Section II). Thus if we replace ω by $f = \omega - iy$, we have

$$\Delta F(T) = -(\hbar/2\pi)\int_0^1 d\lambda(1/\lambda)\,\mathrm{Re}\, i\sum_{\mathbf{k},\mathbf{k}'}\int_{-\infty}^{\infty} df\chi_{\mathbf{k},\mathbf{k}'}(f;\lambda)G_{\mathbf{k}',\mathbf{k}}(f;\lambda) \times \coth(\hbar f/2k_{\mathrm{B}}T), \tag{63}$$

where the contour is taken along a semicircle in the lower half-plane, avoiding the pole at the origin by a half-circle indentation from below. The contribution from the large circle tends to zero as f goes to infinity because of the analytic behavior of the susceptibilities. The hyperbolic cotangent, on the other hand, has an infinite number of singularities along the imaginary axis at the points $f = -iy_l$ where $y_l = 2\pi k_{\mathrm{B}}T\hbar^{-1}l$ with residue equal to $2k_{\mathrm{B}}T\hbar^{-1}$. Using the residue theorem, we get

$$\Delta F(T) = -2k_{\mathrm{B}}T\int_0^1 d\lambda(1/\lambda)\sum_{\mathbf{k},\mathbf{k}'}\sum_{l=0}^{\infty}{}' \chi_{\mathbf{k},\mathbf{k}'}(-iy_l;\lambda)G_{\mathbf{k}',\mathbf{k}}(-iy_l;\lambda), \tag{64}$$

where the prime on the summation sign denotes that the leading term ($l = 0$) must be multiplied by $\frac{1}{2}$. The functional dependence of the susceptibilities on y_l is, in accordance with (29),

$$\chi_{\mathbf{k},\mathbf{k}'}(-iy_l) = \frac{2}{\pi}\int_0^\infty d\omega \frac{\omega\chi''_{\mathbf{k},\mathbf{k}'}(\omega)}{\omega^2 + (2\pi k_B T\hbar^{-1}l)^2}; \tag{65}$$

a similar expression exists for $G_{\mathbf{k}',\mathbf{k}}(-iy_l)$.

In order to reduce Eq. (64) to a more tractable form we now decouple the spatial correlations between multiple reflections in a manner similar to the decorrelation between multiple excitations discussed earlier. This is accomplished by formally writing

$$\begin{aligned}\sum_{\mathbf{k},\mathbf{k}'}\chi_{\mathbf{k},\mathbf{k}'}(\lambda)G_{\mathbf{k},\mathbf{k}'}(\lambda) &= \lambda^2\sum_{\mathbf{k},\mathbf{k}'}\chi_{\mathbf{k}',\mathbf{k}}K^{(2)}_{\mathbf{k}',\mathbf{k}} + \lambda^4\sum_{\mathbf{k},\mathbf{k}',\mathbf{k}'',\mathbf{k}'''}\sum\chi_{\mathbf{k},\mathbf{k}'}K^{(2)}_{\mathbf{k}',\mathbf{k}''}\chi_{\mathbf{k}'',\mathbf{k}'''}\\ &\quad\times K^{(2)}_{\mathbf{k}''',\mathbf{k}}\delta_{\mathbf{k}'',\mathbf{k}} + \cdots,\\ &= \lambda^2\sum_{\mathbf{k}}\sum_{\mathbf{k}'}\chi_{\mathbf{k},\mathbf{k}'}K^{(2)}_{\mathbf{k}',\mathbf{k}} + \lambda^4\sum_{\mathbf{k}}\left(\sum_{\mathbf{k}'}\chi_{\mathbf{k},\mathbf{k}'}K^{(2)}_{\mathbf{k}',\mathbf{k}}\right)^2 + \cdots,\\ &= \sum_{\mathbf{k}}\frac{\lambda^2\sum_{\mathbf{k}'}\chi_{\mathbf{k},\mathbf{k}'}K^{(2)}_{\mathbf{k}',\mathbf{k}}}{1-\lambda^2\sum_{\mathbf{k}'}\chi_{\mathbf{k},\mathbf{k}'}K^{(2)}_{\mathbf{k}',\mathbf{k}}}.\end{aligned} \tag{66}$$

Expression (64) then becomes

$$\Delta F(T) = k_B T\sum_{\mathbf{k}}\sum_{l=0}^{\infty}{}'\ln\left[1 - \sum_{\mathbf{k}'}\chi_{\mathbf{k},\mathbf{k}'}(-iy_l)K^{(2)}_{\mathbf{k},'\mathbf{k}}(-iy_l)\right]. \tag{67}$$

1. *High and Low Temperature Limits*

In the limit as $T \to \infty$ (strict classical limit) all but the zero-frequency susceptibilities vanish, as is readily ascertained by the form of (65). The free energy is then given by the leading ($l = 0$) term in (67). The corresponding energy (in the thermodynamic sense) can be gotten from the Gibbs–Helmholtz equation

$$\partial(T^{-1}\Delta F(T))/\partial(T^{-1}) = \Delta E(T). \tag{68}$$

For a system of harmonic oscillators, the static susceptibilities are temperature-independent and the classical value for E is zero. In the limit as $T \to 0$ (strict quantal limit), the spacing between the poles tends to zero and the summation can be replaced by an integration, i.e.,

$$\sum_{l=0}^{\infty}{}' \to \int_0^\infty dl = (\hbar/2\pi k_B T)\int_0^\infty dy \tag{69}$$

2. *Collective Behavior*

A further interpretation of the general result is obtained by considering the functional behavior of the integrand in (63) along the positive real ω axis. This equation can now be written

$$\Delta F(T) = \frac{\hbar}{2\pi} \operatorname{Re} i \sum_{\mathbf{k}} \int_0^\infty df \ln\left[1 - \sum_{\mathbf{k}'} \chi_{\mathbf{k},\mathbf{k}'}(f) K^{(2)}_{\mathbf{k}',\mathbf{k}}(f)\right] \coth(\hbar f/2k_B T). \quad (70)$$

Integration by parts yields

$$\Delta F(T) = -\frac{k_B T}{\pi} \operatorname{Re} i \sum_{\mathbf{k}} \int_0^\infty df \left(\ln \sinh \frac{\hbar f}{2k_B T}\right) \times \frac{(\partial/\partial f)[1 - \sum_{\mathbf{k}'} \chi_{\mathbf{k},\mathbf{k}'}(f) K^{(2)}_{\mathbf{k}',\mathbf{k}}(f)]}{1 - \sum_{\mathbf{k}'} \chi_{\mathbf{k},\mathbf{k}'}(f) K^{(2)}_{\mathbf{k}',\mathbf{k}}(f)}. \quad (71)$$

As path of integration we choose the ω axis avoiding the singularities by half-circle indentations from below. Along this axis, the function $[1 - \sum_{\mathbf{k}'} \chi_{\mathbf{k},\mathbf{k}'} K^{(2)}_{\mathbf{k}',\mathbf{k}}]$ has zeros at the points $\omega^{(c)}_{\eta\gamma}(\mathbf{k})$ which are the eigenfrequencies of the coupled system (see Section V, B). The integrand has poles also along the ω axis at the singularities of the susceptibilities $\chi_1(\omega)$ and $\chi_2(\omega)$; these occur at the transition frequencies $\omega^{(1)}_{mn}$ and $\omega^{(2)}_{pq}$ of the isolated molecules. The residues of the integrand (e.g., Hille, 1959) are $\ln \sinh(\hbar\omega^{(c)}_{\eta\gamma}(\mathbf{k})/2k_B T)$ at the zeros $\omega^{(c)}_{\eta\gamma}(\mathbf{k})$, $-\ln \sinh(\hbar\omega^{(1)}_{mn}/2k_B T)$ at $\omega^{(1)}_{mn}$ and similarly at $\omega^{(2)}_{pq}$. In carrying out the integration, we need not consider the segments between the singularities, since these are real and drop out when multiplied by Re *i*. From the residues we obtain

$$\Delta F(T) = k_B T\left[\sum_{\mathbf{k}} \sum_{\eta,\gamma} \ln \sinh(\hbar\omega^{(c)}_{\eta\gamma}(\mathbf{k})/2k_B T) - \sum_{m,n} \ln \sinh(\hbar\omega^{(1)}_{mn}/2k_B T) - \sum_{p,q} \ln \sinh(\hbar\omega^{(2)}_{pq}/2k_B T)\right]. \quad (72)$$

In the limit as $T \to 0$

$$\Delta F(0) = \Delta E(0) = (\hbar/2)\left[\sum_{\mathbf{k}} \sum_{\eta} \omega^{(c)}_{\eta 0}(\mathbf{k}) - \sum_{m} \omega^{(1)}_{m0} - \sum_{p} \omega^{(2)}_{p0}\right]. \quad (73)$$

This result has a simple physical interpretation: It is the change in the zero-point energy of the normal modes of the charge (-density) motion brought about by the Coulomb interaction. Thus, the energy shift is shown to depend explicitly on the collective behavior of the total system.

IV. The Dipolar Approximation

Most treatments of dispersion forces that include retardation are formulated in terms of dipolar interactions. We now present an elementary discussion of the retarded dipolar approximation based on the infinite-order reaction field scheme. For small molecules or molecules which are composites of small nonoverlapping units, the dipolar approximation furnishes an adequate description of the dispersion interaction. We now consider each molecule as one polarizable center.

In the dipole model of dispersion interaction, the results are generally expressed in terms of molecular polarizabilities, which are the transforms of the response functions to an electric field. The perturbation series can then be generated by considering directly the coupling between a fluctuating dipole moment and its reaction field. In complete analogy with the foregoing (see also Linder, 1967, and references therein), we find that in first approximation

$$\hat{\mathbf{E}}^{(2)}_{s\leftarrow 1}(t) = \int_{-\infty}^{t} dt' \hat{\boldsymbol{\kappa}}^{(2)}(t, t') \cdot \hat{\mathbf{m}}_1(t'), \tag{74}$$

where $\hat{\mathbf{E}}^{(2)}_{s\leftarrow 1}$ is the reaction-field operator produced by the moment $\hat{\mathbf{m}}_1$ and $\hat{\boldsymbol{\kappa}}^{(2)}(t, t')$, the response function. This leads to

$$F^{(2)}(T) = -(\hbar/4\pi) \operatorname{Re} i \int_{-\infty}^{\infty} d\omega \operatorname{tr} \boldsymbol{\alpha}_1(\omega) \cdot \boldsymbol{\kappa}^{(2)}(\omega) \coth(\hbar\omega/2k_B T). \tag{75}$$

In order to obtain an explicit expression for $\boldsymbol{\kappa}^{(2)}(\omega)$, we consider a field at a point $\mathbf{R}$ due to a system of charges and currents, at points $\mathbf{r}'$ centered about the origin:

$$\mathbf{E}(\mathbf{R}, t) = -\nabla\phi(\mathbf{R}, t) - \frac{1}{c}\frac{\partial \mathbf{A}(\mathbf{R}, t)}{\partial t} \tag{76}$$

or, in terms of their Fourier components,

$$\mathbf{E}(\mathbf{R}, \omega) = -\nabla\phi(\mathbf{R}, \omega) - \frac{i\omega}{c}\mathbf{A}(\mathbf{R}, \omega), \tag{77}$$

where

$$\phi(\mathbf{R}, \omega) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}', \omega)}{|\mathbf{R} - \mathbf{r}'|} \exp\left\{-\frac{i\omega}{c}|\mathbf{R} - \mathbf{r}'|\right\} \tag{78}$$

and

$$\mathbf{A}(\mathbf{R},\omega)=\frac{1}{c}\int d\mathbf{r}'\,\frac{\mathbf{j}(\mathbf{r}',\omega)}{|\mathbf{R}-\mathbf{r}'|}\exp\left\{-\frac{i\omega}{c}|\mathbf{R}-\mathbf{r}'|\right\}. \tag{79}$$

If d is of the order of the dimensions of the source, then for $R \gg d$

$$|\mathbf{R}-\mathbf{r}'| \cong R-\mathbf{R}\cdot\mathbf{r}'/R. \tag{80}$$

If also $d \ll 2\pi c\omega^{-1}=\lambda$, i.e., the wavelength of the emitted radiation is much larger than the source dimensions, then to terms linear in r'

$$\phi(\mathbf{R},\omega)\,\mathbf{R}\,\frac{\exp\{-i(\omega/c)R\}}{R}\left[\frac{\mathbf{R}}{R^2}+\frac{i\omega}{c}\frac{\mathbf{R}}{R}\right]\cdot\int\rho(\mathbf{r}',\omega)\mathbf{r}'\,d\mathbf{r}' \tag{81}$$

and

$$\mathbf{A}(\mathbf{R},\omega)=\frac{\exp\{-i(\omega/c)R\}}{R}\int d\mathbf{r}'\,\mathbf{j}(\mathbf{r}',\omega). \tag{82}$$

We note that $\int d\mathbf{r}'\,\rho(\mathbf{r}',\omega)\mathbf{r}'=\mathbf{m}(\omega)$ and $\int d\mathbf{r}'\,\mathbf{j}(\mathbf{r}',\omega)=i\omega\mathbf{m}(\omega)$. The latter can be inferred from the definition of $\mathbf{j}(\mathbf{r}',t)[\mathbf{j}(\mathbf{r}',t)=\sum_i e_i\dot{\mathbf{r}}_i'(t)\delta(\mathbf{r}'-\mathbf{r}_i'(t))]$ which leads to $\int d\mathbf{r}'\,\mathbf{j}(\mathbf{r}',t)=\dot{\mathbf{m}}(t)$. Using (81) and (82) then produces

$$\mathbf{E}(\mathbf{R},\omega)=-\mathbf{T}(\mathbf{R},\omega)\cdot\mathbf{m}(\omega), \tag{83}$$

where

$$\mathbf{T}(\mathbf{R},\omega)=\exp\{-i(\omega/c)R\}\left[\mathbf{I}\left(-\frac{\omega^2}{c^2R}+\frac{i\omega}{cR^2}+\frac{1}{R^3}\right)+\frac{\mathbf{RR}}{R^2}\left(\frac{\omega^2}{c^2R}-\frac{3i\omega}{cR^2}-\frac{3}{R^3}\right)\right] \tag{84}$$

or, more compactly,

$$\mathbf{T}(\omega)=-(\boldsymbol{\nabla\nabla}+\mathbf{I}\nabla^2)\exp[-i(\omega/c)R]/R. \tag{85}$$

For $d \ll R \ll \lambda$ the $\mathbf{T}$ tensor reduces to the static value, which varies as R^{-3}. For $R \gg \lambda \gg d$, $\mathbf{T}$ varies as $R^{-1}\exp\{-i(\omega/c)R\}$.

We now return to Eq. (75) and assume that the separation between the centers of molecules 1 and 2 (or between units in these molecules, as the case may be) is R. Since we took 1 to be the "signal generator," it is clear that the field produced at 2 is $\mathbf{E}_{s\leftarrow1}^{(1)}(\omega)=-\mathbf{T}(\omega)\cdot\mathbf{m}_1(\omega)$ and the reaction field is $\mathbf{E}_{s\leftarrow1}^{(2)}(\omega)=\mathbf{T}(\omega)\cdot\boldsymbol{\alpha}_2(\omega)\cdot\mathbf{T}(\omega)\cdot\mathbf{m}_1(\omega)$ hence

$$\boldsymbol{\kappa}^{(2)}(\omega)=\mathbf{T}(\omega)\cdot\boldsymbol{\alpha}_2(\omega)\cdot\mathbf{T}(\omega). \tag{86}$$

(The parametric dependence on R has been omitted.) Thus an explicit expression is obtained for $F^{(2)}(T)$ in terms of the properties of the isolated molecules. In a similar manner we generate the higher-order terms and, in the decorrelation approximation, get a closed form expression for the infinite-order free-energy shift

$$\Delta F(T) = -\frac{\hbar}{\pi} \operatorname{Re} i \int_0^1 \frac{d\lambda}{\lambda} \operatorname{tr} \int_0^\infty d\omega \frac{\lambda^2 \boldsymbol{\alpha}_1(\omega) \cdot \mathbf{T}(\omega) \cdot \boldsymbol{\alpha}_2(\omega) \cdot \mathbf{T}(\omega)}{\mathbf{I} - \lambda^2 \boldsymbol{\alpha}_1(\omega) \cdot \mathbf{T}(\omega) \cdot \boldsymbol{\alpha}_2(\omega) \cdot \mathbf{T}(\omega)} \times \coth \frac{\hbar\omega}{2k_B T}, \qquad (87)$$

$$= -\frac{\hbar}{\pi} \operatorname{Re} i \int_0^1 \frac{d\lambda}{\lambda} \operatorname{tr} \int_0^\infty d\omega \lambda^2 \boldsymbol{\alpha}_1(\omega) \cdot \mathbf{g}(\omega; \lambda) \coth \frac{\hbar\omega}{2k_B T}, \qquad (88)$$

where $\mathbf{g}(\omega; \lambda)$ is the dipolar analog of $G_{\mathbf{k},\mathbf{k}'}(\omega; \lambda)$ given in (62). Upon integrating,

$$\Delta F(T) = k_B T \sum_{l=0}' \operatorname{tr} \ln[\mathbf{I} - \boldsymbol{\alpha}_1(-iy_l) \cdot \mathbf{T}(-iy_l) \cdot \boldsymbol{\alpha}_2(-iy_l) \cdot \mathbf{T}(-iy_l)]. \qquad (89)$$

Small and Large Separations

In order to illustrate the functional dependence of the interaction on R let us assume the molecules to be isotropic and consider $F^{(2)}(0)$ as an integral along the y axis:

$$F^{(2)}(0) = E^{(2)}(0) = -(\hbar/2\pi) \int_0^\infty dy\, \alpha_1(-iy)\alpha_2(-iy) \operatorname{tr} \mathbf{T}(-iy) \cdot \mathbf{T}(-iy) \qquad (90)$$

Along the y axis, the $\mathbf{T}$ tensor takes the form

$$\mathbf{T}(-iy) = -(\nabla\nabla + \mathbf{I}\nabla^2) \exp[-(y/c)R]/R \qquad (91)$$

For small separation, $\mathbf{T}$ is effectively frequency independent and (90) reduces to

$$E^{(2)}(0) = -\frac{3\hbar}{\pi R^6} \int_0^\infty dy\, \alpha_1(-iy)\alpha_2(-iy)$$

$$= -\frac{6\hbar}{\pi^2 R^6} \int_0^\infty d\omega_1 \int_0^\infty d\omega_2 \frac{\alpha_1''(\omega_1)\alpha_2''(\omega_2)}{\omega_1 + \omega_2} \qquad (92)$$

on remembering that $\operatorname{tr} \mathbf{T}(0) \cdot \mathbf{T}(0) = 6\, R^{-6}$. This expression is a form of the London formula (London, 1937). On the other hand, for large R, $\mathbf{T}$ decreases very rapidly with y. Since $\alpha(-iy)$ decreases relatively slowly and monotonically when y goes from 0 to ∞, the major contribution comes from zero frequency. By replacing the $\alpha(-iy)$ by their static values, we get

$$E^{(2)}(0) = -(\hbar/2\pi)\alpha_1(0)\alpha_2(0) \int_0^\infty dy \, \mathrm{tr}\, \mathbf{T}(-iy) \cdot \mathbf{T}(-iy). \tag{93}$$

The latter reduces to the Casimir–Polder formula (1948)

$$E^{(2)}(0) = -(23\hbar c/4\pi R^7)\alpha_1(0)\alpha_2(0) \tag{94}$$

as shown by McLachlan (1963a).

For very high temperatures (strict classical limit), $F^{(2)}(T)$ is rigorously given by the leading ($l = 0$) term inasmuch as $\alpha(-iy_l)$ drops off very rapidly with increasing l [see Eq. (65)]. Therefore,

$$F^{(2)}(T) = -3k_BT[\alpha_1(0)\alpha_2(0)/R^6] \tag{95}$$

irrespective of distance. It appears that the retarded potential changes from an R^{-7} to an R^{-6} dependence as the temperature increases. There is, however, an overall weakening of the forces as the quantum fluctuations give way to thermal ones.

V. Relation to Other Theories

A. The Charge-Density Formulation of Longuet-Higgins (1956; Longuet-Higgins and Salem, 1960–1961)

If we substitute (44) into (45), switch to the y axis, we obtain for $T = 0$

$$F^{(2)}(0) = E^{(2)}(0) = -(\hbar/2\pi)\int d\mathbf{r}_1 \int d\mathbf{r}_1' \int d\mathbf{r}_2 \int d\mathbf{r}_2' \int_0^\infty dy$$
$$\times \chi_1(\mathbf{r}_1', \mathbf{r}_1, -iy)v(\mathbf{r}_1, \mathbf{r}_2)\chi_2(\mathbf{r}_2, \mathbf{r}_2', -iy)v(\mathbf{r}_2', \mathbf{r}_1'). \tag{96}$$

Substituting (29) and (35) yields, upon integrating out the y,

$$E^{(2)}(0) = -\frac{\hbar}{\pi^2}\int d\mathbf{r}_1 \int d\mathbf{r}_1' \int d\mathbf{r}_2 \int d\mathbf{r}_2' \int_0^\infty d\omega_1 \int_0^\infty d\omega_2$$
$$\times \frac{\chi_1''(\omega_1)\chi_2''(\omega_2)}{(\omega_1 + \omega_2)|\mathbf{r}_1 - \mathbf{r}_2|\,|\mathbf{r}_1' - \mathbf{r}_2'|}, \tag{97}$$

which is further reduced to

$$E^{(2)}(0) = -\frac{1}{\hbar}\int d\mathbf{r}_1 \cdots \int d\mathbf{r}_2' \, \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \, \frac{1}{|\mathbf{r}_1' - \mathbf{r}_2'|} \times \sum_{n \neq 0,\, p \neq 0} \frac{\rho_{0n}(\mathbf{r}_1)\rho_{n0}(\mathbf{r}_1')\rho_{0p}(\mathbf{r}_2)\rho_{p0}(\mathbf{r}_2')}{\omega_{n0}^{(1)} + \omega_{p0}^{(2)}} \tag{98}$$

on replacing the χ's by their respective matrix elements given in (15). Equation (98) is the charge-density formulation for the dispersion interaction obtained by Longuet-Higgins on the basis of ordinary time-independent perturbation theory.

B. The Coupled-Molecule Susceptibility

Equation (87) can be written

$$\Delta F(T) = (\hbar/\pi)\,\mathrm{Re}\, i \int_0^1 d\lambda (1/\lambda) \int_0^\infty d\omega \,\mathrm{tr}\, \boldsymbol{\alpha}_{12}^{(c)}(\omega; \lambda) \cdot \mathbf{T}(\omega) \coth(\hbar\omega/2k_{\mathrm{B}}T) \tag{99}$$

where

$$\boldsymbol{\alpha}_{12}^{(c)}(\omega; \lambda) = -\frac{\lambda^2 \boldsymbol{\alpha}_1(\omega) \cdot \mathbf{T}(\omega) \cdot \boldsymbol{\alpha}_2(\omega)}{\mathbf{I} - \lambda^2 \boldsymbol{\alpha}_1(\omega) \cdot \mathbf{T}(\omega) \cdot \boldsymbol{\alpha}_2(\omega) \cdot \mathbf{T}(\omega)} \tag{100}$$

The foregoing expression was first obtained by McLachlan *et al.* (1963–1964) on the basis of time-dependent Hartree theory. The emphasis in this and similar methods (Lundqvist and Sjölander, 1964; Mahan, 1965; Doniach, 1963; Lucas, 1967; Linderberg, 1964) is on the collective properties of the total system. In the Hartree approach $\boldsymbol{\alpha}_{12}^{(c)}(\omega)$ is obtained as an off-diagonal element of a generalized coupled molecule polarizability; the meaning of this concept is discussed more fully below.

Although Eq. (99) already establishes the equivalence of the time-dependent Hartree formulation and the reaction-field technique within the decorrelation approximation, it is instructive to analyze the problem from a slightly different point of view. In the time-dependent Hartree theory, the coupled polarizability $\boldsymbol{\alpha}_{12}^{(c)}$ is obtained from the response of a molecule to an external field in the presence of an average field due to the other molecule. We can obtain $\boldsymbol{\alpha}_{12}^{(c)}$ also by our present technique of multiple polarization processes by directly determining the moment induced by an external field.

Let $\mathbf{E}_1(t)$ and $\mathbf{E}_2(t)$ be the field strength at 1 and 2 respectively. The Fourier component of the induced moments are

$$\begin{aligned}\langle\hat{\mathbf{m}}_1(\omega)\rangle = {} & [\boldsymbol{\alpha}_1 + \boldsymbol{\alpha}_1\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_2\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_1 + \cdots]\cdot\mathbf{E}_1(\omega)\\ & - [\boldsymbol{\alpha}_1\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_2 + \boldsymbol{\alpha}_1\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_2\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_1\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_2 + \cdots]\cdot\mathbf{E}_2(\omega)\end{aligned} \tag{101}$$

and

$$\begin{aligned}\langle\hat{\mathbf{m}}_2(\omega)\rangle = {} & [\boldsymbol{\alpha}_2 + \boldsymbol{\alpha}_2\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_1\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_2 + \cdots]\cdot\mathbf{E}_2(\omega)\\ & - [\boldsymbol{\alpha}_2\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_1 + \boldsymbol{\alpha}_2\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_1\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_2\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_1 + \cdots]\cdot\mathbf{E}_1(\omega).\end{aligned} \tag{102}$$

(The dependence of $\mathbf{T}$ and $\boldsymbol{\alpha}$ on ω has here been suppressed.) The brackets indicate an average over unperturbed states. For example, $\langle\hat{\mathbf{m}}_1(\omega)\rangle$ is a Fourier component of the expectation value of $\hat{\mathbf{m}}(t)$, which is the dipole moment operator for 1 corrected to infinite order for the presence of the other molecule and to first-order in the external field. The leading term in the first series (101) is the moment induced by the applied field; the second term represents a process whereby the field is first scattered from 1, then from 2 and then returns to 1 to polarize it; etc. In the second series, the field first scatters from 2, and eventually polarizes 1.

The series can be summed to give

$$\langle\hat{\mathbf{m}}_1(\omega)\rangle = \frac{\boldsymbol{\alpha}_1}{\mathbf{I} - \boldsymbol{\alpha}_1\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_2\cdot\mathbf{T}}\,\mathbf{E}_1(\omega) - \frac{\boldsymbol{\alpha}_1\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_2}{\mathbf{I} - \boldsymbol{\alpha}_1\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_2\cdot\mathbf{T}}\,\mathbf{E}_2(\omega) \tag{103}$$

and

$$\langle\hat{\mathbf{m}}_2(\omega)\rangle = \frac{\boldsymbol{\alpha}_2}{\mathbf{I} - \boldsymbol{\alpha}_2\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_1\cdot\mathbf{T}}\,\mathbf{E}_2(\omega) - \frac{\boldsymbol{\alpha}_2\ \mathbf{T}\cdot\boldsymbol{\alpha}_1}{\mathbf{I} - \boldsymbol{\alpha}_2\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_1\cdot\mathbf{T}}\,\mathbf{E}_1(\omega), \tag{104}$$

which leads to

$$\begin{pmatrix}\langle\mathbf{m}_1(\omega)\rangle\\ \langle\mathbf{m}_2(\omega)\rangle\end{pmatrix} = \begin{pmatrix}\boldsymbol{\alpha}_{11}^{(c)} & \boldsymbol{\alpha}_{12}^{(c)}\\ \boldsymbol{\alpha}_{21}^{(c)} & \boldsymbol{\alpha}_{22}^{(c)}\end{pmatrix}\begin{pmatrix}\mathbf{E}_1(\omega)\\ \mathbf{E}_2(\omega)\end{pmatrix}, \tag{105}$$

where

$$\begin{pmatrix}\boldsymbol{\alpha}_{11}^{(c)} & \boldsymbol{\alpha}_{12}^{(c)}\\ \boldsymbol{\alpha}_{21}^{(c)} & \boldsymbol{\alpha}_{22}^{(c)}\end{pmatrix} = \begin{pmatrix}\dfrac{\boldsymbol{\alpha}_1}{\mathbf{I} - \boldsymbol{\alpha}_1\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_2\cdot\mathbf{T}} & \dfrac{-\boldsymbol{\alpha}_1\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_2}{\mathbf{I} - \boldsymbol{\alpha}_1\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_2\cdot\mathbf{T}}\\ \dfrac{-\boldsymbol{\alpha}_2\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_1}{\mathbf{I} - \boldsymbol{\alpha}_2\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_1\cdot\mathbf{T}} & \dfrac{\boldsymbol{\alpha}_2}{\mathbf{I} - \boldsymbol{\alpha}_2\cdot\mathbf{T}\cdot\boldsymbol{\alpha}_1\cdot\mathbf{T}}\end{pmatrix}. \tag{106}$$

It should be noted that if we factor out $\boldsymbol{\alpha}_1 \cdot \mathbf{T}$ in (101) from all the terms but the first, we get

$$\langle \mathbf{m}_1(\omega) \rangle = \boldsymbol{\alpha}_1(\omega) \cdot \mathbf{E}_1(\omega) - \boldsymbol{\alpha}_1 \cdot \mathbf{T}(\omega) \cdot \langle \mathbf{m}_2(\omega) \rangle, \tag{107}$$

and similarly,

$$\langle \mathbf{m}_2(\omega) \rangle = \boldsymbol{\alpha}_2(\omega) \cdot \mathbf{E}_2(\omega) - \boldsymbol{\alpha}_2(\omega) \cdot \mathbf{T}(\omega) \cdot \langle \mathbf{m}_1(\omega) \rangle. \tag{108}$$

These equations are the starting points for MacLachlan's formulation. It must be emphasized that this reduction is possible only under the assumption of decorrelation. The equivalence of the decorrelation and Hartree approximation is apparent.

The matrix element representation of $\boldsymbol{\alpha}_{12}^{(c)}$ is obtained in the usual manner. In particular,

$$\boldsymbol{\alpha}_{12}^{(c)}(\omega) = \lim_{\varepsilon \to 0} \frac{1}{\hbar} \sum_{\eta\gamma} \sigma_{\eta\eta}^{0} \left[\frac{(\mathbf{m}_1)_{\eta\gamma}(\mathbf{m}_2)_{\gamma\eta}}{\omega + \omega_{\gamma\eta} - i\varepsilon} - \frac{(\mathbf{m}_2)_{\eta\gamma}(\mathbf{m}_1)_{\gamma\eta}}{\omega - \omega_{\gamma\eta} - i\varepsilon} \right], \tag{109}$$

where the η, γ are states of the *coupled* system.

It is instructive to split (99) into two parts:

$$\begin{aligned} \Delta F(T) = \frac{\hbar}{\pi} \operatorname{tr} \int_0^1 \frac{d\lambda}{\lambda} \int_0^\infty & d\omega \{ \boldsymbol{\alpha}_{12}^{(c)''}(\omega; \lambda) \cdot \mathbf{T}'(\omega) \\ & + \boldsymbol{\alpha}_{12}^{(c)'}(\omega; \lambda) \cdot \mathbf{T}''(\omega) \} \coth \frac{\hbar\omega}{2k_{\mathrm{B}}T} \end{aligned} \tag{110}$$

The first term represents an interaction which arises from the fluctuation in the two-molecule system; the second term arises from fluctuation which originates in the field. At moderate distances only the first term prevails since $\mathbf{T}$ is independent of ω and, therefore $\mathbf{T}'' = 0$. In this case we can use the relation

$$\langle \mathbf{m}_1(-\omega)\mathbf{m}_2(\omega) + \mathbf{m}_2(-\omega)\mathbf{m}_1(\omega) \rangle = (h/\pi)\boldsymbol{\alpha}_{12}^{(c)''}(\omega) \coth(h\omega/2k_{\mathrm{B}}T), \tag{111}$$

which is the fluctuation–dissipation theorem (Landau and Lifshitz, 1958) specialized to the coupled-molecule polarizability, and obtain after integrating over ω

$$\Delta F(T) = \int_0^1 \frac{d\lambda}{\lambda} \langle \mathbf{m}_1(t; \lambda) \cdot \mathbf{T} \cdot \mathbf{m}_2(t) \rangle. \tag{112}$$

It should be emphasized that even though the operators are functions of time, the expectation value is not. This must be so since the correlation functions on which this formula is based depend only on time differences and not on the time itself, and this is consistent with the notion that the system is one of equilibrium. The states, as remarked before, are the unperturbed Heisenberg states, and the operators are unperturbed operators corrected to infinite order for the presence of the other moment. Since the expectation value is invariant under a unitary transformation (Löwdin, 1967), Eq. (112) can be written also as

$$\Delta F(T) = \int_0^1 \frac{d\lambda}{\lambda} \langle t | \hat{\mathbf{m}}_1(\lambda) \cdot \mathbf{T} \cdot \hat{\mathbf{m}}_2 | t \rangle, \tag{113}$$

where $|t\rangle$ and $\hat{\mathbf{m}}$ are now in the Schrödinger picture. The time dependence of the state functions actually drops out and (113) can be written in terms of the stationary states as

$$\Delta F(T) = \int_0^1 d\lambda (1/\lambda) \operatorname{tr} \hat{V}(\lambda) \hat{\sigma}(\lambda), \tag{114}$$

where $\hat{V}(\lambda) = \hat{\mathbf{m}}_1(\lambda) \cdot \mathbf{T} \cdot \hat{\mathbf{m}}_2$ and $\hat{\sigma}(\lambda)$ is the statistical operator in terms of $\mathscr{H}(\lambda) = \mathscr{H}_0 + \hat{V}(\lambda)$. Equation (114) has the standard form for the interaction free energy in equilibrium quantum-statistical mechanics.

The same analysis applies to the more general case in which the dipolar approximation is not made. In the latter case, the external probe would be a potential and the response a charge density. The susceptibility of the combined two-molecule system is obtained by using both the time and spatial decorrelation approximations. For example, the 1,2-element of the coupled susceptibility is

$$\chi^{(c)}_{1,2}(\mathbf{k}) = \sum_{\mathbf{k}'} \chi^{(1)}_{\mathbf{k},\mathbf{k}'} v_{\mathbf{k}'} \chi^{(2)}_{\mathbf{k}',\mathbf{k}} \Big/ \left(1 - \sum_{\mathbf{k}'} \chi^{(1)}_{\mathbf{k},\mathbf{k}'} v_{\mathbf{k}'} \chi^{(2)}_{\mathbf{k}',\mathbf{k}} v_{\mathbf{k}}\right). \tag{115}$$

The eigenfrequencies of the combined system are the poles of $\chi^{(c)}$. These occur at the zeros of $[1 - \sum \chi v \chi v]$. The eigenfrequencies are then the solutions of

$$\det\left| 1 - \sum_{k'} \chi^{(1)}_{\mathbf{k},\mathbf{k}'}(\omega) v_{\mathbf{k}'} \chi^{(2)}_{\mathbf{k}',\mathbf{k}}(\omega) v_{\mathbf{k}} \right| = 0; \tag{116}$$

and thus a definite relationship is established between the transition frequencies $\omega^{(c)}_{\eta\gamma}(\mathbf{k})$ and the $\chi_{\mathbf{k},\mathbf{k}'}(\omega)$ and $v_{\mathbf{k}}$.

VI. Harmonic Oscillators

As an illustration of the use of the susceptibility method we employ the formula for ΔF and treat the interaction between two isotropic harmonic oscillators in detail. For such a system, an exact result for ΔF is obtained.

Starting from formula (88) and neglecting retardation we have

$$\Delta F(T) = -(\hbar/\pi)\,\mathrm{Re}\, i \int_0^\infty d\lambda (1/\lambda) \int_0^\infty d\omega\, \mathrm{tr}\, \lambda^2 \alpha_1(\omega) \mathbf{g}(\omega; \lambda) \coth(\hbar\omega/2k_B T). \tag{117}$$

Let us examine α_1 and $\mathbf{g}$ as functions of the complex frequency $f = \omega - iy$. These are

$$\alpha_1(f) = \alpha_1(0)\omega_1{}^2/(\omega_1{}^2 - f^2), \tag{118}$$

where $\alpha_1(0)$ is the static polarizability of the isolated oscillator and ω_1 the natural frequency,

$$\mathrm{tr}\, \mathbf{g}(f;\lambda) = \mathrm{tr} \frac{\alpha_2(f)\mathbf{T}\cdot\mathbf{T}}{\mathbf{I} - \lambda^2 \alpha_1(f)\alpha_2(f)\mathbf{T}\cdot\mathbf{T}} \tag{119}$$

The latter reduces to

$$\mathrm{tr}\, \mathbf{g}(f; \lambda) = \sum_j T_{jj}^2 \frac{\alpha_2(0)\omega_2{}^2(\omega_1 + f)(\omega_1 - f)}{(f - \omega_j{}^+)(f + \omega_j{}^+)(f - \omega_j{}^-)(f + \omega_j{}^-)}, \tag{120}$$

where $T_{jj}^2 = (\mathbf{T}\cdot\mathbf{T})_{jj}$ and

$$\omega_j{}^\pm(\lambda) = \{\tfrac{1}{2}(\omega_1{}^2 + \omega_2{}^2) \pm \tfrac{1}{2}[(\omega_1{}^2 - \omega_2{}^2)^2 + 4\lambda^2\alpha_1(0)\alpha_2(0)\omega_1{}^2\omega_2{}^2 T_{jj}^2]^{1/2}\}^{1/2},$$

which are the zeros of the denominator.

Only the imaginary part of the integrand of (117) makes a contribution to the integral. On the real ω axis the integrand contains $\mathrm{tr}(\alpha_1''\mathbf{g}' + \alpha_1'\mathbf{g}'')$. The expressions for $\mathrm{tr}\,\mathbf{g}'$ and $\mathrm{tr}\,\mathbf{g}''$ are

$$\begin{aligned} \mathrm{tr}\, \mathbf{g}' = {} & \tfrac{1}{2}\alpha_2(0)\omega_2{}^2 \\ & \times \sum_j T_{jj}^2 \mathscr{P}\left[\frac{\omega_1{}^2 - (\omega_j{}^+)^2}{\omega_j{}^+(\omega_j{}^-)^2 - (\omega_j{}^+)^3}\left(\frac{1}{\omega - \omega_j{}^+} - \frac{1}{\omega + \omega_j{}^+}\right)\right. \\ & \left. + \frac{(\omega_j{}^-)^2 - \omega_1{}^2}{(\omega_j{}^-)^3 - (\omega_j{}^+)^2\omega_j{}^-}\left(\frac{1}{\omega - \omega_j{}^-} - \frac{1}{\omega + \omega_j{}^-}\right)\right] \end{aligned} \tag{121}$$

and

$$\operatorname{tr} \mathbf{g}'' = \tfrac{1}{2}\pi\alpha_2(0)\omega_2{}^2 \times \sum_j T_{jj}^2 \left[\frac{\omega_1{}^2 - (\omega_j{}^+)^2}{\omega_j{}^+(\omega_j{}^-)^2 - (\omega_j{}^+)^3}\left(\delta(\omega - \omega_j{}^+) - \delta(\omega + \omega_j{}^+)\right) + \frac{(\omega_j{}^-)^2 - \omega_1{}^2}{(\omega_j{}^-)^3 - (\omega_j{}^+)^2\omega_j{}^-}\left(\delta(\omega - \omega_j{}^-) - \delta(\omega + \omega_j{}^-)\right).\right] \tag{122}$$

Upon substituting for α_1', α_1'', $\operatorname{tr} \mathbf{g}'$ and $\operatorname{tr} \mathbf{g}''$ in (117) and integrating over ω we get

$$\Delta F(T) = \frac{\hbar}{2}\int_0^1 \frac{d\lambda}{\lambda}\sum_j \lambda^2 T_{jj}^2 \omega_1{}^2\omega_2{}^2\alpha_1(0)\alpha_2(0) \times \left\{\frac{\coth[\hbar\omega_j{}^+(\lambda)/2k_{\mathrm{B}}T]}{\omega_j{}^+(\lambda)[(\omega_j{}^+(\lambda))^2 - (\omega_j{}^-(\lambda))^2]} + \frac{\coth[\hbar\omega_j{}^-(\lambda)/2k_{\mathrm{B}}T]}{\omega_j{}^-(\lambda)[(\omega_j{}^-(\lambda))^2 - (\omega_j{}^+(\lambda))^2]}\right\}. \tag{123}$$

Integrating over λ yields

$$\Delta F(T) = k_{\mathrm{B}}T\sum_j\left(\ln\sinh\frac{\hbar\omega_j{}^+}{2k_{\mathrm{B}}T} + \ln\sinh\frac{\hbar\omega_j{}^-}{2k_{\mathrm{B}}T}\right) - 3k_{\mathrm{B}}T\left(\ln\sinh\frac{\hbar\omega_1}{2k_{\mathrm{B}}T} + \ln\sinh\frac{\hbar\omega_2}{2k_{\mathrm{B}}T}\right) \tag{124}$$

This expression is identical with the one obtained from statistical mechanics. It was derived also by Das (1964) by direct summation of Eq. (89) which McLachlan *et al.* (1963–1964) had derived on the basis of the time-dependent Hartree formulation.

The energy shift is obtained at once by the use of the Gibbs–Helmholtz equation:

$$\Delta E(T) = \frac{\hbar}{2}\sum_j\left(\omega_j{}^+\coth\frac{\hbar\omega_j{}^+}{2k_{\mathrm{B}}T} + \omega_j{}^-\coth\frac{\hbar\omega_j{}^-}{2k_{\mathrm{B}}T}\right) - \tfrac{3}{2}\hbar\omega_1\coth\frac{\hbar\omega_1}{2k_{\mathrm{B}}T} - \tfrac{3}{2}\hbar\omega_2\coth\frac{\hbar\omega_2}{2k_{\mathrm{B}}T}. \tag{125}$$

At finite temperature a second-order result is obtained by expanding $\mathbf{g}$ in Eq. (117), keeping the first term, and integrating over ω and λ. This yields

$$F^{(2)}(T) = -\frac{3}{2}\frac{\hbar\alpha_1(0)\alpha_2(0)\omega_1\omega_2}{R^6}$$

$$\times\left(\frac{\omega_1}{\omega_1{}^2-\omega_2{}^2}\coth\frac{\hbar\omega_2}{2k_BT}-\frac{\omega_2}{\omega_1{}^2-\omega_2{}^2}\coth\frac{\hbar\omega_1}{2k_BT}\right). \quad (126)$$

VII. Summary and Conclusions

The treatment presented here of the van der Waals interaction is based on a physically intuitive procedure for generating the perturbation terms for the free energy. The use of the decorrelation approximation provides a closed-form expression for the series. The connection between this treatment and those formulations based on the lowering of the zero-point energy of the collective modes of motion is established. The general expression for the free energy takes account of the correlative contributions from different parts of the molecules; this is important for the treatment of systems with delocalized electrons. There seems to be no simple way to include retardation except in a formal way or for special limiting cases.

The dipolar model for dispersion interaction is, generally, a good approximation for small molecules, and often also for some large molecules such as saturated hydrocarbons. The treatment of unsaturated hydrocarbons on the other hand, requires the general formulation. These and other special cases will be discussed in a future paper.

The theory presented here is based on the notion that the interaction results from the charge fluctuations of the molecules. If permanent moments are present, they give rise to generalized orientation (Keesom, 1921) and induction (Falkenhagen, 1922) forces in addition to the dispersion forces. This was explicitly shown for the dipolar case in a previous paper (Linder, 1964).

Slight complications arise in case of identical molecules at finite temperatures. Resonance interaction gives rise to terms in the free energy that are not accounted for by the adiabatic susceptibilities on which the present theory is based. Those terms correct for the redistribution of the population among the resonance states, the degeneracy of which is removed by the interaction (Kromhout and Linder, 1968). For high temperatures (classical limit), these correction terms are vanishingly small; they are absent at $T = 0$ inasmuch as the molecules are initially in their ground states, which are non degenerate. Ordinary room temperature is for most molecules effectively "zero" for the dispersion interaction and "very high" for orientation interaction. The adiabatic approximation is therefore valid for the cases of practical interest. The induction interaction arises from the correlation between electronic and rotational motion. The possibility of resonance states cannot arise.

The decorrelation approximation presents a more serious problem. In essence it neglects the distortion of the charge distributions resulting from the interaction. There is at present no reliable data available of the magnitude of this effect. Rough estimates of the static polarizability changes for interacting noble gas atoms at distances of closest approach seem to indicate that they are of the order of a few percent of the polarizability of the free atoms (e.g. Lim *et al.*, 1970; see also Jansen and Mazur, 1955; and Mazur and Jansen, 1955). The decorrelation approximation is expected to introduce small errors in the fourth-order perturbation term but will affect the higher-order terms in a more pronounced way. The leading term does not depend on the decorrelation approximation and it is essentially exact. The decorrelation approximation was shown to be equivalent to the time dependent Hartree, or other self-consistent field approximations (e.g., the RPA) and these theories suffer from the same shortcomings. A possible way to avoid these difficulties is to formulate a theory in terms of hypersusceptibilities. We must wait to see whether such a program can be pursued.

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Natural Orbitals

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I. Introduction

It has long been assumed that the charge and bond-order matrix (first-order reduced density matrix in modern terminology) contains most of the essential information about chemical bonding and electron distribution in a molecule. Numerous methods have been developed for extracting quantities of physical significance from the density matrix. Mulliken (1955) exemplifies attempts to base the analysis on minimum-basis-set atomic-orbital populations. Ruedenberg (1962) bases his analysis on the energy contribution arising from the changes in the density matrix upon going from the free atom to the molecule. Several other attempts to interpret this difference density have also appeared.

The basis of the assumption that the density matrix contains all information of chemical significance lies mainly in the fact that the Roothaan–Hartree–Fock self-consistent-field (SCF) wave function is easily reconstructed from the density matrix. Thus, to the extent that the SCF approximation is a sufficiently accurate description, all information is contained in the charge and bond-order matrix. It is now recognized, of course, that for most molecules the SCF approximation (a) gives a molecular energy above the separated atom SCF energy, (b) gives a potential curve with an R^{-1} dependence on internuclear separation at moderate to large

R, and (c) appears to give an energy minimum only because the wave function is constrained to go to the wrong limit at large R.

Hence inclusion of correlation effects is essential in a qualitatively correct interpretation of chemical bonding. The natural question then is to what extent the correlation effects can be interpreted in terms of the one-particle density matrix. The answer to this is now fairly clear. For a many-electron system, one can extract from the one-matrix a set of "natural" orbitals that are particularly efficient for describing the electron correlation in the molecule. In order to understand the correlation effects produced by these orbitals, however, one must reconstruct the wave function by a configuration-interaction calculation and then extract the two-particle density matrix. The one-matrix alone is not sufficient to regenerate the wave function for a correlated many-electron system or to understand how electrons correlate their distributions.

Natural spin-orbitals were first defined by Löwdin (1955). Soon after that, Löwdin and Shull (1956) showed that natural orbitals could be used to write a two-electron wave function in a simple canonical form. This form gave much more rapid convergence than the usual configuration-interaction wave function. Shull and Löwdin (1955, 1959) applied this theory to the helium ground state. Shull (1959) converted most of the then existent hydrogen molecule ground-state wave functions to natural orbital form. This early work has been the inspiration for most of the use of natural orbitals.

For many-electron systems, the simplicity introduced in the two-electron system by natural orbitals does not appear. Only for certain restricted classes of wave functions are the number of terms reduced. Nevertheless, there has been a steady stream of papers, beginning with work on carbon monoxide (Hurley, 1960), reporting natural orbitals for many-electron systems. By careful study of the wave function in natural orbital form it has been possible to develop an intuition about correlation effects which was missing earlier. Configuration-interaction wave functions based on natural orbitals are among the most accurate ever produced for many-electron systems. The extent of progress in interpretation of correlation effects is partially reflected in a comparison of the recent review by Smith (1968) with the earlier reviews by Löwdin (1959) and McWeeny (1960).

II. General Properties

Every electron may be described by a three-dimensional position vector $\mathbf{r}$, and a discrete spin variable ξ. For convenience, we will use the four-vector $\mathbf{x}$ to stand for $(\mathbf{r}, \xi)$ and $\int d\mathbf{x}$ to stand for $\sum_\xi \int d\tau$. Then the first-order reduced density matrix for a normalized, antisymmetric N-electron wave function may be defined (in Löwdin's normalization) as

$$D(\mathbf{x};\mathbf{x}') = N\int \psi(\mathbf{x},\mathbf{x}_2,\ldots,\mathbf{x}_N)\psi^*(\mathbf{x}',\mathbf{x}_2,\ldots,\mathbf{x}_N)\,d\mathbf{x}_2\cdots d\mathbf{x}_N. \quad (1)$$

In atomic units, the diagonal ($\mathbf{x}=\mathbf{x}'$) part of this matrix gives the probable number of electrons per bohr^3 near the point $\mathbf{r}$ with spin ξ.

The average value of any local one-electron operator

$$\mathcal{O} = \sum_{i=1}^{N} \mathcal{O}_1(\mathbf{x}_i)$$

may be obtained from D by

$$\langle\mathcal{O}\rangle = \int d\mathbf{x}\,d\mathbf{x}'\,\delta(\mathbf{x}-\mathbf{x}')\mathcal{O}_1(\mathbf{x})D(\mathbf{x};\mathbf{x}').$$

For a nonlocal operator defined by

$$\mathcal{O}_1 f = \int d\mathbf{x}'\mathcal{O}_1(\mathbf{x};\mathbf{x}')f(\mathbf{x}'), \qquad \langle\mathcal{O}\rangle = \int d\mathbf{x}\,d\mathbf{x}'\mathcal{O}_1(\mathbf{x}';\mathbf{x})D(\mathbf{x};\mathbf{x}').$$

In either case $\langle\mathcal{O}\rangle$ may be conveniently abbreviated as

$$\langle\mathcal{O}\rangle = \mathrm{Tr}(\mathcal{O}_1 D). \quad (2)$$

One particular example of a nonlocal operator of importance is associated with the " occupation number " or probable number of electrons in spin-orbital ϕ. This is given by

$$n_\phi = \mathrm{Tr}(|\phi\rangle\langle\phi|\,D) = \int d\mathbf{x}\,d\mathbf{x}'\phi^*(\mathbf{x})D(\mathbf{x},\mathbf{x}')\phi(\mathbf{x}'). \quad (3)$$

Only if two orbitals ϕ and ϕ' are orthogonal is the probability of finding an electron in one mutually exclusive with finding the electron in the other. The sum of n_ϕ over any complete orthonormal set is the trace of D (which by definition is N).

The form of these equations suggest that D itself should be regarded as the kernel of an integral operator $\mathcal{D}$,

$$\mathcal{D}f = \int d\mathbf{x}'\,D(\mathbf{x},\mathbf{x}')f(\mathbf{x}'). \quad (4)$$

From this viewpoint $\mathcal{D}$ is easily seen to be hermitian and positive semidefinite. The rank r of $\mathcal{D}$, defined as the number of nonzero eigenvalues, may be either finite or infinite. Löwdin (1955) has given the name "natural spin-orbitals" (NSO) to the eigenfunctions of $\mathscr{D}$.

Clearly, if

$$\mathscr{D}\chi_i = \lambda_i \chi_i, \tag{5}$$

λ_i is just the occupation number of the NSO χ_i. It is easily shown that $0 \le \lambda_i \le 1$ as expected from the Pauli exclusion principle. If ψ is a configuration-interaction wave function constructed from a finite number R of spin-orbital basis functions, then $r \le R$ and each χ_i is a linear combination of the basis orbitals. A more subtle theorem shown by Coleman (1963) is that for finite r, ψ may be expressed exactly in terms of the χ_i with nonzero λ_i.

Coleman (1963) also reviews the optimal properties of the NSO's. They offer the most rapidly convergent series approximation to D in the sense that, among all expansions of the form

$$D \approx \sum_{i,j}^{K} d_{ij} g_i(\mathbf{x}) g_j^*(\mathbf{x}')$$

with orthonormal g_i, the series

$$D \approx \sum_{i=1}^{K} \lambda_i \chi_i(\mathbf{x}) \chi_i^*(\mathbf{x}') \tag{6}$$

has the minimum possible least-square error for fixed K. Similarly, among all expansions of ψ of the form

$$\psi \approx \sum_{i,j}^{K} g_i(\mathbf{x}_1) h_j(\mathbf{x}_2, \ldots, \mathbf{x}_N),$$

the most rapidly convergent is

$$\psi \approx \sum_{i=1}^{K} \chi_i(\mathbf{x}_1) \phi_i(\mathbf{x}_2, \ldots, \mathbf{x}_N), \tag{7}$$

where

$$\phi_i = \int \chi_i^*(\mathbf{x}_1) \psi \, d\mathbf{x}_1.$$

A third sense in which the NSO's are optimal may be seen from considering an expansion of ψ in Slater determinants as

$$\psi = \sum_K C_K \Phi_K,$$

where

$$\Phi_K = (N!)^{-1/2} \operatorname{Det}\{g_{k_1} \cdots g_{k_N}\}; \qquad K = \{k_1 < k_2 \cdots < k_N\}.$$

Then the occupation number of g_k is

$$n_k = \sum_{\{K|k\in K\}} |C_K|^2. \tag{8}$$

Because the χ_i are the set of orbitals with maximum occupation number, each successive χ_i makes maximum contribution to the final complete wave function. This does not mean that the least-squares error using only $p(<r)$ of the NSO's is minimum since χ_i does not reach its maximum contribution λ_i until all other orbitals are included.

A. Perturbation Approach

The effect of electron correlation on the density matrix has been discussed by McWeeny (1960), Hirschfelder *et al.* (1964), and Davidson (1968). If ε is some relevant measure of the size of the correlation effect, ψ may be written in a perturbation expansion with ψ_{SCF} used for $\psi^{(0)}$ as

$$\psi = \psi_{\text{SCF}} + \varepsilon\psi_{\text{d}}^{(1)} + \varepsilon^2(\psi_{\text{s}}^{(2)} + \psi_{\text{d}}^{(2)} + \psi_{\text{t}}^{(2)} + \psi_{\text{q}}^{(2)}) + \cdots,$$

where ψ_{d} consists of double excitations from ψ_{SCF}, ψ_{s} of single, ψ_{t} of triple, and ψ_q of quadruple excitations. The density matrix arising from this expansion is

$$D = D_{\text{SCF}} + \varepsilon^2 D^{(2)} + \cdots,$$

where

$$D^{(2)} = \int d\mathbf{x}_2 \cdots d\mathbf{x}_N[\psi_{\text{d}}^{(1)}\psi_{\text{d}}^{(1)*} + \psi_{\text{s}}^{(2)}\psi_{\text{SCF}}^* + \psi_{\text{SCF}}\psi_{\text{s}}^{(2)*}].$$

If D is expressed in matrix form as

$$D = \sum d_{ij}\, g_i(\mathbf{x})g_j(\mathbf{x}')^*,$$

then the matrix $\mathbf{D}$ may be partitioned into blocks corresponding to the SCF occupied (o) and unoccupied (u) orbitals as

$$\mathbf{D} = \left(\begin{array}{c|c} \mathbf{D}_{\text{o,o}} & \mathbf{D}_{\text{o,u}} \\ \hline \mathbf{D}_{\text{u,o}} & \mathbf{D}_{\text{u,u}} \end{array}\right)$$

where

$$\mathbf{D}_{\text{SCF}} = \left(\begin{array}{c|c} \mathbf{1} & \mathbf{0} \\ \hline \mathbf{0} & \mathbf{0} \end{array}\right).$$

The product $\psi_{\text{d}}^{(1)}\psi_{\text{d}}^{(1)*}$ contributes to $\mathbf{D}_{\text{o,o}}^{(2)}$ and $\mathbf{D}_{\text{u,u}}^{(2)}$ while

$$\psi_{\text{s}}^{(2)}\psi_{\text{SCF}}^* + \psi_{\text{SCF}}\psi_{\text{s}}^{(2)*}$$

contributes to $\mathbf{D}_{\text{u,o}}^{(2)}$ and $\mathbf{D}_{\text{o,u}}^{(2)}$.

The eigenvectors of **D** give the coefficients for the expansion of the NSO's in the basis $\{g_i\}$ of SCF occupied and virtual orbitals. By applying perturbation theory to the calculation of the eigenvectors of **D** one can now reach the following conclusions.

(a) There are N natural spin orbitals with occupation numbers differing from unity by $\mathcal{O}(\varepsilon^2)$.

(b) The rest of the natural spin orbitals have occupation number $\mathcal{O}(\varepsilon^2)$.

(c) The mixing coefficients of occupied and unoccupied SCF orbitals in any natural orbital are of size $\mathcal{O}(\varepsilon^2)$.

(d) The highly occupied NSO's in zeroth order are a linear transformation of the occupied SCF orbitals, but this transformation is completely determined by $\psi_d^{(1)}$.

(e) The weakly occupied NSO's in zeroth order are a linear transformation of the virtual SCF orbitals, and this transformation is completely determined by $\psi_d^{(1)}$.

Thus while the χ_i are generally quite different from the SCF orbitals, the first natural configuration

$$\psi_{\mathrm{FNC}} = (N!)^{-1/2}\mathrm{Det}\{\chi_1 \cdots \chi_N\} \tag{9}$$

differs only by $\mathcal{O}(\varepsilon^2)$ from ψ_{SCF}. It should also be clear from this discussion that the NSO's are quite sensitive to the choice of configurations in a CI wave function. For many-electron systems of low symmetry, the NSO's from quite similar wave functions may differ significantly. This, of course, complicates the problem of approximating the NSO's of the exact wave function by NSO's of approximate wave functions. Generally the zeroth-order mixing of the SCF occupied orbitals is confined to those of nearly equal orbital energy. For this reason, the shell structure of atoms, where all orbitals of similar energy are of different symmetry, is nearly undisturbed by this zeroth-order mixing, while molecular valence orbitals may be strongly affected.

For two electron atomic ions with nuclear charge Z, the usual scaling transformation shows that ε is proportional to Z^{-1} (Byers Brown and Nazaroff, 1967). Hence the slightly occupied natural orbitals have occupation numbers proportional to Z^{-2}, and ψ_{FNC} or ψ_{SCF} becomes a better approximation to ψ as Z increases. It is well known, on the other hand, that the correlation energy for this system is nearly independent of Z. For atoms, one can see from the virial theorem that

$$E = -T = -\sum \lambda_i \langle \chi_i | -\tfrac{1}{2}\nabla^2 | \chi_i \rangle.$$

By the scaling procedure, the kinetic energy of any orbital should be proportional to Z^2 so the term-by-term contribution to E from the weakly occupied NSO's should be approximately independent of Z.

This effect may lead to difficulties with many-electron atoms. Each shell, with effective charge Z_{eff}, has a set of correlation orbitals associated with it whose occupation numbers are proportional to Z_{eff}^{-2}. For neon, for example, the occupation numbers for the main correlating orbitals of the 1s shell are more than an order of magnitude smaller than those for the 2s, 2p shell even though they are equally important to the energy. Properties other than the energy will scale in still different ways. In a calculation of ψ from a set of approximate natural orbitals, the choice of which orbitals to include must be influenced by what properties are to be predicted. Generally speaking, all orbitals making significant contributions to

$$\langle \mathcal{O} \rangle = \sum \lambda_i \langle \chi_i | \mathcal{O} | \chi_i \rangle$$

as well as all those contributing to E must be included correctly in ψ if an accurate value for $\langle \mathcal{O} \rangle$ is desired.

B. Cusp Constraint

A few general analytical properties of the NSO's are known. These are mainly related to cusp conditions, spin dependence, and symmetry properties.

If ψ is an eigenfunction of the usual Born–Oppenheimer hamiltonian, given by

$$H = \sum_i \left(-\tfrac{1}{2}\nabla_i^2 - \sum_\alpha Z_\alpha r_{i\alpha}^{-1} \right) + \sum_{i<j} r_{ij}^{-1} \tag{10}$$

for electrons i and nuclei α, then ψ satisfies the cusp condition (Pack and Byers Brown, 1966)

$$\lim_{r_{i\alpha} \to 0} [(l+1)\, \partial/\partial r_{i\alpha} + Z_\alpha] r_{i\alpha}^{-l} \int d\Omega_{i\alpha}\, Y_{l,m}^{*}(\Omega_{i\alpha}) \psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = 0 \tag{11}$$

for all l, m, α. It has been shown by Poling *et al.* (1971) that a necessary and sufficient condition for ψ to satisfy this cusp condition is that every NSO with λ_i nonzero satisfy this same condition. Thus, if it is desired to constrain an approximate wave function to satisfy one of the cusp conditions, it is necessary and sufficient to constrain the occupied natural orbitals to satisfy that condition. If the NSO's are expanded in a set of basis orbitals that do not satisfy the cusp conditions, it can be shown that each cusp condition requires the exclusion of one linear combination of the basis orbitals from the space spanned by the NSO's.

Bingel (1963) has discussed the cusp condition for the density matrix. For $l = 0$, (11) yields

$$\lim_{r_\alpha \to 0} [\partial/\partial r_\alpha + 2Z_\alpha] \sum_\xi \int d\Omega_\alpha D(\mathbf{x}, \mathbf{x}) = 0.$$

C. Spin Dependence

The spin dependence of the NSO's is relatively simple if ψ is an eigenfunction of $\mathscr{S}^2$ and $\mathscr{S}_z$ with eigenvalues $S(S+1)$ and M. In this case D may be written as (McWeeney, 1960)

$$D = \tfrac{1}{2}[\alpha(\xi)\alpha(\xi')^* + \beta(\xi)\beta(\xi')^*]\rho(\mathbf{r}, \mathbf{r}') + \tfrac{1}{2}[\alpha(\xi)\alpha(\xi')^* - \beta(\xi)\beta(\xi')^*]\gamma(\mathbf{r}, \mathbf{r}') \tag{12}$$

where

$$\operatorname{Tr} \rho = N = N_\alpha + N_\beta, \qquad \operatorname{Tr} \gamma = 2M = N_\alpha - N_\beta .$$

The function ρ is called the charge density matrix and gives the electron spatial distribution,

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{\xi, \xi'} \delta_{\xi, \xi'} D(\mathbf{x}, \mathbf{x}'). \tag{13}$$

The diagonal elements of ρ are the probable numbers of electrons per bohr^3. The function $(2M)^{-1}\gamma$ is usually called the spin-density matrix,

$$\gamma(\mathbf{r}, \mathbf{r}') = 2 \sum_{\xi, \xi'} \delta_{\xi, \xi'} \mathscr{S}_z D(\mathbf{x}, \mathbf{x}'). \tag{14}$$

It can be shown (Kutzelnigg, 1963c; Bingel, 1960) that $M^{-1}\gamma$ and ρ are independent of M within a set of $\psi_{S,M}$ connected by $\mathscr{S}_\pm$. From the formula (2) for the expectation values it follows that, if $\mathscr{O}$ is spin free,

$$\langle \mathscr{O} \rangle = \operatorname{Tr}(\mathscr{O}_1 \rho)$$

is independent of M. If $\mathscr{O}_1$ is of the form $u(\mathbf{r})\mathscr{S}_z$ then

$$\langle \mathscr{O} \rangle = \tfrac{1}{2} M \operatorname{Tr}(u M^{-1} \gamma)$$

is linear in M.

The natural spin-orbitals of $\psi_{S,M}$ can be chosen to be eigenfunctions of $\mathscr{S}_z$. The spatial dependence of the NSO's is computed from the integral kernel $\rho + \gamma$ for α spin and $\rho - \gamma$ for β spin. Only if $M = 0$ will these sets of spatial orbitals coincide.

Thus the NSO's are the natural basis for use in a configuration-interaction extension of an unrestricted SCF calculation. Because of the large difference in computer time and computer storage between CI calculations with Slater determinants built from unrestricted spin-orbitals compared with spin-restricted orbitals, few CI calculations have actually been done with NSO's (for $M \neq 0$). Besides this practical difficulty, the fact that the spatial dependence of each NSO would be different for each M makes the NSO's conceptually undesirable.

Most calculations for $S \neq 0$ are performed with spin-restricted orbitals because formation of spin eigenfunctions from Slater determinants in such a basis is trivial. A "best" basis for such a calculation are the natural orbitals (NO's). These are defined as α or β times the eigenfunctions of ρ,

$$\int \rho(\mathbf{r}, \mathbf{r}')g_i(\mathbf{r}')d\tau' = \mu_i g_i(\mathbf{r}). \tag{15}$$

The occupation number μ_i of the NO g_i lies between zero and two. The charge density has an expansion in the g_i of the form

$$\rho(\mathbf{r}, \mathbf{r}') = \sum \mu_i g_i(\mathbf{r})g_i^*(\mathbf{r}').$$

The comments made previously about the optimal properties of the NSO's apply with only slight modification to the NO's. The NO's, of course, are independent of M and coincide with the NSO's for $M = 0$.

D. Symmetry Properties

There have been numerous papers on the symmetry properties of density matrices and natural orbitals (Bingel, 1960, 1962, 1970; Bingel and Kutzelnigg, 1968, 1969; McWeeny and Kutzelnigg, 1968). The basic result is that, if ψ belongs to a nondegenerate irreducible representation of a point group, then the NO's and NSO's can be chosen to be symmetry adapted with all partners for an irreducible representation equally occupied. If ψ is degenerate due to symmetry, then the NO's will generally not be of pure symmetry. The most common failing in this respect is that the partner functions to a natural orbital belonging to a degenerate representation will not themselves be natural orbitals. For example, in the $\sigma_g \pi_u {}^3\Pi_u$ state of H_2, the complex conjugates of the natural π_u orbitals are not the natural π_u^* orbitals.

Most calculations are done in the spirit of the Hartree atomic calculations with forced equivalence of partner orbitals in degenerate irreducible representations. Again this is primarily for computational advantage as use of different radial parts for $2p_1$, $2p_0$, and $2p_{-1}$ would lead to unnecessary complications in the CI calculation. Also there is a conceptual advantage to using the same set of orbitals for all of the wave functions in the degenerate state. The symmetry-constrained natural orbitals (SCNO's) are usually generated by diagonalizing a symmetrized density matrix. This matrix is easily generated in practice by averaging the density matrix over the ensemble of degenerate states. Except for some two-electron calculations, most extensive CI calculations have been done with SCNO's.

For this ensemble averaged density, all SCNO's related by symmetry as partners in an irreducible representation will have the same occupation numbers. Many tabulations of these orbitals list only the total occupation number for all the partners. In this case the total occupation number is bounded by $2d$ where d is the dimension of the irreducible representation.

III. Two-Electron Wave Functions

Wave functions for two-electron systems are an important special case in the theory of natural orbitals. In this case the form of the wave function is greatly simplified by the natural orbital expansion. This simplification was first pointed out by Löwdin and Shull (1956) and has been discussed in detail by Carlson and Keller (1961), Davidson (1962), and Rothenberg and Davidson (1966).

Suppose ψ is a two-electron function, with spin included. Then the minimum of the expression

$$\int d\mathbf{x}_1\, d\mathbf{x}_2 |\psi - \sum_{i,j}^{K} \mu_{ij} f_i(\mathbf{x}_1) t_j^*(\mathbf{x}_2)|^2,$$

where $\{f_i\}$ and $\{t_i\}$ are orthonormal sets, is achieved if

$$\int \psi(\mathbf{x}_1, \mathbf{x}_2) f_i^*(\mathbf{x}_1)\, d\mathbf{x}_1 = \mu_i t_i^*(\mathbf{x}_2) \tag{16a}$$

$$\int \psi(\mathbf{x}_1, \mathbf{x}_2) t_i(\mathbf{x}_2)\, d\mathbf{x}_2 = \mu_i f_i(\mathbf{x}_1) \tag{16b}$$

and

$$\psi \approx \sum_{i=1}^{K} \mu_i f_i(\mathbf{x}_1) t_i^*(\mathbf{x}_2). \tag{17}$$

That is, $\mu_i t_i^*$ is the Fourier coefficient of f_i and $\mu_i f_i$ is the Fourier coefficient of t_i^*. This factorization is quite similar to that given for the density matrix in the previous section except that ψ, treated as an integral kernel, is neither hermitian nor positive.

It is informative to multiply (16a) by $\psi^*(\mathbf{x}_1', \mathbf{x}_2)$ and integrate over $\mathbf{x}_2$ to obtain

$$\int \psi^*(\mathbf{x}_1', \mathbf{x}_2)\psi(\mathbf{x}_1,\mathbf{x}_2)f_i^*(\mathbf{x}_1)\, d\mathbf{x}_1\, d\mathbf{x}_2 = \mu_i \int \psi^*(\mathbf{x}_1', \mathbf{x}_2)t_i^*(\mathbf{x}_2)\, d\mathbf{x}_2$$

or

$$\frac{1}{2}\int D(\mathbf{x}_1', \mathbf{x}_1)f_i(\mathbf{x}_1)\, d\mathbf{x}_1 = |\mu_i|^2 f_i(\mathbf{x}_1'). \tag{18}$$

similarly, one can show

$$\frac{1}{2}\int D(\mathbf{x}_1, \mathbf{x}_1')t_i(\mathbf{x}_1') = |\mu_i|^2\, t_i(\mathbf{x}_1). \tag{19}$$

Hence the orbitals which lead to the best factored form for ψ are NSO's. The converse is not generally true, however, as (16) associates a unique t_i with each f_i whereas (18) and (19) allow considerable freedom in the selection of f and t if the occupation numbers $2|\mu|^2$ are degenerate. Any arbitrary choice of NSO's can be used for the f_i if the corresponding t_i are found by (16a).

Often some particular choice of the f_i are of obvious conceptual convenience. These usually lead to a correspondingly convenient choice for the t_i. For example, for a singlet state wave function

$$\psi = \Phi(\mathbf{r}_1, \mathbf{r}_2)(\alpha\beta - \beta\alpha)/2^{1/2}$$

the natural orbitals $g_i\alpha$ and $g_i\beta$ defined in (15) are also NSO's. Clearly if $f = g_i\alpha$ the corresponding t is $\tilde{g}_i\beta$ where

$$\int \Phi(\mathbf{r}_1, \mathbf{r}_2)g_i^*(\mathbf{r}_1)\, d\tau_1 = \gamma_i\tilde{g}_i^*(\mathbf{r}_2) \qquad \text{and} \qquad \gamma_i = 2^{1/2}\mu_i.$$

Hence a convenient natural expansion of ψ is

$$\psi = \sum_i \gamma_i g_i(\mathbf{r}_1)\tilde{g}_i^*(\mathbf{r}_2)(\alpha\beta - \beta\alpha)/2^{1/2} \tag{20}$$

or

$$\Phi = \sum_i \gamma_i g_i(\mathbf{r}_1)\tilde{g}_i^*(\mathbf{r}_2). \tag{21}$$

If the eigenvalues of $\rho(\mathbf{r}_1, \mathbf{r}_2)$ are nondegenerate, this expansion for Φ is unique and g_i and $\tilde{g}_i$ differ by a multiplicative constant which can be chosen to be unity. If the eigenvalues of ρ are degenerate, as they would be if g_i were a π orbital in a Σ state of a diatomic molecule, then a degree of arbitrariness remains which allows either

$$2p_x(\mathbf{r}_1)2p_x(\mathbf{r}_2) + 2p_y(\mathbf{r}_1)2p_y(\mathbf{r}_2) \qquad \text{or} \qquad 2p\pi(\mathbf{r}_1)2p\pi^*(\mathbf{r}_2) + 2p\pi^*(\mathbf{r}_1)2p\pi(\mathbf{r}_2)$$

to be used in the natural expansion of Φ.

A more complicated case arises if the degenerate eigenvalues of ρ belong to different irreducible representations. For a ${}^1\Pi_u$ state of H_2, the natural orbitals of ρ can be chosen to be σ_g and π_u which leads to the convenient form

$$\sigma_g(\mathbf{r}_1)\pi_u(\mathbf{r}_2) + \pi_u(\mathbf{r}_1)\sigma_g(\mathbf{r}_2)$$

in the natural expansion of Φ. As mentioned previously, in this case the $\pi_u{}^*$ orbitals, which occur in terms such as

$$\pi_u{}^*(\mathbf{r}_1)\delta_g(\mathbf{r}_2) + \delta_g(\mathbf{r}_1)\pi_u{}^*(\mathbf{r}_2),$$

are not the complex conjugates of the π_u natural orbitals.

If the eigenvalues of ρ are nearly, but not quite, degenerate the natural expansion often assumes a highly nonintuitive form. For the $1\sigma_g 2\sigma_g {}^1\Sigma_g{}^+$ state of H_2 (or similarly for the $1s2s\,{}^1S$ state of helium), the first two eigenvalues of ρ differ slightly. The NO's turn out, in this case, to be approximately given as

$$g_1 \approx 2^{-1/2}(1\sigma_g + 2\sigma_g), \qquad g_2 \approx 2^{-1/2}(1\sigma_g - 2\sigma_g)$$

so the expansion

$$\gamma_1 g_1(\mathbf{r}_1)g_1(\mathbf{r}_2) - \gamma_2 g_2(\mathbf{r}_1)g_2(\mathbf{r}_2)$$

looks quite different from the intuitive form,

$$1\sigma_g(\mathbf{r}_1)2\sigma_g(\mathbf{r}_2) + 2\sigma_g(\mathbf{r}_1)1\sigma_g(\mathbf{r}_2).$$

To get around this difficulty, it is convenient to introduce the (u, v) form for singlet wavefunctions. Let

$$b_1 = |\gamma_1|/(\gamma_1{}^2 + \gamma_2{}^2)^{1/2}, \qquad b_2 = |\gamma_2|/(\gamma_1{}^2 + \gamma_2{}^2)^{1/2},$$

$$u = (b_1^{1/2}g_1 + b_2^{1/2}g_2)/(b_1 + b_2)^{1/2}, \qquad v = (b_1^{1/2}g_1 - b_2^{1/2}g_2)/(b_1 + b_2)^{1/2}.$$

Then for γ_1 and γ_2 positive, the two terms in g_1 and g_2 may be rewritten identically as

$$\tfrac{1}{2}(b_1 + b_2)[u(\mathbf{r}_1)v(\mathbf{r}_2) + v(\mathbf{r}_1)u(\mathbf{r}_2)].$$

For an open-shell state, γ_1 and γ_2 will be about equal so that u and v will be nearly orthogonal. For a closed-shell ground state, this (u, v) form corresponds to the split-shell approximation $(1s, 1s')$ for He or

$$((1s_a + \lambda 1s_b), (\lambda 1s_a + 1s_b))$$

for H_2.

For the triplet state wavefunction

$$\Psi = \Phi(\mathbf{r}_1, \mathbf{r}_2)\alpha\alpha$$

the NO's are the same as the α type NSO's. If f is $g_i\alpha$ and t is $\tilde{g}_i\alpha$, then

$$\Psi = \sum \gamma_i g_i(\mathbf{r}_i)\tilde{g}_i^*(\mathbf{r}_2)\alpha\alpha \tag{22}$$

and Φ is given by (21). Now if Φ is to be antisymmetric, the product $g_i(\mathbf{r}_1)\tilde{g}_i^*(\mathbf{r}_2)$ must be of rank two; i.e., $\tilde{g}_i^*$ must be orthogonal to g_i and the eigenvalues of ρ must be evenly degenerate. Just as for singlet states, if the degenerate eigenvalues of ρ belong to different irreducible representations or different partners within one representation, the natural orbitals are most conveniently chosen to be symmetry adapted. For the $1\sigma_g 2\sigma_g\,{}^3\Sigma_g{}^+$ state of H_2, there is no nonarbitrary way to pick the σ_g or σ_u NO's since the degenerate occupation numbers occur within the same symmetry subspace of ρ.

A. Calculation of the Natural Orbitals

There are three main methods for obtaining NO's for two-electron systems. The first of these (Löwdin and Shull, 1956), and by far the simplest and most widely applied, is to construct a CI wave function in a finite basis set $\{\varphi_i\}$ and then to solve (16) in the matrix form

$$\Phi_{lk} = \int \varphi_l^*(\mathbf{r}_1)\Phi(\mathbf{r}_1, \mathbf{r}_2)\varphi_k(\mathbf{r}_2)\, d\tau_1\, d\tau_2, \tag{23}$$

$$g_i = \sum g_{ki}\, \varphi_k(\mathbf{r}), \tag{24}$$

$$\tilde{g}_i = \sum \tilde{g}_{ki}\, \varphi_k(\mathbf{r}), \tag{25}$$

$$S_{lk} = \int \varphi_l^*(\mathbf{r})\varphi_k(\mathbf{r})\, d\tau, \tag{26a}$$

$$\mathbf{\Phi}\tilde{g}_i = \gamma_i \mathbf{S}\mathbf{g}_i, \tag{26b}$$

$$\mathbf{\Phi}^\dagger \mathbf{g}_i = \gamma_i^* \mathbf{S}\tilde{g}_i,$$

Because

$$\boldsymbol{\rho} = 2\boldsymbol{\Phi}^{\dagger}\mathbf{S}^{-1}\boldsymbol{\Phi}, \tag{27}$$

we have

$$\boldsymbol{\rho}\mathbf{g}_i = 2|\gamma_i|^2\mathbf{S}\mathbf{g}_i, \tag{28a}$$

and

$$\boldsymbol{\rho}\tilde{g}_i = 2|\gamma_i|^2\mathbf{S}\tilde{g}_i. \tag{28b}$$

Since Φ is expressible in this basis set $\{\varphi_i\}$, these equations are exact. If Φ is written as

$$\Phi = \sum c_{ij}\,\varphi_i(\mathbf{r}_1)\varphi_j^*(\mathbf{r}_2) \tag{29}$$

then

$$\boldsymbol{\Phi} = \mathbf{SCS}$$

and $\boldsymbol{\rho} = 2\mathbf{SC}^{\dagger}\mathbf{SCS}$. Equations (28a) and (26b) are easily solved to yield an exact NO expansion of the approximate wavefunction Φ.

For both He and H_2 there exist much better wave functions than those formed from finite CI expansions. These involve the $\mathbf{r}_{12}$ coordinate explicitly and have infinite rank. If one approximates a Φ of this form by an expansion of the form

$$\sum_{i,j}^{K} \gamma_{ij}\,g_i(\mathbf{r}_1)\tilde{g}_j^*(\mathbf{r}_2)$$

where g_i and $\tilde{g}_j$ are themselves expanded in a finite basis set $\{\varphi_i\}$, the least-squares deviation is minimum for Φ approximated as in (21) with the g_i and $\tilde{g}_i$ computed from (23)–(28) (Davidson, 1962). Convergence can be measured by the approach of $\sum |\gamma_i|^2$ to unity. Deviations from unity will be corrected as the basis set is enlarged by the appearance of additional γ_i and by variations in those found previously. If the $\boldsymbol{\rho}$ matrix were merely bordered by the enlargement of the basis $\{\varphi_i\}$, the $|\gamma_i|^2$ would be lower bounds to their true values. But since all the elements of $\boldsymbol{\rho}$ given by (27) change as they converge toward the true matrix elements of $\rho(\mathbf{r}_1\mathbf{r}_2)$ in this basis, no rigorous statement can be made about the sign of the error in the $|\gamma_i|^2$. A heuristic argument that the $|\gamma_i|^2$ tend to be too small may be made by defining P as the projection operator onto the N-particle subspace spanned by products of the φ_i, and Q as the projection onto the orthogonal complement. Then

$$\begin{aligned}\frac{1}{2}\int g_i{}^*\rho g_i\,d\tau\,d\tau' &= \int g_i{}^*(1)\Phi(1,2)(P^2+Q^2)\Phi^*(1',2)g_i(1')d\tau_1\,d\tau_1'\,d\tau_2\\ &= |\gamma_i|^2 + \int (Q\Phi^*g_i)^*(Q\Phi^*g_i)\,d\tau_1\,d\tau_1'\,d\tau_2\\ &\geq |\gamma_i|^2\end{aligned}$$

and

$$\frac{1}{2}\int g_i{}^*\rho g_j\,d\tau_1\,d\tau_1' = \int g_i{}^*\Phi Q^2\Phi^* g_j\,d\tau \qquad (i \neq j)$$

$$\int |Q\Phi|^2\,d\tau = 1 - \sum |\gamma_i|^2.$$

Thus for the true ρ operator, instead of the approximate one defined by (27), the diagonal elements would be larger than $|\gamma_i|^2$, and the off-diagonal elements should be small as convergence is approached. Hence the $|\gamma_i|^2$ should approach their limiting values from below. Clearly, as in the CI method, the accuracy is limited by the basis set. For any particular finite basis, the results from the CI method and this method would be different and the energy from the CI method would be lower.

A third approach to natural orbitals is to attempt a direct calculation from the Schrödinger equation without first finding a wave function. Löwdin (1955), Kutzelnigg (1963a), Reid and Öhrn (1963), and Nazaroff (1968) all discuss coupled integro-differential equations for the NO's. Linderberg (1964) and Reinhardt and Doll (1969) discuss the direct calculation of natural orbitals by perturbation theory. Of these approaches, only Kutzelnigg has pursued his procedure to obtain results of meaningful accuracy.

Kutzelnigg's approach takes advantage of the fact that, for a closed-shell state, a reasonable choice for the g_i is the one for which $\tilde{g}_i = g_i$ and Φ becomes

$$\Phi = \sum \gamma_i g_i(\mathbf{r}_1) g_i{}^*(\mathbf{r}_2), \tag{30}$$

where the γ_i are real. For the atomic ions and for molecules at small R, the first γ is nearly unity, while the remaining γ_i are small. If H is written as

$$H = h(1) + h(2) + r_{12}^{-1},$$

then

$$\bar{E} = \langle H \rangle = \sum \gamma_i \gamma_j [2h_{ii}\delta_{ij} + K_{ij}]$$

where K_{ij} is the usual exchange integral. Variation of $\bar{E}$ with respect to the g_k subject to orthonormality constraints gives

$$[\gamma_k{}^2 h + \sum_i \gamma_k \gamma_i \mathscr{K}_i] g_k = \sum_i \lambda_{ik} g_i \tag{31}$$

or

$$\gamma_k{}^2 G_k g_k = \sum_i \lambda_{ik} g_i, \tag{32}$$

where

$$G_k = h + \sum_i \gamma_i \gamma_k^{-1} \mathscr{K}_i. \tag{33}$$

This gives rise to a double iteration procedure with the natural orbitals calculated from (32) at one stage and the γ_k calculated from ordinary CI for the configurations in (30) at the next stage.

Although Kutzelnigg did not do so, (32) can be put into a different form by elimination of the off-diagonal Lagrangian multipliers. In order for (32) to be valid, λ must be hermitian. This is easily accomplished by using

$$\lambda_{ik} = \lambda_{ki}^* = \gamma_k{}^2 \langle g_i | G_k | g_k \rangle \qquad \text{for} \quad i < k. \tag{34}$$

Substitution of this into (32) and insertion of some terms which are zero but are needed to preserve hermiticity gives,

$$\mathscr{G}_k = P_k\{G_k - \sum_{i>k} (\gamma_i/\gamma_k)^2 [|g_i\rangle\langle g_i| G_i + G_i |g_i\rangle\langle g_i|]\} P_k, \tag{35}$$

$$\gamma_k{}^2 \mathscr{G}_k g_k = \lambda_{kk} g_k, \tag{36}$$

$$P_k = \mathbf{1} - \sum_{i<k} |g_i\rangle\langle g_i|. \tag{37}$$

The energy is given by

$$\bar{E} = \sum \lambda_{kk} + \gamma_k{}^2 h_{kk} = \sum \gamma_k{}^2 \langle g_k | G_k + h | g_k \rangle$$

or

$$\bar{E} = \sum \gamma_k{}^2 (\varepsilon_k + h_{kk}), \tag{38}$$

where

$$\lambda_{kk} = \gamma_k{}^2 \varepsilon_k.$$

Now for $\gamma_1 \approx 1$, and the NO's numbered in order of decreasing $|\gamma_i|$, (36) can be conceptually approximated as

$$P_k\{h + (\gamma_1/\gamma_k)\mathscr{K}_1\}P_k g_k \approx \varepsilon_k g_k, \qquad k \neq 1, \tag{39}$$

$$\{h + \mathscr{K}_1\}g_1 \approx \varepsilon_1 g_1. \tag{40}$$

Hence to the first approximation, g_1 is just the SCF orbital. Since the CI equation for γ_i gives

$$\gamma_i \approx -K_{1i}(\varepsilon_i - \varepsilon_1)^{-1}, \tag{41}$$

γ_i is negative. Hence the g_k are bound not only by the nuclear potential, but also by the very large exchange potential

$$-(\varepsilon_i - \varepsilon_1)K_{1i}^{-1}\mathscr{K}_1.$$

As k increases, γ_k decreases; so the potential felt by the higher NO's is much more attractive than for the lower ones. As a consequence, the NO's remain strongly localized in the region of space occupied by the SCF orbital. In fact, they resemble the eigenfunctions of a particle in a box the size of g_1. They do not at all resemble the virtual SCF orbitals or the Rydberg orbitals.

The difference between g_1 and g_{SCF} has been discussed at length by several authors (Nazaroff and Hirschfelder, 1963). From (36), to the next approximation

$$\{h + \mathscr{K}_1 - \sum_{i>1} |\gamma_i| \mathscr{K}_i\}g_1 \approx \varepsilon_1 g_1. \tag{42}$$

Hence g_1 would be expected to be contracted relative to g_{SCF} due to the exchange potentials of the other NO's. This effect is small, however, for since $\mathscr{K}_i g_1$ is small, γ_i is small, and $\varepsilon_2 - \varepsilon_1$ is large. The overlap of g_1 and g_{SCF} for H_2 is about 0.99998.

B. Results for Simple Systems

There have been numerous calculations on the ground state of the helium isoelectronic series. Shull and Löwdin (1955, 1959) analyzed an accurate CI wave function for helium. Kutzelnigg (1963b) and Ahlrichs *et al.* (1966a) solved approximate equations for the direct calculation of the NO's in an extensive basis set for H^-, He, ..., 0^{6+}. Davidson (1963) obtained approximate natural orbitals for a Kinoshita type wave function of He. Banyard and Baker (1969) found NO's for the Weiss wave functions for H^-, He, and Li^+. Finally Cressy *et al.* (1969) have attempted to find more compact expansions of the natural orbitals of He.

For the ^{1}S states of He, the wave function can always be written as

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = \sum_l \phi_l(r_1, r_2) P_l(\cos\theta_{12}).$$

The natural orbitals $g_{i,l,m}$ of Φ can be chosen to be the natural radial orbitals of ϕ_l multiplied by a spherical harmonic,

$$\int_0^\infty \phi_l(r_1, r_2)\mathscr{R}_{i,l}(r_2){r_2}^2\,dr_2 = \alpha_{i,l}\mathscr{R}_{i,l}(r_i),$$

$$g_{i,l,m}(\mathbf{r}) = \mathscr{R}_{i,l}(r)\,Y_{l,m}(\theta, \varphi),$$

because

$$P_l(\cos\theta_{12}) = \frac{4\pi}{2l+1}\sum_m Y_{l,m}(\theta_1, \varphi_1)\,Y^*_{l,m}(\theta_2\,\varphi_2).$$

Thus only the $\mathscr{R}_{i,l}$ need be computed.

Table I gives the values of γ_{il} in the natural expansion,

$$\Phi = \sum_{i,l}\gamma_{il}\sum_m g_{i,l,m}(\mathbf{r}_1)g^*_{i,l,m}(\mathbf{r}_2)$$

TABLE I

COEFFICIENTS IN THE NATURAL EXPANSION OF HELIUM

	Davidson (1963)	Ahlrichs *et al.* (1966a)	Shull and Löwdin (1959)	Banyard and Baker (1969)
1s	0.99599	0.99622	0.99592	0.99598
1p	−0.03563	−0.03467	−0.03582	−0.03574
2s	−0.06148	−0.06003	−0.06204	−0.06163
1d	−0.00566	−0.00545	−0.00599	−0.00566
2p	−0.00638	−0.00552	−0.00673	−0.00643
3s	−0.00786	−0.00681	−0.00735	−0.00790
1f	−0.00169	−0.00161	−0.00112	−0.00169
2d	−0.00178	−0.00148	−0.00099	−0.00174
3p	−0.00180	−0.00134	−0.00124	−0.00189
4s	−0.00197	−0.00144	−0.00221	−0.00192

(note that many authors differ by a factor of $(2l + 1)^{1/2}$ in the definition of γ_{il}). The agreement between the results of Davidson and the NO's from the Weiss wave function is quite good. The results of Shull and Löwdin show a greater difference because this is a complete list of their NO's. The results of

Ahlrichs *et al.* is surprisingly quite different in spite of an energy close to that obtained by Weiss. This must arise because they used the approximate equations (39)–(41) rather than (35)–(37) in determining the natural orbitals. Even though these orbitals give a good energy when used in (30), they still differ significantly from the true NO's.

Most of these papers discuss the convergence of properties other than the energy (note that the values of $\langle r_{12}^{-1} \rangle$ given by Davidson should be divided by $\langle \psi | \psi \rangle$ for the truncated wave function). The general conclusion is that correlation affects $\langle r^n \rangle$ very little and then mostly in the change from g_{SCF} to g_1. The quantity r_{12}^{-1} is reduced by correlation by about twice the energy improvement and $\langle -\frac{1}{2}\nabla_1{}^2 - \frac{1}{2}\nabla_2{}^2 \rangle$ is increased by about half as much.

For other ions the coefficients γ_{ll}, other than the first one, tend like $2Z^{-1}$ times those for helium. For H^-, whose Z is close to the critical Z for binding the second electron, the coefficient of the 2s orbital is larger than expected from this rule. For $Z < 1$ the wave function approaches the open shell (u, v) form, $2^{-1/2}(1s\,2s + 2s\,1s)$ where 2s is a very diffuse orbital. Consequently for $Z < 1$, $\gamma_{1,0}$ approaches $2^{-1/2}$ and $\gamma_{2,0}$ approaches $-2^{-1/2}$ and the natural orbitals approach 1s ± 2s.

The first correlation orbital for helium introduces angular correlation and the next introduces in–out correlation. For all ions from H^- to 0^{6+} the contribution from the first two correlation orbitals accounts for about 90% of the correlation energy. The ratio of in–out to angular correlation energy changes, though, from about 1.5 to 1 in H^- to 1 to 1.5 in 0^{6+}.

The ground state of the hydrogen molecule has been the subject of numerous natural orbital analyses. Shull (1959) reported the natural orbitals of most of the extant H_2 wave functions. Hagstrom and Shull (1959), and later, Ahlrichs *et al.* (1966b) reported natural orbitals for one-center wave functions. Hirschfelder and Löwdin (1959, 1965) calculated the natural orbitals at large R. Eliason and Hirschfelder (1959) analyzed the Hirschfelder–Linnet wavefunction for the ${}^1\Sigma_g{}^+$ and ${}^3\Sigma_u{}^+$ states over a wide range of internuclear distance. Konowalow *et al.* (1968) analyzed the somewhat better Fraga and Ransil function for the ${}^1\Sigma_g{}^+$ state over the same range of R. Davidson and Jones (1962a) reported wave functions approaching the σ_g and $\sigma_g + \sigma_u$ CI limit, the natural orbitals from these, and the best SCF and (u, v) functions for small internuclear distances.

The most extensive work at the equilibrium internuclear separation was done by Hagstrom and Shull (1963) using a CI wave function and by Davidson and Jones (1962b) who analyzed the Kolos and Roothaan wave function. Stewart *et al.* (1965) used the charge density reconstructed from the Davidson and Jones work (note this latter paper reports some corrections to misprints in the original paper) to compute the coherent X-ray scattering factors for bonded hydrogen. An extended CI calculation, similar to the Hagstrom and Shull work, was reported at an internuclear separation of 2 a.u. by Rothenberg and Davidson (1967) in connection with a study of the convergence of transition probabilities as a function of natural orbital expansion length. The most accurate NO's over a large range of R are probably those reported by Das and Wahl (1966) who calculated the first six natural orbitals with their multiconfiguration SCF program.

Although many calculations on excited states of H_2 exist in the literature, relatively few natural orbitals have been reported. Davidson (1961) reported the NO's for the first excited ${}^1\Sigma_g{}^+$ state and used these to show the difference between the wave functions at the two minima in the potential curve. Rothenberg and Davidson (1966) published extensive tables and drawings of excited-state natural orbitals at an internuclear distance of 2.0 a.u. Davidson (1970) has pointed out that, while the correlation effects in the excited states are small, the rate of convergence of the correlation energy in a NO expansion is similar to that for the ground state.

Correlation effects in the ground state of H_2 have been of considerable interest. Clearly as R approaches zero, the wave function must approach the helium limit. Hence as R goes to zero, the natural orbital expansion coefficients must approach those in Table I.

At very large R, the wavefunction approaches

$$2^{-1/2}[\tfrac{1}{2}(1\mathrm{s}_a + 1s_b)_1(1s_a + 1s_b)_2 - \tfrac{1}{2}(1s_a - 1s_b)_1(1s_a - 1s_b)_2]$$

so γ_1 approaches $2^{-1/2}$ and γ_2 approaches $-2^{-1/2}$. Hirschfelder and Löwdin's results for large R show that the next term is of the form

$$-R^{-3}[p_{ax}(1)p_{bx}(2) + p_{ay}(1)p_{by}(2) + p_{az}(1)p_{bz}(2) + p_{bx}(1)p_{ax}(2) \\ + p_{by}(1)p_{ay}(2) + p_{bz}(1)p_{az}(2)].$$

They point out, as expected, that the p orbitals involved are the size of the 1s orbital rather than of the Rydberg orbitals of the hydrogen atom. Consequently, the usual perturbation expansion using excited states is slowly convergent while this one correlation orbital gives the coefficients of R^{-6} and R^{-8} in the energy formula to better than 1 %. The p_x and p_y part of this function provide angular correlation while p_z provides a form of localized in–out. That is, if the electron near "a" is between the nuclei, the electron near "b" is slightly more likely to be found on the side of "b" away from "a."

As R is decreased from this large value, the p type correlation is better expressed with π_u, π_g, σ_u and σ_g molecular orbitals. The π_u orbital persists to the united atom limit as the dominant angular correlation effect. The π_g and σ_g orbitals become part of the first d correlation orbitals while σ_u becomes the σ part of the first f orbitals of He·

The coefficients in Table II show that H_2 at R_e is clearly still close to the united atom limit although the R derivatives of the coefficients are large. The coefficients in this table are believed to be accurate to ±0.001.

TABLE II

COEFFICIENTS IN THE NATURAL EXPANSION OF H_2

R	0[a]	1.4009[b]	2.0[c]	4.0[d]	∞[e]
$1\sigma_g$	0.99599	0.99106	0.98320	0.8673	$2^{1/2}$
$1\sigma_u$	−0.03563	−0.09947	−0.16183	−0.4973	$-2^{1/2}$
$1\pi_u$	−0.03563	−0.04604	−0.04648	−0.0112	$-1.1R^{-3}$
$2\sigma_g$	−0.06148	−0.05481	−0.05039	−0.0081	
$1\pi_g$	−0.00566	−0.00838	−0.00961	−0.0038	$1.1R^{-3}$
$3\sigma_g$	−0.00566	−0.00997	−0.01233	0.0123	$1.1R^{-3}$
$2\sigma_u$	−0.00638	−0.00975	−0.01155		$-1.1R^{-3}$
$1\delta_g$	−0.00566	−0.00688	−0.00619		
$2\pi_u$	−0.00638	−0.00662	−0.00612		
$4\sigma_g$	−0.00786	−0.00655	−0.00509		

[a] From Column 1 of Table I

[b] Davidson and Jones (1962b).

[c] Rothenberg and Davidson (1967).

[d] Das and Wahl (1966).

[e] Hirschfelder and Löwdin (1959).

There are no results of comparable accuracy for R larger than 2.0 although the Hirschfelder–Linnet function is very similar to the Hirschfelder–Löwdin function and so should become accurate at large R. The Das and Wahl calculation omits the $2\sigma_u$ orbital so it cannot approach the correct limit at large R. Probably as a consequence of this omission of $2\sigma_u$, the $3\sigma_g$ orbital which should combine with $2\sigma_u$ at large R to give $2p_{za}2p_{zb}$ is poorly behaved. It would seem that there should be a crossing of the occupation numbers of $2\sigma_g$ and $3\sigma_g$ at some R value.

The total correlation energy of H_2 is nearly constant for $R < 2.0$ a.u. This must be regarded as a fortuitous cancelation of errors, however, as the rapid increase in occupation of the σ_u orbital is compensated for by a decrease in the dynamical correlation of the electrons. If the (u, v) form rather than the SCF were picked as the standard, it would appear that the correlation energy had significantly decreased from $R = 0$ to $R = 2$.

The type of correlation introduced by a natural orbital configuration with negative coefficient can be judged by considering the corresponding (u, v) orbitals $g_1 \pm \lambda g_i$. Thus the $1\sigma_u$ orbital, which resembles $1s_a - 1s_b$, produces left–right correlation. The π_u orbital produces angular correlation around the bond axis. The $2\sigma_g$ orbital, which resembles a 2s united atom orbital, produces a radial in–out correlation. These three orbitals account for 90% of the correlation energy at R_e. The distribution of correlation energy among these three is quite different from the helium atom although their combined effect is quite similar. The $1\pi_g$ orbital, which resembles a $d\pi$ united atom orbital, produces local angular correlation between an electron on "a" and one on "b." The $3\sigma_g$ orbital resembles a $d\sigma$ orbital and produces a horizontal in–out correlation along the bond axis.

Another way to visualize correlation effects is to introduce the two-particle probability distribution $|\Phi|^2$ If γ_i^2 is neglected $(i > 1)$, the g_i are chosen to be real functions, and γ_i is assumed to be negative $(i > 1)$,

$$|\Phi|^2 \approx g_1^2(\mathbf{r}_1)g_1^2(\mathbf{r}_2) - 2\sum |\gamma_i| g_1(\mathbf{r}_1)g_1(\mathbf{r}_2)g_i(\mathbf{r}_1)g_i(\mathbf{r}_2)$$

and

$$\tfrac{1}{2}\rho \approx g_1^2(\mathbf{r}_1).$$

Thus $g_1^2(\mathbf{r})$ is approximately the independent particle distribution and $g_1^2(\mathbf{r}_1)g_1^2(\mathbf{r}_2)$ is the uncorrelated two-particle distribution. Then

$$|\Phi|^2 = g_1^2(\mathbf{r}_1)g_1^2(\mathbf{r}_2)f,$$

where the correlation factor f is approximately given by

$$f = 1 - 2\sum_i |\gamma_i|(g_i/g_1)_{\mathbf{r}_1}(g_i/g_1)_{\mathbf{r}_2}.$$

Thus f is increased if $\mathbf{r}_1$ and $\mathbf{r}_2$ are such that (g_i/g_1) has opposite signs at the two points. Similarly if (g_i/g_1) has the same sign at both points f is diminished. Clearly $1\sigma_u/1\sigma_g$ favors finding electrons at opposite ends of the molecule, π_x/σ_g favors electrons on opposite sides of the bond axis, etc.

Shull has considered the problem of defining ionic and atomic character in homopolar (Shull, 1960) and heteropolar (Shull, 1962) diatomic molecules. His definition, based on the fractional probability of finding both electrons in the same half of the molecule compared with the alternative of finding them in opposite halves, gives the ionicity as

$$I = \tfrac{1}{2} + \gamma_1\gamma_2(\gamma_1^2 + \gamma_2^2)^{-1/2}$$

for the homopolar case (provided γ_2 refers to a σ_u orbital). This definition gives zero at large R but suffers from the same defects as the concept of ionicity itself at small R. That is, it gives about $\frac{1}{2} + \gamma_2$ or 0.46 for the ionicity of the helium atom. For H_2 at R_e this definition gives about 40% for the ionicity. By way of comparison, the first excited ${}^1\Sigma_g{}^+$ state at its outer minimum has a 93% ionic character. This is in good agreement with that states potential curve which behaves like $-R^{-1}$ and, were it not for crossing with other states, would approach H^+H^- at large R.

There are a few other two electron systems for which the natural orbitals have been found. Shull and Prosser (1964) investigated He_2^{2+} to see if the strange potential curve was associated with any peculiarities in the wave function. The Frage and Ransil wave function which they analyzed contained no angular correlation. The natural orbital expansion closely resembled that for H_2 if one allows for scaling.

To see the expected relationship as the nuclear charge Z is changed, consider replacing all distances by $r' = Zr$ so

$$H = Z^2\left\{\sum_{i=1,2}\left[-\tfrac{1}{2}\nabla_i'^2 - \sum_{\alpha}(r'_{\alpha i})^{-1}\right] + Z^{-1}(r'_{12})^{-1}\right\}$$

so the scaled wave function at (Z, R) for one molecule is nearly the same as for H_2 at $(1, ZR)$ except that the electron repulsion is scaled down by Z^{-1}. Thus the small coefficients in the natural orbital expansion are approximately related by

$$\gamma_i(Z, R) \approx Z^{-1}\gamma_i(1, ZR).$$

The coefficients other than $\gamma_{1\sigma_g}$ and $\gamma_{1\sigma_u}$ at least qualitatively obey this relationship for He_2^{2+}. There was no apparent anomaly in the wavefunction to account for the relative minimum or maximum in the potential curve.

Anex and Shull (1964) reported the natural orbitals for HeH^+ in a basis set which contained σ, π, and δ orbitals. The results were much closer to the separated atom He limit than to the united atom Li^+ limit. For instance, the total π occupation was 0.0020 for HeH^+ compared with 0.0028 π character for He and about 0.0012 for Li^+. This is in agreement with the relatively larger value of ZR in HeH^+ compared with H_2.

There have been several calculations on the $H_3{}^+$ molecule. Shull (1964) reported an analysis of the relatively crude Hirschfelder, Eyring, and Rosen wave function for linear $H_3{}^+$. Christofferson and Shull (1968) calculated NO's for a much better CI wave function for triangular $H_3{}^+$. Kutzelnigg *et al.* (1967) reported a direct calculation of the NO's in a gaussian basis set as a function of bond angle. Banyard and Tait (1968) studied the two-electron ion $(ZHZ)^{2Z-1}$ as a function of bond angle for $Z = 1.0(0.4)2.2$.

The results for equilateral H_3^+ support the view that the SCF energy is -1.30 hartrees, and the total energy is about -1.34 with about the same -0.04 correlation energy as H_2 or He. The natural orbital occupations for H_3^+ are close to the united atom values. For the linear form of H_3^+, Kutzelnigg, *et al.*, report a decrease of correlation energy to -0.052. This is largely due to the fact that the end atoms of H_3^+ are about 3.1 a.u. apart. At this large distance the correlation energy of H_2 greatly exceeds -0.05. The calculated left–right correlation energy (-0.028) of linear H_3^+ is reached in H_2 at $R = 2.0$ a.u. Thus the linear molecule H_3^+ is somewhat further from the united atom limit than the more compact equilateral triangle.

IV. Few-Electron Wave Functions

There are now numerous calculations for atoms and molecules with 3 to 20 electrons. Most of the calculations for these systems which have achieved accuracy beyond the SCF limit have been based, in one way or another, on natural orbitals. The advantage of NO's for these systems is only that the CI expansion is as rapidly convergent as possible. For more than two electrons, there is no simplification in the form of the wave function.

There are many ways of incorporating natural orbital concepts into a many-electron wave function. Some obvious ways which have been tried are NO analysis of existing wave functions, direct calculation of pseudonatural orbitals followed by a CI calculation for the wave function, and iterative natural orbital calculations. Even MC–SCF methods, which have no apparent direct connection with natural orbitals, have in fact been strongly influenced by NO's in setting up the initial choice of configurations.

Analysis of existent wave functions has been limited by a lack of accurate wave functions. Hurley (1960) reported the natural orbitals for a minimum basis valence bond calculation of carbon monoxide. Barnett *et al.* (1965) analyzed several beryllium atom wave functions and one LiH function. D. Smith and Fogel (1965) also reported an analysis of Watson's Be atom function. V. Smith (1967) analyzed Boys' function for $C(^1S)$. V. Smith and Larsson (1968) analyzed some functions for Li with r_{12} explicitly included. Macías (1968) has studied a wave function for H_3^-. Olympia (1970) reported natural orbitals for the first excited ^1S state of Be.

Olympia and Fung (1970) gave the results for a one center expansion for CH_3^-, NH_3 and OH_3^+. Kouba and Öhrn (1970) did an extensive CI study of the electronic states of boron carbide with natural orbitals used to reduce their wave functions to understandable form.

These analyses for beryllium have established that the wave function is nearly separable into an inner shell and an outer shell. The correlation orbitals tend to be localized in one shell or the other. The $1s^2$ pair of electrons, for example, have a whole set of p, d, f... orbitals the size of the 1s core. These are disturbed only slightly by the presence of the outer shell electrons. The work of Allan and Shull (1962) supports the idea of Hurley *et al.* (1953) that the Be wave function can be approximated as

$$\psi = \mathscr{A} g_1(1, 2) g_2(3, 4)$$

where g_1 and g_2 are strongly orthogonal geminals,

$$\int g_1^*(1, 2) g_2(1, 3)\, d\tau_1 = 0$$

and $\mathscr{A}$ is the antisymmetric projection. The error in such an approximation for Be seems to be about 10% of the correlation energy.

Since g_1 and g_2 are two-electron functions they have natural expansions of the form (20). Arai (1960) has proven that the natural expansions of g_1 and g_2 span disjoint subspaces if g_1 and g_2 are strongly orthogonal. That is, in this case, the natural orbitals of g_1 and g_2 are also NO's of ψ and the NO's appearing in g_1 do not appear in g_2. This very important result also holds for the generalized form

$$\psi = \mathscr{A} g_1(1, 2) g_2(3, 4) \cdots g_{N/2}(N-1, N)$$

known as an antisymmetrized product of strongly orthogonal geminals (APSG). This wave function has a very simple form with $N/2$ "intra" pairs correlated just as in two-electron problems, and $\binom{N}{2} - N/2$ uncorrelated "inter" pairs.

Ebbing and Henderson (1965) reported a direct calculation of the APSG function for LiH. Miller and Ruedenberg (1965, 1968) calculated the APSG function for Be. Both of these calculations proceeded by solving iteratively a complicated coupled set of equations for the natural orbitals and expansion coefficients. The relatively high accuracy achieved in these two examples have inspired many calculations for other systems with more electrons. Hindsight has shown, however, that the good results for LiH and Be resulted because the electron pairs were localized with little mutual penetration, rather than from any general tendency for interpair correlation to be small.

For more than four electrons, the direct calculation of the APSG function is difficult and time consuming. Nevertheless Silver *et al.* (1970a,b) and Mehler *et al.* (1970) solved the appropriate equations for expansion of the geminals in a finite basis set for LiH, BH, and NH. The results of these calculations agree with estimates derived by methods to be discussed later that the APSG correlation energy is seriously in error for more than four electrons. For NH they recovered only 22% of the correlation energy, so 78% is due to interpair correlation. Further, about 64% of the correlation error in the dissociation energy is due to interpair effects.

Kutzelnigg (1964) and Ahlrichs and Kutzelnigg (1968b) have developed an algorithm for finding approximate natural orbitals. This method begins with SCF orbitals and finds the approximate g for each pair correlation independently by solving equations like those given previously for two-electron systems. A difficulty with this method is that the SCF orbitals, and hence the pairs, are arbitrary within a unitary transformation. Calculations as done by Silver, Mehler, and Ruedenberg get this transformation correct but the decoupled pair approximation of Ahlrichs and Kutzelnigg requires much additional work to find the best transformation. A study of the best results so far obtained has shown that the canonical SCF orbitals are generally closer to the best orbitals than are the localized SCF orbitals. Besides Be and LiH, the method has been applied to BeH_2 (Ahlrichs and Kutzelnigg, 1968a), BH_3, CH_4, BeH, BH_2^+, and BH (Jungen and Ahlrichs, 1970), and Be_2H_4, Be_3H_6 (Ahlrichs, 1970). In most of these calculations, independent electron pair calculations were made for each of the $\binom{N}{2}$ pairs in natural orbital form. Again the conclusion is drawn that, in aggregate, interpair effects are larger than intrapair effects for most molecules.

In a somewhat similar approach, Edmiston and Krauss (1966, 1968) and Sanders and Krauss (1968) have found natural orbitals for independent electron pairs by doing a CI calculation including only excitations from a particular pair and then factoring into natural orbital form. By repeating this for each of the intrapair correlations, a set of pseudonatural orbitals can be developed that are suitable as a basis for a full CI calculation. While these are not really natural orbitals, they span the essential correlation orbital subspace. In these calculations the authors have generally used localized SCF orbitals to define the uncorrelated pairs. This tends to maximize the intrapair contribution to the correlation energy.

Bender and Davidson have developed an iterative method for calculation of natural orbitals. In this scheme an initial CI wave function is analyzed into NO's and these are used as basis orbitals in a new CI calculation. Improvement in the wave function is usually dramatic for the first few iterations although convergence is slow if it occurs at all. The difficulties with convergence are closely associated with the fact that the NO's are determined in zeroth order by second-order terms in the density matrix. Hence the NO's are very sensitive to the wave function.

This procedure has been applied to a series of molecules [Bender and Davidson, 1966 (HeH, LiH), 1967 (HF), 1968a (HF), 1968b (LiH), 1969a (BH), 1969b (LiH, BH, CH, NH, OH, HF); Chan and Davidson, 1968 (BeH), 1970 (MgH); Matsumoto *et al.*, 1967 (He_2); Siu and Davidson, 1970 (CO)] and atoms [A. Bunge, 1970 (C); C. F. Bunge, 1968 (Be)].

The two major problems in any CI calculation are the choice of orbitals and the selection of configurations. If natural orbitals are to be used, a good initial guess is still required. Various schemes have been tried for getting an initial guess to the NO's. For the first work on HeH, LiH, and He_2, the occupied and virtual orbitals were chosen by the Roothaan SCF procedure. Since only 1s shells are present in these molecules (to the first approximation), this starting set was good enough to get convergence. The slightly occupied NO's finally obtained were quite different, of course, from the virtual SCF orbitals. For the hydrogen fluoride molecule, the virtual SCF orbitals were so bad an initial guess that no reasonable results could be obtained by that method. For this molecule, a method similar to that developed independently by Edmiston and Krauss was employed. The natural orbitals for all $\binom{N}{2}$ pairs of electrons were found by independent-electron-pair calculations followed by factorization of the wave function. The energy contribution from the individual terms in each pair and the overlap between natural orbitals from different pairs was examined in detail (Bender and Davidson, 1968a). From this it was obvious that the interpair contributions were about two-thirds of the correlation error in the dissociation energy. It was also obvious that the idea of strongly orthogonal geminals, even for the intrapair part of the correlation, was not a good approximation since the correlating orbitals for many of the pairs were very similar. These pseudonatural orbitals were merged to form a linearly independent set which spanned the most important correlation effects. These were then used to start the iterative NO procedure.

For BeH another procedure was tried. This procedure maximized a weighted average of the square of the exchange integral between a slightly occupied NO and the occupied SCF orbitals. This was time consuming but gave a reasonable first guess to the NO's. A better procedure, which requires less computer time, is to calculate the wave function to first order by perturbation theory (based on virtual orbitals) and then to take the initial NO's from the resulting density matrix. This was used in several subsequent calculations. At present this is probably the best procedure in terms of accuracy achieved per unit of computer cost.

The choice of configurations is a great problem when very few are used. For large scale calculations with over 1000 configurations, a useful procedure is to estimate the contribution of each possible double replacement by perturbation theory. Then the more important of these (based either on energy, or coefficients, or contribution to some other property) plus all single excitations and any other configurations believed to be important can be used in a CI calculation. This eliminates the need for arbitrary choices of configurations implicit in MC–SCF and APSG wave functions. The single excitations, while making very small contributions to the energy, are essential if better than SCF results are wanted for molecular properties. Generally ψ_{FNC} gives much better values for one electron operators than does ψ_{SCF}. This is partly because the singly excited configurations actually have smaller coefficients in the NO basis than in the SCF basis.

The results from these extended iterative NO calculations warned that much of the effort expanded on APSG functions would be unsuccessful. The dominant correlation effect in the HF molecule, for example, is of the form $3\sigma 1\pi \rightarrow 4\sigma 2\pi$. This represents a ($\pi$ in, σ left)–(π out, σ right) correlation between the bonding pair and the π electrons. This is as responsible as the expected $3\sigma^2 \rightarrow 4\sigma^2$ excitation for the correlation error in the dissociation energy. This type of effect is missing from the APSG function and is suppressed in most MC–SCF calculations.

Independent-electron-pair calculations have shown that the interpair effects are large. But these same calculations have shown that the pair energies fail to be additive by as much as 20–30% for diatomics with full octets (CO, HF). This suggests that for larger polyatomic molecules such as naphthalene the independent pair approach may collapse completely. The sum of the independent-pair correlation energies depends on a unitary transformation among the occupied orbitals (Davidson and Bender, 1968; Bender and Davidson, 1969a). This suggests that methods which seek to maximize the intrapair energy may run into trouble for large molecules because that also seems to nearly maximize the sum of all the pair energies and hence to maximize the error in the independent-pair method.

A fair question to pose is "are natural orbitals worth the trouble it takes to get them?" In terms of maximum accuracy for a fixed cost the answer to this is "probably not." Use of pseudonatural orbitals found by perturbation theory is probably more economical. Certainly use of some type of approximate natural orbitals for large basis sets is essential since any other basis set leads to intolerable costs. For small basis sets with all single and double replacements included in the CI calculation, natural orbitals raise the cost with little change in the results. The real advantage of natural orbitals is in getting maximum understanding for a fixed cost. Reduction of wave functions to easily interpreted canonical terms makes possible an understanding of the correlation effects. This should prevent heading up blind alleys by assumption of unsuitable simplified wave functions. In this respect, it is now clear that the results for two- and four-electron systems were misleading for ten-electron systems. It is probable that the independent-electron-pair calculations for up to ten electrons may be deceptively accurate if used as a basis for extrapolation to many-electron polyatomics such as naphthalene. The insignificance of higher excitations for ten-electron systems may also break down in polyatomics with large numbers of interlocking octet centers. At this point in time NO-based CI calculations for polyatomic molecules are feasible; but it is premature to try to predict which types of configurations will prove important.

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Matrix Elements and Density Matrices for Many-Electron Spin Eigenstates Built from Orthonormal Orbitals*

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I. Introduction

For an important class of many-electron problems, namely, those governed by spin-free or nearly spin-free Hamiltonians, it is practically and theoretically useful to formulate many-electron wavefunctions which, in addition to being antisymmetric, are also eigenfunctions of the total spin operators $\mathcal{S}^2$ and $\mathcal{S}_z$.

The most widespread method of constructing *antisymmetric* wavefunctions is by an expansion in terms of Slater determinants of orthonormal orbitals (Slater, 1929). Thereby quantum mechanical problems are transformed into matrix problems and the matrix elements are integrals involving two Slater determinants and certain dynamical operators. The formulas expressing these matrix elements in terms of one- and/or two-electron integrals between orbitals, known as the Slater-Condon rules (Slater, 1929; Condon, 1930), are particularly simple for Slater determinants, and this has been a major attraction of this approach. The generalization of the Slater-Condon rules to operators involving more than two electrons and to nonorthogonal orbitals has been given by Löwdin (1955).

Slater determinants have, however, one shortcoming: In general, they are not eigenfunctions of the total spin operator $\mathcal{S}^2$. Only certain linear combinations of Slater determinants have this property. Over the years a variety of formalisms have therefore been invented for the construction of many-electron wavefunctions that are antisymmetric as well as eigenfunctions of $\mathcal{S}^2$.

The earliest approach, known as "the method of bonded functions," grew out of the work of Heitler and Rumer (1931). Related to it is Pauling's (1933) method for singlet states. Matsen (1960) and Matsen *et al.* (1966) showed that Pauling's approach is equivalent to projecting spin eigenfunctions by means of Young operators (Rutherford, 1968) and on this basis made a generalization to the case of arbitrary spin eigenvalues. Other generalizations were given by McLachlan (1960) and by Shull (1969). General matrix element formulas for the bonded-functions approach were derived by Boys (1952) and Reeves (1966), by McWeeny (1954, 1961), by Cooper and McWeeny (1966), and by Sutcliffe (1966). The bonded spin eigenfunctions are linearly independent, but non-orthogonal.

A second route can be considered as originating with Dirac's vector model (1929, see also Corson, 1951). An interesting modification was suggested by Serber (1934). Yamanouchi (1935, 1936, 1937, 1938, 1948) and Kotani *et al.* (1955) reformulated and generalized this method with the help of the representation theory of the symmetric group, as developed by Schur (1904), Frobenius (1907), and Young (1931). In this approach orthogonal representations are deployed, in contrast to the aforementioned method of bonded functions, which is based on the nonorthogonal representations generated by the Young operators. It was shown by Koster (1956) and, in greater depth, by Matsen (1960) that this approach can be elegantly formulated in terms of projection operators that can be constructed with the help of the Frobenius algebra (see, e.g., Boerner, 1963) of the symmetric group. Such an algebraic approach has also been followed by Goddard (1967, 1968, 1969), Gallup (1968), Sullivan (1968), Gerratt and Lipscomb (1968), and Poshusta and Kramling (1968) in the context of self-consistent-field theory. It has also been pursued by Kaplan (1961, 1963, 1965, 1967) in the context of atomic and molecular calculations. This second route is closely related to methods used by nuclear theorists (Jahn and van Wieringen, 1951; Jahn, 1954) as exhibited, for example, in the derivations of nuclear matrix elements by Kramer and Seligman (1969a,b). In a recent investigation, Salmon (1972) has shown how to modify Young operators so that they can be used to algebraically construct the *orthogonal* projection operators required for the Yamanouchi-Kotani approach. The basic drawback of the latter is that the matrix elements contain complicated sums over many permutational terms, whose number increases rapidly with the number of particles. The method is therefore practical only for systems with few electrons.

A third route was initiated by Löwdin's suggestion (1955, 1960, 1964) to construct spin eigenfunctions with the help of projection operators that are not derived from group theory. This construction was computationally implemented by Rotenberg (1963). Formulas for special matrix elements in this approach were obtained by Pauncz *et al.* (1962), by de Heer and Pauncz (1963), and by Pauncz (1967, 1969). Harris (1967b) has extended this approach to handle general superpositions of this type of spin-projected determinants with arbitrary spin values that are composed of orthonormal orbitals. The resulting matrix element expressions require the evaluation of so-called Sanibel coefficients which have been the subject of considerable study (Percus and Rotenberg, 1962; Sasaki and Ohno, 1963; Smith, 1964; Shapiro, 1965; Smith and Harris, 1967; Harris, 1967b; Manne, 1966). Reviews of this approach have been given by Harris (1967a) and Pauncz (1967).

In all of these methods, the construction of wavefunctions with the desired characteristics is the simpler task. It is in the evaluation of the expectation values and matrix elements of the many-electron operators that complexities and complications arise. It is always possible, of course, to decompose the antisymmetric spin eigenfunctions in terms of Slater determinants, if the space part is a superposition of orbital products, and then to apply the simple Slater-Condon rules. This procedure leads to lengthy summations, however, and does not exploit the available group theoretical knowledge concerning the spin representations. In several of the aforementioned methods, "direct" matrix-element formulas, that do not rely on a decomposition in Slater determinants, have therefore been derived. The resulting expressions for expectation values and matrix elements have, however, remained more cumbersome than one would wish and no really simple expressions have been available.

The Yamanouchi-Kotani method and the Slater method can be considered as two extremes. The former takes advantage of the group theoretical relations resulting from the orthogonal representations of the symmetric group, but largely ignores the fact that the dynamical operators involve only two (or in general p) electrons. The latter, on the other hand, embodies the simplifications characteristic for two-body (or p-body) operators, but does not take into account the representation properties of the spin functions. A synthesis of these two approaches is clearly desirable and this is the goal of the present investigation. Our formulation of antisymmetric spin eigenfunctions is similar to that of Kotani. However, certain essential additional conventions are introduced, in particular, Serber's (1934) spin eigenfunctions are used, as had been done previously by Miller and Ruedenberg (1968). Explicit direct formulas are derived for the matrix elements of p-particle operators. The spatial factors are clearly separated from the spin-dependent factors and the latter are simply identified in terms of representation matrices of permutations. The resulting formulas are very similar to the Slater-Condon-Löwdin rules and contain them as special cases. They are finally used to obtain corresponding expansions for reduced density matrices. The specialized formulas resulting for one- and two-electron operators, which are also given in the sequel, have been previously reported (Ruedenberg, 1971) and for them an alternate derivation is possible (Salmon and Ruedenberg, 1972).

II. *N*-Electron Basis Functions

A. Definition

Antisymmetric N-electron functions which are eigenstates of $\mathscr{S}^2$ and $\mathscr{S}_z$ can be expressed as expansions of the form

$$\Psi(\text{spin, space}) = \sum_{K,s} c_{Ks}\Psi_{Ks}^{SM}(\text{spin, space}) \tag{1}$$

with the Ψ_{Ks}^{SM} defined by

$$\Psi_{Ks}^{SM}(\text{spin, space}) = N_{Ks}^{SM}\mathscr{A}\{\Theta_s^{SM}(\text{spin})U_K(\text{space})\}, \tag{2}$$

where N_{Ks}^{SM} are normalization constants to be determined below and

$$\mathscr{A} = (N!)^{-1/2}\sum_{\mathscr{P}}(-1)^p\mathscr{P}$$

is the antisymmetrizer over N electrons. Here and in the entire paper, permutations apply to electron coordinates unless otherwise specified.[1]

The functions $\Theta_1^{SM}, \Theta_2^{SM}, \ldots, \Theta_{f^S}^{SM}$ form a complete basis of

$$f^S = \frac{(2S+1)}{(N+1)}\binom{(N+1)}{\frac{1}{2}N - S} \tag{3}$$

pure spin functions which satisfy

$$\mathscr{S}^2\Theta_s^{SM} = \hbar^2 S(S+1)\Theta_s^{SM}, \qquad \mathscr{S}_z\Theta_s^{SM} = \hbar M\Theta_s^{SM}, \tag{4}$$

where S can assume the values $(\frac{1}{2}N)$, $(\frac{1}{2}N - 1)$, $(\frac{1}{2}N - 2), \ldots$, ($\frac{1}{2}$, if N is odd) or (0 if N is even), and M is limited by $-S \leq M \leq S$.

The functions U_K (space) form a complete basis of N-electron functions. In cases of spatial symmetry, they may be restricted to the irreducible representations of the appropriate point group. In principle, the number of U's is infinite; in practical applications, it is large but finite. In the present analysis, we consider those complete bases which are obtained by choosing all possible products of the members of a complete set of orthonormal real one-electron functions (orbitals): $f_1(\mathbf{r}), f_2(\mathbf{r}), f_3(\mathbf{r}), \ldots$.

The spin-eigenfunctions Θ_s^{SM} are linear superpositions of the $[N!/(\frac{1}{2}N + M)!(\frac{1}{2}N - M)!]$ products which can be obtained from the one-electron spin functions α and β by choosing α for $(\frac{1}{2}N + M)$ electrons and β for $(\frac{1}{2}N - M)$ electrons. The N-electron basis functions can therefore be expressed as linear combinations of Slater determinants, and it follows then that any one of the space orbitals f_ν cannot occur more than twice as a factor in any one of the products U_K; i.e., any orbital can only be "unoccupied," "singly occupied," or "doubly occupied."

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[1] The following notation will be used for permutations: $\mathscr{P}$ for permutations on electrons, P for permutations on orbital indices, $\mathbf{P}$ for the representation matrix corresponding to P.

B. Relation to the Symmetric Group

The spin eigenfunctions Θ_s^{SM} can be chosen to form an orthonormal basis for an irreducible representation of the symmetric group of N elements, S_N. This is to say that the relations

$$\mathscr{P}\Theta_t^{SM} = \sum_{s=1}^{f_S} \Theta_s^{SM}\langle\Theta_s^{SM}|\mathscr{P}|\Theta_t^{SM}\rangle \tag{5}$$

hold for any permutation $\mathscr{P}$ out of S_N, where the matrices $\langle\Theta_s^{SM}|\mathscr{P}|\Theta_t^{SM}\rangle$ form an irreducible and orthonormal representation of S_N.

This fact leads to a reduction in the number of U_K's which are required to form a complete set. Namely, let $U^{(0)}$, $U^{(1)}$, $U^{(2)}, \ldots, U^{(a)}$ be all those among the basis functions U_K which differ from each other merely by permutations among the electrons, then *only one of these functions* must be included in the basis set. This is so because the set of functions $\mathscr{A}\{\Theta_s^{SM}U\}$, $s = 1, 2, \ldots, f_S$, and the set of functions $\mathscr{A}\{\Theta_s^{SM}(\mathscr{P}U)\}$, $s = 1, 2, \ldots, f_S$, both span the same linear space if $\mathscr{P}$ is an arbitrary permutation out of S_N. Indeed, one finds

$$\begin{aligned}\mathscr{A}\{\Theta_t^{SM}(\mathscr{P}U)\} &= (\mathscr{A}\mathscr{P})\{(\mathscr{P}^{-1}\Theta_t^{SM})U\}\\ &= (-1)^p\mathscr{A}\left\{\sum_s \Theta_s^{SM}\langle\Theta_s^{SM}|\mathscr{P}^{-1}|\Theta_t^{SM}\rangle U\right\}\\ &= \sum_{s=1}^{f_S}\langle\Theta_s^{SM}|(-1)^p\mathscr{P}^{-1}|\Theta_t^{SM}\rangle\mathscr{A}\{\Theta_s^{SM}U\}.\end{aligned} \tag{6}$$

Consequently, for any one choice of N orbitals $f_{\nu_1}, f_{\nu_2}, f_{\nu_3}, \ldots, f_{\nu_N}$, there exists *exactly one set of functions* Ψ_{Ks}, $s = 1, 2, \ldots, f_S$, and a unique order can be arbitrarily chosen for the arrangement of the orbitals in the product U_K. In the present analysis the following ordering principle is adopted. Let $U_K = U$, and denote the orbitals in U by $u_1, u_2, u_3, \ldots, u_N$, i.e.,

$$U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = u_1(\mathbf{r}_1)u_2(\mathbf{r}_2)\cdots u_N(\mathbf{r}_N), \tag{7}$$

and suppose that U contains the orbitals $f_{i_1}, f_{i_2}, \ldots, f_I$ with "double occupancy" and the orbitals $f_{j_1}, f_{j_2}, \ldots, f_J$ with "single occupancy." Then the ordering in U is fixed by the identity

$$\{u_1\, u_2\, u_3 \cdots u_N\} = \{f_{i_1} f_{i_1} f_{i_2} f_{i_2} \cdots f_I f_I f_{j_1} f_{j_2} \cdots f_J\}, \tag{8}$$

where the orbital indices follow the order

$$i_1 < i_2 < i_3 < \cdots < I; \qquad j_1 < j_2 < j_3 < \cdots < J. \tag{9}$$

That is, the doubly occupied space orbitals are written first in the order of ascending indices, then the singly occupied orbitals are written in the ordering of ascending indices.

C. Geminal Spin Harmonics

There exists considerable freedom in choosing an orthogonal basis in the space spanned by the f_S spin eigenfunctions Θ_s^{SM}, $s = 1, \dots, f_S$, and, correspondingly, there exist various explicit forms of the irreducible representations of S_N. The most common choice is that of the spin eigenfunctions obtained by adding the spin of one electron at a time and using the angular momentum addition rules. This method has been described by Kotani *et al.* (1955). The irreducible representations can be obtained by the methods of Yamanouchi (1935 to 1948) and Kotani (1955), or, alternatively by the older method of Young's orthogonal representations, which, recently, has been adapted by Goddard (1967–1969).[2] The equivalence of the two has been proven by Pauncz (1967).

In the present treatment we find it useful to make a different choice, which was first suggested by Serber (1934). A detailed discussion of these spin functions, and a method for their construction is given in separate investigations (Salmon 1972; Salmon and Ruedenberg, 1972; Salmon *et al.*, 1972). They are characterized by the fact that all of them have the property

$$\mathscr{Q}\Theta_s^{SM} = \varepsilon_s^{\,S}(\mathscr{Q})\Theta_s^{SM} \tag{10}$$

where $\mathscr{Q}$ is any one of the transpositions (12), (34), (56), (78), ..., $(N-2, N-1)$ or $(N-1, N)$, depending upon N being odd or even, and where $\varepsilon_s^{\,S}(\mathscr{Q})$ can be either $+1$ or -1. The same holds for any product of the transpositions mentioned, i.e., for all elements of the *geminal subgroup of* S_N which is defined as the direct product of the groups {1, (12)}, {1, (34)}, ..., $\{1, (N-2, N-1)\}$ or $\{1, (N-1, N)\}$. These spin eigenfunctions will be called *geminal spin harmonics.* That is is possible to choose spin-functions satisfying Eq. (10) is evident from the fact that the "geminal spin-operators" $(\mathscr{S}_1 + \mathscr{S}_2)^2, (\mathscr{S}_3 + \mathscr{S}_4)^2, (\mathscr{S}_5 + \mathscr{S}_6)^2, \dots$ etc., all commute with the total spin $\mathscr{S}^2$ and with each other.

Specifically the geminal spin harmonics can be written in the form

$$\Theta_s^{SM} = (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)\cdots(\alpha\beta - \beta\alpha)\hat{\Theta}_s^{SM}, \tag{11}$$

That is, first the factor $(\alpha\beta - \beta\alpha)$ occurs $m_s^{\,S}$ times, corresponding to the electrons 1, 2, ..., $2m_s^{\,S}$, then follows a factor $\hat{\Theta}_s^{SM}$ which is symmetric in the electron pair $(2m_s^{\,S} + 1, 2m_s^{\,S} + 2)$ at least. Hence, $\varepsilon_s^{\,S}(\mathscr{Q}) = -1$ for $\mathscr{Q} = (12), (34), \dots, (2m_s^{\,S} - 1, 2m_s^{\,S} + 1)$, but $+1$ for $\mathscr{Q} = (2m_s^{\,S} + 1, 2m_s^{\,S} + 2)$. Furthermore, the order of the geminal spin harmonics can be chosen such that, as the index t of Θ_t^{SM} increases, the number of factors $(\alpha\beta - \beta\alpha)$ in Eq. (11), i.e., $m_t^{\,S}$, decreases, or remains the same.

A first consequence of this choice of spin eigenfunctions is that for a space product U of the type characterized by Eq. (8), where the first I

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[2] The best introduction to Young's theory is Rutherford (1948, 1968).

orbitals appear with double occupancy, a *nonzero* basis function Ψ of the kind defined in Eq. (2) results only for those geminal spin harmonics for which

$$\mathscr{R}\Theta_s^{SM} = -\Theta_s^{SM}, \tag{12}$$

where $\mathscr{R}$ is any of the transpositions (12), (34), ..., $(2I-1,\ 2I)$. This means that only the geminal harmonics Θ_t^{SM} which have $m_t^S \geq I$ can combine with U to give nonzero antisymmetric Ψ's. Because of the ordering these will be geminal harmonics whose index does not exceed a certain value $f_S(U)$. *Thus, there will only be* $f_S(U)$ *nonzero basis functions of the type defined in Eq.* (2), *corresponding to the s index values* $s = 1, 2, 3, \ldots, f_S(U)$.

D. Normalization

With the aforementioned choices and conventions the normalization constants in Eq. (2) can be evaluated. Considering the space function U defined in Eqs. (7)–(9), one finds, by a familiar rearrangement[3]

$$\begin{aligned}\langle \mathscr{A}\Theta_s^{SM}U \mid \mathscr{A}\Theta_s^{SM}U\rangle &= \sum_P (-1)^P \langle \Theta_s^{SM}U \mid \mathscr{P}\Theta_s^{SM}U\rangle \\ &= \sum_P (-1)^P \langle \Theta_s^{SM} \mid \mathscr{P} \mid \Theta_s^{SM}\rangle\langle U \mid \mathscr{P} \mid U\rangle \end{aligned}\tag{13a}$$

In view of Eq. (8) and the orthogonality of the orbital basis, one has

$$\langle U \mid \mathscr{P} \mid U\rangle = \langle u_1u_2\cdots u_N \mid \mathscr{P} \mid u_1u_2\cdots u_N\rangle = \begin{cases}1 & \text{if } \mathscr{P} \text{ belongs to } \mathrm{S}_U, \\ 0 & \text{otherwise.}\end{cases}\tag{13b}$$

Here S_U is that subgroup of S_N which consists of the transpositions (12), (34), (56), $(2I-1,\ I)$ and all their products. It is the direct product of the groups $\{1, (12)\}$, $\{1, 34\}$, ..., $\{1, (2I-1, I)\}$. It is a subgroup of the geminal subgroup of S_N. It contains all permutations which leave the product U invariant and is therefore called the invariance group of U. It contains $2^{\pi(U)}$ permutations, where $\pi(U)$ is the number of orbitals with double occupancy in U.

From Eq. (12) it follows, on the other hand, that

$$\langle \Theta_s^{SM} \mid \mathscr{P} \mid \Theta_s^{SM}\rangle = (-1)^P \qquad \text{if } \mathscr{P} \text{ belongs to } \mathrm{S}_U. \tag{13c}$$

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[3] If $\Phi(1, 2, \ldots, N)$ and $\Psi(1, 2, \ldots, N)$ are arbitrary and the operator $\mathscr{G}(x_1 \cdots x_n)$ is totally symmetric, then

$$\begin{aligned}\langle \mathscr{A}\Phi \mid \mathscr{G} \mid \mathscr{A}\Psi\rangle &= (N!)^{-1/2}\sum_P \langle (-1)^P\mathscr{P}\Phi \mid \mathscr{G} \mid \mathscr{A}\Psi\rangle \\ &= (N!)^{-1/2}\sum_P \langle \Phi \mid \mathscr{G} \mid (-1)^P\mathscr{P}^{-1}\mathscr{A}\Psi\rangle \\ &= (N!)^{-1/2}\sum_P \langle \Phi \mid \mathscr{G} \mid \mathscr{A}\Psi\rangle \\ &= (N!)^{1/2}\langle \Phi \mid \mathscr{G} \mid \mathscr{A}\Psi\rangle = \sum_P (-1)^P\langle \Phi \mid \mathscr{G} \mid \mathscr{P}\Psi\rangle\end{aligned}$$

Hence, Eq. (13a) together with Eqs. (13b) and (13c) yields

$$\begin{aligned}\langle \mathscr{A}\Theta_s^{SM}U \,|\, \mathscr{A}\theta_s^{SM}U\rangle &= \text{number of permutations in } \mathrm{S}_U \\ &= 2^{\pi(U)}.\end{aligned}$$

The normalization constant for the function Ψ_{Ks}^{SM} of Eq. (2) is therefore

$$N_{Ks}^{SM} = 2^{-\pi(K)/2} \tag{14}$$

where $\pi(K)$ is the number of orbitals with double occupancy in U_K. It may be noted that the normalization constant is independent of the indices S, M, s.

III. Matrix Elements for p-Electron Operator

A. Prototype Matrix Element

If the electronic wave functions Ψ is expressed by an expansion such as given in Eq. (1), then all quantum-mechanical calculations are reduced to matrix problems, involving matrices of the form $\langle \Psi_{Ks}^{SM} | \mathscr{G} | \Psi_{K's'}^{S'M'}\rangle$. Here $\mathscr{G}$ stands for any one of a number of linear operators, all of which have the following properties: They are symmetric in all electrons and they can be classified as no-particle, one-particle, two-particle, etc. operators, a p-particle operator having the form

$$\mathscr{G} = \sum_{(i)} g(i), \tag{15}$$

where the summation is p-fold and goes over the electron indices as follows

$$\sum_{(i)} = \sum_{i_1=1}^{N} \sum_{i_2=1}^{N} \sum_{i_3=1}^{N} \cdots \sum_{i_p=1}^{N} \qquad \text{with} \quad i_1 < i_2 < i_3 < \cdots < i_p \tag{16}$$

and $g(i)$ is an operator that operates on the coordinates of electrons $i_1, i_2, \ldots, i_p$ in symmetric fashion. Thus, if $\mathscr{P}$ is a permutation between the electrons $i_1, i_2, \ldots, i_p$, then

$$\mathscr{P}g(i) = \mathscr{P}g(i_1, i_2, \ldots, i_p) = g(i_1, i_2, \ldots, i_p) = g(i). \tag{17}$$

In the present analysis we limit ourselves to spin independent operators. In this case nonvanishing matrix elements occur only between basis function Ψ_{Ks}^{SM} with the same value of S and M. In the sequel, these superscripts are therefore omitted from the derivation, unless their presence is necessary. We, furthermore, eliminate the subscript K by writing the two basis functions occurring in the prototype matrix element in the form

$$\Psi_{Us} = |\, Us\rangle = 2^{-\pi(U)/2}\mathscr{A}\{\Theta_s U\}, \tag{18}$$

$$\Psi_{Vt} = |\, Vt\rangle = 2^{-\pi(V)/2}\mathscr{A}\{\Theta_t V\}, \tag{19}$$

with

$$U = u_1 u_2 \cdots u_N, \tag{20}$$

$$V = v_1 v_2 \cdots v_N. \tag{21}$$

Here and in the sequel the orbitals are occupied by the electrons 1, 2, ... N in the order in which they are written. It should also be remembered that nonzero Ψ functions exist only for $s \leq f_S(U)$, $t \leq f_S(V)$ due to double occupancies.

With these assumptions and conventions the prototype matrix element becomes

$$\langle Us|\mathscr{G}|Vt\rangle = 2^{-[\pi(U)+\pi(V)]/2}\langle \mathscr{A}\Theta_s U|\mathscr{G}|\mathscr{A}\Theta_t V\rangle. \tag{22}$$

Since $\mathscr{G}$ is symmetric in all electrons, a familiar arrangement yields[4]

$$\langle Us|\mathscr{G}|Vt\rangle = 2^{-[\pi(U)+\pi(V)]/2}\sum_P(-1)^P\langle \Theta_s U|\mathscr{G}|\mathscr{P}\Theta_t V\rangle,$$

and since $\mathscr{G}$ is spin independent

$$\langle Us|\mathscr{G}|Vt\rangle = 2^{-[\pi(U)+\pi(V)]/2}\sum_{\mathscr{P}}\mathbf{P}_{st}\langle U|\mathscr{G}|\mathscr{P}V\rangle \tag{23}$$

where the matrix P_{st} is defined as

$$P_{st} = (-1)^P\langle \Theta_s|\mathscr{P}|\Theta_t\rangle. \tag{24}$$

If we define the matrix,

$$\mathbf{G}(U, V) = \{G_{st}(U, V)\} = \{\langle Us|\mathscr{G}|Vt\rangle\}, \tag{25}$$

the result of Eq. (23) can be expressed as the matrix identity

$$\mathbf{G}(U,V) = 2^{-[\pi(U)+\pi(V)]/2}\sum_{\mathscr{P}}\langle U|\mathscr{G}|\mathscr{P}V\rangle\mathbf{P}. \tag{26}$$

It should be remembered that nonzero matrix elements for this matrix exist only for

$$1 \leq s \leq f_S(U), \qquad 1 \leq t \leq f_S(V). \tag{27}$$

It should also be noted that the matrices $\mathbf{P}$ depend on S but not on M:

$$P_{st} = P_{st}^S = (-1)^P\langle \Theta_s^{SM}|\mathscr{P}|\Theta_t^{SM}\rangle. \tag{28}$$

The matrices $\mathbf{P}^{-1}$ form the irreducible representation of S_N which is conjugate to that given by $\langle \theta_s^{SM}|\mathscr{P}|\theta_s^{SM}\rangle$.

B. The Line-Up Permutation

An essential role in the calculation of $\mathbf{G}(U, V)$ is played by the permutation $\mathscr{L}(U, V)$ which "lines up V with U."

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[4] See footnote 3 page 273.

Suppose that V and U have $(N-q)$ orbitals in common, i.e., among the orbitals $u_1, u_2, \ldots, u_N$ there are $(N-q)$ which are identical with certain ones of the orbitals $v_1, v_2, \ldots, v_N$. The remaining q orbitals in U have no orbitals in common with the remaining q orbitals in V. Then there exists a permutation $\mathscr{L}$ such that the orbital product $W = \mathscr{L}V$ has the following properties:

(1) The $(N-q)$ orbitals which V and U have in common are occupied by the same electrons in W and in U;

(2) the remaining q orbitals occur in W in the order of ascending orbital index with ascending index of the occupying electron, i.e., they occur in the same order as in V.

For example, if $U = f_1 f_2 f_3 f_4 f_5$ and $V = f_2 f_4 f_6 f_7 f_8$ then $W = f_6 f_2 f_7 f_4 f_8$. In general, we shall use the indices $j_1, j_2, \ldots, j_q$ to denote those electrons which occupy *different* orbitals in U and W. Hence, the orbitals occupied by the remaining electrons are identical in U and W. Thus, if

$$\mathscr{L}V = W = w_1(1)\, w_2(2) \cdots w_N(N), \tag{29}$$

then

$$\begin{aligned} w_n &= u_n \qquad \text{for} \quad n \neq j_1, j_2, \ldots, j_q, \\ w_n &\neq u_n \qquad \text{for} \quad n = j_1, j_2, \ldots, j_q. \end{aligned} \tag{30}$$

For the example given, one has $q = 3$ and $j_1, j_2, j_3 = 1, 3, 5$.

A line-up permutation exists always. It depends of course upon U and V: $\mathscr{L} = \mathscr{L}(U, V)$. However, in the presense of doubly occupied orbitals it is not unique. In those cases, we require $\mathscr{L}$ to satisfy the following conventions. Suppose that the orbital f_α is doubly occupied in U so that, e.g., $u_\beta = u_{\beta+1} = f_\alpha$, where β is an odd number. Suppose, furthermore, that the orbital f_α occurs *once* among the orbitals of V. Then we stipulate that $w_\beta \neq u_\beta$, $w_{\beta+1} = f_\alpha$, so that the index β belongs to the indices $j_1, \ldots, j_q$, and the index $(\beta + 1)$ does not. Similarly, if f_γ occurs twice in V, say $v_\delta = v_{\delta+1} = f_\gamma$ ($\delta = \text{odd}$), and once in U, then $\mathscr{L}$ should line up $v_{\delta+1}$ (and not v_δ) with the identical orbital, f_γ, in U. Finally, if f_α is doubly occupied in U and V: $f_\alpha = u_\beta = u_{\beta+1} = v_\gamma = v_{\gamma+1}$, then the permutation $\mathscr{L}$ should line up u_β with v_γ and $u_{\beta+1}$ with $v_{\gamma+1}$. With these conventions, one has $\mathscr{L}(V, U) = \mathscr{L}^{-1}(U, V)$ and hence, for the corresponding matrices of Eq. (24), $L_{st}(V, U) = L_{ts}(U, V)$, since the representation of S_N is orthogonal.

When the permutation $\mathscr{P}$ runs through the whole symmetric group S_N, then the permutation $\mathscr{P}' = \mathscr{P}\mathscr{L}$, does too. Hence the basic equation (26) can also be written in the form

$$\mathbf{G}(U, V) = 2^{-[\pi(U)+\pi(V)]/2} \sum_{\mathscr{P}} \langle U \,|\, \mathscr{G} \,|\, \mathscr{P}W \rangle \mathbf{PL} \tag{31}$$

where W is lined up with U according to Eqs. (29) and (30).

For a p-particle operator, such as defined in Eqs. (15), (16), (17), the basic equation (31) becomes

$$\mathbf{G}(U, V) = 2^{-[\pi(U)+\pi(V)]/2} \sum_{(i)} \mathbf{G}_{(i)}(U, V) \tag{32}$$

with

$$\begin{aligned} \mathbf{G}_{(i)}(U, V) &= \sum_{\mathscr{P}} \langle U | g(i) | \mathscr{P} W \rangle \mathbf{PL} \\ &= \sum_{\mathscr{P}} \langle u_1 u_2 \cdots u_N | g(i_1 i_2 \cdots i_p) | \mathscr{P} w_1 w_2 \cdots w_N \rangle \mathbf{PL}, \end{aligned} \tag{33}$$

where the summation over (i) covers the indices

$$1 \le i_1 \le N, \qquad 1 \le i_2 \le N, \qquad \cdots \qquad 1 \le i_p \le N, \tag{34}$$

subject to the conditions

$$i_1 < i_2 < i_3 < \cdots < i_p. \tag{35}$$

C. Reduction of Sum Over $(i_1\, i_2 \cdots i_p)$

In Eq. (33), the orbitals u_n with indices $n \neq (i_1 i_2 \cdots i_p)$ form overlap integrals with certain orbitals among the $w_1, \ldots, w_N$. In order that these be nonzero, all orbitals u_n with $n \neq (i_1 i_2 \cdots i_p)$ must occur among the orbitals $w_1, \ldots, w_N$, and hence among the orbitals of V. This can however be the case only for certain selected index sets $(i_1 i_2 \cdots i_p)$, because W is lined up with U.

A first case is that when the index set $(i_1 i_2 \cdots i_p)$ contains the entire index set $(j_1 j_2 \cdots j_q)$ which, according to Eq. (30), labels the electrons which occupy *different* orbitals in U and W. Clearly, the remaining orbitals are identical in U and W. The sum over all possible index sets of this kind can be written

$$\sum_{(i)}{}^{*} g(i) = \sum_{k_1} \sum_{k_2} \cdots \sum_{k_{p-q}} g(j_1 j_2 \cdots j_q k_1 k_2 \cdots k_{p-q}) \tag{36}$$

where the k's are summed according to

$$\begin{aligned} &1 \le k_1 \le N, \qquad 1 \le k_2 \le N, \qquad \ldots, \qquad 1 \le k_{p-q} \le N; \\ &\qquad\qquad\qquad\qquad\qquad\qquad k_1 < k_2 < \cdots < k_{p-q} \end{aligned} \tag{37}$$

and none of them assumes any of the values $j_1, \ldots, j_q$. In writing Eq. (36) use has been made of the fact that $g(i_1 i_2 \cdots i_p)$ is symmetric in all its indices [see Eq. (17)].

Other cases arise only when U has doubly occupied orbitals which are singly occupied in V. Let $u_\beta = u_{\beta+1}$ be such an orbital in U, then β is among the indices $j_1, j_2 \ldots, j_q$ and $(\beta + 1)$ is not, as discussed in the previous section. In this case, it is clearly only necessary that the index set $(i_1, i_2,$

$\ldots, i_p)$ contain *either* the index β *or* the index $(\beta + 1)$ in order that the remaining orbitals can have matches in W. Let us, then, consider an index set (i) which contains the index β and another index set $(\hat{\imath})$ which differs from (i) merely by having β replaced by $(\beta + 1)$. Then both $g(i)$ and $g(\hat{\imath})$ give nonzero contributions, and one can write

$$\begin{aligned}\langle U|g(\hat{\imath})|\mathscr{P}W\rangle &= \langle U|(\beta, \beta+1)g(i)(\beta, \beta+1)|\mathscr{P}W\rangle \\ &= \langle(\beta, \beta+1)U|g(i)(\beta, \beta+1)|\mathscr{P}W\rangle \\ &= \langle U|g(i)(\beta, \beta+1)|\mathscr{P}W\rangle,\end{aligned}$$

where $(\beta, \beta + 1)$ denotes the transposition between the odd electron β and the even electron $(\beta + 1)$. Now, if $(\beta + 1)$ does *not* occur among the indices $(k_1, k_2, \ldots, k_{p-q})$, then $g(\hat{\imath})$ yields an *additional* non-zero term, that is not contained in Eq. (36). However, if it so happens that $(\beta + 1)$ *does* occur among the indices $(k_1, k_2, \ldots, k_{p-q})$, then one has $g(i) = g(\hat{\imath})$, and this term is already contained in Eq. (36). Hence all cases yielding a nonzero $\mathbf{G}_{(i)}$ are taken into account by expanding Eq. (36) to the following form

$$\sum{}^* g(i) = \sum_{k_1} \sum_{k_2} \sum_{kp-q} \sum_{\mathscr{Q}^*} (j_1 j_2 \cdots j_q k_1 k_2 \cdots k_{p-q})\mathscr{Q}^* 2^{-\pi'(U,i)} \tag{38}$$

where the $k_1, k_2, \ldots, k_{p-q}$ sum over the same indices as defined in Eq. (37) and where the summation over $\mathscr{Q}^*$ *covers the elements of the subgroup obtained as the direct product of all geminal subgroups of the form* $\{1, (\beta, \beta + 1)\}$ *corresponding to orbital pairs* $(u_\beta, u_{\beta+1})$, *which represent doubly occupied orbitals in* U *that are singly occupied in* V. Furthermore, $\pi'(U, i)$ is the number of *these* orbital pairs, for which the indices of both partners are contained in the set $(i_1, i_2, \ldots, i_p)$.

Consequently Eq. (26) can be rewritten as

$$\mathbf{G}(U, V) = 2^{-\pi'(U,i)-[\pi(U)+\pi(V)]/2} \sum_{(k)} \mathbf{G}_{(k)}(U, V) \tag{39}$$

with

$$\mathbf{G}_{(k)}(U, V) = \sum_{\mathscr{Q}^*} \sum_{\mathscr{P}} \langle U|g(j_1 \cdots j_p k_1 \cdots k_{p-q})|\mathscr{Q}^*\mathscr{P}W\rangle \mathbf{PL}$$

where the sum over (k) is given by Eq. (37). Replacing now the sum over $\mathscr{P}$ by a sum over $\mathscr{P}' = \mathscr{Q}^*\mathscr{P}$ and using the fact that $(\mathscr{Q}^*)^{-1} = \mathscr{Q}^*$ (being a product of commuting transpositions), we obtain

$$\mathbf{G}_{(k)}(U, V) = \sum_{\mathscr{P}} \langle u_1 u_2 \cdots u_N|g(i_1 i_2 \cdots i_p)|\mathscr{P} w_1 w_2 \cdots w_N\rangle \Big(\sum_{Q^*} \mathbf{Q}^*\Big)\mathbf{PL} \tag{40}$$

with

$$(i_1 i_2 \cdots i_p) = (j_1 j_2 \cdots j_q k_1 k_2 \cdots k_{p-q}). \tag{41}$$

The sum over (k) is defined as follows: Each of the indices $k_1, k_2, \ldots, k_{p-q}$ runs from 1 to N, but cannot assume the value $j_1, j_2, \ldots, j_q$. Furthermore, they are subject to the inequalities $k_1 < k_2 \cdots < k_{p-q}$. The sum over Q^* has been characterized after Eq. (38).

D. Analysis of Sum over P

The sum over $\mathscr{P}$ in Eq. (40) runs over the entire symmetric group S_N. In order to make further progress, this has to be decomposed according to certain subgroups.

Consider first the subgroups $\mathrm{S}_{(i)}$ and $\hat{\mathrm{S}}_{(i)}$, where $\mathrm{S}_{(i)}$ is the subgroup of $p!$ permutations among the electrons $(i_1, \ldots, i_p)$ and $\hat{\mathrm{S}}_{(i)}$ is the subgroup of $(N-p)!$ permutations among the electrons with indices different from $(i_1, i_2, \ldots, i_p)$. Furthermore, let $\mathrm{T}_{(1)}$ be a collection of $[N!/p!(N-p)!] = \binom{N}{p}$ nonequivalent right coset generators of the subgroup $\mathscr{S}_{(i)} \times \mathscr{P}_{(i)}$, so that

$$\mathrm{S}_N = \mathrm{S}_{(i)} \times \hat{\mathrm{S}}_{(i)} \times \mathrm{T}_{(i)} \tag{42}$$

If we denote the elements of S_N by $\mathscr{P}$, those of $\mathrm{S}_{(i)}$ by $\mathscr{R}$, those of $\hat{\mathrm{S}}_{(i)}$ by $\mathscr{S}$, those of $\mathrm{T}_{(i)}$ by $\mathscr{T}$, then Eq. (42) implies the summation decomposition

$$\sum_{\mathscr{P}} f(\mathscr{P}) = \sum_{\mathscr{R}} \sum_{\mathscr{S}} \sum_{\mathscr{T}} f(\mathscr{R}\mathscr{S}\mathscr{T}) \tag{43}$$

for any function of $\mathscr{P}$.

The elements of $\mathrm{T}_{(i)}$ are defined as $N!/p!(N-p)!$ permutations $\mathscr{T}_1, \mathscr{T}_2, \mathscr{T}_3, \ldots$ with the following properties: Each $\mathscr{T}_\alpha$ establishes an interchange between electrons with labels $(i_1, i_2, \ldots, i_p)$ and electrons with labels $\neq (i_1, i_2, \ldots, i_p)$. Furthermore, for any two such permutations, $\mathscr{T}_\alpha$ and $\mathscr{T}_\beta$ say, *the product* $\mathscr{T}_\alpha \mathscr{T}_\beta^{-1}$ *must not belong to the subgroup* $\mathrm{S}_{(i)} \times \hat{\mathrm{S}}_{(i)}$, since otherwise $\mathscr{T}_\alpha$ and $\mathscr{T}_\beta$ would generate the same right coset.

Secondly, we have to consider the invariance group S_V of V, and its relation to the coset decomposition of Eq. (42). If V contains the doubly occupied orbitals $v_1 = v_2$, $v_3 = v_4, \ldots, v_d = d_{d+1}$, then the invariance group S_V consists of all elements $\mathscr{Q}$ in the direct product

$$\mathrm{S}_V = \{1, (12)\} \times \{1, (34)\} \cdots \{1, (d-1, d)\} = \{\mathscr{Q}\}. \tag{44}$$

Furthermore, since the invariance $\mathscr{Q}V = V$ yields the invariance $(\mathscr{L}\mathscr{Q}\mathscr{L}^{-1})W = W$, it is apparent that the invariance group of W is given by

$$\mathrm{S}_W = \mathscr{L}\mathrm{S}_V \mathscr{L}^{-1}, \tag{45}$$

i.e.,

$$\mathscr{L}\mathscr{Q}\mathscr{L}^{-1} w_1 w_2 \cdots w_N = w_1 w_2 \cdots w_N \tag{46}$$

for all elements $\mathscr{Q}$ of S_V. Since all elements of S_V commute, the same holds for S_W. We shall now show that S_W can be expressed as the direct product of three commuting subgroups, $\mathrm{S}_W^{(i)}$, $\hat{\mathrm{S}}_W^{(i)}$, $\mathrm{T}_W^{(i)}$, which have the properties that $\mathrm{S}_W^{(i)}$ is a subgroup of $\mathrm{S}_{(i)}$, $\hat{\mathrm{S}}_W^{(i)}$ is a subgroup of $\hat{\mathrm{S}}_{(i)}$, and $\mathrm{T}_W^{(i)}$ is part of the right coset generator collection $\mathrm{T}^{(i)}$. Thus,

$$\mathrm{S}_W = \mathrm{S}_W^{(i)} \times \mathrm{S}_W^{(i)} \times \mathrm{T}_W^{(i)}. \tag{47}$$

Furthermore, the three subgroups are given by

$$\mathrm{S}_W^{(i)} = \mathscr{L}\mathrm{A}_{(i)}\mathscr{L}^{-1} \tag{48a}$$

$$\hat{\mathrm{S}}_W^{(i)} = \mathscr{L}\mathrm{B}_{(i)}\mathscr{L}^{-1} \tag{48b}$$

$$\mathrm{T}_W^{(i)} = \mathscr{L}\mathrm{C}_{i)}\mathscr{L}^{-1} \tag{48c}$$

where $\mathrm{A}_{(i)}$, $\mathrm{B}_{(i)}$, $\mathrm{C}_{(i)}$ are certain commuting subgroups of $\mathscr{S}_V$ such that

$$\mathrm{S}_V = \mathrm{A}_{(i)} \times \mathrm{B}_{(i)} \times \mathrm{C}_{(i)} \tag{49}$$

In order to show these contentions let us denote by $v_a = v_{a+1}$ the doubly occupied orbital in V which corresponds to the transposition $(a, a+1)$. Then the generating transpositions $(1, 2)$, $(3, 4), \ldots, (d-1, d)$ occurring in Eq. (44) can be divided into three categories. First category: Both orbitals v_a and v_{a+1} are among the orbitals w_n with $n = (i_1, i_2, \ldots i_p)$. If $\mathscr{A}_1, \mathscr{A}_2, \ldots, \mathscr{A}_\alpha$ are all transpositions of this type, then $\mathrm{A}_{(i)}$ is defined by

$$\mathrm{A}_{(i)} = \{1, \mathscr{A}_1\} \times \{1, \mathscr{A}_2\} \times \cdots \times \{1, \mathscr{A}_\alpha\}. \tag{50}$$

Clearly $\mathscr{L}\mathrm{A}_{(i)}\mathscr{L}^{-1}$ leaves W invariant and, moreover, interchanges only electrons between orbitals w_n with $n = (i_1, i_2, \ldots, i_p)$. Hence, it is a subgroup of $\mathrm{S}_{(i)}$.

Second category: Both orbitals v_a and v_{a+1} are among the orbitals w_n with $n \neq (i_1, i_2, \ldots, i_p)$. If $\mathscr{B}_1, \mathscr{B}_2, \ldots, \mathscr{B}_\beta$ are all transpositions of this type, then $\mathrm{B}_{(i)}$ is defined as

$$\mathrm{B}_{(i)} = \{1, \mathscr{B}_1\} \times \{1, \mathscr{B}_2\} \times \cdots \times \{1, \mathscr{B}_\beta\}. \tag{51}$$

Clearly $\mathscr{L}\mathrm{B}_{(i)}\mathscr{L}^{-1}$ leaves W invariant and, moreover, interchanges only electrons between orbitals w_n with $n \neq (i_1, i_2, \ldots, i_p)$. Hence, it is a subgroup of $\hat{\mathrm{S}}_{(i)}$.

Third category: One of the orbitals v_a and v_{a+1} is among the orbitals w_n with $n = (i_1, i_2, \ldots, i_p)$, the other is among the orbitals w_n with $n \neq (i_1, i_2, \ldots, i_p)$. If $\mathscr{C}_1, \mathscr{C}_2, \ldots, \mathscr{C}_\gamma$ are all transpositions of this kind, then $\mathrm{C}_{(i)}$ is defined by

$$\mathrm{C}_{(i)} = \{1, \mathscr{C}_1\} \times \{1, \mathscr{C}_2\} \times \cdots \times \{1, \mathscr{C}_\gamma\} \tag{52}$$

Clearly $\mathscr{L}\mathsf{C}_{(i)}\mathscr{L}^{-1}$ leaves W invariant. Moreover, the product decomposition (49) and, hence the decomposition (47) holds.

In order to prove that all elements of $\mathscr{L}\mathsf{C}_{(i)}\mathscr{L}^{-1}$ belong to the collection $\mathsf{T}_{(i)}$ of right coset generators of $\mathsf{S}_{(i)} \times \hat{\mathsf{S}}_{(i)}$, we note that all transpositions in Eq. (52) commute and are their own inverses. It is then readily seen that any product $(\mathscr{L}\mathscr{C}_\nu\mathscr{L}^{-1})(\mathscr{L}\mathscr{C}_\mu\mathscr{L}^{-1})^{-1} = \mathscr{L}\mathscr{C}_\nu\mathscr{C}_\mu\mathscr{L}^{-1}$ still results in an interchange between electrons with $n = (i_1, i_2, \ldots, i_p)$ and electrons with $n \neq (i_1, i_2, \ldots, i_p)$. Hence this product does not belong to $\mathsf{S}_{(i)} \times \hat{\mathsf{S}}_{(i)}$ and, thus, $\mathscr{L}\mathscr{C}_\nu\mathscr{L}^{-1}$ and $\mathscr{L}\mathscr{C}_\mu\mathscr{L}^{-1}$ belong to different cosets of $\mathsf{S}_{(i)} \times \hat{\mathsf{S}}_{(i)}$. All 2^γ elements of the subgroup $\mathsf{T}_W^{(i)}$, defined by Eq. (48c) and (52), can therefore be chosen to be among the elements of the collection $\mathsf{T}_{(i)}$ of right coset generators of $\mathsf{S}_{(i)} \times \hat{\mathsf{S}}_{(i)}$.

In view of the direct product decomposition of Eq. (47), the sum over all permutations which leave W invariant can therefore be decomposed as

$$\sum_{\mathscr{Q}} f(\mathscr{L}\mathscr{Q}\mathscr{L}^{-1}) = \sum_{\mathscr{R}'}\sum_{\mathscr{S}'}\sum_{\mathscr{T}'} f(\mathscr{R}'\mathscr{S}'\mathscr{T}'), \tag{53}$$

where $\mathscr{Q}$ runs over S_V, $\mathscr{R}'$ runs over $\mathsf{S}_W^{(i)}$, $\mathscr{S}'$ runs over $\hat{\mathsf{S}}_W^{(i)}$, and $\mathscr{T}'$ runs over $\mathsf{T}_W^{(i)}$.

E. Reduction of Sum over P

By virtue of the coset decomposition of Eqs. (42) and (43), the summation of Eq. (40) can be reexpressed as

$$\mathbf{G}_k(U, V) = \sum_{\mathscr{R}}\sum_{\mathscr{S}}\sum_{\mathscr{T}} \langle u_1 \cdots u_N | g(i_1 \cdots u_p) | \mathscr{R}\mathscr{S}\mathscr{T} w_1 \cdots w_N\rangle \Big(\sum_{Q^*} \mathbf{Q}^*\Big)\mathbf{RSTL} \tag{54}$$

where $\mathscr{R}, \mathscr{S}, \mathscr{T}$ sum over $\mathsf{S}_{(i)}$, $\hat{\mathsf{S}}_{(i)}$, and $\mathsf{T}_{(i)}$, respectively.

In order that the integral $\langle U | g | \mathscr{R}\mathscr{S}\mathscr{T} W\rangle$ be nonzero, the integration over the u_n, with $n \neq (i_1, i_2, \ldots, i_p)$, must give nonzero overlap integrals. Now W is lined up with U and, hence, we have $u_n = w_n$ for all $n \neq (j_1, j_2, \ldots, j_q)$, hence in particular for $n \neq (i_1, i_2, \ldots, i_p)$. A nonzero contribution is therefore obtained for $\mathscr{R}\mathscr{S}\mathscr{T} = 1$ and for any other product $\mathscr{R}\mathscr{S}\mathscr{T}$ which leaves *these* orbitals w_n unchanged. In the summations over $\mathscr{S}$ and $\mathscr{T}$, this is the case only for those elements of $\hat{\mathsf{S}}_{(i)}$ and $\mathsf{T}_{(i)}$ which belong to the subgroups $\hat{\mathsf{S}}_W^{(i)}$ and $\mathsf{T}_W^{(i)}$ defined in Eqs. (48b), (48c). The summation of Eq. (54) can therefore be reduced according to

$$\sum_{\mathscr{R}}\sum_{\mathscr{S}}\sum_{\mathscr{T}} f(\mathscr{R}\mathscr{S}\mathscr{T}) = \sum_{\mathscr{R}}\sum_{\mathscr{S}'}\sum_{\mathscr{T}'} f(\mathscr{R}\mathscr{S}'\mathscr{T}') \tag{55}$$

where $\mathscr{S}'$ and $\mathscr{T}'$ run over $\hat{\mathsf{S}}_W^{(i)}$ and $\mathsf{T}_W^{(i)}$, respectively [see Eq. (53)].

Finally, it is possible to make a left coset decomposition of $\mathrm{S}_{(i)}$ according to the subgroup $\mathrm{S}_W^{(i)}$ defined in Eq. (48a):

$$\mathrm{S}_{(i)} = \mathrm{S}_{(i)}^W \times \mathrm{S}_W^{(i)}. \tag{56}$$

Denoting the elements of the left coset $\mathrm{S}_{(i)}^W$ by $\mathscr{R}''$, we can then write Eq. (55) as

$$\sum_{\mathscr{R}} \sum_{\mathscr{S}} \sum_{\mathscr{T}} f(\mathscr{R}\mathscr{S}\mathscr{T}) = \sum_{\mathscr{R}''} \sum_{\mathscr{R}'} \sum_{\mathscr{S}'} \sum_{\mathscr{T}'} f(\mathscr{R}''\mathscr{R}'\mathscr{S}'\mathscr{T}'),$$

and by virtue of Eq. (53) as

$$\sum_{\mathscr{R}} \sum_{\mathscr{S}} \sum_{\mathscr{T}} f(\mathscr{R}\mathscr{S}\mathscr{T}) = \sum_{\mathscr{R}''} \sum_{\mathscr{Q}} f[\mathscr{R}''(\mathscr{L}\mathscr{Q}\mathscr{L}^{-1})] \tag{57}$$

where $\mathscr{Q}$ runs over the invariance group of V.

Introducing the identity (57) into Eq. (54), and noting that the summation over $\mathscr{Q}$ generates all permutations $(\mathscr{L}\mathscr{Q}\mathscr{L}^{-1})$ which leave W invariant, one finds

$$\mathbf{G}_{(k)}(U, V) = \sum_{\mathscr{R}''} \langle u_1 \cdots u_N | g(i_1 \cdots i_p) | \mathscr{R}'' w_1 \cdots w_N \rangle \Big(\sum_{Q^*} \mathbf{Q}^*\Big) \mathbf{R}'' \Big(\sum_{Q} \mathbf{L}\mathbf{Q}\mathbf{L}^{-1}\Big) \mathbf{L}.$$

Since $\mathscr{R}''$ affects only the electrons $(i_1, i_2, \ldots, i_p)$, the integration over the remaining electrons can now be carried out, giving a product of unity overlap integrals. The summation over $\mathscr{R}''$ covers the left coset $\mathrm{S}_{(i)}^W$ of Eq. (56). However, since the elements of the subgroup $\mathrm{S}_W^{(i)}$ leave the product $(w_{i_1}, w_{i_2}, \ldots, w_{i_p})$ invariant, the permutations $\mathscr{R}''$ can be replaced by $\mathscr{R}''\mathscr{R}'$ in the integral, where $\mathscr{R}'$ is an arbitrary element of $\mathrm{S}_W^{(i)}$. According to Eq. (48a), the permutation $\mathscr{R}'$ can, however, be written as $\mathscr{L}\mathscr{A}_{R'}\mathscr{L}^{-1}$, with $\mathscr{A}_{R'}$ belonging to the geminal subgroup of Eq. (50). In the matrix factor of the expression for $\mathbf{G}_k$, we can therefore write

$$\mathbf{R}''\mathbf{L}\mathbf{Q}\mathbf{L}^{-1} = \mathbf{R}''\mathbf{R}'\mathbf{R}'^{-1}\mathbf{L}\mathbf{Q}\mathbf{L}^{-1} = \mathbf{R}''\mathbf{R}'\mathbf{L}\mathbf{A}_{R'}\mathbf{Q}\mathbf{L}^{-1}.$$

Since $\mathscr{R}'$ may be any element of $\mathrm{S}_W^{(i)}$, the summation over $\mathscr{R}''$ in the expression for $\mathbf{G}_k$ may be replaced by a summation over $\mathscr{P}$, where $\mathscr{P} = \mathscr{R}''\mathscr{R}'$ covers the whole subgroup $\mathrm{S}_{(i)}$, if the result is divided by the number of elements in $\mathrm{S}_W^{(i)}$. The latter is $2^{\pi(V, i)}$, with $\pi(V, i)$ being the number of doubly occupied orbitals among $w_{i_1}, w_{i_2}, \ldots, w_{i_p}$. Thus one obtains

$$\mathbf{G}_{(k)}(U, V) = \sum_{\mathscr{P}} \langle u_{i_1} u_{i_2} \cdots u_{i_p} | g(i_1 i_2 \cdots i_p | \mathscr{P} w_{i_1} w_{i_2} \cdots w_{i_p} \rangle \mathbf{M}(\mathscr{P}), \tag{58}$$

with

$$\mathbf{M}(\mathscr{P}) = \Big(\sum_{Q^*} \mathbf{Q}^*\Big) \mathbf{P}\mathbf{L}\mathbf{A}_{\mathscr{P}} \Big(\sum_{Q} \mathbf{Q}\Big) 2^{-\pi(V, i)}. \tag{59}$$

Here, the summation over $\mathscr{P}$ covers the subgroup $S_{(i)}$; the summation over Q covers S_V, the invariance group of V; and Q^* runs over that geminal subgroup which is the direct product of all transposition groups $\{1, (\beta, \beta + 1)\}$, which correspond to orbital pairs $\{u_\beta, u_\beta + 1\}$ representing doubly occupied orbitals of U that are singly occupied in V.

We now note that the Q, the Q^*, and the $A_{\mathscr{P}}$ are all products of geminal transpositions. By virtue of the property expressed in Eq. (10) for the Serber-type representations, they are all diagonal, with values $+1$ or -1. We furthermore recall that, according to Eq. (27), the matrix elements G_{st} are nonzero only if $s \leq f_S(U)$ and $t \leq f_S(V)$. According to Eqs. (12) and (24), the diagonal elements will be $+1$ for these index choices, since the Q^* belong to the invariance group of U and the Q and $A_{\mathscr{P}}$ belong to the variance group of V. All matrices Q^*, Q, and $A_{\mathscr{P}}$ can therefore be replaced by unit matrices, and one obtains for Eq. (59)

$$\mathbf{M}(\mathscr{P}) = \mathbf{PL}2^{\pi'(U)+\pi(V)-\pi(V,i)} \tag{60}$$

where $\pi(V)$ is the number of doubly occupied orbitals in V, $\pi'(U)$ is the number of orbitals that are doubly occupied in U, but only singly occupied in V.

We now substitute Eq. (60) in Eq. (58) and, then, Eq. (58) back in Eq. (39). In order to combine the numerical factors in Eq. (60) and Eq. (39), we note that

$$\pi(U) = \pi(UV) + \pi'(U) + \pi^0(U) \tag{61a}$$

$$\pi(U, i) = \pi(UV, i) + \pi'(U, i) + \pi^0(U) \tag{61b}$$

where

$\pi(U)$ = number of doubles in U,
$\pi(UV)$ = number of doubles common to U and V,
$\pi'(U)$ = number of doubles in U which are single in V,
$\pi^0(U)$ = number of doubles in U whose orbitals do not occur in V,
$\pi(U, i)$ = number of doubles in U that occur among $u_1, u_2, \ldots, u_{i_p} = U(i)$.
$\pi(UV, i)$ = number of doubles common to U and V *and* occurring in $U(i)$.
$\pi'(U, i)$ = number of doubles in U that are singles in V *and* occur in $U(i)$.

Hence the identity

$$\pi(U) - \pi(UV) - \pi(U, i) + \pi(UV, i) = \pi'(U) - \pi'(Ui)$$

holds, and the exponent of 2, resulting from combining Eqs. (60) and (39), will be

$$\begin{aligned}&\{-\tfrac{1}{2}[\pi(U)+\pi(V)]-\pi'(U,i)\}+\{\pi'(U)+\pi(V)-\pi(V,i)\}\\&\quad=-\tfrac{1}{2}[\pi(U)+\pi(V)]+[\pi(U)-\pi(UV)-\pi(U,i)+\pi(UV,i)]\\&\qquad+[\pi(V)-\pi(V,i)]\\&\quad=\tfrac{1}{2}[\pi(U)+\pi(V)]-\pi(UV)-\pi(U,i)-\pi(V,i)+\pi(UV,i).\end{aligned}$$

The resulting expression is therefore

$$\mathbf{G}(U,V)=\sum_{(i)}\sum_{\mathscr{P}}^{(i)}\langle u_{i1}\cdots u_{i_p}|g|\mathscr{P}w_{i_1}\cdots w_{i_p}\rangle\mathbf{PL}2^{\Delta(U,i)+\Delta(V,i)} \tag{62}$$

with

$$\Delta(U,i)=\delta(U)-\delta(U,i) \tag{63}$$

where

$$\delta(U)=\tfrac{1}{2}\{\pi(U)-\pi(UV)\} \tag{64a}$$

$$\delta(U,i)=\pi(U,i)-\tfrac{1}{2}\pi(UV,i). \tag{64b}$$

The constants $\Delta(V,i)$ are defined in an entirely analogous manner with $\pi(V)$ = number of doubles in V, $\pi(V,i)$ = number of doubles in V that occur in $(w_{i_1}w_{i_2}\cdots w_{i_p})$, and $\pi(UV,i)$ = number of doubles common to U and V that occur in $(w_{i_1}w_{i_2}\cdots w_{i_p})$. The two definitions for $\pi(UV,i)$ are not in conflict because if both orbitals of a double, that is common to U and V, occur in $(u_{i_1}\cdots u_{i_p})$, then both must also occur in $(w_{i_1}\cdots w_{i_p})$, since zero overlap integrals would result otherwise.

F. General Result

In order to arrive at the master formula, we finally transform the permutations $\mathscr{P}$, applying to electrons, into permutations P, applying to orbital indices.

Since $\mathscr{P}$ is a unitary operator and $g(i_1i_2\cdots i_p)$ is symmetric in $(i_1\cdots i_p)$, one has

$$\begin{aligned}&\langle u_{i_1}u_{i_2}\cdots|g(i_1\,i_2\cdots|\mathscr{P}w_{i_1}w_{i_2}\cdots\rangle\\&\qquad\qquad=\langle\mathscr{P}^{-1}u_{i_1}u_{i_2}\cdots|g(i_1\,i_2\cdots)|w_{i_1}w_{i_2}\cdots\rangle\end{aligned}$$

and, here, the permutation $\mathscr{P}^{-1}$, which applies to the electron coordinates can now be replaced by the permutation P which applies to the corresponding orbital indices, whence

$$\langle u_{i_1}u_{i_2}\cdots|g(i_1\,i_2\cdots)|\mathscr{P}w_{i_1}w_{i_2}\cdots\rangle=\langle Pu_{i_1}u_{i_2}\cdots|g(i_1\,i_2\cdots)|w_{i_1}w_{i_2}\cdots\rangle.$$

In this formulation the electrons serve only as integration variables and their labeling becomes arbitrary. Moreover, since $g(i_1 i_2 \cdots i_p)$ is symmetric in the electron coordinates, the order of the integration variables in g is irrelevant. The only essential point is that the orbital u_{i_k} (before applying P) has the same integration variable as the orbital w_{i_k}.

Furthermore, the order in which the orbitals are written in forming the products $(u_{i_1} u_{i_2} \cdots)$ and $(w_{i_1} w_{i_2} \cdots)$ does not matter. It is therefore possible to place the orbitals in which U and V differ ahead of those in which they agree. Let the former be denoted by

$$\begin{aligned} &u_{j_1} = u_{\alpha_1},\ u_{j_2} = u_{\alpha_2}, \ldots, u_{j_q} = u_{\alpha_q}; \qquad \alpha_1 < \alpha_2 < \cdots < \alpha_q, \\ &w_{j_1} = v_{\beta_1},\ w_{j_2} = v_{\beta_2}, \ldots, w_{j_q} = v_{\beta_q}; \qquad \beta_1 < \beta_2 < \cdots < \beta_q, \end{aligned}$$

(where $j_k = \alpha_k$, but $j_k \neq \beta_k$), and observe that, for the latter, we have $w_k = u_k$. Then Eq. (62) can be written in the final form

$$\begin{aligned} \mathbf{G}(U, V) &= \{\langle Us|g|Vt\rangle\} \\ &= \sum_{(k)} \sum_{P}^{(i)} P\mathbf{L}(UV) 2^{\Delta(U,i)+\Delta(V,i)} \\ &\quad \times \langle Pu_{\alpha_1} \cdots u_{\alpha_q} u_{k_1} \cdots u_{k_{p-q}} | g | v_{\beta_1} \cdots v_{\beta_q} u_{k_1} \cdots u_{k_{p-q}} \rangle, \end{aligned} \tag{65}$$

where the order of the orbitals indicates the integration variables which may be labeled $(x_1 x_2 \cdots x_p)$. The sum over (k) is defined as

$$\begin{aligned} &1 \le k_\gamma \le N, \qquad k_1 < k_2 < \cdots < k_{p-q}, \\ &k_\gamma \neq \alpha_1, \alpha_2, \ldots, \alpha_q \qquad \text{for all values of } \gamma. \end{aligned} \tag{66}$$

The set (i) denotes the collection of indices $(j_1, j_2, \ldots j_q, k_1, k_2, \ldots, k_{p-q})$. The summation $\sum^{(i)}$ over P covers all permutations among the indices of the set (i). These permutations apply to the actual *values* of the orbital indices and not to the positions of the orbitals. Thus, for the permutation $P = (1347)$ one would have, e.g.,

$$Pu_3(x_1)u_7(x_2)u_1(x_3)u_4(x_4) = u_4(x_1)u_1(x_2)u_3(x_3)u_7(x_4).$$

Among the u orbitals and among the v orbitals, there may occur doubles. The summations over (k) and (P) count the two members of each couple as different orbitals and, hence, may generate certain identical terms which can be collected.

The constants $\Delta(U, i)$ and $\Delta(V, i)$ were defined in Eqs. (64a) and (64b). The matrix $\mathbf{L}(UV)$ is the representation matrix of the permutation $\mathscr{L}(UV)$ which lines V up with U in the manner discussed in connection with Eqs. (29) and (30).

Equation (65) appears to treat the functions U and V differently. In order to bring out that the expression is in fact symmetric in U and V, let $\tilde{\mathcal{Q}}$ be a permutation of the integration variables in Eq. (65). Then, due to the symmetry in g, we have

$$\langle P\tilde{\mathcal{Q}}u_{\alpha_1}\cdots|g|\tilde{\mathcal{Q}}v_{\beta_1}\cdots\rangle = \langle Pu_{\alpha_1}\cdots|g|v_{\beta_1}\cdots\rangle.$$

Let us use again the original integration variables, so that the electron labels are identical with the indices of the orbitals u_i and w_i, used in Eq. (62). Hence, on the left of g, $\tilde{\mathcal{Q}}$ can be replaced by $\tilde{Q}^{-1}$, where $\tilde{Q}$ acts on the orbital indices. To the right of g, the situation is not as simple. There one has to keep in mind, that the *original* electron labels are identical with the orbital indices in V. It follows from this that

$$W = \mathcal{L}(\text{electrons})V = L^{-1}(\text{orbitals})V$$

and

$$\begin{aligned}\tilde{\mathcal{Q}}(\text{electrons})W &= \tilde{\mathcal{Q}}(\text{electrons})\mathcal{L}(\text{electrons})V\\ &= L^{-1}(\text{orbitals})\tilde{Q}^{-1}(\text{orbitals})V\\ &= L^{-1}(\text{orbitals})\tilde{Q}^{-1}(\text{orbitals})L(\text{orbitals})W\end{aligned}$$

whence

$$\langle Pu_{\alpha_1}\cdots|g|v_{\beta_1}\cdots\rangle = \langle P\tilde{Q}^{-1}u_{\alpha_1}\cdots|g|L^{-1}\tilde{Q}^{-1}Lv_{\beta_1}\cdots\rangle$$

Choosing now $\mathcal{Q} = \mathcal{L}^{-1}\tilde{\mathcal{Q}}^{-1}\mathcal{L}$, so that

$$L^{-1}\tilde{Q}^{-1}L = Q, \qquad P\tilde{Q}^{-1} = PLQL^{-1} = P^*,$$

one can replace the summation over P by a summation over P^*, if $\mathbf{PL}$ is replaced by

$$\mathbf{PL} = \mathbf{P^*LQ}^{-1} = \mathbf{P^*LQ}^{\dagger},$$

with $\mathbf{Q}^{\dagger}$ indicating the transposed matrix. These considerations can be made for any of the $p!$ permutations Q among the orbital indices to the right of g. Hence we can reexpress Eq. (65) in the form

$$\begin{aligned}\mathbf{G}(U, V) = \sum_{(k)}\sum_{P}^{(i)}\sum_{Q}^{(j)} 2^{\Delta(U,i)+\Delta(V,j)}(p!)^{-1}\mathbf{PL}(UV)\mathbf{Q}^{\dagger}\\ \cdot\langle Pu_{\alpha_1}\cdots u_{\alpha_q}u_{k_1}\cdots u_{k_{p-q}}|g|Qv_{\beta_1}\cdots v_{\beta_q}v_{l_1}\cdots v_{l_{p-q}}\rangle, \qquad (67)\end{aligned}$$

where $l_1 < l_2\cdots < l_{p-q}$ are the indices of those orbitals v_i for which $v_{l_\gamma} = u_{k_\gamma}$, after V has been lined up with U. Altogether, there are of course $(N-q)$ such orbitals

$$v_{l_\gamma} = u_{k_\gamma}, \qquad \text{with} \quad l_1 < l_2\cdots < l_{N-q}; \quad k_1 < k_2 < \cdots < k_{N-q}, \qquad (68)$$

so that one can write $l_\gamma = l(k_\gamma)$, and the summation over $(k) = (k_1 \cdots k_{p-q})$ also implies substitution of the appropriate l_γ values. The summation over Q covers all $p!$ permutations among the index collection $(j) = (\beta_1 \cdots \beta_q\ l_1 \cdots l_{p-q})$. The summation over P covers all $p!$ permutations among the index collection $(i) = (\alpha_1 \cdots \alpha_q\ k_1 \cdots k_{p-q})$.

In order to see that $G_{st}(U, V) = \langle Us|g|Vt\rangle$ is symmetric in U and V we have to show that the expression (67) remains invariant if (Us) is interchanged with (Vt). Since interchanging U and V in the integral is equivalent to interchanging P and Q, the total result of interchanging Us and Vt is, therefore, equivalent to replacing $(\mathbf{PL}(UV)\mathbf{Q}^\dagger)_{st}$ by $(\mathbf{QL}(V, U)\mathbf{P}^\dagger)_{ts}$ in Eq. (67). However, we have discussed earlier that $\mathscr{L}(V, U) = \mathscr{L}^{-1}(U, V)$ and, furthermore, the matrix $\mathbf{L}$, like all representation matrices, is orthogonal. Consequently, we find

$$(\mathbf{QL}(V, U)\mathbf{P}^\dagger)_{ts} = (\mathbf{QL}^\dagger(U, V)\mathbf{P}^\dagger)_{st}^\dagger = (\mathbf{PL}(U, V)\mathbf{Q}^\dagger)_{st},$$

which establishes the invariance of the expression (67).

IV. Matrix Elements for Special Cases

A. Extreme Values of q

From the final result expressed in Eq. (65) it is apparent that q cannot be larger than p, i.e., for a p-particle operator, U and V cannot "differ in more than p orbitals." Otherwise, one of the orbitals which are different in U and V would be occupied by electrons other than $(i_1 i_2 \cdots i_p)$ and hence yield a zero overlap integral.

The case $q = 0$ corresponds to U and V being identical. One has, therefore, $\mathscr{L} = 1$, $(i_1 i_2 \cdots i_p) = (k_1 k_2 \cdots k_p)$, $\pi(U) = \pi(V) = \pi(U, V)$, and $\pi(U, i) = \pi(V, i) = \pi(UV, i)$. It follows that

$$\mathbf{G}(U, U) = \sum_{k_1 < k_2 \cdots < k_p} \sum_{P}{}^{(k)} \langle P u_{k_1} \cdots u_{k_p} | g | u_{k_1} \cdots u_{k_p} \rangle \mathbf{P} 2^{-\pi(U, k)} \tag{69}$$

The opposite extreme $q = p$ corresponds to U and V differing in p orbitals. In this case one has $(i_1 \cdots i_p) = (j_1 \cdots j_p)$ and there is no sum over (k). The integrals do not contain any of the orbitals which are identical in U and V, whence $\pi(UV, i) = 0$. Then, one finds

$$\mathbf{G}(U, V) = \sum_{P} \langle P u_{\alpha_1} \cdots u_{\alpha_p} | g | v_{\beta_1} \cdots v_{\beta_p} \rangle \mathbf{PL} 2^{\Delta(U, i) + \Delta(V, i)} \tag{70}$$

where $\Delta(U, i)$ and $\Delta(V, i)$ are given by Eqs. (63), (64a), (64b) with the term $\pi(UV, i)$ omitted.

If U and V differ in $(p - 1)$ orbitals, one has $q = p - 1$. In this case, the summation over (k) is a single sum. Hence the integrals cannot contain any "doubles" which are common to U and V, and one still has $\pi(UV, i) = 0$. Then one finds

$$\mathbf{G}(U, V) = \sum_k \sum_P{}^{(i)} \langle P u_{\alpha_1} \cdots u_{\alpha_{p-1}} u_k | g | v_{\beta_1} \cdots v_{\beta_{p-1}} u_k \rangle \mathbf{PL} 2^{\Delta(U, i) + \Delta(V, i)} \quad (71)$$

where k runs from 1 to N, omitting the values $(\alpha_1 \alpha_2 \cdots \alpha_{p-1})$ and the definitions of $\Delta(U, i)$ and $\Delta(V, i)$ have again $\pi(UV, i)$ omitted.

B. Unity Operator ($p = 0$)

The operator $\mathscr{G} = 1$ yields the overlap integrals $\langle Us | Vt \rangle$. In this case, the subgroup $\mathscr{S}_{(i)}$ is $\mathscr{S}_{(i)} = 1$, so that the sum over P reduces to the term $P = 1$. Furthermore, the only possible value of q is $q = p = 0$, so that Eq. (69) and (70) both apply. Equation (70) shows that there is no sum over (k) and that $\pi(U, i) = 0$. Equation (69) shows then that $\mathbf{G} = \mathbf{I}$, i.e.,

$$\langle Us | Vt \rangle = \delta_{UV} \delta_{st} \quad (72)$$

Thus, the Ψ_{ks} of Eq. (2) form an orthonormal basis.

C. One-Particle Operator ($p = 1$)

For a one-particle operator,

$$\mathscr{G} = \sum_i g(i)$$

where $i = 1, 2, \ldots, N$ is a single index, the subgroup $\mathrm{S}_{(i)}$ is still $\mathrm{S}_{(i)} = 1$ and, hence, the sum over P still reduces to the term $P = 1$. Furthermore, the integrals contain only one u orbital and one v orbital, so that the terms $\delta(U, i)$ and $\delta(V, i)$, as given by Eq. (64b), vanish. There are two possible values of q, namely, $q = p - 1 = 0$, and $q = p = 1$.

If U and V are identical ($q = 0$), Eqs. (69) and (71) both apply. Equation (71) shows that the sum over (k) is a single sum. Hence, Eq. (69), with $P = 1$ only, yields

$$\langle Us | \sum_i g(i) | Ut \rangle = \delta_{st} \sum_{k=1}^{N} \langle u_k | g | u_k \rangle. \quad (73)$$

$$= \delta_{st} \sum_k{}' \, (u_k | g | u_k) N(k, U). \quad (74)$$

In Eq. (73) the sum runs over all orbitals in U, repeating the doubly occupied ones. In Eq. (74) the sum runs only over the distinct orbitals in U, and $N(k, U)$ is defined as

$$N(k, U) = \text{occupation number of } u_k \text{ in } U \quad (75)$$

If U and V differ in one orbital ($q = 1$), Eq. (70) applies. If the two differing orbitals are denoted by $u_j = u_\alpha$, $w_j = v_\beta$, one obtains

$$\langle Us|\sum_i g(i)|Vt\rangle = \langle u_\alpha|g|v_\beta\rangle L_{st} 2^{\delta(U)+\delta(V)},$$

where $\delta(U)$ and $\delta(V)$ are defined in Eq. (64a). It is readily seen that $\delta(U) = 0$ if u_α is single and $\delta(U) = \frac{1}{2}$ if u_α is part of a double; and similarly for $\delta(V)$. Hence this equation can be rewritten as

$$(Us|\sum_i g(i)|Vt) = \langle u_\alpha|g|u_\beta\rangle L_{st}(U, V)[N(\alpha, U)N(\beta, V)]^{1/2} \tag{76}$$

D. Two-Particle Operator ($p = 2$)

For a two-particle operator,

$$\mathscr{G} = \sum_{i_1}\sum_{i_2} g(i_1\, i_2), \qquad i_1 < i_2$$

the subgroup $S_{(i)}$ is the transposition group $S_{(i)} = \{1, (i_1\, i_2)\}$, so that the sum over P yields the "direct terms" and the "exchange terms,"

$$\sum_P f(P) = f[1] + f[(i_1\, i_2)]$$

There are three possible values of q: $q = 0$, $q = p - 1 = 1$, and $q = p = 2$.

If U and V are identical ($q = 0$), Eq. (69) is applicable and yields

$$\begin{aligned}\langle Us|&\sum_{i_1<i_2} g(i_1\, i_2)|Ut\rangle \\ &= \sum_{k=1}^{N}\sum_{l=1}^{N}\{\langle u_k u_l|g|u_k u_l\rangle\delta_{st} + \langle u_l u_k|g|u_k u_l\rangle(\mathbf{kl})_{st}\}2^{-\pi(U,kl)}\end{aligned} \tag{77}$$

where $(\mathbf{kl})_{st}$ denotes the matrix element for the transposition (lk), and $\pi(U, kl) = 1$ or 0, depending upon $(u_k u_l)$ being a double or not. If U contains doubles, then both partners of each couple occur in the summation over k and l, subject of course to the restriction $k < l$. Therefore, the case $u_k = u_l$ can arise only if $k =$ odd and $l = k + 1$. Thus we have here

$$\pi(U, kl) = \begin{cases} 1 & \text{if} \quad (kl) = (12), (34), \ldots, (2I - 1, 2I), \\ 0 & \text{otherwise} \end{cases} \tag{77a}$$

where I is the index introduced in Eqs. (7), (8), (9). It follows that Eq. (77) can also be written as

$$\begin{aligned}\langle Us|\sum\sum_{i_1<i_2} g(i_1\, i_2)|Ut\rangle = \sum_k{}' \sum_l{}' &[N(k, U)N(l, U)/(1 + \hat{\delta}_{kl})^3] \\ &\times\{\langle u_k u_l|g|u_k u_l\rangle\delta_{st} + \langle u_l u_k|g|u_k u_l\rangle(\mathbf{kl})_{st}\}.\end{aligned} \tag{78}$$

Here the summations go again over distinct orbitals only (with $k < l$) and $\hat{\delta}_{kl}$ has the meaning

$$\hat{\delta}_{kl} = \begin{cases} 1 & \text{if} \quad u_k = u_l \\ 0 & \text{if} \quad u_k \neq u_l \end{cases} \tag{79}$$

If U and V differ in two orbitals ($q = 2$), Eq. (70) is applicable. Furthermore, one has $\pi(UV, i) = 0$ in Eq. (64b). If the different orbitals are denoted by $u_{j_1} = u_\alpha$, $u_{j_2} = u_\beta$, $w_{j_1} = v_\gamma$, $w_{j_2} = v_\delta$ with $\alpha < \beta$, $\gamma < \delta$, Eq. (70) yields

$$\begin{aligned} &\langle Us | \sum_{i_1 < i_2} g(i_1\, i_2) | Vt \rangle \\ &\quad = \{\langle u_\alpha u_\beta | g | v_\gamma v_\delta \rangle \mathbf{L}_{st} + \langle u_\beta u_\alpha | g | v_\gamma v_\delta \rangle [(\boldsymbol{\alpha\beta})\mathbf{L}]_{st}\} 2^{\Delta(U, \alpha\beta) + \Delta(V, \gamma\delta)} \end{aligned} \tag{80}$$

where

$$\Delta(U, \alpha\beta) = \delta(u) - \pi(U, \alpha\beta),$$

with $\delta(U)$ being given by Eq. (64a) and $\pi(U, \alpha\beta)$ by Eq. (77a). From these two equations it can be seen that, in this case,

$$\Delta(U, \alpha\beta) = \begin{cases} -\tfrac{1}{2} & \text{if } u_\alpha = u_\beta \\ 0 & \text{if } u_\alpha,\ u_\beta \text{ both are singles} \\ \tfrac{1}{2} & \text{if one of the two orbitals is single and the other part of a double} \\ 1 & \text{if both } u_\alpha \text{ and } u_\beta \text{ are parts of two different doubles.} \end{cases}$$

Analogous statements hold for $\Delta(V, \gamma\delta)$. Hence Eq. (80) can be written in the form

$$\begin{aligned} &\langle Us | \sum_{i_1 < i_2} g(i_1\, i_2) | Vt \rangle \\ &\quad = [N(\alpha, U) N(\beta, U) N(\gamma, V) N(\delta, V) / (1 + \hat{\delta}_{\alpha\beta})^3 (1 + \hat{\delta}_{\gamma\delta})^3]^{1/2} \\ &\qquad \times \{\langle u_\alpha u_\beta | g | v_\gamma v_\delta \rangle \mathbf{L}_{st} + \langle u_\beta u_\alpha | g | v_\gamma v_\delta \rangle [(\boldsymbol{\alpha\beta})\mathbf{L}]_{st}\}. \end{aligned} \tag{81}$$

Finally, if U and V differ in one orbital ($q = 1$), Eq. (71) applies and, as before $\pi(UV, i) = 0$. Denoting by $u_j = u_\alpha$, $w_j = v_\beta$ the differing orbitals, one obtains

$$\begin{aligned} &\langle Us | \sum_{i_1 < i_2} g(i_1\, i_2) | Vt \rangle \\ &\quad = \sum_{k=1}^{N} \{\langle u_\alpha u_k | g | v_\beta u_k \rangle \mathbf{L}_{st} + \langle u_k u_\alpha | g | v_\beta u_k \rangle [(\boldsymbol{\alpha}\mathbf{k})\mathbf{L}]_{st}\} 2^{\Delta(U, \alpha k) + \Delta(V, \beta k)}, \end{aligned} \tag{82}$$

where

$$\Delta(U, \alpha k) = \delta(U) - \pi(U, \alpha k),$$

with $\delta(U)$ and $\pi(U, \alpha k)$ again defined by Eqs. (64a) and (77a). It can be seen that, in this case,

$$\Delta(U, \alpha k) = \begin{cases} -\frac{1}{2} & \text{if } u_\alpha \text{ is double and } u_k = u_\alpha, \\ 0 & \text{if } u_\alpha \text{ is single}, \\ \frac{1}{2} & \text{if } u_\alpha \text{ is double and } u_k \neq u_\alpha. \end{cases}$$

Analogous statements hold for $\Delta(V, \beta k)$. Consequently Eq. (82) can be expressed as

$$\begin{aligned} &\langle Us | \sum_{i_1 < i_2} g(i_1 i_2) | Vt \rangle \\ &\quad = \sum_k{}' \, [N(\alpha, U) N(k, U) N(\beta, V) N(k, V) / (1 + \hat{\delta}_{\alpha k})^3 (1 + \hat{\delta}_{\beta k})^3]^{1/2} \\ &\quad \times \{ \langle u_\alpha u_k | g | v_\beta u_k \rangle \mathbf{L}_{st} + \langle u_k u_\alpha | g | v_\beta u_k \rangle [(\boldsymbol{\alpha}\mathbf{k})\mathbf{L}]_{st} \}, \end{aligned} \tag{83}$$

where the summation runs over all distinct orbitals $u_k \neq u_\alpha$.

In the case of doubly occupied orbitals, only one of the two occurs in the sums over k and l in Eqs. (78) and (83). Thus, there appears to exist an ambiguity as to which of the two to choose in the transposition matrices $(\boldsymbol{\alpha}\mathbf{k})$ and $(\mathbf{kl})$. It can, however, be shown that the choice is immaterial. In the case of Eq. (78), let k, k' and l, l' be two different doubles in U. Then one has

$$(\mathbf{k'l'})_{st} = [(\mathbf{kk'})(\mathbf{ll'})(\mathbf{kl})(\mathbf{kk'})(\mathbf{ll'})]_{st} = (\mathbf{kl})_{st}$$

The last equality follows because s, $t \leq f_S(U)$ and, hence, the matrices $(\mathbf{kk'})$, $(\mathbf{ll'})$ both can be replaced by unity, as discussed before Eq. (60). In the case of Eq. (83), let k, k' be a double in U and l, l' be that double in V which consists of the identical orbitals. Then it is readily seen that $(kk')\mathscr{L} = \mathscr{L}(ll')$. By similar arguments as before, one finds therefore

$$[(\boldsymbol{\alpha}\mathbf{k'})\mathbf{L}]_{st} = [(\mathbf{kk'})(\boldsymbol{\alpha}\mathbf{k})(\mathbf{kk'})L]_{st} = [(\mathbf{kk'})(\boldsymbol{\alpha}\mathbf{k})L(\mathbf{ll'})]_{st} = [(\boldsymbol{\alpha}\mathbf{k})\mathbf{L}]_{st}$$

Thus, Eqs. (78) and (83) are invariant against substituting k' for k and l' for l.

V. Density Matrices

A. *p*th Order Reduced Spinless Density Matrix

The operator $g(x_1 \cdots x_p)$ of Eq. (17) can be expressed as

$$g = \sum_{\mathbf{n}} \sum_{\mathbf{m}} |f_{n_1}\rangle |f_{n_2}\rangle \cdots |f_{n_p}\rangle g(\mathbf{n} | \mathbf{m}) \langle f_{m_1} | \langle f_{m_2} | \cdots \langle f_{m_p} | \tag{84}$$

where

$$\begin{aligned} \mathbf{n} &= (n_1\, n_2 \cdots n_p), & \sum_{\mathbf{n}} &= \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \cdots \sum_{n_p=1}^{\infty}, \\ \mathbf{m} &= (m_1\, m_2 \cdots m_p), & \sum_{\mathbf{m}} &= \sum_{m_1=1}^{\infty} \sum_{m_2=1}^{\infty} \cdots \sum_{m_p=1}^{\infty}, \end{aligned} \tag{85}$$

and

$$g(\mathbf{n}|\mathbf{m}) = \langle f_{n_1}(x_1) \cdots f_{n_p}(x_p) | g(x_1 \cdots x_p) | f_{m_1}(x_1) \cdots f_{m_p}(x_p) \rangle \tag{86}$$

The functions $f_n(x)$ are the orthonormal basis introduced after Eq. (4), and the projection operators $|f_n\rangle\, \langle f_m|$ are defined by

$$\begin{aligned} &|f_{n_1}\rangle \cdots |f_{n_p}\rangle \langle f_{m_1}| \cdots \langle f_{m_p}| \Psi(x_1 \cdots x_p\, x_{p+1} \cdots x_N) \\ &\quad = f_{n_1}(x_1) \cdots f_{n_p}(x_p) \int d\xi_1 \cdots d\xi_p f_{m_1}(\xi_1) \cdots f_{m_p}(\xi_p) \Psi(\xi_1 \cdots \xi_p\, x_{p+1} \cdots x_N). \end{aligned} \tag{87}$$

Since g is symmetric in $(x_1 \cdots x_p)$, the matrix $g(\mathbf{n}|\mathbf{m})$ has the symmetries

$$g(\mathbf{n}|\mathbf{m}) = g(\mathbf{m}|\mathbf{n}), \tag{88}$$

$$g(Qn_1\, n_2 \cdots n_p | Qm_1\, m_2 \cdots m_p) = g(n_1\, n_2 \cdots n_p | m_1\, m_2 \cdots m_p), \tag{89}$$

where Q is an arbitrary permutation of the indices $(1, 2, \ldots, p)$ in $\mathbf{n}$ and $\mathbf{m}$.

By virtue of Eq. (84) and the antisymmetry of Ψ, the expectation value of $\mathcal{G}$ can be expressed as

$$\langle \Psi | \mathcal{G} | \Psi \rangle = \sum_{\mathbf{nm}} p(\mathbf{m}|\mathbf{n}) g(\mathbf{n}|\mathbf{m}), \tag{90}$$

with

$$p(\mathbf{m}|\mathbf{n}) = \langle f_{m_1}(x_1') \cdots f_{m_p}(x_p') | \pi(x_1' \cdots x_p' | x_1'' \cdots x_p'') | f_{n_1}(x_1'') \cdots f_{n_p}(x_p'') \rangle, \tag{91}$$

where

$$\begin{aligned} \pi(x_1' \cdots x_p' | x_1'' \cdots x_p'') = \binom{N}{p} \int ds_1 \cdots ds_N \int dx_{p+1} \cdots x_N \\ \times \Psi(x_1' s_1 \cdots x_p' s_p\, x_{p+1} s_{p+1} \cdots x_N\, s_N) \\ \times \Psi^*(x_1'' s_1 \cdots x_p'' s_p\, x_{p+1} s_{p+1} \cdots x_N\, s_N). \end{aligned} \tag{92}$$

It is apparent that this is the kernel of the integral operator

$$\pi = \sum_{\mathbf{n}} \sum_{\mathbf{m}} |f_{m_1}\rangle \cdots |f_{m_p}\rangle p(\mathbf{m}|\mathbf{n}) \langle f_{n_1}| \cdots \langle f_{n_p}| \qquad (93)$$

and that the expectation value of Eq. (90) can be written

$$(\Psi|\mathcal{G}|\Psi) = \mathrm{Trace}(\pi g) = \mathrm{Trace}(g\pi) \qquad (94)$$

The operator π is the pth order spinless density operator of Ψ (Löwdin, 1955; McWeeney, 1954, 1955). The coefficients $p(\mathbf{n}|\mathbf{m})$ form the corresponding density matrix in the basis $f_{n_1}, f_{n_2}, \ldots$ and, in correspondence to Eqs. (88) and (89), can be chosen to have the symmetries

$$p(\mathbf{n}|\mathbf{m}) = p(\mathbf{m}|\mathbf{n}) \qquad (95)$$

$$p(Qn_1 n_2 \cdots n_p | Qm_1 m_2 \cdots m_p) = p(n_1 n_2 \cdots n_p | m_1 m_2 \cdots m_p) \qquad (96)$$

B. Expansion of $p(\mathbf{n}|\mathbf{m})$

If the wave function Ψ is expressed according to Eq. (1), then the expectation value of $\mathcal{G}$ is

$$\langle\Psi|\mathcal{G}|\Psi\rangle = \sum_{Is} \sum_{Jt} C_{Is} C_{Jt} \langle Is|\mathcal{G}|Jt\rangle \qquad (97)$$

and Eqs. (65) or (67) are applicable. With g given by Eq. (84), there will occur in Eq. (67) terms of the type

$$\langle u_{\alpha_1} \cdots u_{k_{p-q}} | g | v_{\beta_1} \cdots v_{l_{p-q}} \rangle = \sum_{\mathbf{n}} \sum_{\mathbf{m}} g(\mathbf{n}|\mathbf{m}) \times \langle f_{n_1}|u_{\alpha_1}\rangle \cdots \langle f_{n_p}|u_{k_{p-q}}\rangle \langle v_{\beta_1}|f_{m_1}\rangle \cdots \langle v_{l_{p-q}}|f_{m_p}\rangle.$$

Since $g(\mathbf{n}|\mathbf{m})$ satisfies the symmetry of Eq. (89) or, equivalently, since g is symmetric in $(x_1 \cdots x_p)$, the symmetrical formula

$$\langle u_{\alpha_1} \cdots u_{k_{p-q}} | g | v_{\beta_1} \cdots v_{l_{p-q}} \rangle = \sum_{\mathbf{n}} \sum_{\mathbf{m}} g(\mathbf{n}|\mathbf{m}) \times (p!)^{-1} \sum_{R} R \langle n_{j_1}|u_{\alpha_1}\rangle \cdots \langle n_{j_p}|u_{k_{p-q}}\rangle \langle v_{\beta_1}|m_{j_1}\rangle \cdots \langle v_{l_{p-q}}|m_{j_p}\rangle \qquad (98)$$

is equally valid. Here $\langle n_v|$ stands for f_{n_v} and $\sum_R$ runs over all $p!$ permutations $(j_1 j_2 \cdots j_p)$ of the indices $(1, 2, \ldots, p)$. It is now necessary to identify U and V with the indices I and J, and the orbitals u_a, u_b with certain orbitals among the basic set $f_1, f_2, \ldots$. It may be noted that, e.g., u_a denotes a certain orbital f_n *which occurs in U and does not occur in V* and, hence, *depends on I and J*. The following index notation is therefore adequate and consistent:

$$\begin{aligned}
n &= (IJ\alpha_\nu) && \text{if } f_n = u_{\alpha_\nu}, && U = I, && V = J \\
n &= (IJk_\nu) && \text{if } f_n = u_{k_\nu}, && U = I, && V = J \\
n &= (JI\beta_\nu) && \text{if } f_n = v_{\beta_\nu}, && U = I, && V = J \\
n &= (JIl_\nu) && \text{if } f_n = v_{l_\nu}, && U = I, && V = J
\end{aligned} \tag{99}$$

Note that α_ν, β_ν denote orbitals in which I and J differ, whereas k_ν, l_ν denote orbitals in which I and J agree.

With these notations, Eq. (67) can be rewritten as

$$\langle Is|\mathscr{G}|Jt\rangle = \sum_{\mathbf{nm}} \hat{p}_{Is,Jt}(\mathbf{n}|\mathbf{m})g(\mathbf{n}|\mathbf{m}) \tag{100}$$

with the coefficients

$$\begin{aligned}
\hat{p}_{Is,Jt}(\mathbf{n}|\mathbf{m}) = \sum_{(k)} \sum_P{}^{(i)} \sum_Q{}^{(j)} 2^{\Delta(I,i)+\Delta(J,j)}(p!)^{-2}[\mathbf{PL}(IJ)Q^\dagger]_{st} \\
\times \sum_R R\{P\langle n_{j_1}|IJ\alpha_1\rangle \cdots \langle n_{j_q}|IJ\alpha_q\rangle \\
\times \langle n_{j_{q+1}}|IJk_1\rangle \cdots \langle n_{j_p}|IJk_{p-q}\rangle \\
\times Q\langle m_{j_1}|JI\beta_1\rangle \cdots \langle m_{j_q}|JI\beta_q\rangle \\
\times \langle m_{j_{q+1}}|JIl_1\rangle \cdots \langle m_{j_p}|JIl_{p-q}\rangle\}.
\end{aligned} \tag{101}$$

In this equation the definitions and conventions are exactly the same as those used in Eq. (67). The summation $\sum_R$ covers all $p!$ permutations $(j_1 j_2 \cdots j_p)$ of the indices $(1, 2, \ldots p)$, thereby ensuring the symmetry required by Eq. (96). Furthermore, by virtue of arguments of the type made after Eq. (68), it is seen that

$$\hat{p}_{Is,Jt}(\mathbf{n}|\mathbf{m}) = \hat{p}_{Jt,Is}(\mathbf{m}|\mathbf{n}). \tag{102}$$

Insertion of Eq. (100) into Eq. (97) and comparison with Eq. (90) shows that the density matrix has the expansion

$$p(\mathbf{n}|\mathbf{m}) = \sum_{Is} \sum_{Jt} C_{Is} C_{Jt} p_{Is,Jt}(\mathbf{n}|\mathbf{m}) \tag{103}$$

with

$$\begin{aligned}
p_{Is,Jt}(\mathbf{n}|\mathbf{m}) &= \{\hat{p}_{Is,Jt}(\mathbf{n}|\mathbf{m}) + \hat{p}_{Jt,Is}(\mathbf{n}|\mathbf{m})\}/2 \\
&= \{\hat{p}_{Is,Jt}(\mathbf{n}|\mathbf{m}) + \hat{p}_{Is,Jt}(\mathbf{m}|\mathbf{n})\}/2.
\end{aligned} \tag{104}$$

These expansion coefficients are defined so that, individually, they possess the symmetries of Eqs. (95) and (96).

VI. Special Density Matrices

A. First-Order Density Matrix

Combining Eqs. (100), (101), (104) with the previous results of Eqs. (73) to (76), one obtains for the first order density matrix

$$\rho(x' \mid x'') = \sum_n \sum_m f_n(x') f_m(x'') p(m, n), \tag{105}$$

with the "bond orders"

$$p(n \mid m) = \sum_I \sum_J C_{Is} C_{Jt} p_{Is, Jt}(n \mid m), \tag{106}$$

The coefficients are given by

$$p_{Is, Jt}(n \mid m) = S(n, m)[N(n, I) N(m, J)]^{1/2} D(nI, mJ) L_{st}(I, J) \tag{107}$$

where

$$S(n, m) = \tfrac{1}{2}\{1 + (n, m)\}, \tag{108}$$

and

$$D(nI, mJ) = \begin{cases} \delta_{nm} & \text{if } I = J, \\ \langle n \mid IJ\alpha\rangle\langle m \mid JI\beta\rangle & \text{if } I \text{ and } J \text{ differ in one orbital,} \\ 0 & \text{if } I \text{ and } J \text{ differ in more than} \\ & \quad \text{one orbital.} \end{cases} \tag{109}$$

Here, α and β denote the orbitals in I and J respectively, in which these two wave functions differ. It may also be noted that, for $I = J$, $L_{st} = \delta_{st}$. Furthermore, the symbols $N(nI)$, etc. are defined by Eq. (75).

B. Second-Order Density Matrix

The expansion of the second order density matrix has the form

$$\pi(x_1{}'x_2{}' \mid x_1''x_2'') = \sum_{n_1 n_2} \sum_{m_1 m_2} f_{n_1}(x_1{}') f_{n_2}(x_2{}') f_{m_1}(x_1'') f_{m_2}(x_2'') \times p(n_1 n_2 \mid m_1 m_2) \tag{110a}$$

with the "pair bond orders"

$$p(n_1 n_2 \mid m_1 m_2) = \sum_{Is} \sum_{Jt} C_{Is} C_{Jt} p_{Is, Jt}(n_1 n_2 \mid m_1 m_2). \tag{110b}$$

Combining Eqs. (100), (101), (104) with the previous results of Eqs. (77) to (83), one obtains

$$p_{Is, Jt}(n_1 n_2 \mid m_1 m_2) = S(\mathbf{n} \mid \mathbf{m}) \left[\frac{N(n_1 I) N(n_2 I) N(m_1 J) N(m_2 J)}{(1 + \delta_{n_1 n_2})^3 (1 + \delta_{m_1 m_2})^3}\right]^{1/2} \times \{D'(\mathbf{n}I, \mathbf{m}J) M'_{st}(IJ) + D''(\mathbf{n}I, \mathbf{m}J) M''_{st}(IJ)\} \tag{111}$$

where

$$P(\mathbf{n}, \mathbf{m}) = \tfrac{1}{2}[1 + (n_1 m_1) \otimes (n_2 m_2)]. \tag{112}$$

and the symbol ⊗ denotes that the two transpositions apply independently of each other.

The matrices $\mathbf{M}'$ and $\mathbf{M}''$ are given by

$$\begin{aligned} \mathbf{M}' &= \tfrac{1}{2}\{\mathbf{L}(IJ) + (\mathbf{k}_{n_1}\mathbf{k}_{n_2}) \cdot \mathbf{L}(IJ) \cdot (\mathbf{l}_{m_1}\mathbf{l}_{m_2})\} \\ \mathbf{M}'' &= \tfrac{1}{2}\{(\mathbf{k}_{n_1}\mathbf{k}_{n_2}) \cdot \mathbf{L}(I, J) + \mathbf{L}(IJ) \cdot (\mathbf{l}_{m_1}\mathbf{l}_{m_2})\} \end{aligned} \tag{113}$$

where k_n denotes the position held by the orbital f_n in the orbital product I, and l_m denotes the position held by the orbital f_m in the orbital product J.

The quantities D' and D'' are defined as follows:

If $I = J$,

$$D'(\mathbf{n}I, \mathbf{m}J) = \delta_{n_1 m_1} \delta_{n_2 m_2} \tag{115}$$

$$D''(\mathbf{n}I, \mathbf{m}J) = \delta_{n_1 m_2} \delta_{m_1 n_2} \tag{116}$$

If I and J differ in one orbital (α in I, β in J),

$$D'(\mathbf{n}I, \mathbf{m}J) = S'(\mathbf{n}, \mathbf{m}) \langle n_1 | IJ\alpha \rangle \langle m_1 | JI\beta \rangle \, \delta_{n_2 m_2} \tag{117}$$

$$D''(\mathbf{n}I, \mathbf{m}J) = S'(\mathbf{n}, \mathbf{m}) \langle n_1 | IJ\alpha \rangle \langle m_2 | JI\beta \rangle \, \delta_{n_2 m_1} \tag{118}$$

If I and J differ in two orbitals (α, β in I; γ, δ in J),

$$D'(\mathbf{n}I, \mathbf{m}J) = S'(\mathbf{n}, \mathbf{m}) \langle n_1 | IJ\alpha \rangle \langle n_2 | IJ\beta \rangle \langle m_1 | JI\gamma \rangle \langle m_2 | JI\,\delta \rangle \tag{119}$$

$$D''(\mathbf{n}I, \mathbf{m}J) = S'(\mathbf{n}, \mathbf{m}) \langle n_1 | IJ\alpha \rangle \langle n_2 | IJ\beta \rangle \langle m_2 | JI\gamma \rangle \langle m_1 | JI\,\delta \rangle \tag{120}$$

If I and J differ in more than two orbitals,

$$D'(\mathbf{n}I, \mathbf{m}J) = D''(\mathbf{n}I, \mathbf{m}J) = 0 \tag{121}$$

In Eqs. (117) to (120) S' denotes the symmetrizer

$$S'(\mathbf{n}, \mathbf{m}) = \tfrac{1}{2}\{1 + (n_1 n_2) \otimes (m_1 m_2)\}. \tag{122}$$

If the two-electron operator g consists of multiplication by a function, as is the case for the electron repulsion operator $g(x_1 x_2) = r_{12}{}^{-1}$, then only the diagonal elements $\pi(x_1 x_2 | x_1 x_2)$ of the density kernel are required, and it is apparent from Eq. (93) that the further symmetries

$$p(n_1 n_2 | m_1 m_2) = p(n_2 n_1 | m_1 m_2) = p(n_1 n_2 | m_2 m_1) \tag{123}$$

may be imposed upon the density matrix elements. This can be achieved by substituting the symmetrizer

$$S''(\mathbf{n}, \mathbf{m}) = \{1 + (n_1 n_2)\} \otimes \{1 + (m_1 m_2)\} \tag{124}$$

for the symmetrizer S' in Eqs. (117) to (118), and by applying it also in Eqs. (115) and (116).

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Upper and Lower Bounds to Quantum-Mechanical Properties

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I. Introduction

The properties of atoms and molecules are increasingly investigated by direct mathematical attack on the fundamental quantum-mechanical Schrödinger equation. This *ab initio* theoretical approach has been stimulated not only by the availability of high-speed computing machines, but also by developments in the experimental domain itself, where new technology is often furnishing accurate and detailed information of an increasingly fundamental nature.

But as chemical theory has reached a new prominence, the question of the *reliability* of theoretical predictions has become increasingly acute. The dilemma originates in the fact that the Schrödinger equation cannot usually be solved exactly, so that approximation methods must be introduced which are often of uncertain accuracy and dubious predictive value. One generally hopes that accumulated computational experience and compari-

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sons with experimental data may help to establish the reliability of a particular theoretical result, but such rules of thumb will be unavailable in precisely those cases where theory could be most uniquely valuable, i.e., where little or no experimental guidance is available. In addition, the "agreement with experiments" is too frequently found to deteriorate as the theoretical methods (or the experiments!) are refined, and this has sometimes led to a certain prevailing skepticism concerning the value of the theoretical calculations.

Particular importance attaches therefore to a special class of approximation procedures which lead to *upper and lower bounds* for the properties of interest, so that rigorous error limits are attached to the theoretical estimate. Such procedures provide the theory with *internal* criteria of reliability, which are independent of whether experimental data are available for comparison. They also permit the theoretical predictions to be systematically improved in an unambiguous fashion. Of course, error limits are routinely demanded of any experimental result, and one should also hope for a corresponding standard of reliability from the theoretical side.

In this article we attempt to survey some aspects of the recent progress in the development of upper and lower bounds to quantum-mechanical properties. The survey is necessarily incomplete, with several important topics barely mentioned or even omitted entirely, and special emphasis has been placed throughout on the particular line of developments associated with determinantal inequalities (Weinhold, 1967). In this connection we wish to refer the reader to the recent review articles of Gordon (1969), Rebane (1970), Langhoff and Karplus (1970), Langhoff *et al.* (1971), and Goscinski and Brändas (1971), and the monograph of Arthurs (1970), where certain aspects of the general problem are discussed from alternative points of view.

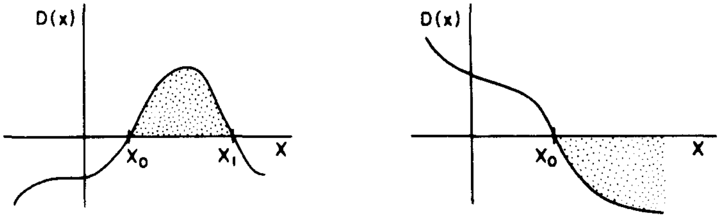
In Section II we describe in some detail the general procedure for obtaining upper and lower bounds from determinantal inequalities, and the connection with certain other approaches. Then Section III describes the application of these and other methods to various quantum-mechanical properties such as energy eigenvalues, scattering phase shifts, overlap, expectation values, transition moments, and second-order properties. Section IV offers some concluding remarks and discusses future prospects in this area.

II. Method of Determinantal Inequalities

A general approach to the problem of bounding an unknown quantity x may be posed quite simply:

Suppose x appears in one element or in several elements of a *deter-*

minant D whose sign can somehow be determined, and whose other elements are all known. Then D may be viewed as a polynomial in x, $D = D(x)$, whose *zeros* delimit the permissible values of the unknown x, and thus give upper and lower bounds. Some schematic examples are sketched in Figs. 1a and b for the cases $D \geq 0$ and $D \leq 0$, respectively.



$D>0$: $x_0 \leq x \leq x_1$

(a)

$D<0$: $x \geq x_0$

(b)

Fig. 1

In view of the simple prescription given above, it is only necessary to inquire (i) how the sign of the determinant D can be determined, and (ii) how the roots of the determinantal polynomial $D(x) = 0$ are found. These two questions are taken up in turn in Sections II,A and II,B, respectively.

A. Determinants of Fixed Sign

An $n \times n$ determinant D may be written in the general case as

$$D = \det\begin{vmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{vmatrix} = \det|\mathrm{A}^{(n)}|, \tag{1}$$

but we shall assume at the outset that the matrix $\mathrm{A}^{(n)} = \{a_{ij}\}$ is at least real and symmetric,[1]

$$a_{ij} = a_{ij}^{*} = a_{ji}.$$

It is further convenient to assume that the a_{ij} are matrix elements of a self-adjoint operator $\mathscr{A}$,

$$a_{ij} = \langle f_i | \mathscr{A} | f_j \rangle, \tag{2}$$

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[1] A more general matrix may possibly lead to *complex* values of D. Since inequalities cannot be written involving complex numbers, but only their real or imaginary parts, the restriction to real a_{ij} and symmetric $\mathrm{A}^{(n)}$ is implicit in the spirit of the approach (though it could also be relaxed in certain special cases).

where the f_i are some suitably chosen set of wave functions. Although the formulas of Section II,B are independent of this assumption, the definiteness of the sign of D will most frequently arise from the special properties of such an operator. The eigenvalue problem for $\mathscr{A}$ is

$$\mathscr{A}|\alpha_i\rangle = \alpha_i|\alpha_i\rangle, \qquad \alpha_1 \le \alpha_2 \le \cdots, \tag{3}$$

while that for $\mathbf{A}^{(n)}$ is

$$\mathbf{A}^{(n)}\mathbf{c}_i^{(n)} = a_i^{(n)}\mathbf{c}_i^{(n)}, \qquad a_1^{(n)} \le a_2^{(n)} \le \cdots, \tag{4}$$

and according to the general "interleaving theorem" of Hylleraas and Undheim (1930) and MacDonald (1933), the ordered eigenvalues satisfy

$$a_i^{(n)} \ge a_i^{(n+1)} \ge \alpha_i, \qquad i = 1, 2, \ldots, n. \tag{5}$$

Although the spectrum of the operator $\mathscr{A}$ may be partly or wholly continuous (thereby rendering the ordering relation (5) inapplicable), the finite matrix $\mathbf{A}^{(n)}$ has always n discrete eigenvalues, and the determinant D satisfies the familiar relation

$$D = \prod_{i=1}^{n} a_i^{(n)} = \det|\mathbf{A}^{(n)}|, \tag{6}$$

which is a useful starting point for many of the later developments.

We recall that an operator $\mathscr{A}$ is *positive semidefinite*, $\mathscr{A} \ge 0$, if

$$\langle\varphi|\mathscr{A}|\varphi\rangle \ge 0 \tag{7}$$

for every wave function φ. The definition (7) is equivalent to the requirement that $\mathscr{A}$ have only nonnegative eigenvalues,

$$\alpha_i \ge 0, \qquad \text{all} \quad i, \tag{8}$$

and we note that the condition $\mathscr{A} \ge 0$ implies also that

$$\mathbf{A}^{(n)} \ge 0 \tag{9}$$

for each n, since with the definition (for normalized $\mathbf{c}_i^{(n)}$),

$$\varphi_i = \sum_k (\mathbf{c}_i^{(n)})_k f_k,$$

the eigenvalues $a_i^{(n)}$ satisfy

$$a_i^{(n)} = \mathbf{c}_i^{(n)\dagger}\mathbf{A}^{(n)}\mathbf{c}_i^{(n)} = \langle\varphi_i|\mathscr{A}|\varphi_i\rangle \ge 0 \tag{10}$$

according to (7). A more general classification of operators according to the signs of their eigenvalues is given in Table I. Here we will often use

TABLE I

Type of operator	Signs of eigenvalues
Positive definite, $\mathscr{A} > 0$	all $\alpha_i > 0$
Positive semidefinite, $\mathscr{A} \geq 0$	all $\alpha_i \geq 0$
Indefinite	some $\alpha_i > 0$, some $\alpha_j < 0$
Negative semidefinite, $\mathscr{A} \leq 0$	all $\alpha_i \leq 0$
Negative definite, $\mathscr{A} < 0$	all $\alpha_i < 0$

the simpler term "positive" to describe a positive semidefinite operator $\mathscr{A} \geq 0$.

The types of determinantal inequalities to be obtained now depend primarily on the choice of the operator $\mathscr{A}$, whether definite or indefinite, etc. We consider below the principal choices which lead to a determinant D of definite sign.

1. Gram Determinants

If $\mathscr{A}$ is the identity operator, the elements a_{ij} are simply scalar products between the basic functions f_i,

$$a_{ij} = \langle f_i | f_j \rangle.$$

Then $\mathrm{A}^{(n)}$ is known as a *Gram matrix*, and the corresponding determinant

$$D = \det|\mathrm{A}^{(n)}| = \det|\langle f_i | f_j \rangle|$$

is called the *Gram determinant* (or *Gramian*) for the functions f_i. The positivity of the identity operator implies that the Gram matrix $\mathrm{A}^{(n)}$ is also positive semidefinite, and that the Gram determinant must have a positive sign

$$D = \det|\langle f_i | f_j \rangle| \geq 0 \tag{11}$$

in view of (6) and (10). Inequality (11) is the basis for most of the determinantal inequalities that have been developed.

The Gram determinant is a well-known measure of the linear independence of the functions f_i, and of the volume spanned by the corresponding vectors in Hilbert space (as discussed, e.g., by Shilov, 1961). The condition $D \geq 0$ may also be regarded as a many-dimensional generalization of the *Schwarz inequality*, to which it reduces when $n = 2$. Since the positivity of the Gram matrix is both the necessary and sufficient condition for the existence of *any* set of functions having the specified scalar products $\langle f_i | f_j \rangle$, the constraint (11) is the strongest possible restriction that can be placed on a given scalar product in terms of the internal geometry of the vectors $|f_i\rangle$.

The general case of a positive semidefinite operator $\mathscr{A} \geq 0$ can be handled in essentially the same manner. Such an operator can always be written in the form (see e.g., Shilov, 1961)

$$\mathscr{A} = \mathscr{B}^\dagger \mathscr{B}$$

for a suitable operator $\mathscr{B}$ (e.g., $\mathscr{B} = \mathscr{A}^{1/2}$), so that the matrix elements a_{ij} may be written as

$$a_{ij} = \langle f_i | \mathscr{A} | f_j \rangle = \langle \mathscr{B} f_i | \mathscr{B} f_j \rangle = \langle g_i | g_j \rangle,$$

where $g_i \equiv \mathscr{B} f_i$. Thus for any positive $\mathscr{A} \geq 0$ the determinant $D = \det|\langle f_i | \mathscr{A} | f_j \rangle|$ may again be regarded as a Gram determinant, and again

$$D = \det|\langle f_i | \mathscr{A} | f_j \rangle| \geq 0. \tag{12}$$

Of course, the treatment of negative definite and semidefinite operators $\mathscr{A} \leq 0$ presents no difficulties, since D again has a definite sign, $(-1)^n$. Alternatively we can find bounds for the matrix element $\langle f_i | -\mathscr{A} | f_j \rangle$ of the positive operator $-\mathscr{A}$.

2. *Indefinite Operators: Use of Interleaving Theorem*

When the operator $\mathscr{A}$ is indefinite, i.e., has one or more negative eigenvalues $\alpha_i \leq 0$, then one or more of the eigenvalues $a_i^{(n)}$ of $\mathrm{A}^{(n)}$ may also be negative and the sign of D, Eq. (6), requires further study. The problem appears to be soluble only when $\mathscr{A}$ has a known *finite* number ν of negative eigenvalues, and we therefore assume

$$\alpha_1 \leq \alpha_2 \leq \cdots \leq \alpha_\nu < 0 \leq \alpha_{\nu+1} \leq \cdots, \tag{13}$$

where only the number ν, not the detailed values of the eigenvalues, need be known.

According to the Hylleraas–Undheim–MacDonald "interleaving theorem," Eq. (5), the Rayleigh–Ritz estimates $a_i^{(n)}$ approach the true eigenvalues α_i from above as the determinantal order n increases. Then for *some* sufficiently high order μ ($\mu \geq \nu$), the lowest ν eigenvalues $a_i^{(\mu)}$ of the matrix $\mathrm{A}^{(\mu)}$ will also be negative

$$\alpha_1 \leq a_1^{(\mu)} \leq \alpha_2 \leq a_2^{(\mu)} \leq \cdots \leq \alpha_\nu \leq a_\nu^{(\mu)} < 0,$$

and the sign of the determinants can no longer change as the order is increased. That is, since

$$0 \leq \alpha_{\nu+m} \leq a_{\nu+m}^{(\mu+k)}, \qquad \text{all} \quad k, m = 1, 2, \ldots, \tag{14}$$

all new eigenvalues of $\mathbf{A}^{(\mu+k)}$ come in with *positive* sign as the determinantal order increases, and the sign of D remains fixed

$$\operatorname{sgn}\{\det|\mathbf{A}^{(\mu+k)}|\} = (-1)^{\nu} \tag{15}$$

for all k. Equation (15) may also be written in the form

$$\operatorname{sgn}\{\det|\mathbf{A}^{(\kappa)}|\} = \operatorname{sgn}\{\det|\mathbf{A}^{(\lambda)}|\}, \kappa, \lambda \geq \mu,$$

or as

$$\det|\mathbf{A}^{(\kappa)}|/\det|\mathbf{A}^{(\lambda)}| \geq 0, \qquad \kappa, \lambda \geq \mu, \tag{16}$$

which is a convenient form for the applications of Section II,B. Note that inequalities such as (16) apparently no longer have the simple geometrical significance of the corresponding Gramian inequalities (11), (12), but both serve equally well as the basis for developing formulas for upper and lower bounds.

B. Upper and Lower Bounds

1. *Zeros of Determinantal Polynomials*

The problem of determining the roots of the polynomial equation $D(a_{ij}) = 0$ can be settled for the cases of principal interest even when the determinantal order is arbitrarily large (Weinhold, 1971b). We first define the determinants D_i, D_{ij}, d_i, and d_{ij} which are obtained from D, Eq. (1), by the following prescription:

D_i: delete the ith row and column
D_{ij}: delete the ith and jth rows and columns[2] (17)
d_i: set $a_{ii} = 0$
d_{ij}: set $a_{ij} = 0$, and delete row j and column i.

Then for a diagonal element a_{ii}, the root of the polynomial $D = 0$ is

$$a_{ii} = -d_i/D_i, \tag{18}$$

while for an off-diagonal element a_{ij} the result is found to be

$$a_{ij} = \frac{(-1)^{i+j}d_{ij} \pm (D_i D_j)^{1/2}}{D_{ij}}. \tag{19}$$

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[2] Note that when D has only two rows and columns, $D_{12} \equiv 1$.

The results (18) and (19) may also be used to rewrite D in terms of its roots in the alternative forms

$$D/D_i = a_{ii} + (d_i/D_i), \tag{20}$$

$$D/D_{ij} = (r_+ - a_{ij})(a_{ij} - r_-), \tag{21}$$

where $r_\pm$ are the roots

$$r_\pm \equiv \frac{(-1)^{i+j}d_{ij} \pm (D_i D_j)^{1/2}}{D_{ij}} \tag{22}$$

obtained in (19).

To obtain upper and lower bounds, we now consider in turn the special cases of Section II,A.

If D is a *Gram* determinant [Eqs. (11) or (12)], then $D \geq 0$ and we recognize further that the determinants D_i and D_{ij} are *also* Gram determinants of lower order, so that

$$D \geq 0, \qquad D_i > 0, \qquad D_{ij} > 0$$

Then (20) and (21) lead, respectively, to the inequalities

$$a_{ii} + (d_i/D_i) \geq 0,$$
$$(r_+ - a_{ij})(a_{ij} - r_-) \geq 0,$$

which in turn imply the upper and lower bounds

$$a_{ii} \geq -d_i/D_i, \tag{23}$$

$$r_+ \geq a_{ij} \geq r_-, \tag{24}$$

for the elements of D.

In the case of the inequality (16), based on the interleaving theorem, we may momentarily regard i (and j) as the *last* row(s) and column(s) of $\mathbf{A}^{(n)}$; then we only need to assume that $n - 1 \geq \mu$ or $n - 2 \geq \mu$, respectively, in order to ensure that

$$\frac{D}{D_i} = \frac{\det|\mathbf{A}^{(n)}|}{\det|\mathbf{A}^{(n-1)}|} \geq 0, \tag{25}$$

$$\frac{D}{D_{ij}} = \frac{\det|\mathbf{A}^{(n)}|}{\det|\mathbf{A}^{(n-2)}|} \geq 0. \tag{26}$$

In conjunction with (20) and (21), the inequalities (25) and (26) will then again guarantee, respectively, the validity of (23) and (24). More generally, we must only take care to ensure that the matrix left after removing the ith row and column (or, for an off-diagonal element, both the ith and jth rows and columns) from $\mathrm{A}^{(n)}$ still has the *same number of negative eigenvalues* as does $\mathscr{A}$ itself, and the upper and lower bounds (23), (24) are then again guaranteed.

2. *Alternative Forms*

The upper and lower bound formulas (23), (24) may be cast into an alternative form which is computationally convenient, and which permits comparison with certain other approaches in the following Section II,B,3.

Let us first assume that $D = \det|\mathrm{A}^{(n+1)}|$ is a determinant of order $n + 1$, and write out the lower bound (23) for the *last* diagonal element of D in the form

$$a_{n+1,n+1} \geq -d_{n+1}/D_{n+1}\,. \tag{27}$$

We introduce the n-dimensional matrix A and column vector $\mathbf{u}$ by the definitions

$$\mathrm{A} \equiv \begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{12} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & & \vdots \\ a_{1n} & a_{2n} & \cdots & a_{nn} \end{pmatrix}, \qquad \mathbf{u} \equiv \begin{pmatrix} a_{1,n+1} \\ a_{2,n+1} \\ \vdots \\ a_{n,n+1} \end{pmatrix}, \tag{28}$$

and note that the determinants D_{n+1} and d_{n+1} can then be written in the form

$$D_{n+1} = \det|\mathrm{A}|, \tag{29}$$

$$d_{n+1} = \det\begin{vmatrix} \mathrm{A} & \mathbf{u} \\ \mathbf{u}^\dagger & 0 \end{vmatrix}, \tag{30}$$

from the basic definitions (17).

The result we wish to establish is that

$$d_{n+1} = -(\mathbf{u}^\dagger \mathrm{A}^{-1}\mathbf{u})\det|\mathrm{A}|, \tag{31}$$

so that (27) becomes simply

$$a_{n+1,n+1} \geq \mathbf{u}^\dagger \mathrm{A}^{-1}\mathbf{u} \tag{32}$$

and is expressed as a simple expectation value of the inverse matrix A^{-1}. The form (31) may be inferred by expanding d_{n+1} down the final column, then expanding each resulting cofactor along the bottom row to obtain still other cofactors which are recognized to be (up to a constant) the elements of $\mathbf{A}^{-1}$. Here we give a simpler proof which, while not so intuitive, requires less algebra. Write

$$\begin{aligned} 1 &= \frac{D_{n+1}}{\det|\mathbf{A}|} = D_{n+1}\det|\mathbf{A}^{-1}| = D_{n+1}\det\begin{vmatrix}\mathbf{A}^{-1} & \mathbf{0}\\ \mathbf{0}^{\dagger} & 1\end{vmatrix}, \\ &= D_{n+1}\det\begin{vmatrix}\mathbf{A}^{-1} & -\mathbf{A}^{-1}\mathbf{u}\\ \mathbf{0}^{\dagger} & 1\end{vmatrix}. \end{aligned} \tag{33}$$

where $\mathbf{0}$ is an n-dimensional zero vector, and where the partitioning corresponds to that used in Eq. (30). The equivalence of the final two forms in (33) may be verified by expanding both determinants along the bottom row. Then ($\mathbf{I}$ = n-dimensional identity),

$$\begin{aligned} d_{n+1} &= d_{n+1}D_{n+1}\det\begin{vmatrix}\mathbf{A}^{-1} & -\mathbf{A}^{-1}\mathbf{u}\\ \mathbf{0}^{\dagger} & 1\end{vmatrix}, \\ &= D_{n+1}\det\begin{vmatrix}\mathbf{A} & \mathbf{u}\\ \mathbf{u}^{\dagger} & 0\end{vmatrix}\det\begin{vmatrix}\mathbf{A}^{-1} & -\mathbf{A}^{-1}\mathbf{u}\\ \mathbf{0}^{\dagger} & 1\end{vmatrix}, \\ &= D_{n+1}\det\begin{vmatrix}\mathbf{I} & \mathbf{0}\\ \mathbf{u}^{\dagger}\mathbf{A}^{-1} & -\mathbf{u}^{\dagger}\mathbf{A}^{-1}\mathbf{u}\end{vmatrix}, \\ &= D_{n+1}(-\mathbf{u}^{\dagger}\mathbf{A}^{-1}\mathbf{u}), \end{aligned}$$

where the final step is confirmed by evaluating the determinant down the last column. The desired result (32) is thus established.

An analogous result can be obtained for the off-diagonal matrix elements, Eq. (24). We now assume that $D = \det|\mathbf{A}^{(n+2)}|$ is of order $n + 2$, and we rewrite (24) for the last off-diagonal element of D as

$$a_{n+1,\,n+2} \substack{\le \\ \ge} \frac{-d_{n+1,\,n+2} \pm (D_{n+1}\,D_{n+2})^{1/2}}{D_{n+1,\,n+2}}. \tag{34}$$

We again adopt the definitions (28) for the n-dimensional matrix $\mathbf{A}$ and column vector $\mathbf{u}$, and we introduce in addition

$$\mathbf{v} = \begin{pmatrix} a_{1,\,n+2} \\ a_{2,\,n+2} \\ \vdots \\ a_{n,\,n+2} \end{pmatrix}, \tag{35}$$

so that the various determinants can be written as

$$D_{n+1,n+2} = \det|\mathbf{A}|, \tag{36}$$

$$D_{n+2} = \det\begin{vmatrix} \mathbf{A} & \mathbf{u} \\ \mathbf{u}^\dagger & a_{n+1,n+1} \end{vmatrix}, \tag{37}$$

$$D_{n+1} = \det\begin{vmatrix} \mathbf{A} & \mathbf{v} \\ \mathbf{v}^\dagger & a_{n+2,n+2} \end{vmatrix}, \tag{38}$$

$$d_{n+1,n+2} = \det\begin{vmatrix} \mathbf{A} & \mathbf{v} \\ \mathbf{u}^\dagger & 0 \end{vmatrix}. \tag{39}$$

The identities analogous to (33) are then

$$1 = D_{n+1,n+2} \det\begin{vmatrix} \mathbf{A}^{-1} & -\mathbf{A}^{-1}\mathbf{u} \\ \mathbf{0}^\dagger & 1 \end{vmatrix}, \tag{40}$$

$$1 = D_{n+1,n+2} \det\begin{vmatrix} \mathbf{A}^{-1} & -\mathbf{A}^{-1}\mathbf{v} \\ \mathbf{0}^\dagger & 1 \end{vmatrix}, \tag{41}$$

and, for example, from (39) and (41),

$$\begin{aligned} d_{n+1,n+2} &= D_{n+1,n+2} \det\begin{vmatrix} \mathbf{A} & \mathbf{v} \\ \mathbf{u}^\dagger & 0 \end{vmatrix} \det\begin{vmatrix} \mathbf{A}^{-1} & -\mathbf{A}^{-1}\mathbf{v} \\ \mathbf{0}^\dagger & 1 \end{vmatrix}, \\ &= D_{n+1,n+2} \det\begin{vmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{u}^\dagger\mathbf{A}^{-1} & -\mathbf{u}^\dagger\mathbf{A}^{-1}\mathbf{v} \end{vmatrix}, \\ &= -D_{n+1,n+2}(\mathbf{u}^\dagger\mathbf{A}^{-1}\mathbf{v}). \end{aligned} \tag{42}$$

Similarly,

$$D_{n+2} = D_{n+1,n+2}(a_{n+1,n+1} - \mathbf{u}^\dagger\mathbf{A}^{-1}\mathbf{u}), \tag{43a}$$

$$D_{n+1} = D_{n+1,n+2}(a_{n+2,n+2} - \mathbf{v}^\dagger\mathbf{A}^{-1}\mathbf{v}). \tag{43b}$$

Then with (42) and (43) we obtain finally from (34),

$$a_{n+1,n+2} \lesseqgtr \mathbf{u}^\dagger\mathbf{A}^{-1}\mathbf{v} \pm [(a_{n+1,n+1} - \mathbf{u}^\dagger\mathbf{A}^{-1}\mathbf{u})(a_{n+2,n+2} - \mathbf{v}^\dagger\mathbf{A}^{-1}\mathbf{v})]^{1/2}, \tag{44}$$

which again requires only the inversion of the matrix A, Eq. (28), and is thus a numerically convenient form. We recall that the bounds (32), (44) are quite generally valid so long as the matrix A has the *same number of negative eigenvalues* as does the operator $\mathscr{A}$, though of course this is no restriction when D is a Gramian determinant.

3. *Operator Inequalities*

Although the determinantal inequalities were developed to set upper and lower bounds on *elements* of a general determinant, the forms (32) and (44) make it particularly easy to infer certain general inequalities for the operator $\mathscr{A}$ from which the determinantal elements arise. We recall the definitions (28) for A and u in terms of the matrix elements $a_{ij} = \langle f_i|\mathscr{A}|f_j\rangle$, and write out (32) explicitly in the form

$$\begin{aligned}\langle f_{n+1}|\mathscr{A}|f_{n+1}\rangle &\geq \mathbf{u}^{\dagger}\mathbf{A}^{-1}\mathbf{u},\\ &= \sum_{i,j=1}^{n}(\mathbf{u}^{\dagger})_i(\mathbf{A}^{-1})_{ij}(\mathbf{u})_j,\\ &= \sum_{i,j=1}^{n}\langle f_{n+1}|\mathscr{A}|f_i\rangle(\mathbf{A}^{-1})_{ij}\langle f_j|\mathscr{A}|f_{n+1}\rangle. \qquad (45)\end{aligned}$$

Since (45) is valid for *every* choice of the function f_{n+1} (so long as A has the proper number of negative eigenvalues), it implies the *operator inequality*

$$\mathscr{A} \geq \sum_{i,j=1}^{n}\mathscr{A}|f_i\rangle(\mathbf{A}^{-1})_{ij}\langle f_j|\mathscr{A}, \qquad (46)$$

where the notation "$\mathscr{A} \geq \mathscr{B}$" means that the operator $\mathscr{A} - \mathscr{B}$ is positive semidefinite.

The operator inequality (46) is usually written in a convenient and suggestive notation (Sugar and Blankenbecler, 1964; Löwdin, 1965a) based on the definitions

$$\begin{aligned}\langle\mathbf{f}|\mathscr{A}|\mathbf{f}\rangle &\equiv \mathbf{A} = \{\langle f_i|\mathscr{A}|f_j\rangle\},\\ |\mathbf{f}\rangle &\equiv \textit{row}\text{ vector of the } |f_i\rangle\text{'s}, \qquad (47)\\ \langle\mathbf{f}| &\equiv \textit{column}\text{ vector of the } \langle f_i|\text{'s},\end{aligned}$$

where f represents the set of functions $f_1, f_2, \ldots, f_n$. Then (46) is

$$\mathscr{A} \geq \mathscr{A}|\mathbf{f}\rangle\langle\mathbf{f}|\mathscr{A}|\mathbf{f}\rangle^{-1}\langle\mathbf{f}|\mathscr{A}, \qquad (48)$$

where the choice of f is evidently arbitrary so long as $\mathscr{A}$ and the matrix $\langle\mathbf{f}|\mathscr{A}|\mathbf{f}\rangle$ have the same number of negative eigenvalues. Different forms of the inequality (48) result from different choices of the basis set f. For example, the choice $|\mathbf{g}\rangle = \mathscr{A}|\mathbf{f}\rangle$ leads to the form

$$\mathscr{A} \geq |\mathbf{g}\rangle\langle\mathbf{g}|\mathscr{A}^{-1}|\mathbf{g}\rangle^{-1}\langle\mathbf{g}|, \qquad (49)$$

and still other forms have been described by Löwdin (1965a,b, 1966) for the case when $\mathscr{A}$ is a positive operator.

Operator inequalities of the type (49) were employed by Bazley and Fox (1961a,b), and were then further developed by Sugar and Blankenbecler

(1964) and by Löwdin (1965a,b, 1966) for the special case of the positive operators, $\mathscr{A} \geq 0$. For the more general case of an indefinite operator with a finite number of negative eigenvalues, the essential step was taken by Rosenberg *et al.* (1960), and the results were then further developed by Sugar and Blankenbecler (1964), Miller (1969), and others. In addition to the applications to be discussed in Section III,A, the operator inequalities have been fruitfully applied (see, e.g., Goscinski, 1967; Brändas and Goscinski, 1970a,b, Goscinski and Brändas, 1971) to the analysis of perturbation series, Padé approximants, and other problems.

III. Upper and Lower Bounds to Properties

The discussion of Section II describes only one set of techniques which may be useful in the general problem of developing upper- and lower-bound formulas for quantum-mechanical properties. In the present section we wish to survey the various quantum-mechanical properties for which bounds may be sought, and describe the rigorous bound formulas which have been developed by various methods.

A. Energy Levels and Phase Shifts

Historically, upper- and lower-bound formulas were associated mainly with the determination of bound-state energy eigenvalues E_k, due of course to the central importance of the Schrödinger equation

$$\mathscr{H}\Psi_k = E_k\Psi_k, \qquad E_0 \leq E_1 \leq \cdots \tag{50}$$

in the complete description of a quantum-mechanical system. The best known *upper*-bound formula in quantum mechanics is undoubtedly the Ritz *variational principle*

$$\langle\Phi|\mathscr{H}|\Phi\rangle/\langle\Phi|\Phi\rangle \geq E_0, \tag{51}$$

and the related inequalities furnished by the "interleaving theorem" (5) for the higher eigenvalues E_k. Formula (51) is remarkably accurate in that first-order errors in the approximate wave function Φ are easily shown (see, e.g., Pilar, 1968, p. 235) to lead only to second-order errors in the estimate of E_0. Thus, even crude functions Φ can lead to eigenvalue estimates which are unexpectedly accurate and are, in addition, rigorous bounds to the true E_0. This happy conjunction of virtues is the basis for much of the success of modern atomic and molecular physics. But it has sometimes stimulated unrealistic expectations with respect to other calculations in quantum mechanics.

With (51) in hand it is natural to seek a corresponding *lower* bound to E_0 so that the true value can be bracketed between rigorous theoretical limits. The early formulas were based principally on the idea that the operator $(\mathscr{H} - E_0)(\mathscr{H} - \alpha)$ could have no negative eigenvalues so long as α lay below E_1, the first excited state of the same symmetry as E_0, so that

$$\langle\Phi|(\mathscr{H} - E_0)(\mathscr{H} - \alpha)|\Phi\rangle \geq 0 \qquad \text{if} \quad \alpha \leq E_1. \tag{52}$$

Unfortunately, the resulting formulas usually involve the "width" $\Delta\mathscr{H}$,

$$(\Delta\mathscr{H})^2 = \langle\Phi|\mathscr{H}^2|\Phi\rangle - \langle\Phi|\mathscr{H}|\Phi\rangle^2, \tag{53}$$

and thus require the difficult matrix elements of $\mathscr{H}^2$. The maximum choice $\alpha = E_1$ is optimal in a certain sense[3] and leads to the time-honored Temple (1928) formula (see also Kato, 1949)

$$E_0 \geq \langle\Phi|\mathscr{H}|\Phi\rangle - \frac{(\Delta\mathscr{H})^2}{E_1 - \langle\Phi|\mathscr{H}|\Phi\rangle}. \tag{54}$$

Similar formulas of Weinstein (1934) and Stevenson and Crawford (1938) have also been extensively studied. More recently Switkes (1967) pointed out that the transition energy δ

$$\delta \equiv E_1 - E_0 \tag{55}$$

is the quantity much more likely to be known from experiment[4] so that one can choose

$$\alpha \equiv \delta + E_0 \tag{56}$$

and obtain the useful formula

$$E_0 \geq \langle\Phi|\mathscr{H}|\Phi\rangle - (\delta/2) + \{(\delta/2)^2 - (\Delta\mathscr{H})^2\}^{1/2}. \tag{57}$$

The difficulty of calculating $\mathscr{H}^2$ integrals largely prevented any serious applications of the Temple-like bounds, the notable exceptions being Wilets and Cherry (1956), Kinoshita (1959), Pekeris (1962), and Conroy (1964). The numerical results were generally of low quality compared to the variational upper bound, and various reasons have been proposed. Thus, Caldow

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[3] Formula (54) is known (Kato, 1949) in fact to be the *best possible* lower bound to E_0 for the specific amount of information ($\langle\Phi|\mathscr{H}|\Phi\rangle$, $\langle\Phi|\mathscr{H}^2|\Phi\rangle$, E_1) which it contains. See the discussions of Walmsley (1967b) and of Schmid and Schwager (1968).

[4] Although energy differences such as (55) are directly measured in spectroscopic experiments, these generally involve transitions between states of *different* symmetry, so that at least two spectral lines (e.g., $E_0 \rightarrow E^*$, $E_1 \rightarrow E^*$) will be required to get an experimental δ.

and Coulson (1961) pointed out that the *virial theorem* was not satisfied by trial functions chosen to optimize lower bounds, and Fröman and Hall (1961) discussed more generally the proper choice of scale in lower-bound calculations. Schwartz (1967) stressed the unfavorable emphasis on regions of high kinetic energy in the lower-bound formulas, and this effect was noted also by Keaveny and Christoffersen (1969). These latter authors discuss the evaluation of the $\mathscr{H}^2$ matrix elements in terms of Gaussian-type orbital basis sets, while Conroy (1967) and Goodisman and Secrest (1966) have advocated numerical methods, and Birss and co-workers (Solony *et al.*, 1966; Messmer, 1969; Messmer *et al.*, 1969) have developed formulas for these integrals in the Slater-type orbital basis.

Interest in this area was strongly revived with the papers of Bazley (1959, 1960) and of Bazley and Fox (1961a,b, 1962, 1966b), based on the methods of Weinstein and his school (see Gould, 1966). The key to this approach is the "ordering theorem"[5] which states that if operators $\mathscr{A}$, $\mathscr{B}$ satisfy

$$\mathscr{A} \geq \mathscr{B}, \tag{58a}$$

then their *ordered* eigenvalues α_i, β_j, respectively, must satisfy

$$\alpha_k \geq \beta_k, \qquad \text{all} \quad k. \tag{58b}$$

Note that the converse is not generally true unless the operators commute.

Bazley and Fox then construct "intermediate Hamiltonians" $\mathscr{H}^{(n)}$ with the property

$$\mathscr{H}^{(n)} \leq \mathscr{H}^{(n+1)} \leq \cdots \leq \mathscr{H}, \tag{59}$$

and where each $\mathscr{H}^{(n)}$ is explicitly solvable:

$$\mathscr{H}^{(n)}\psi_k^{(n)} = \varepsilon_k^{(n)}\psi_k^{(n)}.$$

Then in view of the ordering theorem (58), the eigenvalues $\varepsilon_k^{(n)}$ furnish a nondecreasing sequence of lower bounds to the true E_k,

$$\varepsilon_k^{(n)} \leq \varepsilon_k^{(n+1)} \leq \cdots \leq E_k. \tag{60}$$

The construction of intermediate Hamiltonians $\mathscr{H}^{(n)}$ is based usually on a splitting of the Hamiltonian $\mathscr{H}$ into a solvable problem $\mathscr{H}_0$ and a multiplicative remainder $\mathscr{V}$,

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{V}, \tag{61}$$

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[5] A simple proof is given by Löwdin (1965a)

with subsequent application of operator inequalities (see Section II,B.3) to either $\mathscr{H}_0$ or $\mathscr{V}$ (or to both). The general features of this approach, and of the related bracketing theorems based on the partitioning technique, were developed from several points of view by Löwdin (1965a,b, 1966), Gay (1964), Miller (1965, 1968, 1969) and others, and various extensions and numerical applications have subsequently been given; see Johnson and Coulson (1964), Bunge and Bunge (1965), Choi and Smith (1965), Reid (1965), Walmsley and Coulson (1966), Larsson (1967), Jennings (1967a), Walmsley (1967a), Wilson (1967a,b), and Wang (1968). Wilson (1965) was able to show how the older Temple-like formulas could be recovered in this approach by applying operator inequalities to the *full* $\mathscr{H}$ (up to a constant) instead of to $\mathscr{H}_0$ or $\mathscr{V}$. Indeed, this choice seems to be necessary when (as appears usual in three- or more electron systems) the convenient $\mathscr{H}_0$ has an *infinite* number of eigenvalues below the lowest eigenvalue of $\mathscr{H}$, and the treatments based on the splitting (61) break down, as discussed, e.g., by Jennings (1967b). Recent work by Miller (1969) based on the operator inequalities has therefore tended back toward the Temple-like formulas and their many-dimensional generalizations.

Although determinantal inequalities have not been extensively applied to the problems of bounds to eigenvalues (see, however, Weinhold, 1969a; Cohen and Feldmann, 1969), many of the results in the "method of intermediate Hamiltonians" end up in determinantal form, and it is possible that the point of view developed in Section II could shed additional light on these problems.

A wholly different approach to energy bounds has been given by Rosenthal and Wilson (1967, 1968, 1970), based on the asymptotic form of integrated solutions of the wave equation for incorrect eigenvalues. The method was applied successfully by them to $H_2{}^+$, H_3^{2+}, and He, and by Alexander (1969a) to the Stark effect in hydrogen, but a number of difficulties have thus far prevented applications to more complex systems.

Finally, we may mention that the calculation of upper and lower bounds to bound-state energy levels is closely tied to the calculation of *scattering phase shifts* in the unbound problem. Early work of Kato (1951) was extended in a powerful manner by Spruch and co-workers (see Spruch, 1968, and references cited therein) to provide bounds on the *scattering length*, which characterizes the zero-energy limit of the elastic process.[6] Then Sugar

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[6] As stressed by Burke and Smith (1962), the extrema principles of Spruch and coworkers played a significant role in the proper understanding of the low-energy scattering of electrons from hydrogen.

and Blankenbecler (1964) showed how one could obtain bounds for all the scattering phase shifts and cross sections under very general circumstances. The important result is that the phase shift is *monotonic* in the strength of the potential, so that if the true potential is replaced by an upper or lower bound (whose scattering problem is solvable), one obtains corresponding bounds to the true phase shift. To construct such solvable "intermediate potentials," one can employ the various operator inequalities, very much as in the bound-state problem. For further details, we refer the reader to the original papers cited above.

B. Overlap of Wave Functions

A central problem in the evaluation of upper and lower bounds to quantum-mechanical properties is the estimation of the *overlap integral* $S = \langle \Phi | \Psi \rangle$ between an approximate wave function Φ and the unknown true Ψ. Since S cannot be determined exactly so long as Ψ is unknown, we must instead seek upper and lower bounds S_+, S_-, $(S_- \leq S \leq S_+)$ where the lower bound S_- is particularly important. We assume that Φ and Ψ are normalized and that their phases are properly chosen so that S is a real number lying in the interval $0 \leq S \leq 1$.

Generally speaking, the available bounds for overlap require some knowledge of the true eigenvalues E_k; e.g., the well-known Eckart (1930) criterion for the ground state Ψ_0

$$S^2 = \langle \Phi | \Psi_0 \rangle^2 \geq \frac{E_1 - \langle \Phi | \mathscr{H} | \Phi \rangle}{E_1 - E_0} \tag{62}$$

bounds S from below in terms of known values of E_0, E_1, the two lowest states of the same symmetry. But in general the energy levels E_k are known much more accurately (often from direct experimental measurements) than are the other properties whose error we seek to estimate, so their use in formulas such as (62) is quite reasonable. In any event one can usually, as in (62), simply replace the true values E_0, E_1 by corresponding lower bounds if a strictly theoretical result is necessary.

The method of determinantal inequalities proves to be a valuable tool for comparing, unifying, and extending the various formulas for upper and lower bounds to overlap, and here we shall simply refer the reader to a rather comprehensive treatment (Weinhold, 1970b), where many additional references can be found.[7] A similar approach was also taken by Cohen and

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[7] Formula (2.6) of this paper should be credited to James and Coolidge (1937).

Feldmann (1970a,b), and by Bonelli and Majorino (1970). Other aspects of overlap bounds have been discussed recently by Bazley and Fox (1969), Wang (1970a,b), Shimamura (1970), Rebane (1970), and Weinhold and Wang (1971).

C. Expectation Values

Given the Gramian determinantal inequalities of Section II one can readily write down several formulas for *lower* bounds to the expectation value $\langle\Psi|F|\Psi\rangle$ of a positive operator $F \geq 0$ (Weinhold, 1968a). A simple example can be obtained from the 3×3 Gram determinant D of the functions Ψ, $F\chi$, and Φ

$$D = D(\Psi, F\chi, \Phi) = \begin{vmatrix} 1 & \langle\chi|F|\Psi\rangle & S \\ \langle\chi|F|\Psi\rangle & \langle\chi|F^2|\chi\rangle & \langle\chi|F|\Phi\rangle \\ S & \langle\chi|F|\Phi\rangle & 1 \end{vmatrix} \geq 0, \tag{63}$$

where Ψ is regarded as the true wave function, and χ and Φ are arbitrary variational functions. We solve the determinantal inequality (63) for the unknown $\langle\chi|F|\Psi\rangle$ *to obtain the important inequality* (Weinhold, 1970a),

$$\langle\chi|F|\Psi\rangle \lesseqgtr S\langle\chi|F|\Phi\rangle \pm \varepsilon[\langle\chi|F^2|\chi\rangle - \langle\chi|F|\Phi\rangle^2]^{1/2}, \tag{64}$$

where

$$S = \langle\Phi|\Psi\rangle, \qquad \varepsilon = (1 - S^2)^{1/2}, \tag{65}$$

and where S must be replaced by appropriate bounds; see Section III,B. Introducing the assumption that $F \geq 0$, we employ the Schwarz inequality

$$\langle\chi|F|\Psi\rangle \leq \langle\chi|F|\chi\rangle^{1/2}\langle\Psi|F|\Psi\rangle^{1/2} \tag{66}$$

together with the lower member of (64) to complete the rigorous lower-bound formula

$$\langle\Psi|F|\Psi\rangle \geq \frac{\{S\langle\chi|F|\Phi\rangle - \varepsilon[\langle\chi|F^2|\chi\rangle - \langle\chi|F|\Phi\rangle^2]^{1/2}\}^2}{\langle\chi|F|\chi\rangle}, \tag{67}$$

where the term in braces must be positive. A slight modification of the argument gives the more general result

$$\langle\Psi|F|\Psi\rangle \geq \frac{\{S\langle\chi|F^\nu|\Phi\rangle - \varepsilon[\langle\chi|F^{2\nu}|\chi\rangle - \langle\chi|F^\nu|\Phi\rangle^2]^{1/2}\}^2}{\langle\chi|F^{2\nu-1}|\chi\rangle}, \tag{68}$$

where the exponent ν can be chosen freely (along with Φ and χ) to maximize the lower bound.

The limit $\nu \to 0$ leads, for the special choice $\Phi = \chi$, to the result

$$\langle\Psi|F|\Psi\rangle \geq \langle\Psi|\Phi\rangle\langle\Phi|F^{-1}|\Phi\rangle^{-1}\langle\Phi|\Psi\rangle = S^2/\langle\Phi|F^{-1}|\Phi\rangle, \tag{69}$$

which is suggested by the operator inequality (49). But clearly the general formula (68) is capable of much greater flexibility. For example, the lower bound (68), for $\Phi = \chi$, converges to the true value $\langle\Psi|F|\Psi\rangle$ as $S \to 1$, whereas (69) does not.

A variety of more complicated, but more accurate, formulas are obtained by including additional functions in the Gramian determinant (Weinhold, 1968b, 1969b, 1971b), but these may involve matrix elements of $F\mathscr{H}$ or $\mathscr{H}^2$.

These lower bound formulas have been numerically tested on several properties of the ground-state helium atom in the simple *screening approximation*

$$\Phi = (c^3/\pi)\exp(-cr_1 - cr_2), \tag{70}$$

and an overview of the results can be gained from the plot in Fig. 2 for each of the operators $F = r_1{}^n, r_{12}^n, n = \pm 1, \pm 2$. The two envelopes represent the span of the various lower-bound formulas for two different estimates of the overlap S: (i) the Eckart formula (62), and (ii) an "improved" method described, e.g., by Weinhold (1968b). For comparison, the ordinary estimate $\langle\Phi|F|\Phi\rangle$ (computed with the energy-optimized Φ) is included in the figure, and all results have been expressed as percentages of the essentially exact Pekeris (1959) values. As one can see, the rigorous bounds may occasionally rival or even surpass the accuracy of the direct estimates $\langle\Phi|F|\Phi\rangle$ when the overlap S is accurately calculated.

A related set of lower-bound formulas were suggested by Wang (1969a,b) which can be regarded as Gram determinantal inequalities based on the choice

$$\mathscr{A} = P(\mathscr{H} - E_1)P, \qquad \text{where} \quad P \equiv 1 - |\Psi_0\rangle\langle\Psi_0|$$

for the positive operator $\mathscr{A}$ of Section II,A.1. However, these formulas appear less satisfactory than those based on the choice $\mathscr{A} = 1$, because of the more difficult matrix elements which arise (such as $F\mathscr{H}F$, even in the simplest formula of this type) and because the bounds may not reduce to the true values even in the limit $S \to 1$.[8] Figure 2 includes the best results

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[8] For example, when an exponent ν, analogous to that of (68), is chosen to optimize the simplest Wang formula in the screening approximation (70), the result is usually $\nu_{\text{opt}} \to 0$, which corresponds again to the simple formula (69).

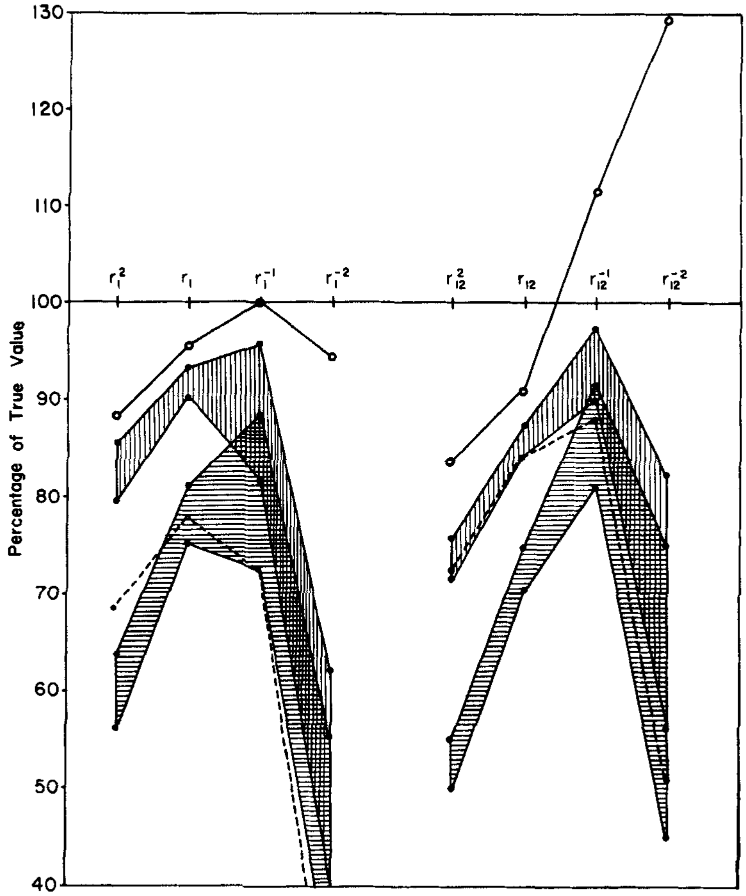

Fig. 2. Lower bounds to helium expectation values in the screening approximation as calculated with the Eckart overlap (horizontal shading) and an "improved" overlap (vertical shading). Wang's lower bounds (o---o), using improved overlap, and the conventional estimate $\langle\Phi|F|\Phi\rangle$ (o—o) are included for comparison.

obtainable from the Wang formula with the "improved" value of overlap, and shows that they compare unfavorably with the previous bounds.

The foregoing formulas provide only the *lower* limit to $\langle\Psi|F|\Psi\rangle$, and are restricted to the particular class of positive semi-definite operators, $F \geq 0$. Of course, we eventually seek both upper and lower limits for arbitrary operators F, but for this more general problem the situation seems less secure.

Apparently the first significant work on error bounds to expectation values was carried out by Kinoshita (1959), who attempted to account for certain relativistic corrections in his careful calculation on the helium atom ground-state energy. This work was extended by Rédei (1963) to Fermi contract terms, spin densities, and atomic form factors; but the bounds, while rigorous, were quite crude. Similar methods were applied more recently by Aranoff and Percus (1967) to a wider variety of properties. A general characteristic in this approach is that a different formula is constructed for each operator considered.

The general problems of bounding expectation values were more formally posed[9] by Bazley and Fox (1963, 1966a), who obtained certain bounds based on pointwise estimates of the wave function Ψ, as well as a simple formula for the positive operators. A significant forward step was then achieved by Jennings and Wilson (1966, 1967) who developed error-bound formulas which, while not mathematically rigorous, were expected to give a good indication of the true error, and which could be readily applied to a variety of problems with good results. For positive operators, their formula could be shown (Weinhold, 1968a) to coincide with the rigorous formula (67) in the limit $S \to 1$. Somewhat similar formulas were recently developed by Alexander (1969b) for the special case of one-electron operators and Hartree–Fock wave functions, but again the results are only semi-rigorous.[10]

More recently an interesting approach has been suggested by Mazziotti and Parr (1970), based essentially on *eigenvalue* bounds for perturbed Hamiltonian operators of the form

$$\bar{\mathscr{H}} = \mathscr{H} + \mu F.$$

Upper and lower bounds to eigenvalues of $\bar{\mathscr{H}}$ can then be converted to upper and lower limits for the expectation value of F. Unfortunately, these formulas suffer from the usual difficulties of the eigenvalue bounds (Section III,A), including the difficult $\mathscr{H}^2$ matrix elements, and in addition special problems arise when, for many choices of F, the operator $\bar{\mathscr{H}}$ is no longer bounded below.

As we shall show in Section III,E, it is also possible to apply the determinantal inequalities such as (64) to calculate *both* upper and lower bounds to $\langle\Psi|F|\Psi\rangle$ for arbitrary operators F. However, this approach requires in advance some finite *upper* limit (perhaps very crude) to the true value of $\langle\Psi|F^2|\Psi\rangle$, which might in turn be obtained from one of the formulas discussed above.

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[9] Cf. also the stimulating remarks of Löwdin (1960) and Preuss (1961, 1962).

[10] In fact, to the same order that these bounds are rigorous, the Hartree–Fock one-electron expectation values are already formally *correct*, so that the significance of these "bounds" is problematical.

A number of authors have discussed the related problems of finding variational principles[11] for expectation values (Delves, 1963; Aranoff and Percus, 1968; Shustek and Krieger, 1971), or of calculating first-order corrections to the zero-order estimate $\langle\Phi|F|\Phi\rangle$ (Dalgarno and Stewart, 1956, 1960; Schwartz, 1959a,b; Hall, 1964; Sanders and Hirschfelder, 1965). Since these alternative approaches, while often useful in improving the numerical accuracy, leave unresolved the basic question of the possible error in the results, we do not discuss them further here.

D. Overlap of Density Matrices

The formulas of the previous Section III,C, such as (67) for the particular choice $\Phi = \chi$, typically provide a bound for the expectation value $\langle\Psi|F|\Psi\rangle$ in terms of other expectation values (such as $\langle\Phi|F|\Phi\rangle$ and $\langle\Phi|F^2|\Phi\rangle$) and the overlap S of the corresponding wave functions Φ and Ψ. However, it is well known that expectation values of one- and two-electron operators can equally well be written in terms of the corresponding one- and two-particle reduced density matrices $\Gamma^{(1)}$ and $\Gamma^{(2)}$ (Husimi, 1940)[12]

$$\Gamma_\Psi^{(1)}(1\,|\,1') \equiv \int \Psi^*(1', 2, 3, \ldots, N)\Psi(1, 2, 3 \ldots, N)\, d2\, d3 \ldots dN, \tag{71a}$$

$$\Gamma_\Psi^{(2)}(1, 2\,|\,1', 2') \equiv \int \Psi^*(1', 2', 3 \ldots, N)\Psi(1, 2, 3 \ldots, N)\, d3 \ldots dN. \tag{71b}$$

Corresponding definitions hold for the reduced density matrices $\Gamma_\Phi^{(1)}$, $\Gamma_\Phi^{(2)}$ of the approximate wave function Φ. The variable 1 denotes the collective space–spin variable of particle 1, etc. Then if F is a one-electron operator, $F = F_1$, a sequence of simple operations (based essentially on the Pauli principle) permits one to write

$$\langle\Psi|F|\Psi\rangle = \mathrm{Tr}\{F\Gamma_\Psi^{(1)}\} \equiv \int \{F\Gamma_\Psi^{(1)}(1\,|\,1')\}_{1'\to 1}\, d1 \tag{72a}$$

where F works only on the unprimed variable of the density matrix, after which the prime is removed and the integration performed. Similarly, if F is a two-particle operator, $F = F_{12}$,

$$\langle\Psi|F|\Psi\rangle = \mathrm{Tr}\{F\Gamma_\Psi^{(2)}\} \equiv \int \{F\Gamma_\Psi^{(2)}(1, 2\,|\,1', 2')\}_{1'\to 1, 2'\to 2}\, d1\, d2, \tag{72b}$$

with a similar convention on primed and unprimed variables.

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[11] That is, stationary or saddle-point principles, as opposed to the true extremum principles we have been discussing.

[12] We adopt the normalization convention of Coleman (1963).

It is of interest to inquire what forms the bound formulas might take in a formalism based on the reduced density matrices instead of the wave functions. For this purpose, we introduce the natural spin orbitals θ_i and their occupation numbers n_i for the wave function Ψ in the usual manner (Löwdin, 1955),

$$\Gamma_{\Psi}^{(1)}(1\,|\,1') = \sum_i n_i \theta_i(1)\theta_i^*(1'). \tag{73}$$

The corresponding quantities for the approximate function Φ will be denoted with tildes,

$$\Gamma_{\Phi}^{(1)}(1\,|\,1') = \sum_i \tilde{n}_i \tilde{\theta}_i(1)\tilde{\theta}_i^*(1'). \tag{74}$$

It is now useful to introduce a *new scalar product* $[\xi, \eta]$ between vectors ξ and η, whose components are spin orbitals,

$$\xi = \begin{pmatrix} \xi_1(1) \\ \xi_2(1) \\ \vdots \end{pmatrix}, \qquad \eta = \begin{pmatrix} \eta_1(1) \\ \eta_2(1) \\ \vdots \end{pmatrix},$$

by the definition

$$[\xi, \eta] \equiv \sum_k \int \xi_k^*(1)\eta_k(1)\,d1. \tag{75}$$

In particular, for the vectors γ_Ψ, γ_Φ defined by

$$\gamma_\Psi \equiv \begin{pmatrix} n_1^{1/2}\theta_1(1) \\ n_2^{1/2}\theta_2(1) \\ \vdots \end{pmatrix}, \qquad \gamma_\Phi \equiv \begin{pmatrix} \tilde{n}_1^{1/2}\tilde{\theta}_1(1) \\ \tilde{n}_2^{1/2}\tilde{\theta}_2(1) \\ \vdots \end{pmatrix}, \tag{76}$$

we can write, using (72) and (73),

$$\langle\Psi|F|\Psi\rangle = [\gamma_\Psi, F\gamma_\Psi], \qquad \langle\Phi|F|\Phi\rangle = [\gamma_\Phi, F\gamma_\Phi]$$

for any one-electron operator F.

The scalar product [,] of (75) allows us to construct the Gram determinant D from the vectors γ_Ψ, $F\gamma_\Phi$, and γ_Φ:

$$D = \begin{vmatrix} [\gamma_\Psi, \gamma_\Psi] & [\gamma_\Psi, F\gamma_\Phi] & [\gamma_\Psi, \gamma_\Phi] \\ [F\gamma_\Phi, \gamma_\Psi] & [F\gamma_\Phi, F\gamma_\Phi] & [F\gamma_\Phi, \gamma_\Phi] \\ [\gamma_\Phi, \gamma_\Psi] & [\gamma_\Phi, F\gamma_\Phi] & [\gamma_\Phi, \gamma_\Phi] \end{vmatrix},$$

$$= \begin{vmatrix} 1 & [\gamma_\Psi, F\gamma_\Phi] & \sigma \\ [\gamma_\Psi, F\gamma_\Phi] & \langle\Phi|F^2|\Phi\rangle & \langle\Phi|F|\Phi\rangle \\ \sigma & \langle\Phi|F|\Phi\rangle & 1 \end{vmatrix} \geq 0, \tag{77}$$

where σ is defined by

$$\sigma = \sigma_1 = [\gamma_\Phi, \gamma_\Psi] = \sum_k (n_k \tilde{n}_k)^{1/2} \int \tilde{\theta}_k^*(1)\theta_k(1)\, d1, \tag{78}$$

and will be called the (one-particle) *density matrix overlap*. The unknown $[\gamma_\Psi, F\gamma_\Phi]$ from (77) will satisfy the Schwarz inequality if $F \geq 0$, exactly as in (66),

$$[\gamma_\Psi, F\gamma_\Phi] \leq [\gamma_\Phi, F\gamma_\Phi]^{1/2}[\gamma_\Psi, F\gamma_\Psi]^{1/2} = \langle\Phi|F|\Phi\rangle^{1/2}\langle\Psi|F|\Psi\rangle^{1/2},$$

so that we shall be led by analogy to the result

$$\langle\Psi|F|\Psi\rangle \geq \frac{\{\sigma\langle\Phi|F|\Phi\rangle - (1-\sigma^2)^{1/2}[\langle\Phi|F^2|\Phi\rangle - \langle\Phi|F|\Phi\rangle^2]^{1/2}\}^2}{\langle\Phi|F|\Phi\rangle} \tag{79}$$

which is identical in form to (67) for $\Phi = \chi$, *except* that the overlap integral $S = \langle\Phi|\Psi\rangle$ has been everywhere replaced by the overlap σ, Eq. (78), of the one-particle density matrices. Similarly, if we considered two-particle operators $F = F_{12}$, we would be led again to (79) with σ now defined as

$$\sigma = \sigma_2 = \sum_k (p_k \tilde{p}_k)^{1/2} \int \tilde{g}_k^*(1,2) g_k(1,2)\, d1\, d2, \tag{80}$$

where g_k are natural spin geminals of Ψ, p_k their pair occupation numbers, and where tildes again label the corresponding quantities for the approximate wave function Φ.

We can use available literature data to estimate, in a simple case, the relative advantage of using the σ's in place of the wave function overlap S. For the Li atom ground state, Larsson and Smith (1969) have carefully analyzed some very accurate wave functions (Larsson, 1968) in terms of the natural spin orbitals. If Φ is taken to be the Hartree–Fock wave function Φ_{HF}, the overlap with the (essentially[13]) exact wave function Ψ was calculated as $S = \langle\Phi_{HF}|\Psi\rangle = 0.99813$ while the corresponding overlap σ_1 of the one-particle density matrices can be worked out from their data to be $\sigma = [\gamma_{HF}, \gamma_\Psi] = 0.99877$. The overlaps enter most critically in the combinations

$$(1 - S^2)^{1/2} = 0.0611, \qquad (1 - \sigma_1{}^2)^{1/2} = 0.0497,$$

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[13] Actually, Ψ is a 25-term Hylleraas-type function (labeled W4) giving about 99.9% of the correlation energy.

so that in a typical case ($\langle\Phi|F|\Phi\rangle \approx \Delta F$),[14] σ_1 might serve to tighten the error limits by about 20%.

Thus it appears that the one- and two-particle density overlaps σ_1, σ_2 of (78), (80) might be preferred to the wave function overlap S as basic criteria of accuracy. It would be interesting to obtain bounds for σ_1, σ_2 analogous to those available for S, and this problem should certainly be studied further.

E. Transition Moments and Oscillator Strengths

The basic inequality (64) of Section III,C

$$\langle\chi|F|\Psi\rangle \lesseqgtr S\langle\chi|F|\Phi\rangle \pm \varepsilon[\langle\chi|F^2|\chi\rangle - \langle\chi|F|\Phi\rangle^2]^{1/2} \qquad (64)$$

is quite useful in any situation where an unknown wave function Ψ is to be replaced by a known approximate Φ while still keeping track of the possible error. This idea can be profitably applied to a general *transition value* w_{ab}

$$w_{ab} = \langle\Psi_a|W|\Psi_b\rangle, \qquad (81)$$

where both Ψ_a and Ψ_b are unknown. When (64) is used first to replace Ψ_b with Φ_b (holding $\chi = \Psi_a$), then used again to replace Ψ_a with Φ_a in the integrals $\langle\Psi_a|W|\Phi_b\rangle$, the result is (Weinhold, 1970c)

$$w_{ab} \lesseqgtr S_a S_b \tilde{w}_{ab} \pm \varepsilon_a S_b \Delta_{ab} \pm \varepsilon_b\{\langle\Psi_a|W^2|\Psi_a\rangle - [S_a\tilde{w}_{ab} - \varepsilon_a\Delta_{ab}]^2\}^{1/2}, \qquad (82)$$

where $\tilde{w}_{ab}$ is the ordinary approximation

$$\tilde{w}_{ab} = \langle\Phi_a|W|\Phi_b\rangle \qquad (83)$$

and where

$$S_a = \langle\Phi_a|\Psi_a\rangle,\ S_b = \langle\Phi_b|\Psi_b\rangle,$$
$$\varepsilon_a = (1 - S_a{}^2)^{1/2},\ \varepsilon_b = (1 - S_b{}^2)^{1/2},$$
$$\Delta_{ab} = (\langle\Phi_b|W^2|\Phi_b\rangle - \tilde{w}_{ab}^2)^{1/2}.$$

The overlap integrals S_a, S_b are replaced by appropriate bounds as before, and the matrix element $\langle\Psi_a|W^2|\Psi_a\rangle$ must also be replaced by some *upper* limit to its true value. Because $\varepsilon_b \to 0$ as $S_b \to 1$, the final term will vanish and the upper and lower bounds (82) will converge to the true value w_{ab} even if this upper limit for $\langle\Psi_a|W^2|\Psi_a\rangle$ is quite crude.

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[14] ΔF is defined as in Eq. (53).

The application of formula (82) to the calculation of dipole oscillator strengths has recently been discussed by Weinhold (1971a), to whom the interested reader is referred for complete details. Here we wish to mention only the significant contribution of Rebane and Braun (1969a) to the understanding of these problems.

It appears that direct calculations of oscillator strengths based on the error-bound formulas (82) may in favorable cases be competitive with the conventional methods, and calculations are in progress to explore this prospect numerically for low-lying transition in some light atoms and ions. Of course, both theoretical and experimental determinations of oscillator strengths are subject to very gross errors (see, e.g., Crossley, 1969), so that the prospect of rigorous error limits is unusually attractive in this area.

It is evident that formula (82) applies equally well in the special case $\Psi_a = \Psi_b$ when w_{ab} becomes an ordinary *expectation* value. Since the operator W is in no way restricted to be positive semidefinite, etc., formula (82) gives the desired upper and lower bounds for the general expectation value or transition value of an arbitrary operator W under the fairly modest assumptions:

(i) all matrix elements are assumed real;
(ii) $\tilde{w}_{ab}$ is assumed positive (if necessary, simply by changing the sign of W, rotating the coordinate system, etc.);
(iii) S_a is sufficiently close to unity that

$$S_a/\varepsilon_a \geq \Delta_{ab}/\tilde{w}_{ab}.$$

Even assumption (iii) is an insignificant restriction for any reasonable Φ_a.

F. Second-Order Properties

When an unperturbed atom or molecule

$$\mathscr{H}_0 \varphi_k^{(0)} = \varepsilon_k^{(0)} \varphi_k^{(0)} \tag{84}$$

is placed in a static external field (associated with the perturbation operator $\mathscr{V}$), the resulting wave equation

$$(\mathscr{H}_0 + \mathscr{V})\Psi_k = E_k \Psi_k \tag{85}$$

is customarily solved by developing the eigenfunction and eigenvalue in a perturbation series

$$\Psi_k = \varphi_k^{(0)} + \varphi_k^{(1)} + \varphi_k^{(2)} + \cdots,$$

$$E_k = \varepsilon_k^{(0)} + \varepsilon_k^{(1)} + \varepsilon_k^{(2)} + \cdots,$$

according to powers of the field strength; see the extensive review of Hirschfelder *et al.* (1964). In terms of the perturbative wave function corrections $\varphi_k^{(n)}$, the first few terms in the energy series are

$$\begin{aligned}
\varepsilon_k^{(0)} &= \langle \varphi_k^{(0)} | \mathscr{H}_0 | \varphi_k^{(0)} \rangle, \\
\varepsilon_k^{(1)} &= \langle \varphi_k^{(0)} | \mathscr{V} | \varphi_k^{(0)} \rangle, \\
\varepsilon_k^{(2)} &= \langle \varphi_k^{(0)} | \mathscr{V} - \varepsilon_k^{(1)} | \varphi_k^{(1)} \rangle,
\end{aligned}$$

with the normalization $\langle \varphi_k^{(0)} | \varphi_k^{(0)} \rangle = 1$. Here $\varepsilon_k^{(0)}$ is an eigenvalue and $\varepsilon_k^{(1)}$ an expectation value as considered in Sections III,A and III,C, respectively, but the *second-order property* $\varepsilon_k^{(2)}$ is of a different type. For example, if $\mathscr{V}$ represents the interaction with a uniform electric field, then $\varepsilon_k^{(2)}$ is related to the electric dipole *polarizability* of the atom or molecule in state k. We shall assume here that $\varepsilon_k^{(1)} = 0$ (e.g., no permanent dipole moment)[15] and concentrate for simplicity on the ground state $k = 0$, so that the property of interest is

$$\varepsilon_0^{(2)} = \langle \varphi_0^{(0)} | \mathscr{V} | \varphi_0^{(1)} \rangle. \tag{86}$$

Since the first-order correction $\varphi_0^{(1)}$ cannot usually be found exactly, we can only hope to bracket the true $\varepsilon_0^{(2)}$ between upper and lower bounds. For this purpose, one has the Hylleraas (1930) upper bound

$$\varepsilon_0^{(2)} \leq |\langle \varphi_0^{(0)} | \mathscr{V} | f \rangle|^2 / \langle f | \varepsilon_0^{(0)} - \mathscr{H}_0 | f \rangle \tag{87}$$

and the Prager–Hirschfelder (Prager and Hirschfelder, 1963) lower bound[16]

$$\varepsilon_0^{(2)} \geq \frac{1}{\varepsilon_1^{(0)} - \varepsilon_0^{(0)}} \left\{ \langle \varphi_0^{(0)} | \mathscr{V}^2 | \varphi_0^{(0)} \rangle - \frac{|\langle \varphi_0^{(0)} | \mathscr{V}(\mathscr{H}_0 - \varepsilon_1^{(0)}) | g \rangle|^2}{\langle g | (\mathscr{H}_0 - \varepsilon_0^{(0)})(\mathscr{H}_0 - \varepsilon_1^{(0)}) | g \rangle} \right\}, \tag{88}$$

where f and g are arbitrary variational functions. Only the Hylleraas principle (87) has been extensively applied to the practical calculation of second-order properties; it is equivalent, as shown, e.g., by Slater and Kirkwood (1931), to a variational solution of the perturbed eigenvalue equation (85)

$$\frac{\langle \varphi_0^{(0)} + f | \mathscr{H}_0 + \mathscr{V} | \varphi_0^{(0)} + f \rangle}{\langle \varphi_0^{(0)} + f | \varphi_0^{(0)} + f \rangle} \geq E_0, \tag{89}$$

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[15] Although the assumption $\varepsilon_k^{(1)} = 0$ represents some loss of generality, we note that this condition is often satisfied in situations where the second-order correction $\varepsilon_k^{(2)}$ is important physically.

[16] See Miller (1969) and Lindner and Löwdin (1968) for the derivation of these and more general forms from the operator inequalities of Section II,B.3.

with subsequent identification of $\varepsilon_0^{(2)}$ as the term quadratic in the field strength.

Although the formulas (87) and (88) are completely rigorous, they contain the *exact* solution $\varphi_0^{(0)}$ of the eigenvalue equation (84), which cannot usually be solved for systems more complicated than hydrogen. With any *approximate* eigenfunction, $\tilde{\varphi}_0^{(0)}$, (87) and (88) are no longer rigorous bounds. Moreover, it was noticed even in the earliest calculations of Hassé (1931) and Baber and Hassé (1937) that the variational estimate calculated from (89) is highly sensitive to the particular representation of $\varphi_0^{(0)}$ which is chosen. Thus the apparent utility of the variational formula (87) is severely diminished; for some alarming examples of its failure, see Epstein and Epstein (1964).

It is therefore desirable to replace the exact but unknown function $\varphi_0^{(0)}$ of (87) with a variational approximation $\tilde{\varphi}_0^{(0)}$ in such a way that the strict inequality is maintained. For this purpose, the ubiquitous inequality (64) may again be adapted with

$$\chi = f, \qquad \Psi = \varphi_0^{(0)}, \qquad \Phi = \tilde{\varphi}_0^{(0)}, \qquad F = -\mathscr{V},$$

to give

$$\varepsilon_0^{(2)} \leq \frac{\{-S\langle\tilde{\varphi}_0^{(0)}|\mathscr{V}|f\rangle - \varepsilon[\langle f|\mathscr{V}^2|f\rangle - \langle\tilde{\varphi}_0^{(0)}|\mathscr{V}|f\rangle^2]^{1/2}\}^2}{\langle f|\varepsilon_0^{(0)} - \mathscr{H}_0|f\rangle}, \tag{90}$$

where the term in braces must be positive, and where the overlap S

$$S = \langle\tilde{\varphi}_0^{(0)}|\varphi_0^{(0)}\rangle$$

should again be replaced by any rigorous lower bound. In formula (90) *both* $\tilde{\varphi}_0^{(0)}$ and f may now be freely varied to minimize the upper bound.[17] Formula (90) strengthens and generalizes the related result of Rebane and Braun (1969b) which can be shown to correspond to the particular, but by no means optimal, choice of the *Eckart* formula (62) for the estimation of S.

We note finally that some rigorous bounds have also been developed for third-order energies by Dmitriev and Yuriev (1969), and for Lamb shift corrections by Dmitriev and Labzovsky (1969). Other applications of a related nature are discussed by Rebane (1970) and Ahlrichs (1971).

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[17] In a similar manner the Prager–Hirschfelder formula (88) might be generalized to include the variational $\tilde{\varphi}_0^{(0)}$; the expectation value $\langle\varphi_0^{(0)}|\mathscr{V}^2|\varphi_0^{(0)}\rangle$ could be replaced with a lower bound from Section III,C but the matrix elements which result when the remaining term $\langle\varphi_0^{(0)}|\mathscr{V}(\mathscr{H}_0 - \varepsilon_1^{(0)})|g\rangle$ is treated with (64) would usually be quite complex.

G. Semiempirical Methods

A completely different class of rigorous bound formulas has recently been rather intensively developed. The objective is to find bounds for a *particular* property in terms of the known (measured or calculated) values of other properties, based on a knowledge of the underlying mathematical structure which connects these properties in the quantum-mechanical description. These bounds are thus in the nature of *consistency conditions* among the set of quantum-mechanical properties.

Because such formulas employ measured values of some properties in order to calculate bounds for others, they may be characterized as *semiempirical* in nature. One should be careful to note that the basic formulas are formally correct and rigorous within the framework of quantum mechanics, so that the term "semiempirical" should be divested in this context of some of its normal connotations. But, of course, the rigor of the *numerical* results will be subject to possible uncertainties in the measurements on which the calculations are based. It is remarkable that the error bounds are often so accurate that these uncertainties must indeed be rather carefully investigated to obtain consistent results.

Among the properties which have been treated in this general manner are dispersion interactions, frequency-dependent polarizability, index of refraction, and the class of properties corresponding to the multipole oscillator strength *sum rules* (see, e.g., Dalgarno, 1962). Mathematical methods which have been adopted to such problems include generalized Gaussian quadratures (Gordon, 1968a,b), Padé approximants (Langhoff and Karplus, 1967; Tang, 1969a, 1970), operator inequalities (Goscinski, 1968), linear programming (Futrelle and McQuarrie, 1968), determinantal inequalities (Weinhold, 1968c), continued factors (Tang, 1969b), and others (Alexander, 1970). Here we shall only refer the reader to a recent striking illustration of the power of these techniques by Starkschall and Gordon (1971), as well as to the review articles of Langhoff and Karplus (1970) and Goscinski and Brändas (1971) on the Padé approximants.

IV. Conclusion

It is now possible to write expressions for rigorous upper or lower bounds to many quantum-mechanical properties of interest. These may be used to judge the accuracy of estimates calculated from other methods, or they might themselves be made the basis for new computational procedures. The latter possibility is particularly appealing for properties such as oscillator strengths which are determined only poorly or erratically by the usual energy-minimization procedure. Of course, one should expect the useful domain of the completely rigorous methods to be rather small compared to the full range and scope of chemical phenomena, but even in this context one could recall that the bounds described in Section III,G are being routinely applied to surprisingly complex systems.

An important general question is whether and how additional miscellaneous information can be systematically incorporated into the error bounds. It is often felt that the accuracy of certain calculations is enhanced when the trial wave function satisfies certain auxiliary conditions (e.g., the virial theorem, cusp conditions, Brillouin's theorem), but how could this intuition be converted rigorously into improved limits of error? It seems that the study of such questions could lead to a more complete understanding of the expected reliability of quantum-mechanical calculations.

In the past, theoretical conclusions have been able to directly challenge experimental results only in the event of gross discrepancies, or after the most heroic calculations, and even in such cases there was often ample room for the skeptically inclined to doubt the theoretical findings. While it is perhaps premature to summon up the image of experimentalists struggling to attain agreement with the theoreticians(!), the availability of rigorous theoretical bounds could, in favorable cases, cast a wholly different light on the interplay between theory and experiment. Thus, the upper and lower bounds are potentially of more than purely formal interest, but as yet their numerical potential remains to be thoroughly explored.

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Ab Initio Calculations on Large Molecules

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I. Introduction

During the twenty years since the advent of large-scale digital computers (ca. 1950–1970), enormous advances have taken place in computational quantum chemistry. These include the formulation of procedures that allow the quantification of quantum chemistry via digital computers [e.g., HF–LCAO–MO–SCF theory (Hall, 1951; Roothaan, 1951), techniques for the recovery of correlation energy (Wahl and Das, 1970)[2]], and application of these procedures to the calculation of physical and chemical properties of molecules (Krauss, 1967). Perhaps equally important, many of these developments have created techniques as well as computer programs that are usable by chemists *other* than quantum chemists. Thus, the realization of computational quantum chemistry as an "analytical tool" for chemists in general is now well underway.

However, if computational quantum chemistry is to provide a general "probe" for chemical problems, it must be capable of investigating a broad spectrum of chemical systems, including large, medium, and small

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[1] Alfred P. Sloan Research Fellow, 1971–1973.

[2] This paper reviews recent advances in this area.

molecules, as well as interactions among molecules. The following discussion attempts to review briefly the efforts that have been made to develop procedures for treating large molecules in a practical manner, and describes in some detail a procedure that has been under development in this laboratory.

For the purpose of the following discussion, we shall take an arbitrary and perhaps myopic definition of a large molecule as one in which there are ≥ 36 electrons, and containing atoms including hydrogen and others from the first row of the periodic table. Two notable types of molecules that will be excluded from this definition are molecules containing a large number of electrons but only a few nuclei (e.g., HCl), and molecules containing translational symmetry. However, the definition will not be restricted to single molecules, and small aggregates of molecules will be considered, whenever data are available. This will allow examination of the various procedures as to their capabilities to describe intermolecular forces, as well as intramolecular forces in isolated molecules.

The discussion will also be limited to procedures that are based upon an *ab initio* formalism. In the past, the only viable approaches for examination of large molecules were semiempirical. While several of these approaches [e.g., CNDO (complete neglect of differential overlap) (Pople *et al.*, 1965), EHT (extended Hückel theory) (Wolfsberg and Helmholtz, 1952; Hoffmann, 1963; Hoffmann and Lipscomb, 1962), INDO (intermediate neglect of differential overlap) (Pople *et al.*, 1967; Gordon and Pople, 1968), MINDO (modified INDO) (see Baird and Dewar, 1969, and other references contained therein), MCZDO (multi-center zero differential overlap) (Brown and Roby, 1970), and NEMO (nonempirical molecular orbital theory) (Newton *et al.*, 1966)] have provided useful and informative results, it seems clear that an *ab initio* approach is desired for several reasons. First, the identification and improvement of inadequacies is more straightforward in an *ab initio* approach, since only a model (e.g., Hartree–Fock) plus a basis set need to be examined. Addition of further approximations to the previous two (e.g., neglect of certain integrals) complicate the analysis considerably. This makes it difficult to establish for a given basis set whether improvement is needed in the model or in the approximations used to evaluate the model. Second, the parametrization techniques are developed typically for the determination of the total energy, and will not be applicable in general to other properties. Third, the evaluation of integrals over Slater-type orbitals (STO's, the most commonly employed basis sets for semiempirical calculations) for properties other than the energy present formidable problems, which are solved usually by invoking additional parameterization procedures. Consequently, these and other theoretical and practical difficulties associated with the use of semiempirical techniques have led to the search for alternative formulations of an *ab initio* nature.

The following sections describe some of the progress that has been made using *ab initio* quantum mechanics as the probe. By this it is meant that the complete nonrelativistic Hamiltonian is employed (within the Born–Oppenheimer approximation), and all electrons are considered explicitly. In addition, after the basis set and model (e.g., Hartree–Fock) are chosen, no further approximations are made. In practice, this usually implies that the integrals that arise over the various operators in the Hamiltonian are evaluated using either an analytical formula (in the case of GTO's), or suitable combinations of analytical and numerical techniques (in the case of STO's) so as to guarantee accuracy of the integrals concomitant with the remainder of the calculations. In some cases this implies values which are precise to the extent allowed in single-precision arithmetic (seven to eight significant figures), and in other calculations (usually involving Gaussians) this implies precision consistent with the use of double-precision arithmetic (14–16 significant figures) throughout the calculations.

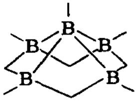
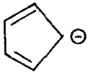
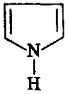
II. Currently Available Procedures

In order to assess the characteristics of the various procedures, it is useful to examine the various applications that have been made to date. Table I presents a summary of *ab initio* calculations that have been carried out on large molecules (as defined previously) to date. As is apparent from even a cursory glance at the entries in this table, a large majority of the investigations to date have been approximate Hartree–Fock calculations on the ground state of the molecule or aggregate of interest. Only a few ions have been investigated [cyclopentadienyl anion (Diercksen and Preuss, 1966; Preuss and Diercksen, 1967), pyrrole cation and anion (Kramling and Wagner, 1969), pyridinium cation (Clementi, 1967c), and benzene cation (Schulman and Moskowitz, 1967)], and attempts to obtain correlation energy of ground and excited states through configuration interaction techniques have been limited to only a few examples [benzene (Buenker *et al.*, 1968; Petke and Whitten, 1969; Gilman and deHeer, 1970; Peyerimhoff and Buenker, 1970), borazine (Peyerimhoff and Buenker, 1970), and thymine (Snyder *et al.*, 1970)].

A few studies have also appeared which involve intermolecular interactions. These have been limited to various aggregates of water, the formic acid dimer, and the cytosine–guanine base pair, and have been at the

TABLE I

BIBLIOGRAPHY OF *AB INITIO* CALCULATIONS ON LARGE MOLECULES[a]

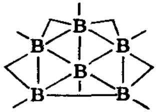
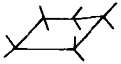
Molecule	No. of electrons	References	Properties[b,c] calculated	Comments
$B_5H_{11}(C_s)$ 	36	Switkes *et al.* (1970a)	$E_T = -129.4281$ hartrees I.P. = 10.92 eV $\mu = 3.17$D	LCAO–MO–SCF; 36 STO basis (minimum basis set). Orbital exponents obtained from a diborane calculation. Electronic structure is discussed using electron density contour maps and a Mulliken population analysis. (Mulliken, 1932, 1935, 1949, 1955, 1962) Relation of electronic structure to magnetic properties and reactivity is also discussed.
Cyclopentadienyl anion 	36	Diercksen and Preuss (1966)	$E_T = -189.42$ hartres Electron affinity $(C_5H_5) = 0.9$ eV $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\pi)^2$ $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\pi)^2(\pi)^2$	SCF–MO–LCGO; 75 GTO, contracted to 40, 45, and 50 "groups." Comments concerning the interspersing of σ and π-MO's are made. The irreducible representations of the individual MO's were not given.
Pyrrole 	36	Clementi *et al.* (1967)	$E_T = -207.93135$ hartrees I.P. = 10.56 eV $(a_1)^2(a_1)^2(b_2)^2(a_1)^2(b_2)^2$ $(a_1)^2(a_1)^2(b_1(\pi))^2(b_2)^2(b_2)^2$ $(a_1)^2(b_1(\pi))^2(a_2(\pi))^2$	LCAO–MO–SCF; 95 Gaussians (obtained from atomic calculations) contracted to a 30 orbital basis for the SCF study. C,N basis:

		1s = 5 contracted GTO. 2s = 2 contracted GTO. 2p = 3 contracted GTO for each component (e.g., $2p_x$) H basis: 1s = 3 contracted GTO. Discussion of the molecular orbital structure and the charge distribution is given, including a Mulliken population analysis (Mulliken, 1932, 1935, 1949, 1955, 1962).
Genson and Christoffersen (to be published)	$E = -178.34748$ hartrees I.P. = 4.17 eV $(a_1)^2(a_1)^2(b_2)^2(a_1)^2(b_2)^2$ $(a_1)^2(a_1)^2(b_2)^2(b_1(\pi))^2(b_2)^2$ $(a_1)^2(b_1(\pi))^2(a_2(\pi))^2$	LCFO–MO–SCF; 30 FSGO basis set, obtained from molecular fragment studies. Discussion of the molecular orbital structure and charge distribution is given.
Kramling and Wagner (1969)	$E_T = -207.93070$ hartrees I.P. = 10.56 eV $(a_1)^2(a_1)^2(b_2)^2(a_1)^2(b_2)^2$ $(a_1)^2(a_1)^2(b_1(\pi))^2(b_2)^2$ $(b_2)^2(a_1)^2(b_1(\pi))^2(a_2(\pi))^2$	SCF–LCAO–MO; 95 Gaussians, contracted to 30 orbital basis set (same basis as Clementi *et al.*, 1967). Discusses the molecular orbital structure of pyrrole cation and anion as well. Gives electron density difference maps for σ- and π-electrons to aid in comparisons. Discusses the validity of σ–π separation, including a Mulliken population analysis (Mulliken, 1932, 1935, 1949, 1955, 1962).

(continued)

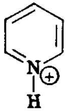
TABLE I—*Continued*

Molecule	No. of electrons	References	Properties^{b,c} calculated	Comments
Pyrrole (continued)	36	Mely and Pullman (1969)	I.P. = 9.73 eV $\mu = 2.16$ D $(a_1)^2(a_1)^2(b_2)^2(a_1)^2(b_2)^2$ $(a_1)^2(a_1)^2(b_2)^2(b_1(\pi))^2$ $(b_2)^2(a_1)^2(b_1(\pi))^2(a_2(\pi))^2$	LCAO–MO–SCF; "Molecule-calibrated" basis set, consisting of 65 GTO, contracted to 30 functions for the SCF study. C,N: 1s = 3 contracted GTO 2s = 1 GTO 2p = 2 contracted GTO per component H: 1s = 3 contracted GTO Analysis of the charge distribution in terms of a Mulliken population analysis (Mulliken, 1932, 1935, 1949, 1955, 1962) is given.
Lithiumcyclopentadiene 	38	Janoschek and Preuss (1967)	$E_T = -196.231$ hartrees $R_{opt} = 1.68$ Å $R = 2.13 \times 10^5$ dyne/cm ($\omega = 750$ cm^{-1}) I.P. = 4.1 eV Binding $E = 6.9$ eV	SCF–MO–LCGO; 72 GTO, contracted to 51 "groups." Eleven different Li-C_5H_5 positions were examined.

$1,2-B_4C_2H_6$ and $1,6-B_4C_2H_6$	38	Epstein *et al.* (1970)	$E_T(1,2) = -177.601$ hartrees $E_T(1,6) = 177.625$ hartrees I.P. $(1,2) = 9.90$ eV I.P. $(1,6) = 9.25$ eV $\mu_{1,2} = 2.95$ D	LCAO–MO–SCF; 36 STO basis (minimum basis set). Orbital exponents taken from B_2H_6 and C_2H_6 calculations. 1,6 isomer is found to be more stable by $\simeq 15$ kcal/mole. Analysis of the charge distribution by means of electron density contours and a Mulliken analysis (Mulliken, 1932, 1935, 1949, 1955, 1962) is given.
Hexaborane (B_6H_{10}) 	40	Epstein *et al.* (1971)	$E_T = -153.5174$ hartrees I.P. $= 10.42$ eV $\mu = 3.69$ D	LCAO–MO–SCF; 40 STO basis (minimum basis set). Orbital exponents taken from an optimized diborane calculation. Localized orbitals were constructed from the SCF orbitals. Comparison of Mulliken analysis (Mulliken, 1932, 1935, 1949, 1955, 1962) for different calculational procedures is given, electron density maps are presented, and a discussion of reactivity is given.
Cyclopentane (C_5H_{10}) 	40	Hoyland (1969)	E_T(half-chair) $= -194.091447$ hartrees E_T(envelope) $= -194.091069$ hartrees E_T(planar) $= -194.078591$ hartrees	LCAO–MO–SCF; 100 GTO, contracted to a 35 orbital basis for the SCF study [called a (5,2,2) basis]: C: 1s = 5 contracted GTO 2s = 5 contracted GTO 2p = 2 contracted GTO for each component H: 1s = 2 contracted GTO

(*continued*)

TABLE I—*Continued*

Molecule	No. of electrons	References	Properties[b,c] calculated	Comments
Water tetramer $(H_2O)_4$	40	Del Bene and Pople (1969), (1970)	$\Delta E(D_{2h}) = -0.027434$ hartrees $\Delta E(C_4) = -0.060468$ hartrees $\Delta E(S_4) = -0.067423$ hartrees $\Delta E(\text{open chain}) = -0.039156$ hartrees	LCAO–MO–SCF; 112 GTO basis (28 GTO/H_2O), contracted to represent a minimum basis set STO calculation (4GTO/STO); orbital exponents optimized in calculations on H_2O monomer. Calculated ΔE = interaction energy = E_T(polymer)-E_T(separated monomers). Cyclic structures are found generally to be more stable than open chain structures. Hydrogen bond energies appear to be nonadditive. Some geometry optimization carried out.
Pyridine ion $(^2A_2)$ 	41	Clementi (1967c)	$E_T = -245.19708$ hartrees I.P. (pyridine) ≈ 13.46 eV	LCAO–MO–SCF; 111 GTO (obtained from atomic calculations) contracted to a 35 orbital contracted basis. Same basis set as for pyridine (Clementi, 1967a). Discussion of the molecular orbital structure and charge distribution is given, including a Mulliken population analysis (Mulliken, 1932, 1935, 1949, 1955, 1959). Discussion of agreement expected for calculated and observed I.P.'s is given.

Benzene 	42	Janoschek *et al.* (1967)	$E_T = -227.27$ hartrees I.P. = 8.5 eV $(\sigma_1)^2(\sigma_2)^2(\sigma_3)^2(\sigma_4)^2(\sigma_5)^2(\sigma_6)^2$ $(\sigma_7)^2(\sigma_8)^2(\sigma_9)^2(\sigma_{10})^2(\pi_1)^2$ $(\sigma_{11})^2(\sigma_{12})^2(\pi_2)^2(\pi_2)^2$	SCF–MO–LCGO; 78 GTO, contracted to 54 "groups". Investigated geometric predictions, and found $R_{CC} = 1.39$ Å. Force constants for the four normal modes are calculated. Some comments concerning the interspersing of σ and π-MO's are made. The irreducible representations of the individual MO's are not given.
		Schulman and Moskowitz (1965)	$E_T(\mathrm{I}) = -219.397$ hartrees $E_T(\mathrm{II}) = -220.068$ hartrees I.P.(I) = 4.53 eV I.P.(II) = 7.83 eV $(a_{1g})^2(e_{1u})^4(e_{2g})^4(a_{1g})^2(b_{1u})^2$ $(e_{1u})^4(a_{2u}(\pi))^2(b_{2u})^2(e_{2g})^4$ $(e_{1g}(\pi))^4$	LCAO–MO–SCF; uncontracted GTO basis; Set I: C: 3 s-type GTO (42GTO) 3 p-type GTO H: 1 s-type GTO Set II: C: 3 s-type GTO (48GTO) 4 p-type GTO H: 1s-type GTO Molecular orbital structure and estimates of excitation energies are discussed.
		Schulman and Moskowitz (1967)	$E_T = -230.463$ hartrees I.P. = 10.15 eV $(a_{1g})^2(e_{1u})^4(e_{2g})^4(a_{1g})^2(b_{1u})^2$ $(b_{2u})^2(e_{1u})^4(a_{2u}(\pi))^2(e_{2g})^4$ $(e_{1g}(\pi))^4$	LCAO–MO–SCF; 162 GTO, contracted to a 60 GTO basis; C: 3 s-type contracted functions (9 GTO) 6 p-type contracted functions (5 GTO) H: 1 s-type contracted function (3 GTO)

(*continued*)

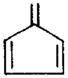
TABLE I—*Continued*

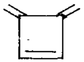
Molecule	No. of electrons	References	Properties^{b,c} calculated	Comments
Benzene (continued)	42	Schulman and Moskowitz (1967)		Molecular orbital structure and charge distribution [via a Mulliken analysis (Mulliken, 1932, 1935, 1944, 1955, 1959)] are given. The benzene cation ($^2E_{1g}$) and ($^2A_{2u}$), molecular orbital structures are also discussed.
		Praud *et al.* (1968)	$E_T = -229.701$ hartrees I.P. = 11.62 eV $(a_{1g})^2(e_{1u})^4(e_{2g})^4(a_{1g})^2(b_{2u})^2$ $(b_{1u})^2(e_{1u})^4(a_{2u}(\pi))^2(e_{2g})^4$ $(e_{1g}(\pi))^4$	LCAO–MO–SCF; 114 GTO, contracted to a 36 orbital basis for the SCF study. C: 1s = 5 contracted GTO 2s = 2 contracted GTO 2p = 3 contracted GTO for each component H: 1s = 3 contracted GTO. Molecular orbital structure and charge distribution [via a Mulliken population analysis (Mulliken, 1932, 1935, 1944, 1955, 1959)] are given.
		Buenker *et al.* (1968) Petke and Whitten (1969)	$E_T(\text{SCF}) = -230.3745$ hartrees $E_T(\text{CI}) = -230.4543$ hartrees I.P. = 10.31 eV $(a_{1g})^2(e_{1u})^4(e_{2g})^4(a_{1g})^2(b_{1u})^2$ $(b_{2u})^2(e_{1u})^4(a_{2u}(\pi))^2(e_{2g})^4$ $(e_{1g}(\pi))^4$	LCAO–MO–SCF plus CI; 180 Gaussian lobe functions, contracted to a 42 orbital basis set for the SCF studies. C: 10 s-type Gaussian lobe functions

		15 p-type Gaussian lobe functions H: 5 s-type Gaussian lobe functions. Considered 400 configurations, corresponding to all possible excitations involving π MO's. Presents CI results for 47 electronic states, and spectral assignments are suggested.
Hehre *et al.* (1969)		Determined optimum orbital exponents for use in GTO representations of STO's for C and H in benzene.
Gilman and de Heer (1970)	$E_T(\text{SCF} - {}^1A_{1g}) = -229.84$ hartrees $E({}^1A_{1g}) - E({}^3B_{1u}) = 4.212$ eV	LCAO–MO–SCF; using 132 GTO, contracted to 48 basis orbitals; studied the $^1A_{1g}$ and $^3B_{1u}$ states. Correlation studied in π-electrons only; σ-core taken from $^1A_{1g}$ state. π-MO's optimized separately in the two states. Basis set taken from Clementi *et al* (1967).
Newton *et al.* (1970)	$R_{CH} = 1.08$ Å $R_{CC} = 1.39$ Å k_{CH}(stretch) = 7.7 mdynes/Å k_{CC}(stretch) = 10.5 mdynes/Å	Minimum basis set STO calculation, with three GTO representing each STO. Extensive geometry optimization carried out. Force constants estimated.

(*continued*)

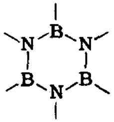
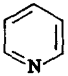
TABLE I—*Continued*

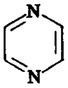
Molecule	No. of electrons	References	Properties[b,c] calculated	Comments
Benzene (continued)	42	Peyerimhoff and Buenker (1970)	$E_T = -230.3934$ hartrees I.P. = 10.29 eV E_T(best CI) = -230.4570 hartrees $(a_{1g})^2(e_{1u})^4(e_{2g})^4(a_{1g})^2(b_{1u})^2$ $(b_{2u})^2(e_{1u})^4(a_{2u}(\pi))^2(e_{2g})^4$ $(e_{1g}(\pi))^4$	LCAO–MO–SCF plus CI; 180 Gaussian lobe functions, contracted to 48 groups for the SCF study; CI involving multiple excitations of the π-MO's is carried out. The theoretical spectrum is compared with experimental results and the results of other calculations.
		Christoffersen *et al.* (1971a) Christoffersen, Maggiora *et al.* (1971)	$E_T = -197.364$ hartrees I.P. = 5.90 eV $(a_{1g})^2(e_{1u})^4(e_{2g})^4(a_{1g})^2(b_{1u})^2$ $(b_{2u})^2(e_{1u})^4(a_{2u}(\pi))^2(e_{2g})^4$ $(e_{1g}(\pi))^4$	SCF–MO–LCFO; 36 FSGO basis, determined in molecular fragment studies. Discussion of electronic structure, compared to other procedures, is given. The aromaticity of benzene is discussed. A variety of one-electron properties are calculated, and their accuracy assessed.
Fulvene (C_{2v}) 	42	Praud *et al.* (1968)	$E_T = -229.630$ hartrees I.P. = 10.74 eV $\mu = 0.97$ D $(a_1)^2(a_1)^2(b_2)^2(a_1)^2(b_2)^2(a_1)^2$ $(a_1)^2(b_2)^2(a_1)^2(b_2)^2(b_1(\pi))^2$ $(a_1)^2(b_2)^2(b_1(\pi))^2(a_2(\pi))^2$	LCAO–MO–SCF; same basis set as described for benzene. Molecular orbital structure and charge distribution [via a Mulliken population analysis (Mulliken, 1932, 1935, 1949, 1955, 1962)] are discussed.

		Christoffersen (1971)	$E_T = -197.23617$ hartrees I.P. = 4.34 eV $(a_1)^2(a_1)^2(b_2)^2(a_1)^2(b_2)^2(a_1)^2$ $(a_1)^2(b_2)^2(a_1)^2(b_2)^2(a_1)^2$ $(b_1(\pi))^2(b_2)^2(b_1(\pi))^2(a_2(\pi))^2$	SCF–MO–LCFO; same basis set as described for benzene. Discussion of the electronic structure is given, and comparisons are made to other procedures and other molecules (e.g., benzene). The aromaticity of fulvene is also discussed.
2,3-Dimethylenecyclobutene (C_{2v}) 	42	Praud *et al.* (1968)	$E_T = -229.576$ hartrees I.P. = 11.02 eV $\mu = 0.56$ D $(a_1)^2(b_2)^2(a_1)^2(a_1)^2(b_2)^2(a_1)^2$ $(b_2)^2(a_1)^2(b_2)^2(a_1)^2(b_1(\pi))^2$ $(b_2)^2(a_1)^2(a_2(\pi))^2(b_1(\pi))^2$	LCAO–MO–SCF; Same basis set as described for benzene. Molecular orbital structure and charge distribution [via a Mulliken analysis (Mulliken, 1932, 1935, 1949, 1955, 1962)] are discussed.
		Christoffersen (1971)	$E_T = -107.15547$ hartrees I.P. = 4.91 eV $(a_1)^2(b_2)^2(a_1)^2(a_1)^2(b_2)^2(b_2)^2$ $(a_1)^2(a_1)^2(b_2)^2(a_1)^2(b_1(\pi))^2$ $(b_2)^2(a_1)^2(a_2(\pi))^2(b_1(\pi))^2$	SCF–MO–LCFO; same basis set as described for benzene. Discussion is similar to that for fulvene and benzene.
Trimethylenecyclopropane (D_{3h}) 	42	Christoffersen (1971)	$E_T = -197.01341$ hartrees I.P. = 5.48 eV $(a_1')^2(e')^4(a_1')^2(e')^4(a_1')^2(e')^4$ $(a_2')^2(a_2''(\pi))^2(e')^4(e''(\pi))^4$	SCF–MO–LCFO: same basis set as described for benzene. Discussion is similar to that for fulvene and benzene.
Dewar benzene (C_{2v}) 	42	Christoffersen (1971)	$E_T = -196.78401$ hartrees I.P. = 1.49 eV $(a_1)^2(b_1)^2(b_2)^2(a_1)^2(a_2)^2(b_2)^2$ $(a_1)^2(b_1)^2(a_1)^2(b_1)^2(b_2)^2(a_2)^2$ $(a_1)^2(b_1)^2(a_1)^2$	SCF–MO–LCFO; same basis set as for benzene, except at bridging carbons, where FSGO from methane fragments were employed. Discussion is similar to that for benzene and fulvene.

(*continued*)

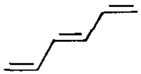
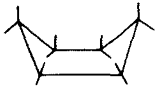
TABLE I—*Continued*

Molecule	No. of electrons	References	Properties[b,c] calculated	Comments
Borazine (D_{3h}) 	42	Peyerimhoff and Buenker (1970)	E_T(SCF) = −240.8970 hartrees I.P. = 11.87 eV $(a_1')^2(e')^4(a_1')^2(e')^4(e')^4$ $(a_2')^2(a_1')^2(a_2''(\pi))^2(e')^4$ $(e''(\pi))^4$	LCAO–MO–SCF + CI; same basis set as for the benzene study. Contour diagrams of various MO's are given, and the charge distribution is discussed. CI involving the π MO's was carried out, and the low-lying states were identified, along with estimates of the energy separations.
Pyridine (C_{2v}) 	42	Clementi (1967a)	E_T = −245.62194 hartrees I.P. = 12.17 eV $(a_1)^2(a_1)^2(b_2)^2(a_1)^2(b_2)^2(a_1)^2$ $(b_2)^2(a_1)^2(b_2)^2(a_1)^2(b_1(\pi))^2$ $(b_2)^2(a_1)^2(b_1(\pi))^2(a_2(\pi))^2$	LCAO–MO–SCF; 111 GTO, contracted to 35 functions for the SCF study. Discussion of the molecular orbital structure and charge distribution is given, including a Mulliken population analysis (Mulliken, 1932, 1935, 1949, 1955, 1962). Comparison between pyrrole and pyridine is made. GTO's obtained from atomic calculations.
		Petke and Whitten (1969), Petke *et al.* (1968)	E_T = −246.3265 hartrees I.P. = 11.05 eV μ = 2.61 D $(a_1)^2(a_1)^2(b_2)^2(a_1)^2(b_2)^2(a_1)^2$	LCAO–MO–SCF and hybrid orbital study. 175 component functions, contracted to 41 functions for the SCF study.

			$(b_2)^2(a_1)^2(b_2)^2(a_1)^2(b_1(\pi))^2$ $(b_2)^2(a_1)^2(b_1(\pi))^2(a_2(\pi))^2$	Comparisons of the adequacy of basis sets of hybrid orbitals with SCF calculations are made. The lone pair MO (highest a_1) is delocalized, in opposition to the result of Clementi (1967a).
		Genson and Christoffersen (1971)	$E_T = -210.47796$ hartrees I.P. = 6.33 eV $(a_1)^2(a_1)^2(b_2)^2(a_1)^2(b_2)^2(a_1)^2$ $(a_1)^2(b_2)^2(b_2)^2(a_1)^2(b_1(\pi))^2$ $(b_2)^2(b_1(\pi))^2(a_1)^2(a_2(\pi))^2$	SCF–MO–LCFO; 36 FSGO basis, determined in molecular fragment studies; Discussion of the molecular orbital structure and charge distribution is given.
Pyrazine (D_{2h}) 	42	Clementi (1967b)	$E_T = -261.55432$ hartrees I.P. = 12.01 eV $(a_1)^2(a_1)^2(b_2)^2(a_1)^2(b_2)^2(a_1)^2$ $(b_2)^2(a_1)^2(b_2)^2(b_1(\pi))^2$ $(b_2)^2$ $(a_1)^2(b_1(\pi))^2(a_2(\pi))^2(a_1)^2$	LCAO–MO–SCF; 108 GTO, contracted to 34 functions for the SCF study. GTO'S obtained from atomic calculations. The HOMO is a lone-pair MO. The two lone-pair MO's appear to be quite different in character. Discussion of the molecular orbital structure and charge distribution is given, including a Mulliken analysis (Mulliken, 1932, 1935, 1949, 1955, 1962). Comparisons to pyridine are given. Orbitals are labeled from C_2v point group instead of D_2h.

(continued)

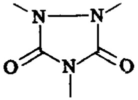
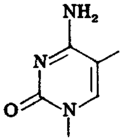
TABLE I—*Continued*

Molecule	No. of electrons	References	Properties[b,c] calculated	Comments
Pyrazine (continued)	42	Petke *et al.* (1968), Petke and Whitten (1969)	$E_T = -262.25466$ hartrees I.P. = 11.97 eV $(a_g)^2(b_{1u})^2(b_{2u})^2(a_g)^2(b_{3g})^2$ $(a_g)^2(b_{2u})^2(b_{1u})^2(b_{2u})^2(b_{3u}(\pi))^2$ $(b_{3g})^2(b_{1u})^2(b_{2g}(\pi))^2(a_g)^2$ $(b_{1g}(\pi))^2$	LCAO–MO–SCF; 170 component functions, contracted to 40 functions for the SCF study. Comparisons with calculations using hybrid orbitals as basis orbitals are made. The HOMO is found to be a π MO, in contrast to the Clementi (1967b) result.
1,3,5-*trans-Hexa*-triene (C_6H_8) (C_{2h}) 	44	Christoffersen (1971)	$E_T = -198.14464$ hartrees I.P. = 4.03 eV $(a_g)^2(b_u)^2(a_g)^2(b_u)^2(a_g)^2$ $(b_u)^2(a_g)^2(b_u)^2(b_u)^2(a_g)^2$ $(a_g)^2(b_u)^2(a_g)^2(a_u(\pi))^2$ $(b_g(\pi))^2(a_u(\pi))^2$	SCF–MO–LCFO; same basis set as for benzene; discussion is similar to that for benzene and fulvene.
Cyclohexane (C_6H_{12}) 	48	Hoyland (1969)	E_T(chair) = -232.910588 hartrees E_T(twisted boat) = -232.90054 hartrees E_T(boat) = -232.899136 hartrees	LCAO–MO–SCF; 120 GTO, contracted to 36 orbitals basis for the SCF study. The transition energy required to go from the chair to the boat form was calculated to be 11.22 kcal/mole.

Formic acid dimer $(HCOOH)_2$	48	Clementi *et al.* (1971)	I.P. $\simeq$ 13.3 eV	LCAO–MO–SCF; variety of contracted GTO bases used to test sensitivity of results to basis set choice. Potential curves for single and coupled motion of hydrogen bonded protons, using a 9/5 basis: C,O: 9 s-type GTO 5 p-type GTO per component H: 4 s-type GTO Orbital energies of the dimer are compared with those for the separated monomers. A double well potential curve is obtained for coupled motion of the two hydrogens.
Water pentamer $(H_2O)_5$	50	Del Bene and Pople (1969)	$\Delta E(C_5) = -0.084769$ hartrees $\Delta E(\text{asymmetric}) = -0.092822$ hartrees	LCAO–MO–SCF; same basis set as for water tetramer calculation. ΔE = interaction energy = E_T(polymer) − E_T (separated monomers). Both polymers have a planar structure for the oxygen atoms, and a chain of OH···OH···OH hydrogen bonds around the ring. Cyclic polymers are found to more stable than open chain polymers. A pentamer structure similar to ice I was also investigated and found to be only slightly more stable than four isolated H-bonds.

(*continued*)

TABLE I—*Continued*

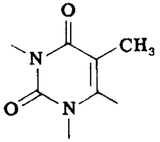
Molecule	No. of electrons	References	Properties^{b,c} calculated	Comments
Urazole ($C_2N_3H_3O_2$) (C_{2v}) 	52	Kramling and Wagner (1969)	$E_T = -338.21540$ hartrees I.P. = 10.99 eV $(a_1)^2(b_2)^2(a_1)^2\,(a_1)^2(b_2)^2$ $(b_2)^2(a_1)^2(a_1)^2(b_1(\pi))^2(b_2)^2$ $(a_1)^2(a_1)^2(a_2(\pi))^2(b_2)^2$ $(b_1(\pi))^2(a_1)^2(b_2)^2(b_1(\pi))^2$ $(a_2(\pi))^2$	LCAO–MO–SCF; 121 GTO, contracted to 38 functions for use in the SCF procedure. Discusses the electronic structure of the urazole anion and cation as well. Discusses the charge distribution via electron density contours and the Mulliken population analysis (Mulliken, 1932, 1935, 1949, 1955, 1962), as well as the validity of σ–π separation. Comparisons are also made to the electronic structure of pyrrole.
Cytosine ($C_4N_3H_5O$) 	58	Mely and Pullman (1969), Pullman *et al.* (1970)	I.P. = 9.79 eV $\mu = 6.76$ D $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2$ $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\pi)^2(\sigma)^2$ $(\pi)^2(\sigma)^2(\pi)^2(\sigma)^2(\pi)^2(\sigma)^2(\pi)^2$	LCAO–MO–SCF; "molecule-calibrated" basis set, consisting of 95 GTO, contracted to 45 functions for the SCF study: C, N, O: 1s = 3 contracted GTO 2s = 1 GTO 2p = 2 contracted GTO per component H: 1s = 3 contracted GTO Molecular orbital structure is discussed, and a Mulliken population analysis (Mulliken, 1932, 1935, 1949, 1955, 1962) is carried out. Electron density contours are also given.

		Clementi *et al.* (1969)	$E_T = -390.93564$ hartrees I.P. = 8.83 eV $\mu = 6.40$ D $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2$ $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\pi)^2(\sigma)^2(\sigma)^2$ $(\pi)^2(\sigma)^2(\pi)^2(\sigma)^2(\sigma)^2(\pi)^2(\pi)^2$	LCAO–MO–SCF; 143 GTO basis, contracted to 45 functions for the SCF study. GTO basis taken from atomic calculations. C, N, O: 1s = 5 contracted GTO 2s = 2 contracted GTO (s-type) 2p = 3 contracted GTO (p-type) for each component H: 1s = 3 contracted GTO (s-type) Discussion of the electronic structure is given, including a Mulliken population analysis (Mulliken, 1932, 1935, 1949, 1955, 1962).
Water Hexamer $(H_2O)_6$	60	Del Bene and Pople (1969)	$\Delta E(C_6) = -0.102926$ hartrees $\Delta E(S_6) = -0.114795$ hartrees $\Delta E(D_{3h}) = -0.041295$ hartrees $\Delta E(\text{chair}) = -0.106385$ hartrees	LCAO–MO–SCF; same basis set as for water tetramer. ΔE = interaction energy = E_T(polymer)-E_T (separated monomers). Most stable form of the hexamer (S_6) has alternate external hydrogens above and below the oxygen plane. Chair form is similar to that of ice I.

(*continued*)

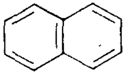
TABLE I—*Continued*

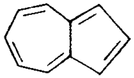
Molecule	No. of electrons	References	Properties[b,c] calculated	Comments
Water Hexamer $(H_2O)_6$ (continued)	60	Sabin *et al.* (1970)	ΔE_2(Ice I) = −0.09211 hartrees $\Delta E_2(D_{6h})$ = −0.10710 hartrees	LCAO–MO–SCF; several basis sets used: Basis Set No. 1: 1 GTO/AO = 42 basis orbitals Basis Set No. 2: 132 GTO, contracted to 42 functions for the SCF study: O: 7 s-type GTO, contracted to two s-type functions. 3 p-type GTO (for each component), contracted to 1 p-type function. H: 3 s-type GTO, contracted to 1 s-type function. Basis Set No. 3: Atomic Hartree-Fock basis [a (10, 5, 5) basis]. Examined the planar hexamer, and an ice I-like puckered configuration. ΔE = interaction energy = E_T(polymer)-E_T (separated monomers). The subscript on ΔE refers to the basis set used. For Basis No. 1, both cyclic hexamers are unstable, relative to six monomers. For Basis No. 3, the planar hexamer is unstable, relative to six monomers.

C_2F_6	66	Newton *et al.* (1969)	E_T(STO-3G) = -663.05394 hartrees E_T(STO-4G) = -667.75554 hartrees	LCAO–MO–SCF; minimum STO basis, with each STO represented by K-GTO. The cases of $K = 3$, 4 are examined. Atomization energies are reported. Comparisons with semiempirical procedures are given.
Thymine ($C_5N_2H_6O_2$) 	66	Mely and Pullman (1969), Pullman *et al.* (1970)	I.P. = 10.16 eV $\mu = 4.22$ D $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2$ $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\pi)^2(\sigma)^2(\sigma)^2$ $(\pi)^2(\sigma)^2(\sigma)^2(\pi)^2(\sigma)^2(\sigma)^2(\sigma)^2$ $(\sigma)^2(\pi)^2(\pi)^2$	LCAO–MO–SCF; basis set chosen in same manner as for cytosine. Discussion is similar to that for cytosine. The labeling for σ and π-orbitals is not strictly correct, due to the CH_3 group.
		Clementi *et al.* (1969)	$E_T = -449.59107$ hartrees I.P. = 10.54 eV $\mu = 3.29$ D	LCAO–MO–SCF; basis set chosen in same manner as for cytosine. Discussion is similar to that for cytosine. Symmetry of MO's relative to approximate σ and π orbitals is not given.
		Snyder *et al.* (1970)	$E_T = -446.790$ hartrees I.P. = 8.6 eV $\mu = 3.450$ D $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2$ $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\pi)^2(\sigma)^2(\pi)^2$ $(\sigma)^2(\sigma)^2(\sigma)^2(\pi)^2(\sigma)^2(\pi)^2(\sigma)^2$ $(\sigma)^2(\pi)^2(\pi)^2$	LCAO–MO–SCF; Minimum AO basis (51 functions), obtained from a contraction of a set of 138 GTO. C, N, O: 1s, 2s = 4 s-type GTO. 2p = 2 p-type GTO for each component. H: 1s = 2 s-type GTO.

(*continued*)

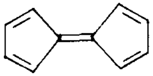
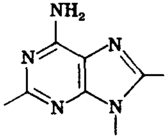
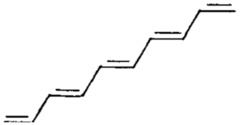
TABLE I—*Continued*

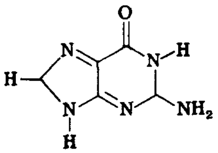
Molecule	No. of electrons	References	Properties[b,c] calculated	Comments
Thymine ($C_5N_2H_6O_2$) (continued)	66	Synder *et al.* (1970)		GTO's obtained from atomic calculations. Calculations were also reported for two anions related to thymine, with protons at each nitrogen removed, respectively. Detailed discussion of the electronic structure and charge distribution is given, including a Mulliken population analysis (Mulliken, 1932, 1935, 1949, 1955, 1962). Discussion of several excited states is also given, using CI techniques.
Naphthalene ($C_{10}H_8$) (D_{2h}) 	68	Preuss (1968)	I.P. = 3.8 eV (equal bond lengths) I.P. = 4.5 eV (experimental geometry)	LCAO–MO–SCF: 40 GTO Some nonlinear parameters chosen from ethylene calculations, and others chosen arbitrarily. Some interspersing of σ- and π-orbitals was reported. Total energy and molecular orbital structure were not reported.
		Buenker and Peyerimhoff (1969)	$E_T = -382.7883$ hartrees I.P. = 9.20 eV $(a_g)^2(b_{3u})^2(b_{2u})^2(a_g)^2(b_{1g})^2(b_{3u})^2$ $(b_{2u})^2(a_g)^2(b_{1g})^2(b_{3u})^2(a_g)^2(b_{2u})^2$	LCAO–MO–SCF; Basis set consists of 140 s-type and 150 p-type Gaussian lobe functions, contracted to 68 groups for the SCF study.

			$(a_g)^2(b_{1g})^2(b_{3u})^2(b_{2u})^2(b_{1u}(\pi))^2$ $(b_{3u})^2(b_{1g})^2(a_g)^2(b_{2g}(\pi))^2$ $(b_{3g}(\pi))^2(b_{1u}(\pi))^2(a_u(\pi))^2$	Comparison of molecular orbital structure with azulene is given, and an analysis of the charge distribution is carried out.
		Christoffersen (1971)	$E_T = -328.109695$ hartrees I.P. = 4.20 eV $(a_g)^2(b_{3u})^2(b_{2u})^2(a_g)^2(b_{1g})^2(b_{3u})^2$ $(b_{2u})^2(a_g)^2(b_{1g})^2(b_{3u})^2(a_g)^2(b_{2u})^2$ $(a_g)^2(b_{1g})^2(b_{3u})^2(b_{2u})^2(b_{1u}(\pi))^2$ $(b_{3u})^2(a_g)^2(b_{1g})^2(b_{2g}(\pi))^2$ $(b_{3g}(\pi))^2(b_{1u}(\pi))^2(a_u(\pi))^2$	LCFO–MO–SCF; 60 FSGO basis set; basis orbitals obtained from study of the .CH_3 molecular fragment. Discussion of the electronic structure is given, and comparisons are made to azulene fulvalene. The concept of aromaticity is also discussed, using the molecular orbital structure. The relative stability of various isomers is discussed.
Azulene ($C_{10}H_8$) (C_{2v}) 	68	Buenker and Peyerimhoff (1969)	$E_T = -382.7082$ hartrees I.P. = 8.26 eV $(a_1)^2(a_1)^2(b_2)^2(a_1)^2(b_2)^2(a_1)^2$ $(b_2)^2(a_1)^2(a_1)^2(b_2)^2(a_1)^2(a_1)^2$ $(b_2)^2(b_2)^2(a_1)^2(a_1)^2(b_2)^2$ $(b_1(\pi))^2(b_2)^2(a_1)^2(b_1(\pi))^2$ $(a_2(\pi))^2(b_1(\pi))^2(a_2(\pi))^2$	LCAO–MO–SCF; same basis set as for naphthalene. Discussion is similar to that concerning naphthalene.
		Christoffersen (1971)	$E_T = -327.96566$ hartrees I.P. = 3.53 eV $(a_1)^2(a_1)^2(b_2)^2(a_1)^2(b_2)^2(a_1)^2(b_2)^2$ $(a_1)^2(a_1)^2(b_2)^2(a_1)^2(a_1)^2(b_2)^2(b_2)^2$ $(a_1)^2(b_2)^2(a_1)^2(b_1(\pi))^2(b_2)^2(a_1)^2$ $(b_1(\pi))^2(a_2(\pi))^2(b_1(\pi))^2(a_2(\pi))^2$	LCFO–MO–SCF; same basis set as for naphthalene. Discussion is similar to that concerning naphthalene.

(*continued*)

TABLE I—*Continued*

Molecule	No. of electrons	References	Properties[b,c] calculated	Comments
Fulvalene ($C_{10}H_8$) (D_{2h}) 	68	Christoffersen (1971)	$E_T = -327.89342$ hartrees I.P. = 4.38 eV $(a_g)^2(b_{3u})^2(a_g)^2(b_{2u})^2(b_{1g})^2(b_{3u})^2$ $(a_g)^2(b_{2u})^2(b_{1g})^2(b_{3u})^2(a_g)^2(b_{3u})^2$ $(b_{2u})^2(b_{1g})^2(a_g)^2(b_{2u})^2(a_g)^2(b_{3u})^2$ $(b_{1u}(\pi))^2(b_{1g})^2(b_{2g}(\pi))^2(b_{1u}(\pi))^2$ $(b_{3g}(\pi))^2(a_u(\pi))^2$	LCFO–MO–SCF; same basis set as for naphthalene. Discussion is similar to that concerning naphthalene.
Adenine ($C_5N_5H_5$) 	70	Mely and Pullman (1969), Pullman *et al.* (1970)	I.P. = 9.41 eV $\mu = 2.83$ D $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2$ $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\pi)^2$ $(\sigma)^2(\sigma)^2(\sigma)^2(\pi)^2(\pi)^2(\sigma)^2(\sigma)^2$ $(\pi)^2(\sigma)^2(\sigma)^2(\pi)^2$	LCAO–MO–SCF; basis set chosen in same manner as for cytosine. Discussion is similar to that for cytosine.
		Clementi *et al.* (1969)	$E_T = -462.55284$ hartrees I.P. = 9.98 eV $\mu = 2.61$ D $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2$ $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\pi)^2$ $(\sigma)^2(\sigma)^2(\sigma)^2(\pi)^2(\pi)^2(\sigma)^2(\pi)^2$ $(\sigma)^2(\pi)^2(\sigma)^2(\pi)^2$	LCAO–MO–SCF; basis set chosen in same manner as for cytosine. Discussion is similar to that for cytosine.
trans-Decapentaene ($C_{10}H_{12}$) 	72	Christoffersen (this chapter)	$E_T = -329.68292236$ hartrees I.P. = 3.55 eV $(a_g)^2(b_u)^2(a_g)^2(b_u)^2(a_g)^2(b_u)^2(a_g)^2$ $(b_u)^2(b_u)^2(a_g)^2(b_u)^2(a_g)^2(b_u)^2(a_g)^2$ $(a_g)^2(b_u)^2(b_u)^2(a_g)^2(a_g)^2(b_u)^2(a_g)^2$ $(a_u(\pi))^2(b_g(\pi))^2(a_u(\pi))^2(b_g(\pi))^2$ $(a_u(\pi))^2$	LCFO–MO–SCF; 60 FSGO basis set. Basis orbitals found by study of $\cdot CH_3$ fragment. Discussion of the electronic structure is given, relative to naphthalene isomers.

Guanine ($C_5N_5H_5O$) 	78	Clementi *et al.* (1969)	$E_T = -537.13942$ hartrees I.P. = 9.11 eV $\mu = 6.94$ D $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2$ $(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2(\sigma)^2$ $(\pi)^2(\sigma)^2(\sigma)^2(\pi)^2(\sigma)^2(\sigma)^2(\pi)^2$ $(\sigma)^2(\pi)^2(\pi)^2(\sigma)^2(\pi)^2(\sigma)^2(\pi)^2$	LCAO-MO-SCF; basis set chosen in same manner as for cytosine. Discussion is similar to that for cytosine.
Cytosine–guanine base pair: ($C_9N_8H_{10}O_2$)	136	Clementi *et al.* (1971)	I.P. $\simeq$ 7.89 eV	LCAO-MO-SCF; 334 GTO, contracted to 105 functions for the SCF study C, N, O: 7-s type functions 3 p-type functions per component H: 3 s-type functions Seven different H_1 positions were examined. Eight different H_2 positions were examined. Eight different H_3 positions were examined. Potential curves for each hydrogen motion are reported. No double well observed for single proton motion. HOMO of dimer is a π-type MO. Orbital energies for the guanine–cytosine pair are compared with those of separated guanine and cytosine.

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[a] The survey is intended to include all papers appearing during 1970 and previously. A few articles from 1971 have also been included. Any additions or corrections to the table would be welcomed.

[b] I.P. = First ionization potential [from Koopmans' theorem (1933)].

[c] Only valence shell molecular orbital structure is given.

approximate Hartree–Fock level. These are very important beginnings, however, since they represent the first *ab initio* studies on large systems that relate to important topics such as solvent effects and other areas involving intermolecular forces.

Examination of these studies reveals that the various methods that have been employed can be classified in terms of three different approaches to the choice of basis set. The first approach, employed by Lipscomb and co-workers (Switkes *et al.*, 1970a, b; Epstein *et al.*, 1970, 1971), uses STO's directly as the basis orbitals of the calculation. These orbitals can be defined as

$$\Psi_{nlm}(r, \theta, \varphi) = Nr^{n-1}e^{-\zeta r}Y_{lm}(\theta, \varphi), \tag{1}$$

where the $Y_{lm}(\theta, \varphi)$ can be employed either in their real or complex form, N is a normalization constant, and ζ is the "orbital exponent" which must be chosen. Since the values of the orbital exponents often vary rather substantially from atomic to molecular systems, the values chosen for molecular computations are usually obtained by direct optimization in small prototype molecules. The advantages of such a basis-set choice are clear, since an exponential function is the correct solution for the hydrogenlike atoms, and a wealth of information on small molecules is available concerning the accuracy to be expected when an STO basis of a given size is employed.

The difficulties of such a basis-set choice are also well known, and are centered around the problems associated with the evaluation of electron repulsion integrals in which basis orbitals on more than two centers are involved. That calculations on large polyatomic molecules are being carried out indicates that progress is being made in this area, but major obstacles remain. First, most available programs are restricted to the use of *s*- and *p*-type STO's only. However, of greater concern is that the accuracy which is usually tolerated as a compromise between economics and the mathematical state-of-the-art of integral evaluation is often of marginal acceptability. For example, if integrals are calculated to five decimal place accuracy (Switkes *et al.*, 1970a, b), and the magnitude of the total energy of the molecules is of the order of 100–500 hartrees, then energetic differences only of the order of 0.01–0.09 hartree (6.3–56.4 kcal/mole) can be discerned. This also assumes that no numerical differencing problems arise in any other phase of the calculation (e.g., the formation and diagonalization of the Fock matrix). Consequently, the calculation of properties dependent upon differences in total energy (e.g., studies of various conformers and isomers, and transition states) will be severely hampered until greater accuracy can be obtained routinely for these integrals.

The second approach avoids the integral accuracy problem by the introduction of Gaussians as basis orbitals. These orbitals can be defined as

$$g_{nlm}(r, \theta, \varphi) = Nr^{n-1}e^{-\alpha r^2}Y_{lm}(\theta, \varphi), \tag{2}$$

where the $Y_{lm}(\theta, \varphi)$ are the spherical harmonics referred to earlier, N is a normalization constant, and α is the "orbital exponent." The immediate advantage that accompanies this choice of basis set is that the troublesome electron repulsion integrals can all be evaluated in closed form (Boys, 1950), and the question of numerical accuracy of individual integrals is no longer present. However, since these orbitals are not the solution to any prototype atomic problem, questions such as how many orbitals, what kind, and what orbital exponents should be chosen, become of major concern.

These questions have been attacked by several different groups (Clementi and Davis, 1966; Hehre *et al.*, 1969; Huzinaga, 1965; Schulman and Moskowitz, 1967; Schulman *et al.*, 1967; Whitten, 1966) although the major emphasis is similar in each case. To begin with, the data management and numerical difficulties associated with the use of each Gaussian as an individual basis orbital have caused most studies to be carried out using "contracted" Gaussian type orbital (GTO) basis sets. However, the basic assumption underlying each of these methods is that, since STO's placed on the various nuclei have provided satisfactory basis sets for small molecules, the Gaussian basis ought to be chosen so that it also resembles an atomic orbital basis set. This procedure consists of consideration of a group of GTO's as a separate entity (i.e., a single orbital),

$$\eta_i = \sum_{j=1}^{P_i} c_{ji}\, g_j, \qquad i = 1, 2, \ldots, N \tag{3}$$

where the g_j are members of the GTO basis, and the contraction coefficients c_{ji} (and orbital exponents of the g_j) are chosen in separate studies. Consequently, the SCF problem typically is reduced considerably in magnitude, since the number of contracted orbitals (N) is usually much less than the number of "primitive" GTO's ($\sum_i P_i$). The particular method of choosing the contraction coefficients and orbital exponents as well as the form of the g_j is where the approaches differ somewhat.

In studies by Pople and co-workers (Hehre *et al.*, 1969), the η_i are used strictly as least-squares mathematical approximations to STO's. They have investigated the number of GTO's that are needed per STO in order to achieve essentially the same results (e.g., for geometric predictions) as when a minimum basis set of STO's is used directly. In the basis sets employed by Clementi and others (Clementi and Davis, 1966; Schulman and Moskowitz, 1967; Schulman *et al.*, 1967), the η_i are also meant to be representations of STO's, but are usually optimized by means of calculations on atomic systems. The basis sets employed by Whitten (1966) and others differ primarily in the choice of the basis functions g_j, where "lobe functions" are used as the basis set. In these calculations, the g_j may themselves be linear combinations of GTO's. However, regardless of the particular method employed, the contraction of the original GTO basis has been an essential ingredient in making the calculations viable.

A third approach has been employed by the current author and co-workers (Christoffersen, 1971; Christoffersen *et al.*, 1971a,b; Maggiora *et al.*, 1971; Shipman and Christoffersen, 1971) and by Preuss and co-workers (Diercksen and Preuss, 1966, 1967; Janoschek and Preuss, 1967; Janoschek *et al.*, 1967; Preuss, 1968; Preuss and Diercksen, 1967). In this approach, the notion that GTO basis sets must be chosen to mimic exponential orbitals based on nuclei is abandoned, and alternative procedures are chosen. The major departure in these procedures consists in allowing the Gaussians to be placed at points of space other than on nuclei (e.g., in bonding regions). Preuss and co-workers have used a variety of techniques to choose the position and orbital exponent of the various Gaussians, including direct optimization on the molecule of interest, transference of parameters from other molecules, and the arbitrary assignment of parameters.

In the following section, another approach that appears to hold some promise for large molecules is described, which attempts to systematize the choice of position and orbital exponent of the basis Gaussians by means of optimization studies on molecular fragments.

III. Molecular Fragment Approach

One of the benefits of the large number of studies that have been carried out on small molecules is that it has been confirmed that, in practice as well as in principle, the role that electronic and geometric structure play in determining the chemistry of a molecule can be extracted from a sufficiently accurate solution of the Schrödinger equation. Perhaps more interesting, however, are the observations that the prediction of many properties of interest may be made with satisfactory accuracy using very approximate wavefunctions (see Allen and Russell, 1967, and other references contained therein; Freed, 1968; Geratt and Mills, 1968; Hall, 1961; Stanton, 1962). Recent efforts in this laboratory have been directed toward exploiting these observations to investigate whether the techniques of *ab initio* quantum mechanics can be modified or reformulated to include consideration of large molecules.

In order to place in perspective the description of the method to follow, it is appropriate first to consider the goals that were sought for a method that was to be applicable to large molecules:

(1) It should be an *ab initio* procedure, applicable in a practical manner to systems containing ≤ 200 electrons, and ≤ 75 nuclei.

(2) It should be capable of easy modification for improvement of accuracy. This implies that accuracy improvements should be possible without having to discard or substantially alter the framework of the approach.

(3) It should be possible to describe and interpret the results in terms of concepts useful and understandable to other chemists, i.e., it should reflect a high degree of chemical intuition.

(4) It is desirable, but not essential, that the method be capable of describing all molecular properties of interest with equal and acceptable accuracy. However, the self-evident desirability of such a capability must be carefully weighed against the effort needed to attain it using currently available theoretical and computational techniques. In fact, it appears that the previous assumption made by quantum chemists that this could be achieved only through very accurate wavefunctions has probably been a significant barrier in the development of *ab initio* computational techniques that can be applied to large molecules. In addition, this type of "dogma" does not take into account the fact, noted earlier, that many properties can be predicted with acceptable accuracy by the use of a very crude approximation to the true wavefunction.

A. Description of Molecular Fragments

The first step in the method consists of examination of small molecules or molecular fragments that appear in larger systems. The intent is to obtain an adequate description of the electron distribution in these fragments using as small a basis set as possible, but not restricting the basis orbitals to lie on nuclei. Of course, many criteria are possible for judgment of the adequacy of the fragment description. In this approach, some consideration is given to the energetics of the various fragment descriptions, but it should be stressed that the ultimate decision as to the acceptability of a fragment description is obtained by an examination of small- and medium-sized prototype molecules containing the fragment.

The first possibility that has been explored for the description of molecular fragments involves a slight generalization of a method suggested and developed by Frost and co-workers (Chu and Frost, 1971; Frost, 1967a,b, 1968a,b; Frost and Rouse, 1968; Frost *et al.*, 1968; Rouse and Frost, 1969). In this procedure, normalized, floating spherical Gaussian orbitals (FSGO) are used as the basis orbitals, and both the location and size of the FSGO are varied until the energy is minimized. The FSGO are defined as

$$G_i(r) = (2\pi/\rho_i^2)^{3/4} \exp\{-(\mathbf{r} - \mathbf{R}_i)^2/\rho_i^2\}, \tag{4}$$

where ρ_i determines the size of the FSGO (and is often referred to as the orbital radius), and $\mathbf{R}_i$ is the location of the FSGO, relative to some arbitrary origin. It is of interest to note that, in the absence of symmetry, there are four nonlinear parameters to be determined for each FSGO. This restricts the practical utility of the procedure to descriptions involving only a relatively small number of FSGO. For molecular fragments that consist of a closed-shell system of $2N$ electrons, the trial wavefunction is taken to be a single, normalized Slater determinant of doubly occupied, nonorthogonal orbitals, i.e.,

$$\begin{aligned}&\Psi(1, 2, \ldots, 2N)\\ &\quad = \{[(2N)!] \det \Delta\}^{-1/2} \det\{\chi_1(1)\alpha(1)\, \chi_1(2)\beta(2) \cdots \chi_N(2N)\beta(2N)\},\end{aligned} \tag{5}$$

where

$$(\Delta)_{ij} = \int \chi_i^* \chi_j \, dv. \tag{6}$$

In some of the studies, χ_i will be taken to be a single FSGO. In other studies, a "split FSGO" description will be used, in which a linear combination of two FSGO is used for a given χ_i. In this case, both the linear and nonlinear parameters are included in the parameter variations. However, neither of these choices represent restrictions on the method, but rather, are convenient for initial investigations. In fact, they illustrate the ease with which the procedures can be modified to improve the accuracy of the description, if needed.

The other type of molecular fragment that arises contains a single unpaired electron, and the trial wavefunction for this open-shell system is taken to be

$$\begin{aligned}&\Psi(1, 2, \ldots, 2N+1) = \{[(2N+1)!] \det \Delta\}^{-1/2}\\ &\qquad \det\{\chi_1(1)\alpha(1) \cdots \chi_N(2N)\beta(2N)\chi_{N+1}(2N+1)^{\alpha(2N+1)}_{\beta(2N+1)}\},\end{aligned} \tag{7}$$

where the $(N + 1)$st orbital may have either α or β spin.

The general expression for the nonrelativistic electronic energy that results from these choices of trial wavefunctions can be written as

$$E_{\text{el}} = 2\sum_{i=1}^{N+P} \langle i|h|i\rangle - \delta_{P,1}\langle N+1|h|N+1\rangle + \sum_{i=1}^{N+P}\sum_{j=1}^{N}\{2\langle ii|jj\rangle - \langle ij|ji\rangle\}, \tag{8}$$

where

$$P = \begin{cases} 0 & \text{for the } 2N\text{-electron case,} \\ 1 & \text{for the } (2N+1)\text{-electron case,} \end{cases} \tag{9}$$

$$h = -\tfrac{1}{2}\nabla^2 = \sum_{\alpha=1}^{\substack{\text{all} \\ \text{nuclei}}} Z_\alpha/r_\alpha, \tag{10}$$

and

$$\langle ij|kl\rangle = \iint \sigma_i^*(1)\sigma_j(1)r_{12}^{-1}\,\sigma_k^*(2)\sigma_l(2)\,dV_1\,dV_2, \tag{11}$$

where σ_i is a member of an orthonormal basis set. The current method uses a nonorthogonal basis set χ, which can be transformed into an orthonormal basis set $\mathbf{\Omega}$ by means of

$$\mathbf{\Omega} = \chi\Delta^{-1/2}. \tag{12}$$

A list of the molecular fragments that have been found to be useful in the description of molecules consisting of C, N, O, F, and H nuclei is given in Table II. Several comments are appropriate regarding the entries in Table II. First, it is interesting to note that only a relatively small number of molecular fragments are needed in order to form an enormous number of molecules of interest to chemists. Second, the number of independent nonlinear parameters that must be varied is reasonable and tractable in each case. However, it should be noted that simple extension of this notion to large molecules is not possible, since the simultaneous determination of both linear and nonlinear parameters for a large molecule of low symmetry is not a viable possibility at this time.

Third, it is not necessary that the molecular fragments correspond to actual stable molecular species, since they are merely useful constructs that approximately describe a variety of anticipated molecular environments. In fact, the purpose of the hydrogen atoms in these fragments is only to allow determination of the basis-set parameters in a polarized

TABLE II

MOLECULAR FRAGMENTS OF INTEREST

		"Nonsplit" Description		"Split" Description[a]	
Molecular fragment	Common use	No. of FSGO	No. of independent nonlinear parameters	No. of FSGO	No. of independent nonlinear parameters
CH_4 (tetrahedral)	Saturated hydrocarbons	5	3	6	5
$\cdot CH_3$ (planar)	Unsaturated hydrocarbons	6^b	5(4)	7^b	7(6)
$:NH_3$ (tetrahedral)	Amines	5	6	6	8
$:NH_3$ (planar)	Amides, pyrrole	6^b	5(4)	7^b	7(6)
$\cdot NH_2$ (planar)	Pyridine	6^b	8(7)	7^b	10(9)
$\cdot NH_3^+$ (planar)	Pyridinium ion	6^b	5(4)	7^b	7(6)
NH_4^+ (tetrahedral)	Ammonium salts	5	3	6	5
H_2O (bent)	Ethers, alcohols	5	7(6)	6	9(8)
$\cdot OH$ (sp^2)	Carbonyls	6^b	9(7)	7^b	11(10)
H_2O (sp^2)	Furan	6^b	8(7)	7^b	10
$H_3{}^+O$ (planar)	Hydronium ion	6^b	5(4)	7^b	7(6)
HF (tetrahedral)	Fluorides	5	6(5)	7	8(7)

[a] This description corresponds to the use of two FSGO for each inner shell χ_i on heavy atoms (C, N, O, F). An alternative or additional description can be obtained by "splitting" lone-pair orbitals.

[b] These fragments employ the π-orbital description of Eq. (13).

environment, similar to that expected in the large molecule. Consequently, the bond distances and angles chosen for the fragment studies do not necessarily correspond to the values observed for the actual molecule.

Finally, in some of the molecular fragments of interest, orbitals appear which will become π-type orbitals in larger molecules. The particular choice for these orbitals is

$$G_\pi = [2(1 - \Delta_{ud})]^{-1/2}(G_u - G_d), \tag{13}$$

where G_u and G_d are FSGO that are symmetrically placed above and below the central atom, on a line perpendicular to the plane of atoms. The choice of CH distance that has been found convenient for fragments containing these orbitals can be illustrated for $\cdot CH_3$, in which the following procedure was used:

$$R_{CH}(\cdot CH_3) = R_{CH}(CH_4) \cdot \frac{R_{C=C}(C_2H_4)}{R_{C-C}(C_2H_6)}$$

In the determination of optimum parameters for fragments containing π-type orbitals, (e.g., $\cdot CH_3$), a computational difficulty arises. If free variation of all parameters is allowed, the FSGO describing the π-orbital will coalesce onto the central atom (Frost, 1967b). Consequently, these FSGO positions need to be chosen using other considerations. After examination of several possibilities (Christoffersen *et al.*, 1971a), it has been found that a placement of these FSGO at 0.1 bohr above and below the plane of the $\cdot CH_3$ fragment provides a satisfactory compromise between the minimum-energy criterion and the linear-dependence problem. This choice has also been suggested by Frost (1967b).

The optimum parameters for several of the molecular fragments are given in Table III, and the details of the energy-minimization procedure

TABLE III

OPTIMIZED MOLECULAR FRAGMENT DATA[a]

Fragment	Orbital radius (ρ)	Distance from the heavy atom	Molecular parameters
CH_4 (tetrahedral)	$\rho_{CH} = 1.67251562$	1.23379402	$R_{CH} = 2.05982176$
	$\rho_C = 0.32784375$	0.0	$E = -33.98985962$
$\cdot CH_3$ (planar, sp^2)	$\rho_{CH} = 1.51399487$	1.13093139	$R_{CH} = 1.78562447$
	$\rho_C = 0.32682735$	0.0	$E = -33.39001656$
	$\rho_\pi = 1.80394801$	± 0.1	
NH_3 (tetrahedral)	$\rho_{NH} = 1.52791683$	0.87735349	$R_{NH} = 1.91242167$
	$\rho_N = 0.27732014$	0.00099090[b]	$E = -47.46744156$
	$\rho_{L.P.} = 1.58328000$	0.25523498	
$\cdot NH_2$ (sp^2)	$\rho_{NH} = 1.43795015$	0.89783593	$R_{NH} = 1.75153951$
	$\rho_N = 0.27701574$	0.00089020[b]	$E = -47.01983881$
	$\rho_{L.P.} = 1.51385733$	0.30432616	
	$\rho_\pi = 1.35806635$	0.08571429	
NH_3 (planar)	$\rho_{NH} = 1.50617853$	0.95498776	$R_{NH} = 1.93131910$
	$\rho_N = 0.27832598$	0.0	$E = -47.46552515$
	$\rho_\pi = 1.50765136$	0.08571429	

[a] See Shull and Hall (1959). All distances and energies in this paper are reported as unscaled quantities using hartree atomic units.

[b] This position is along a line including the lone pair and the nitrogen atom, and is on the hydrogen side of the nitrogen atom.

have been described earlier (Christoffersen *et al.*, 1971a). The entries in this table correspond to what is believed to be the optimum fragment description for the "nonsplit" basis set of one FSGO for each pair of electrons (with the exception of the π-type orbitals). As indicated earlier, the choice of these particular fragment descriptions was made on the basis of calculations carried out on prototype molecules, assembled from these fragments.

Further details of the characteristics of the various fragment choices will be given in later sections. However, it should be reiterated at this point that one of the distinguishing characteristics of this procedure is that a deliberate attempt has been made to avoid using the Gaussian basis as one which somehow mimics the behavior of STO's. In addition, the potential field in which the basis orbitals are determined is a molecular field (as opposed to the use of atomic calculations for this purpose), with hydrogen atoms serving as an approximation to the environment expected when new bonds are formed.

B. Large Molecule Formation

After the description of the appropriate molecular fragments has been completed, the fragments and their associated FSGO are combined appropriately to form large molecules. This procedure can be considered conveniently as consisting of several steps:

(1) Bring the appropriate molecular fragments and their associated FSGO together to the desired distances and angles.

(2) Remove the extra hydrogen atoms (including their electron) from the Hamiltonian. However, retain the FSGO that were used to describe X–H and Y–H bonds, that will now describe a newly formed X–Y bond (a pair of FSGO for each new bond).

(3) Obtain an optimum molecular orbital description for the molecule for this basis set by the solution of the ordinary SCF equations (Hall, 1951; Roothaan, 1951). In particular, the molecular orbitals can be written as

$$\phi_i = \sum_{A=1}^{P} \sum_{k=1}^{N_A} c_{ki}^A \chi_k^A, \tag{14}$$

where the $\chi_k{}^A$ are the previously determined fragment orbitals, ($\chi_k{}^A \equiv G_k{}^A$ for most studies discussed here), and the summations are taken over all fragments P, and all orbitals within a fragment N_A. Thus, the changes in electronic and geometric structure that are brought about by formation of new bonds are reflected in the MO-coefficients (c_{ki}^A).

This procedure is illustrated pictorially for the formation of ethane from two CH_4 fragments in Fig. 1. As is illustrated in the figure, the basis set is no longer a minimum basis set, and the SCF procedure will improve the energy, giving rise to one virtual orbital and nine filled orbitals in this case. We also see the role of the hydrogen atoms more explicitly through this figure. It should be clear from this example that any one or more of the hydrogen atoms in a molecular fragment may be removed, with the formation of an additional bond with each removal.

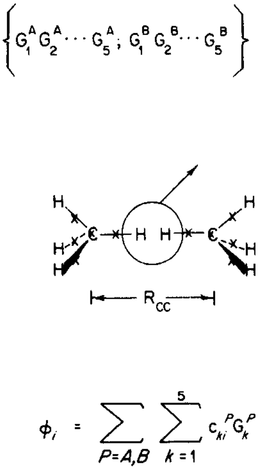


Fig. 1. Formation of ethane from two CH_4 fragments. X denotes the approximate position of the FSGO.

For the closed-shell molecules of interest in these studies, the wave function determined by the SCF procedure has the form

$$\Psi(1, 2, \ldots, 2N) = [(2N)!]^{-1/2} \det\{\phi_1(1)\alpha(1)\phi_1(2)\beta(2) \cdots \phi_N(2N)\beta(2N)\}, \tag{15}$$

and the SCF equations to be solved are given by

$$\mathbf{F}\mathbf{c}_i = \Delta\mathbf{c}_i\,\boldsymbol{\varepsilon}, \tag{16}$$

where

$$(\mathbf{F})_{rs}^{AB} = \langle \chi_r{}^A | h | \chi_s{}^B \rangle + \sum_{C=1}^{Q} \sum_{D=1}^{Q} \sum_{t=1}^{N_C} \sum_{u=1}^{N_D} P_{tu}^{CD} \{ \langle \chi_r{}^A \chi_s{}^B | \chi_t{}^C \chi_u{}^D \rangle - \tfrac{1}{2} \langle \chi_r{}^A \chi_u{}^D | \chi_t{}^C \chi_s{}^B \rangle \}, \tag{17}$$

and ε is a diagonal matrix of orbital eigenvalues. Also, $\mathbf{P}$ is the charge and bond order matrix, defined as

$$P_{tu}^{CD} = 2\sum_{j=1}^{\text{occ}} c_{tj}^{C} c_{uj}^{D}. \tag{18}$$

C. Computational Considerations

Before discussing the results that are obtained by the use of the procedure just described, several comments regarding computational considerations are in order. In fact, the development of procedures in general that are adequate and applicable in a practical manner for large molecules is perhaps a "classic" example of the difference between the solution of a quantum-mechanical problem in principle and in practice. In almost every approach to the treatment of large molecules, at least two aspects of the computational procedure must be considered very carefully. For the procedure considered here, two of the important computational considerations are:

(1) the procedures used for two-electron integral evaluation, and
(2) the efficient manipulation of millions of two-electron integrals in the SCF procedure.

Let us consider the evaluation of integrals over FSGO. The integrals that are most troublesome are the electron repulsion integrals over FSGO, which can be written as

$$\langle ij|kl\rangle = \iint G_i(1)G_j(1)r_{12}^{-1}G_k(2)G_l(2)\,dV_1\,dV_2 \tag{19}$$

where G_i is a normalized FSGO, located at position i. The integral in Eq. (19) can be evaluated analytically (Boys, 1950), and can be written as

$$\langle ij|kl\rangle = N_iN_jN_kN_l\left\{\frac{2\pi^{5/2}}{(a_i+a_j)(a_k+a_l)[a_i+a_j+a_k+a_l]^{1/2}}\right\} \times \exp\left\{-\left(\frac{a_ia_j}{a_i+a_j}\right)\overline{IJ}^2 - \left(\frac{a_ka_l}{a_k+a_l}\right)\overline{KL}^2\right\}F_0(x), \tag{20}$$

where

$$\overline{IJ}^2 = \sum_{t=x,y,z}(I_t-J_t)^2, \qquad \mathbf{I} \equiv \mathbf{R}_i = (I_x, I_y, I_z) \tag{21}$$

$$a_i = 1/\rho_i^2, \qquad N_i = [2/\pi\,\rho_i^2]^{3/4}, \tag{22}$$

$$x = \frac{(a_i + a_j)(a_k + a_l)\overline{PQ}^2}{(a_i + a_j + a_k + a_l)}, \tag{23}$$

$$\overline{PQ}^2 = \sum_{t=x,y,z} (P_t - Q_t)^2, \tag{24}$$

$$\begin{aligned} P_t &= \frac{a_i I_t + a_j J_t}{a_i + a_j}, \qquad t = x, y, z, \\ Q_t &= \frac{a_k K_t + a_l L_t}{a_k + a_l}, \qquad t = x, y, z, \end{aligned} \tag{25}$$

and

$$F_0(x) = \int_0^1 e^{-xu^2}\, du. \tag{26}$$

Several computational aspects of the electron repulsion integral evaluation have been discussed earlier by Shavitt (1963), and several other considerations that have emerged in the current studies are given below.

First, since many intergaussian distances are large in a molecule of the size considered here, there will be a fraction of integrals [Eq. (19)] that will be essentially zero, within the accuracy of the computer. As we shall see shortly, the number of zero integrals is often surprisingly large, and substantial savings in integral evaluation times can be effected by not computing the integrals that are effectively zero. When FSGO are employed, it is a simple matter to establish before calculation of the integral whether or not the integral will be zero due to the position and size of the various FSGO in it. To see this, we rewrite Eq. (20) in the form

$$\langle ij|kl\rangle = K \exp(-v) F_0(x), \tag{27}$$

where

$$K = \frac{2N_i N_j N_k N_l \pi^{5/2}}{(a_i + a_j)(a_k + a_l)(a_i + a_j + a_k + a_l)^{3/2}}, \tag{28}$$

and

$$v = \left(\frac{a_i a_j}{a_i + a_j}\right)\overline{IJ}^2 + \left(\frac{a_k a_l}{a_k + a_l}\right)\overline{KL}^2. \tag{29}$$

Let us assume that an absolute error of less than 10^{-13} is desired in the calculation of $\langle ij|kl\rangle$. It is easily seen from examination of Eq. (26) that

$$0 < F_0(x) \leq 1, \qquad x \geq 0. \tag{30}$$

However, $F_0(x)$ goes to zero so slowly as a function of x $[F_0(x) \sim x^{-1/2}]$ that a test on x to determine whether $F_0(x)$ should be calculated is not a useful test to employ. On the other hand, $\exp(-v) \leq 6 \times 10^{-16}$, when $v \geq 35$. Also, if a minimum value of $a_i \cong 10^{-2}$ is assumed, it is easily seen that

$$K \leq 50. \tag{31}$$

These observations can be combined to provide the desired test. Under worst-case conditions, the integral value will be essentially zero whenever $v \geq 35$, with an error of $\leq 3 \times 10^{-14}$. This test can be made *before* any of the exponential, the constant K, or $F_0(x)$ are calculated, thus reducing the computation times substantially if a significant number of integrals are zero. In the current programs, a test is also performed to establish whether the final value of each "nonzero" integral is $\geq 10^{-13}$. If not, the integral is not stored. This test is useful in eliminating the integrals which are zero by symmetry (e.g., those that are zero due to σ-π interactions).

A detailed estimate of exactly how many integrals will be zero is not easily obtained, since it depends strongly upon the geometry of the large molecule. However, *ad hoc* estimates have been made for several molecules that have been investigated in this laboratory, and are given in Table IV. As is obvious from this table, important economies in calculation of integrals can be effected by implementation of a simple test.

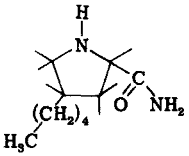
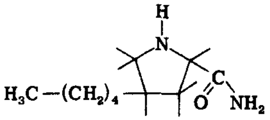
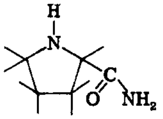
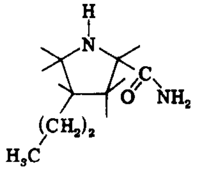
In addition to the noncalculation of zero integrals, it is also important not to use memory or peripheral devices to store the zero integrals. Since the data manipulation problems grow approximately as $(N^4/8)$, where N is the number of basis orbitals, it is important to limit the table of stored integrals to only those that are nonzero. In practice, one usually avoids storing zero integrals by keeping an additional array that indicates how many zero integrals appear between any two nonzero integrals. This additional array adds slightly to the memory requirements, but substantial savings are still possible. In the particular procedure employed in this laboratory, if $2N$ words are required to store N integrals (zero and nonzero) in double precision and f is the fraction of zero integrals, then $3N(1-f)$ words are required to store the nonzero integrals (in double precision) and tabulate where the zeros occur. Thus, when more than one-third of the integrals are zero, a net savings in space occurs.

For those integrals that are nonzero, it is essential that the evaluation of the exponential and $F_0(x)$ be accomplished as rapidly as possible, consistent with the previous accuracy requirements.

The evaluation of $F_0(x)$ is carried out using one of two different procedures (Shipman and Christoffersen, 1971), depending upon the value of

TABLE IV

FRACTION OF ZERO INTEGRALS FOR SEVERAL MOLECULES OF INTEREST

Molecule	Fraction of zero integrals (f)	$F = 3N(1-f)/2N = 3(1-f)/2$
$H_2C=CH_2$	0.43	0.855
	0.55	0.675
	0.56	0.660
	0.149	1.276
	0.389	0.916

the argument x. If $x \geq 28$, an asymptotic formula given by Shavitt (1963) is suitable, i.e.,

$$F_0(x) = \frac{1}{2}\left(\frac{\pi}{x}\right)^{1/2} - \left(\frac{e^{-x}}{2x}\right) \times \left\{1 + \frac{(-1)}{2x} + \frac{(-1)(-3)}{(2x)^2} + \frac{(-1)(-3)(-5)}{(2x)^3} + \cdots + \frac{(-1)(-3)\cdots(-2N+3)}{(2x)^{N-1}}\right\}, \tag{32}$$

where N is the number of terms employed in the asymptotic expansion. Use of this formula guarantees that the relative error will always be less than 8×10^{-14}, since

$$\text{Rel. error} = \left| \frac{F_0(x) - (\pi/x)^{1/2}}{F_0(x)} \right| < \frac{(e^{-x}/2x)}{F_0(x)} < \frac{(e^{-x}/2x)}{\frac{1}{2}(\pi/x)^{1/2} - (e^{-x}/2x)}$$
$$= \frac{1}{e^x(\pi x)^{1/2} - 1}. \tag{33}$$

In the region $0 \leq x < 28$, $F_0(x)$ is approximated by an eight term Chebyshev series in each of several subintervals within three intervals:

$$\begin{aligned} F_0(x) &\cong \sum_{n=0}^{7} a_n T_n(y), \qquad -1 \leq y \leq +1, \\ &= \sum_{n=0}^{7} b_n x^n, \end{aligned} \tag{34}$$

where $T_n(y)$ is the nth order Chebyshev polynomial, and the second form of the series is the rearranged form which is better suited for rapid computation. Also, the various subintervals are mapped onto $-1 \leq y \leq +1$ by the use of

$$y = \frac{m_{ij} - x}{(s_{ij}/2)}, \tag{35}$$

where m_{ij} is the midpoint of subinterval j in interval i, and s_{ij} is the subinterval size. The three intervals that have been found to be convenient are:

$$\begin{aligned} 0 \leq x &< 6.125 && \text{(with 14 subintervals)}, \\ 6.125 \leq x &< 14 && \text{(with 9 subintervals)}, \\ 14 \leq x &< 28 && \text{(with 8 subintervals)}. \end{aligned}$$

Use of this procedure gives a relative error of less than 4×10^{-13} for $0 \leq x < 28$.

Another point concerning numerical procedures is appropriate here. The accuracy of the final eigenvalues and eigenvectors of the SCF procedure will be limited by the accuracy of the various bond distances and angles, which is much less than the approximately seven significant figures which result if single precision arithmetic is employed on most computers. However, when large molecules are studied, the Fock matrices that arise are quite large, (e.g., 100 × 100), and the number of operations that are involved in the formation and diagonalization of the Fock matrix places rather severe requirements on the internal precision that is necessary in order to assure final eigenvalues and eigenvectors whose accuracy is comparable to the bond distances and angles used. Quantitative estimates of the degree of internal precision that is required to achieve this result are difficult to make, since they will depend upon the particular method of coding a given algorithm, as well as computer and programmer idiosyncrasies. However, work in this laboratory indicates that the use of single-precision arithmetic (eight significant figures) does not provide sufficiently high internal precision to give acceptable final results. Consequently, all programs have been written using double precision arithmetic, and the desired accuracy has been obtained successfully for the molecules studied to date.

Even if careful consideration is given to the evaluation of integrals and the precision needed for subsequent manipulation, major problems remain with regard to the SCF portion of the calculation. In fact, the rate-determining step is not the integral evaluation, but in the iterations required for SCF convergence. Two separate problems arise in the SCF iteration sequence. The first of these is whether the initial guess for the **P** matrix is sufficiently close to allow convergence of the SCF procedure to the desired result, and the second is associated with the rate of convergence, i.e., the number of iterations required for convergence.

The studies on hydrocarbons (Christoffersen *et al.*, 1971b) have revealed that satisfactory initial guesses can be obtained by building an initial guess to the **P** matrix of interest from **P** matrices associated with the molecular fragments that are used to form the molecule. Even in cases where the iterative sequence using the "usual" initial guesses fails to converge (e.g., $\mathbf{P} = \mathbf{I}$ or $\mathbf{P} = \mathbf{0}$), use of the **P** matrix formed from the fragments as an initial guess gives rise to a convergent procedure.

The rate of convergence, on the other hand, remains a difficult problem. Use of a good initial guess frequently reduces the number of iterations by one or two, but ~10–15 iterations are often needed to satisfy a convergence criterion of

$$|P_{rs}^{i+1} - P_{rs}^{i}| < 0.00002,$$

for all r and s, where P_{rs}^{i} is the (r, s) element of the **P** matrix associated with the ith iteration. Consequently, much work remains in developing general procedures that can be applied in these calculations to accelerate the rate of convergence.

D. Interpretation of Results

Consistent with the views expressed earlier, the interpretation of the results of these calculations attempts to employ (as far as possible and convenient) concepts and quantities that are related directly to the wave function itself. By this it is meant that, whatever quantity is computed using the wavefunction, it should be done exactly, if possible, in order to keep from introducing approximations in addition to those necessitated earlier (i.e., the model employed and the basis set chosen). Fortunately, there is not a lack of properties that can be employed for comparison purposes. A list of several first-order electronic properties and their corresponding operators that can be used to characterize a molecule once an approximation to its exact wavefunction is available, is given in Table V. In addition to these properties, the use of electron density contours, difference contours, and force constants can also be very helpful in interpreting the charge distribution in molecules.

Differences in total energies are obviously important, but the total energy itself does not seem to be nearly as appropriate as a primary measure of overall wavefunction utility and accuracy as it has been for small molecules. This is due in part to the fact that most total energies, regardless of the procedure employed, will be far above the true energy. In addition, the energy is rather insensitive to the wavefunction, since a first-order change in the wavefunction is accompanied by only a second-order change in the energy. Also, as molecules become larger, the total energy becomes more and more burdened with large (and often chemically uninteresting) contributions from the inner shells. Consequently, other properties, including those given in Table V, may provide more appropriate measures of the balance and utility of a given basis set.

Electron density contours provide a particularly useful source of information concerning the electron distribution in a molecule. Instead of being a weighted average (as the molecular properties of Table V are), resulting from an integration over the entire space of all the electrons that comprise the charge distribution in the molecule, they allow an examination of the details of the electron distribution at specific points or regions in a molecule. This information can be very helpful in rationalizing important characteristics such as the likely points of attack in chemical reactions.

It should be noted that information concerning the details of the total charge distribution are often extracted by the use of the Mulliken population analysis (Mulliken, 1932, 1935, 1949, 1955, 1962), or some modification thereof (e.g. Christoffersen and Baker, 1971). [For other examples of modifications of the Mulliken analysis, see Cusachs and Politzer (1968a,b).] The

TABLE V

PROPERTIES USEFUL FOR CHARACTERIZATION OF MOLECULES

Molecular property	Operator
Molecular dipole moment (at center of mass)	$\mu_\alpha = \sum_K Z_K(\mathbf{R}_K - \mathbf{R}_C)_\alpha - \sum_i (\mathbf{r}_i - \mathbf{R}_C)_\alpha$
Molecular second moment (at center of mass)	$Q_{\alpha\beta} = \sum_K Z_K(\mathbf{R}_K - \mathbf{R}_C)_\alpha(\mathbf{R}_K - \mathbf{R}_C)_\beta - \sum_i (\mathbf{r}_i - \mathbf{R}_C)_\alpha(\mathbf{r}_i - \mathbf{R}_C)_\beta$
Molecular quadrupole moment (at center of mass)	$\Theta_{\alpha\beta} = \frac{1}{2}(3Q_{\alpha\beta} - \delta_{\alpha\beta} \sum_\gamma Q_{\gamma\gamma})$
Potential at a point A	$\Phi(A) = \sum_{K(\neq A)} \frac{Z_K}{\lvert\mathbf{R}_K - \mathbf{R}_A\rvert} - \sum_i \frac{1}{\lvert\mathbf{r}_i - \mathbf{R}_A\rvert}$
Electric field (Hellman–Feynman) at a point A	$\mathscr{E}_\alpha(A) = \sum_{K(\neq A)} \frac{Z_K(\mathbf{R}_K - \mathbf{R}_A)_\alpha}{\lvert\mathbf{R}_K - \mathbf{R}_A\rvert^3} + \sum_i \frac{(\mathbf{r}_i - \mathbf{R}_A)_\alpha}{\lvert\mathbf{r}_i - \mathbf{R}_A\rvert^3}$
Electric field gradient at a point A	$q_{\alpha\beta}(A) = -\sum_{K(\neq A)} Z_K \left\{\frac{3(\mathbf{R}_K - \mathbf{R}_A)_\alpha(\mathbf{R}_K - \mathbf{R}_A)_\beta - \delta_{\alpha\beta}\lvert\mathbf{R}_K - \mathbf{R}_A\rvert^2}{\lvert\mathbf{R}_K - \mathbf{R}_A\rvert^5}\right\} + \sum_i \left\{\frac{3(\mathbf{r}_i - \mathbf{R}_A)_\alpha(\mathbf{r}_i - \mathbf{R}_A)_\beta - \delta_{\alpha\beta}\lvert\mathbf{r}_i - \mathbf{R}_A\rvert^2}{\lvert\mathbf{r}_i - \mathbf{R}_A\rvert^5}\right\}$
One-electron delta function	$\delta(\mathbf{r} - \mathbf{R}_A)$
Nuclear quadrupole coupling constant	$eQ \frac{\partial^2\Phi}{\partial r_{\alpha'}^2} = eQ(-q_{\alpha'\alpha'})$

drawbacks of the use of such an analysis are well known, since the procedure requires an arbitrary division of the charge distribution in order to extract indices for chemical use. On the other hand, electron density contours or difference contours appear to provide a favorable alternative to the Mulliken analysis, since they are calculable directly from the wavefunction.

However, the calculation of electron density contours is a relatively difficult and time-consuming procedure for large molecules. Furthermore, the particular regions of interest in a given molecule may not be apparent at the outset. In these cases, the Mulliken population analysis may prove a useful first step, not as an end in itself, but rather, as a means of defining planes or regions of space that are appropriate for further investigation using density contours.

If the Mulliken analysis is to be used in this manner for the particular method employed here, some modification is required first, to include orbitals that do not lie on nuclei. To do this, we write the electron density at a point **r** in space as

$$\rho(\mathbf{r}) = \sum_i P_{ii} G_i^2(\mathbf{r}) + \sum_{i>j} (2P_{ij} S_{ij}) \left[\frac{G_i(\mathbf{r}) G_j(\mathbf{r})}{\Delta_{ij}} \right], \tag{36}$$

$$= \sum_i n_i d_{ii}(\mathbf{r}) + \sum_{i>j} n_{ij} d_{ij}(\mathbf{r}), \tag{37}$$

where

$$n_i = P_{ii}, \qquad n_{ij} = 2P_{ij} \Delta_{ij}, \qquad \text{and} \qquad d_{ij} = G_i(\mathbf{r}) G_j(\mathbf{r}) / \Delta_{ij} \tag{38}$$

It should be noted that this particular definition of d_{ij} assures that both d_{ii} and d_{ij} are normalized density functions.

In order to employ the Mulliken population analysis, a division of the overlap population (n_{ij}) is necessary. One possible choice that has been found to be useful in these studies is to add the fraction

$$\frac{\int G_{ij} G_i \, dV}{\int G_{ij} G_i \, dV + \int G_{ij} G_j \, dV}$$

to n_i, where G_{ij} is the overlap Gaussian that is formed from the product of G_i and G_j. The remainder of the Mulliken parameters can then be calculated directly. Since these calculations can be carried out quickly and easily, the establishment of planes or regions of interest for further examination can be effected in a reasonably efficient manner.

E. Hydrocarbon Investigations

Much of the emphasis to date has been on examination of hydrocarbons, in order to establish the characteristics of the methods in cases where the complications of lone pairs are not present. In these investigations, the ability of the method to describe three characteristics was investigated:

(1) geometrical structure predictions,
(2) electronic structure predictions, and
(3) the ability to interpret the results in terms of concepts useful to other chemists.

Regarding geometrical considerations, let us consider distance and angle predictions first. Table VI indicates, by means of calculations on specific molecules used as prototypes, the accuracy that might be expected for distance and angle predictions for saturated and unsaturated hydrocarbons. As the entries in the table indicate, the nonsplit representation provides satisfactory results for C=C distance and CCC angle predictions. A split inner-shell description appears necessary in order to predict C–C distances satisfactorily, with the calculated value being 2.82 bohrs for ethane, representing a 2.8% error. These results are very encouraging, for adequate molecular geometry predictions are practically indispensable if the procedure is to be usable as a tool by chemists in general.

TABLE VI

DISTANCE AND ANGLE PREDICTIONS FOR SOME HYDROCARBONS[a]

Prototype molecule	Parameter predicted	Observed value	Calculated value ("Nonsplit" representation)	Error %
Ethane	C–C distance	2.90	2.64	9.0
Ethylene	C=C distance	2.47	2.56	2.8
Propane	∢CCC	110.6°	112.4°	1.6

[a] See Christoffersen *et al.* (1971a) for details.

Another geometrical property that arises from an interaction between molecular fragments is the barrier to internal rotation. For the case of ethane (Christoffersen *et al.*, 1971a), a barrier in the correct direction but whose magnitude is too high is predicted, with the staggered form more stable than the eclipsed form by 5.38 kcal/mole. Furthermore, the magnitude of the error appears to be constant, e.g., in propane the barrier to rotation of a terminal CH_3 group is found to be 5.63 kcal/mole. The slightly higher value of the barrier for propane is consistent with experimental measurements (Kistiakowsky and Rice, 1940; Lide, 1960), indicating that trends in barriers for a series of similar molecules may be extracted from calculations using the molecular fragment method.

Concerning electronic structure predictions, the benzene molecule provides a useful prototype, since several fragments are combined, and a rather large number of different symmetry types are possible for the MO's of the molecule. Consequently, the ability of the procedure to predict the correct ordering of the molecular orbitals (as measured against more accurate calculations) was rather strenuously tested for this case. In fact, this type of test appears to provide a rather sensitive test of the " balance " of a basis set, as will become apparent below. Table VII summarizes the results using the molecular fragment approach, along with comparisons to other types of calculations. Confining our attention for the moment to the non-inner shell "valence" orbitals, we note that the ordering of MO's predicted by the molecular fragment approach is identical to that found by the most accurate study available (Buenker *et al.*, 1968). It is also of interest that extended Hückel theory (Hoffmann, 1963) predicts half of the MO's correctly and INDO (Maggiora, personal communication) predicts the lowest occupied π-orbital to be much too stable, and the other occupied π-orbital to be nearly degenerate with the $3e_{2g}$ orbital. Thus, the desirability of an *ab initio* approach for studying large molecules is again emphasized.

However, the use of *ab initio* techniques does not automatically guarantee the correct determination of electronic structure. For example, the *ab initio* calculations of Schulman and Moskowitz (1965), in which a 48 GTO basis was employed (a 33 % larger basis than used in the molecular fragment approach), predict the ordering correctly for seven of the ten filled orbitals. Consequently, there is a need to maintain the " balance " of the basis set when the size and/or nature is altered, if acceptable results are to be obtained. Additional comments regarding this point will be made later.

In the case of the inner-shell orbitals in the molecular fragment approach, it is not surprising that the ordering is incorrectly predicted. Since the orbitals are nearly degenerate, it is expected that a rather extensive basis may be needed. Also, since the primary energetic deficiency using the molecular fragment approach is in the description of the 1s orbital on the " heavy " atoms, it is not unexpected that the ordering is not correct. It is interesting to note, however, that a similar occurrence sometimes appears even if STO's are employed (Lipscomb, personal communication).

Calculations have also been carried out on a rather large number of benzene and naphthalene isomers (Christoffersen, 1971) and, whenever

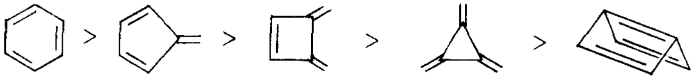
TABLE VII

COMPARISON OF ENERGY LEVEL ORDERING IN BENZENE

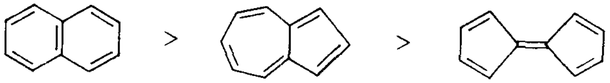
Molecular fragment approach		Extended Hückel Theory (Hoffman, 1963)		INDO (Maggiora, personal communication)		Schulman and Moskowitz (1965)		Buenker *et al.* (1968)	
MO symmetry	$-\varepsilon$	MO symmetry	$-\varepsilon$	MO symmetry	$-\varepsilon$	MO symmetry	$-\varepsilon$	MO symmetry	$-\varepsilon$
$1b_{1u}$	9.454	—	—	—	—	$1a_{1g}$	10.78	$1a_{1g}$	11.35
$1e_{2g}$	9.425	—	—	—	—	$1e_{1u}$	10.77	$1e_{1u}$	11.35
$1e_{1u}$	9.352	—	—	—	—	$1e_{2g}$	10.77	$1e_{2g}$	11.35
$1a_{1g}$	9.268	—	—	—	—	$1b_{1u}$	10.77	$1b_{1u}$	11.35
$2a_{1g}$	1.087	$2a_{1g}$	1.086	$2a_{1g}$	1.9057	$2a_{1g}$	0.9895	$2a_{1g}$	1.173
$2e_{1u}$	0.9686	$2e_{1u}$	0.9476	$2e_{1u}$	1.4096	$2e_{1u}$	0.8909	$2e_{1u}$	1.043
$2e_{2g}$	0.7605	$2e_{2g}$	0.7326	$2e_{2g}$	1.1107	$2e_{2g}$	0.7139	$2e_{2g}$	0.848
$3a_{1g}$	0.5848	$2b_{1u}$	0.6101	$3a_{1g}$	1.0553	$3a_{1g}$	0.5709	$3a_{1g}$	0.741
$2b_{1u}$	0.5566	$3a_{1g}$	0.6092	$1a_{2u}(\pi)$	0.8424	$2b_{1u}$	0.5625	$2b_{1u}$	0.674
$1b_{2u}$	0.5031	$3e_{1u}$	0.5379	$2b_{1u}$	0.7649	$3e_{1u}$	0.4792	$1b_{2u}$	0.660
$3e_{1u}$	0.4783	$1a_{2u}(\pi)$	0.5330	$1b_{2u}$	0.7198	$1a_{2u}(\pi)$	0.4519	$3e_{1u}$	0.626
$1a_{2u}(\pi)$	0.3915	$1b_{2u}$	0.5254	$3e_{1u}$	0.6847	$1b_{2u}$	0.4482	$1a_{2u}(\pi)$	0.538
$3e_{2g}$	0.3900	$3e_{2g}$	0.4718	$3e_{2g}$	0.5002	$3e_{2g}$	0.3742	$3e_{2g}$	0.526
$1e_{1g}(\pi)$	0.2169	$1e_{1g}(\pi)$	0.4703	$1e_{1g}(\pi)$	0.4909	$1e_{1g}(\pi)$	0.2877	$1e_{1g}(\pi)$	0.379
$1e_{2u}(\pi)$	−0.2913	$1e_{2u}(\pi)$	−0.3067	$1e_{2u}(\pi^*)$	−0.1690	$1e_{2u}(\pi)$	−0.1923	$1e_{2u}(\pi)$	−0.139
$1b_{2g}(\pi)$	−0.5441	—	—	$2b_{2u}$	−0.2575	$1b_{2g}(\pi)$	−0.4101	$1b_{2g}(\pi)$	−0.372
$E_T = -197.364$ hartrees						$E_T = -219.706$ hartrees		$E_T = -230.375$ hartrees	

comparisons are possible, the molecular orbital structure has been found to be in essentially exact agreement with the most accurate calculations available. Consequently, the prediction of electronic structure for valence MO's of hydrocarbons appears to be one of the properties that is quite reliable.

Concerning other comparisons of interest to chemists, the relative stability of the various isomers can be easily extracted by simple comparisons of total energies. The relative order of stability that emerges for the benzene isomers (Christoffersen, 1971) is



and for the naphthalene isomers (Christoffersen, 1971) is



In addition to these results, the importance of the σ-orbitals to the results also becomes clear. As shown in Figs. 2 and 3, the molecular orbital structure in each case except the open chain analogue shows a heterogeneous and considerable interspersing of σ- and π-orbitals. Consequently, calculations of electronic structure must include explicit consideration of all σ-orbitals, if reliable conclusions are to be drawn.

The interspersing of σ- and π-orbitals can also be used to rationalize the notion of aromaticity, without the introduction of hypothetical reference molecules. In particular, this concept has arisen as a means of explaining the differences in stability of various ring compounds from corresponding molecules in which all of the orbitals are localized. Since it is the π-orbitals that are involved primarily in this phenomenom, a comparison of the stability of the π-orbitals and their role in the overall molecular structure in various isomers should provide an acceptable framework for the discussion. It must be emphasized at the outset, however, that the relative energies of the π-orbitals are strongly dependent upon the particular σ and nuclear environment that is present, and all effects must be considered simultaneously, if useful results are to be obtained. It should also be noted that, since aromaticity is a concept that is concerned primarily with π-orbitals, the aromaticities of a set of molecules need not necessarily parallel the ordering of overall stability of the molecules.

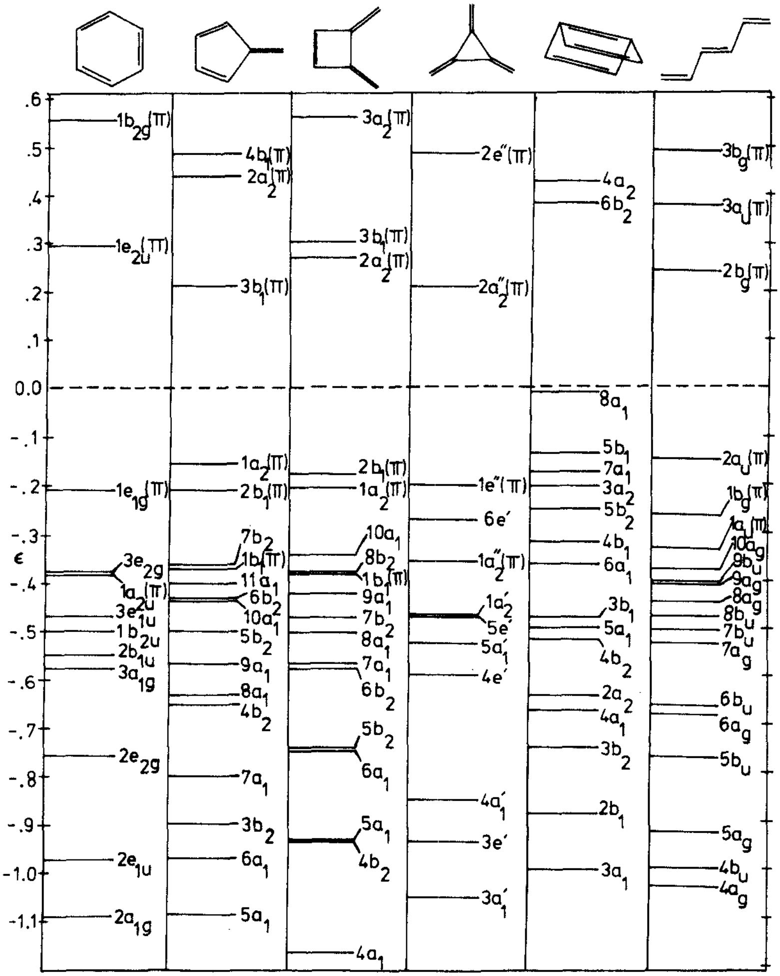


Fig. 2. Valence molecular orbital structure for benzene isomers and hexatriene.

Comparing hexatriene to the benzene isomers in Fig. 2, we note first that the filled π-orbitals in hexatriene all lie above the filled σ-orbitals, and appear relatively unperturbed by the σ and nuclear environment. In fulvene, however, the π-orbitals have been affected sufficiently by their particular environment to stabilize the highest π-orbital, destabilize the second highest π-orbital, and stabilize the lowest π-orbital sufficiently to exchange its

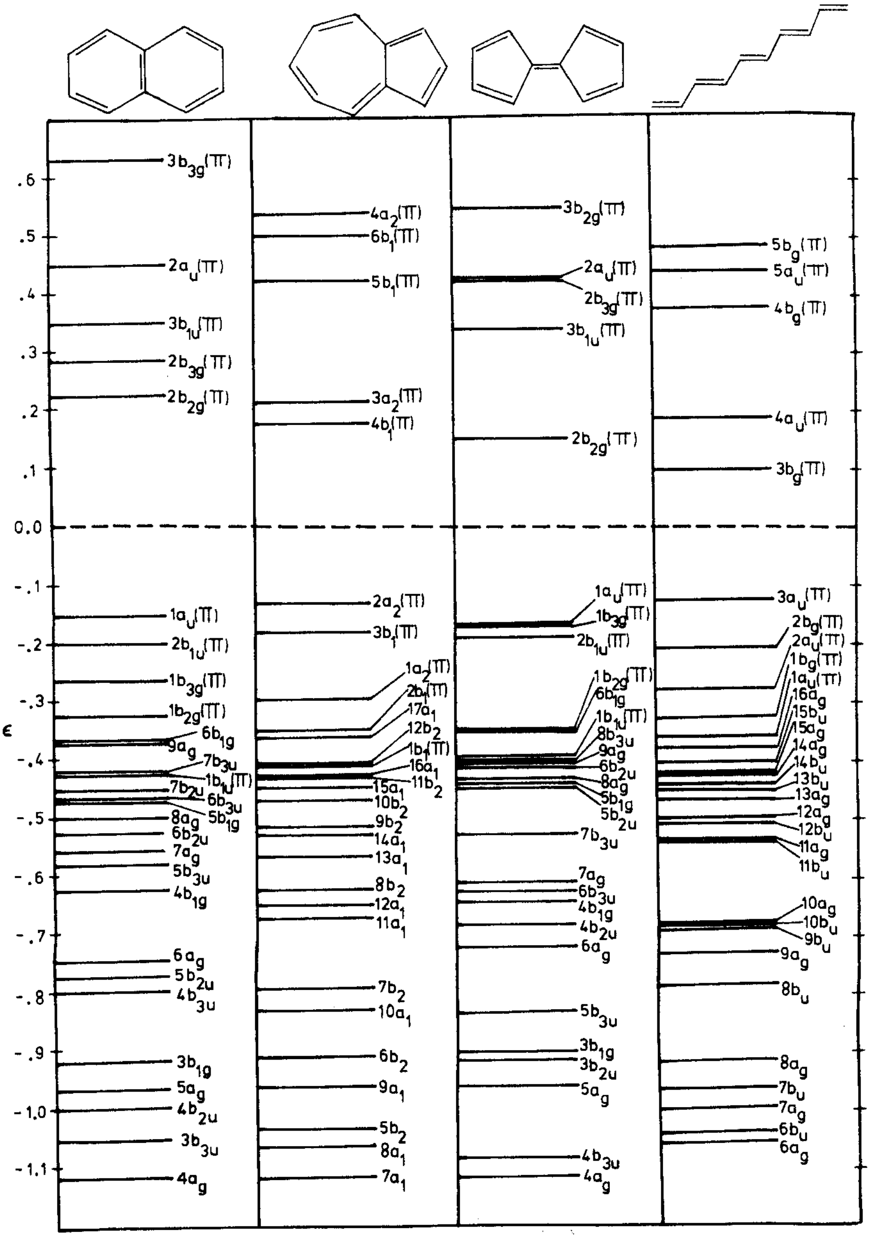


Fig. 3. Valence molecular orbital structure for naphthalene isomers and decapentaene.

position, relative to the highest filled σ-orbital ($7b_2$). In 2,3-dimethylenecyclobutene, trimethylenecyclopropane, and benzene, the set of π-orbitals is affected to an even greater extent, with the most obvious of these effects being the interspersing of a pair of π-orbitals between the lowest π-orbitals. In the naphthalene series, similar observations can be made. In decapentaene, the π-orbitals all appear separated from the σ-orbitals. In fulvalene, one σ-orbital is interspersed between the lowest π-orbitals, while in azulene, two σ-orbitals are interspersed, and in naphthalene three σ-orbitals are interspersed between the lowest π-orbitals. Consequently, a qualitative understanding of the aromaticity of these molecules appears to emerge from an examination of the relative ordering of molecular orbitals.

A quantitative measure of this effect can be made in several ways, depending upon the choice of reference molecule. The open-chain analog provides one possibility (Christoffersen, 1971), but its use in general is mitigated against by the difficulty of choice of open-chain analog in molecules where heteroatoms are present. Another possibility is to compare only molecules which are isomeric. In this case, the sum of all the filled π-orbital energies provides perhaps the simplest and most convenient quantitative measure, since all of the filled π-orbitals contribute to the aromaticity. If one of the isomers is chosen as the reference, then a measure of the aromaticity of one of the isomers (M), relative to the reference isomer, can be defined arbitrarily as:

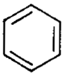
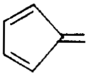
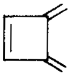
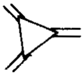
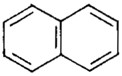
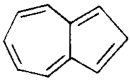
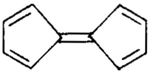
$$A = \left\{1.000 - \left[\frac{E_\pi(\text{ref.}) - E_\pi(\text{M})}{E_\pi(\text{ref})}\right]\right\} * 10, \tag{39}$$

where $E_\pi(i)$ is the sum of the occupied π-orbital energies of the ith isomer. Using benzene and naphthalene as the reference molecules, the aromaticities of the benzene and naphthalene isomers are given in Table VIII. The naphthalene isomers provide no particular surprises, with the decrease in aromaticity paralleling the decrease in overall stability. However, the benzene isomer, fulvene, is quite interesting, since its aromaticity is considerably less than the three- and four-membered ring isomers, even though its total stability is greater than either of these isomers.

Another quantitative measure is also given in Table VIII, which allows comparison between the benzene and naphthalene isomers. This measure, the π-electron energy divided by the number of π-electrons, shows that benzene and naphthalene are about equal in aromaticity, and that fulvene and fulvalene are the least aromatic of these molecules. Regardless of which procedure is chosen to quantify the notion, the point of importance

TABLE VIII

AROMATICITIES OF BENZENE AND NAPHTHALENE ISOMERS

Molecule	Aromaticity (A)[a]	E_π (per π-electron) (hartrees)
	10.000	−0.2751
	9.097	−0.2503
	9.318	−0.2563
	9.222	−0.2537
	10.000	−0.2754
	9.942	−0.2738
	9.173	−0.2526

[a] Calculated by the use of Eq. (39).

is that an examination of the electronic structure of the molecules themselves, without introduction of hypothetical reference molecules, can be used to investigate the concept of aromaticity.

Another concept of chemical interest has also emerged from these studies. This concept involves the transferability of fragment data from one calculation to another. In particular, the calculations on unsaturated hydrocarbons, all of which employ only the $\cdot CH_3$ fragment, have been analyzed to ascertain whether there are portions of the **P** matrix [Eq. (18)] that can be identified as transferable from one molecule to another (Christoffersen *et al.*, 1971b). Two kinds of **P** matrix elements can be distinguished. The first of these, referred to as intrafragment **P**-matrix elements, are shown in Fig. 4. When the various molecules were examined, several of these elements showed remarkable constancy, as indicated in Table IX. The other intrafragment elements are not expected to be constant, since they are ones that are involved with the replacement of CH bonds by CC bonds. However, for the nonconstant intrafragment elements, as well as the important interfragment elements, a simple parameterization procedure involving only the variable R (the bond length of the CC bond to formed) can be used to obtain reliable estimates for those elements. The equation representing this parametrization procedure can be written as

$$P = a\exp[-(bR - c)] + d \tag{40}$$

$$\mathrm{P}\,(\mathrm{CH_3}) = \begin{pmatrix} P_{\mathrm{I,I}} & P_{\mathrm{I,CH1}} & P_{\mathrm{I,CH2}} & P_{\mathrm{I,CH3}} & P_{\mathrm{I},\pi} \\ P_{\mathrm{CH1,I}} & P_{\mathrm{CH1,CH1}} & P_{\mathrm{CH1,CH2}} & P_{\mathrm{CH1,CH3}} & P_{\mathrm{CH1},\pi} \\ P_{\mathrm{CH2,I}} & P_{\mathrm{CH2,CH1}} & P_{\mathrm{CH2,CH2}} & P_{\mathrm{CH2,CH3}} & P_{\mathrm{CH2},\pi} \\ P_{\mathrm{CH3,I}} & P_{\mathrm{CH3,CH1}} & P_{\mathrm{CH3,CH2}} & P_{\mathrm{CH3,CH3}} & P_{\mathrm{CH3},\pi} \\ P_{\pi,\mathrm{I}} & P_{\pi,\mathrm{CH1}} & P_{\pi,\mathrm{CH2}} & P_{\pi,\mathrm{CH3}} & P_{\pi,\pi} \end{pmatrix}$$

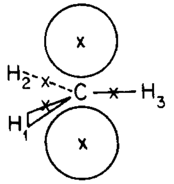


Fig. 4. P-matrix elements of the $\cdot\mathrm{CH_3}$ fragment.

TABLE IX

TRANSFERABILITY OF $\cdot\mathrm{CH_3}$ P-MATRIX ELEMENTS

Matrix element	Average value	No. of points	Variance
$P_{\mathrm{I,I}}$	1.891	31	0.0011
$P_{\mathrm{CH,CH}}$	2.801	23	0.0084
$P_{\pi,\pi}$	0.719	27	0.0069
$P_{\mathrm{I,CH}}$	−0.272	21	0.0005
$P_{\mathrm{CH,CH'}}$	−0.7721	5	0.0005

where *a*, *b*, *c*, and *d* are constants that were fit using a least-squares procedure to existing **P** matrix data.

It is also of interest to note that inclusion of only nearest-neighbor interfragment **P**-matrix estimates appear to be important. This observation, along with the previously mentioned intrafragment interactions, indicate that the molecular fragment model allows a localized interpretation to be given that corresponds well to chemical notions of transferable localized quantities, characteristic of similar chemical environments.

Finally, several first-order molecular properties have been calculated (Maggiora *et al.*, 1971) using the operators of Table V, in order to assess the capability of these small basis sets to predict properties other than the total energy. Summarizing the results of this study, several of these properties, especially regarding trends, appear to be calculated reliably. In particular, the Hellmann–Feynman electric fields (Hellmann, 1937; Feynman, 1939) at the various atoms are quite good, giving accuracies comparable to very extensive calculations where the basis orbitals are restricted to lie on nuclei. In addition to these quantities, relative values of the electric potential and the molecular quadrupole moment (for unsaturated molecules) appear to be satisfactorily calculated.

Properties that are described poorly using these wavefunctions include the one-electron delta function and the electric field gradient. Of course, this is not unexpected, since the nuclear cusp and electronic behavior very near the nuclei are the characteristics most lacking in the wavefunctions formed from the simple FSGO basis.

F. Heteroatom Investigations

The studies to date on molecules containing heteroatoms such as nitrogen and oxygen have been limited primarily, but not exclusively, to reasonably small prototype molecules. This allows consideration of several fragment possibilities, in order to choose the most satisfactory description of small molecules before proceeding to large molecules. The primary difference, and source of complication, that arises in these is the introduction of one or more lone pairs into the molecular fragment.

Considering the fragments involving nitrogen as illustrative of the difficulties associated with heteroatom studies, several observations can be made from these preliminary investigations. Regarding geometrical predictions, the results are, on the whole, similar to those obtained for hydrocarbons. For example, the C–N distance (prototype molecule: methyl amine) is predicted to within 3.2% of the experimental value, the C=N distance (prototype molecule: methylene imine) is predicted to within 1.6%

of an average C=N value, and the CNC angle (prototype molecule: dimethyl amine) is predicted to within 9.1% of the experimental value. Examination of the latter result suggests that perhaps a "split" description of the lone-pair orbital is desirable. This observation also arises for the case of rotation barriers (e.g., N_2H_4).

Regarding electronic structure predictions, the results are generally in excellent agreement with more extensive calculations, even though the total energies are considerably above those of more extensive calculations. Examples of pyrrole and pyridine are given in Tables X and XI. As is

TABLE X

ELECTRONIC STRUCTURE COMPARISONS FOR PYRROLE

Molecular fragment approach[a]		Clementi *et al.* (1967)	
MO Symmetry	$-\varepsilon$	MO Symmetry	$-\varepsilon$
$1a_1$	13.2164	$1a_1$	15.7100
$1b_2$	9.4232	$1b_2$	11.4253
$2a_1$	9.4079	$2a_1$	11.4252
$3a_1$	9.3371	$3a_1$	11.3793
$2b_2$	9.2488	$2b_2$	11.3785
$4a_1$	1.2794	$4a_1$	1.3239
$5a_1$	0.9820	$5a_1$	1.0955
$3b_2$	0.9141	$3b_2$	1.0344
$6a_1$	0.7120	$6a_1$	0.8251
$4b_2$	0.6720	$4b_2$	0.7970
$7a_1$	0.6228	$7a_1$	0.7779
$8a_1$	0.4732	$8a_1$	0.6476
$5b_2$	0.4477	$1b_2(\pi)$	0.6313
$1b_1(\pi)$	0.4260	$5b_2$	0.6243
$6b_2$	0.4256	$6b_2$	0.6022
$9a_1$	0.3948	$9a_1$	0.5766
$2b_1(\pi)$	0.1879	$2b_1(\pi)$	0.4253
$1a_2(\pi)$	0.1532	$1a_2(\pi)$	0.3879
$3b_1(\pi^*)$	−0.3856	$3b_1(\pi^*)$	
$2a_2(\pi^*)$	−0.4461	$2a_2(\pi^*)$	
$E_T = -178.34748$ hartrees		$E_T = -207.93135$ hartrees	

[a] Fragment parameters taken from Table III.

TABLE XI

ELECTRONIC STRUCTURE COMPARISONS FOR PYRIDINE

Molecular fragment approach[a]		Clementi (1967a)		Petke *et al.* (1968)	
M.O. Symmetry	$-\varepsilon$	M.O. Symmetry	$-\varepsilon$	M.O. Symmetry	$-\varepsilon$
$1a_1$	13.0871	$1a_1$	15.6776	$1a_1$	15.6391
$1b_2$	9.4301	$1b_2$	11.4612	$1b_2$	11.4067
$2a_1$	9.4251	$2a_1$	11.4611	$2a_1$	11.4067
$2b_2$	9.3070	$3a_1$	11.4430	$3a_1$	11.3880
$3a_1$	9.2840	$2b_2$	11.4344	$2b_2$	11.3801
$4a_1$	9.2283	$4a_1$	11.4343	$4a_1$	11.3800
$5a_1$	1.2389	$5a_1$	1.3277	$5a_1$	1.2952
$6a_1$	1.0534	$6a_1$	1.1577	$6a_1$	1.1283
$3b_2$	0.9829	$3b_2$	1.1103	$3b_2$	1.0750
$7a_1$	0.7951	$7a_1$	0.9218	$7a_1$	0.8912
$4b_2$	0.7881	$4b_2$	0.9044	$4b_2$	0.8844
$8a_1$	0.5955	$8a_1$	0.7792	$8a_1$	0.7602
$9a_1$	0.5659	$5b_2$	0.7260	$9a_1$	0.6945
$5b_2$	0.5433	$9a_1$	0.7012	$5b_2$	0.6914
$6b_2$	0.4850	$6b_2$	0.6700	$6b_2$	0.6483
$10a_1$	0.4529	$10a_1$	0.6394	$10a_1$	0.6193
$1b_1(\pi)$	0.4364	$1b_1(\pi)$	0.6223	$1b_1(\pi)$	0.5816
$7b_2$	0.4065	$7b_2$	0.5795	$7b_2$	0.5563
$2b_1(\pi)$	0.2675	$11a_1$	0.4654	$11a_1$	0.4425
$11a_1$	0.2408	$2b_1(\pi)$	0.4586	$2b_1(\pi)$	0.4260
$1a_2(\pi)$	0.2328	$1a_2(\pi)$	0.4473	$1a_2(\pi)$	0.4062
$2a_2(\pi^*)$	−0.2783			$2a_2(\pi^*)$	−0.1099
$3b_1(\pi^*)$	−0.2817			$3b_1(\pi^*)$	−0.1107
$E_T = -210.47796$ hartrees		$E_T = -245.62194$ hartrees		$E_T = -246.32653$ hartrees	

[a] Fragment parameters taken from Table III.

apparent from examination of these tables, the only places where discrepancies in the ordering of valence molecular orbitals occur are where lone-pair orbitals are involved. In particular, the ($5b_2$, $1b_1(\pi)$) pair are switched in pyrrole, and the ($11a_1$, $2b_1(\pi)$) pair in pyridine are switched, when compared to the most accurate calculations available. Consequently, even though these results are of a preliminary nature, they suggest that the introduction of lone pairs does not present significant difficulties, although it may be desirable to employ a "split" description of lone-pair orbitals in order to assure satisfactory geometric and electronic structure predictions.

IV. Discussion

One of the striking features of the calculations on large molecules that have been carried out to date is that investigations at the "large" end of the large molecule scale (~200 electrons, as considered here) are practically nonexistent. Consequently, the practical applicability of any of the methods to deal with large molecules must be considered to be an open question at this point. The characteristics that have already emerged, however, are suggestive of what to expect.

In the case of the use of STO basis sets, the rapid and accurate evaluation of integrals still remains a major stumbling block that must be overcome if reliable and practical calculations are to be carried out on large molecules. In the case of GTO approximations to atomic orbitals, the main problem is the one associated with the data management of the large number of orbitals involved. These restrictions, with current technology, will probably be too severe to allow practical application of any of these methods to large molecules. Indeed, a procedure that required that an IBM 360/195 be dedicated for eight days (Clementi *et al.*, 1971) in order to carry out calculations on a 136 electron system cannot be considered to be of practical utility!

On the other hand, the methods employing small basis sets that do not attempt to mimic STO behavior, such as the molecular fragment approach, do appear to be extendable to large systems. However, the problem in this case is the accuracy to be expected of the results. Clearly, not all properties can be expected to be predicted accurately (e.g., total energy). The results on the systems studied to date allow some optimism that other properties of chemical interest (e.g., electronic structure and geometry) may be predicted adequately. The difficulty is that the ultimate proof of acceptability of the approach must be on the basis of "exhaustion," i.e., examination of a large number of cases with satisfactory results. Since very little data is available at the current time, the reliability of this approach for large molecule studies cannot be finally assessed.

Among the other observations that are possible concerning large molecule investigations, perhaps the most appropriate are those concerning the criteria by which a calculation is evaluated. Since a close approach to even the Hartree–Fock result for most large molecules is not a viable possibility at this point, it does not seem appropriate to use the total energy as the primary measure of wavefunction utility. Indeed, a low total energy may simply reflect a good description of the heavy atom inner shell orbitals, although the valence orbitals may be poorly described.

Instead, other measures of overall basis set "balance" are appropriate, and a variety of possibilities can be used for this purpose. The guiding principle, however, perhaps ought to be that the measure of wavefunction "balance" needs to reflect a *relative* (not absolute) quantity. Several examples of properties that reflect the relative balance of the description include: (1) molecular geometry, including bond distances, bond angles, and barriers to rotation; (2) electronic structure (e.g., MO ordering): (3) force constants; (4) electron density contours; (5) properties depending upon energy differences; and (6) first-order electronic properties. These properties also have the advantage, in the case where Gaussians are employed, that they do not require *additional* approximations in order to interpret the wavefunction.

It is difficult to say which, if any, of the procedures currently under development will ultimately be of greatest usefulness. In fact, the difficulty of this recommendation coupled with the lack of substantive amounts of data for large molecules only underscores the need for substantial further efforts in this area. A successful development in this area would indeed be of great interest to nearly all chemists, for it would provide a new "probe" for the investigation of important topics such as the reactivity of molecules (e.g., points of attack), the mechanism of chemical reactions (e.g., transition state studies), and the microscopic modeling of intermolecular interactions (e.g., solvent effects).

GLOSSARY

CNDO: Complete Neglect of Differential Overlap
EHT: Extended Hückel Theory
FSGO: Floating Spherical Gaussian Orbitals
GTO: Gaussian-Type Orbitals
INDO: Intermediate Neglect of Differential Overlap
MCZDO: Multi-Center Zero Differential Overlap
NEMO: Non-Empirical Molecular Orbital (Theory)
STO: Slater-Type Orbitals

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