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Some Recent Advances in Density Matrix Theory

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CONTENTS

I. DENSITY MATRIX

1. Historical Background. Thermodynamic Applications

THIS review is concerned mainly with applications of density matrix theory to the quantum mechanical N-electron problem, in which the system of interest —atom, molecule, or crystal—is assumed to be in a definite eigenstate. The density matrix was, on the other hand, first developed and used in statistical thermodynamics, in which the system of interest is less completely specified and is described by a representative ensemble. The same basic theory (von Neumann[1]; Dirac[2]) applies to both situations, but much progress has been made recently in the study of N-particle systems as a result of the introduction of *reduced* density matrices (Husimi[3]) which determine the *internal* particle distribution functions.

Before proceeding to the N-particle problem, we therefore review very briefly the general nature of the theory and its application in thermodynamics.

1.1. Formulation. Pure States

We are concerned with nonrelativistic quantum mechanics based upon the Schrödinger equation

$$\mathcal{H}\Psi_t(q,t) = -(\hbar/i)(\partial/\partial t)\Psi_t(q,t), \qquad (1)$$

which describes the time development of a system with wave function $\Psi_t(q,t)$. Here q denotes the set $q_1, q_2, \cdots q_n$ of position coordinates and $\mathcal{H}$ is the usual Hamiltonian operator, formed from the classical Hamiltonian by the association[4]

$$q_j \rightarrow q_j, \quad p_j \rightarrow (\hbar/i)(\partial/\partial q_j),$$

p_j being the momentum coordinate conjugate to q_j. $\Psi_t(q,t)$ is a function of the coordinates q_j and the time t such that

$$\Psi_t^*(q_1,\cdots q_n,t)\Psi_t(q_1,\cdots q_n,t)dq_1\cdots dq_n$$

is the probability that the coordinates will simultaneously have values in the ranges (q_1, q_1+dq_1), (q_2, q_2+dq_2), $\cdots (q_n, q_n+dq_n)$.

Equation (1) has solutions of the form $\Psi_t(q,t) = \Psi(q)T(t)$, where $T(t) = \exp(-iEt/\hbar)$, provided $\Psi(q)$ satisfies the time-independent wave equation

$$\mathcal{H}\Psi = E\Psi, \qquad (2)$$

where E is the separation parameter. Well-behaved solutions of (2) exist only for certain values of E: these eigenvalues are the energies for which the system can exist in *stationary states* with $\Psi_t^*(q,t)\Psi_t(q,t) = \Psi^*(q)\Psi(q)$ (time independent).

It is convenient to express $\Psi_t(q,t)$ and $\Psi(q)$ in terms of a complete orthonormal set

$$\Phi_1(q), \Phi_2(q), \Phi_3(q), \cdots \Phi_n(q), \cdots,$$

thus

$$\Psi_t(q,t) = \sum_\kappa C_\kappa(t)\Phi_\kappa(q), \quad \Psi(q) = \sum_\kappa C_\kappa\Phi_\kappa(q). \qquad (3)$$

Orthonormality is expressed by

$$(\Phi_\kappa|\Phi_\lambda) = \int \Phi_\kappa^*(q)\Phi_\lambda(q)dq = \delta_{\kappa\lambda}. \qquad (4)$$

The Dirac-type notation for this scalar product is often abbreviated even further to the symbolic product $\Phi_\kappa^*\Phi_\lambda$.

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[1] J. von Neumann, Nachr. Akad. wiss. Gottingen, Math. physik. Kl. IIa. Math. physik. chem. Abt. **1927**, 245.

[2] P. A. M. Dirac, Proc. Cambridge, Phil. Soc. **25**, 62 (1929); **26**, 376 (1930); **27**, 240 (1931).

[3] K. Husimi, Proc. Phys. Math. Soc. Japan **22**, 264 (1940).

[4] Generally, it may be assumed that the q's are supplemented by spin variables. $\mathcal{H}$ must also be supplemented by nonclassical spin terms, but for many purposes these are negligible and the operator may be assumed spin free.

With $\mathcal{H}$ is associated a matrix **H** with elements

$$H_{\kappa\lambda}=(\Phi_\kappa|\mathcal{H}|\Phi_\lambda)=\int\Phi_\kappa^*(q)\mathcal{H}\Phi_\lambda(q)dq, \tag{5}$$

and Eqs. (1) and (2) then take matrix forms

$$\mathbf{HC}=-(\hbar/i)(d\mathbf{C}/dt)\quad\text{(time-dependent state)}, \tag{6}$$

$$\mathbf{HC}=E\mathbf{C}\quad\text{(stationary state)}, \tag{7}$$

where **C** is the column matrix of components, $C_1, \cdots C_\kappa, \cdots$. Equation (3) may also be abbreviated to

$$\Psi=\mathbf{\Phi C}, \tag{8}$$

where $\mathbf{\Phi}$ is the row matrix $(\Phi_1\Phi_2\cdots\Phi_\kappa\cdots)$ and Ψ, Φ_κ are the vectors or elements of Hilbert space represented by $\Psi(q)$ and $\Phi_\kappa(q)$. It is assumed, for convenience, that the basis is discrete.

We also use integral operators. $A(q;q')$ is called the kernal of an integral operator if it produces from $\Phi(q)$ a new function, denoted by $\mathcal{A}\Phi(q)$, according to

$$\mathcal{A}\Phi(q)=\int A(q;q')\Phi(q')dq'. \tag{9}$$

This serves to define an operator $\mathcal{A}$ which operates on Φ to give $\mathcal{A}\Phi$; $A(q;q')$ is the representative of this operator. With any pair of functions $\Phi_\kappa(q)$, $\Phi_\lambda(q)$, we may associate an integral operator $\mathcal{A}$ with kernal $\Phi_\kappa(q)\Phi_\lambda^*(q')$. This has the property that

$$\mathcal{A}\Phi(q)=\Phi_\kappa(q)\int\Phi_\lambda^*(q')\Phi(q')dq'=\Phi_\kappa(q)(\Phi_\lambda^*\Phi) \tag{10}$$

and may thus be expressed symbolically by $\mathcal{A}=\Phi_\kappa\Phi_\lambda^*$ (starred symbol on the *right*): for then the analog of (10) is simply

$$\mathcal{A}\Phi=(\Phi_\kappa\Phi_\lambda^*)\Phi=\Phi_\kappa(\Phi_\kappa^*\Phi). \tag{11}$$

An operator of this kind is called a dyad—a term borrowed from elementary vector algebra—and any operator in the space spanned by $\Phi_1, \Phi_2, \cdots\Phi_\kappa, \cdots$ can be written as a sum of dyads, a dyadic,

$$\mathcal{A}=\sum_{\kappa,\lambda}\Phi_\kappa A_{\kappa\lambda}\Phi_\lambda^*\quad\left(=\sum_{\kappa,\lambda}A_{\kappa\lambda}\Phi_\kappa\Phi_\lambda^*\right), \tag{12}$$

in which the numerical coefficients are simply the matrix elements of the operator, defined by (5). To verify this we need only note

$$(\Phi_\mu|\mathcal{A}|\Phi_\nu)=\Phi_\mu^*\Big(\sum_{\kappa,\lambda}\Phi_\kappa A_{\kappa\lambda}\Phi_\lambda^*\Big)\Phi_\nu=A_{\mu\nu}\quad[\text{by (4)}].$$

The reader accustomed to Dirac notation[5] will notice that $\Psi\equiv|\,\rangle$ and $\Psi^*\equiv\langle\,|$. The scalar product $\langle\,|\,\rangle$ is identical with $\Psi^*\Psi$ (starred symbol on the *left*) while the operator $|\,\rangle\langle\,|$, with representative $\langle q|\,\rangle\langle\,|q'\rangle$ is identical with $\Psi\Psi^*$ (starred symbol on the *right*), with representative $\Psi(q)\Psi^*(q')$. The notation is otherwise familiar: $\mathcal{A}$ is the operator associated with a dynamical quantity A; **A** is its matrix representative with elements $A_{\kappa\lambda}=(\Phi_\kappa|\mathcal{A}|\Phi_\lambda)$ in the discrete basis $\mathbf{\Phi}=(\Phi_1\Phi_2, \cdots\Phi_\kappa, \cdots)$; and $A(q;q')$ is the "matrix element" of $\mathcal{A}$ in a continuous representation, i.e., the integral operator kernal associated with $\mathcal{A}$. (When lower case script is not available, German letters are substituted.)

1.2. Density Matrix. Pure States

The density operator for a system known to be in state Ψ_K (i.e., for a pure state) may be defined symbolically by

$$\rho^{KK}=\Psi_K\Psi_K^*,\quad \rho^{KK}\Phi=(\Psi_K\Psi_K^*)\Phi=\Psi_K(\Psi_K^*\Phi), \tag{13}$$

where Φ is an arbitrary state vector. Since the scalar product is just a number, ρ^{KK} always produces a multiple of Ψ_K: it is the *projection operator* associated with state K and (assuming Ψ_K is normalized) has the characteristic property $\rho^{KK}\rho^{KK}=\rho^{KK}$. In the Schrödinger representation, ρ^{KK} is represented by an integral operator:

$$\rho(KK|q;q')=\Psi_K(q)\Psi_K^*(q')$$

and

$$\rho^{KK}\Phi(q)=\int\rho(KK|q;q')\Phi(q')dq'=\Psi_K(q)\cdot\Psi_K^*\Phi. \tag{14}$$

$\rho(KK|q;q')$ is usually called the density matrix,[6] q and q' taking the place of subscripts, and in density matrix theory the wave function $\Psi_K(q)$ is eliminated in favor of $\rho(KK|q;q')$. Thus, the expectation value in state K of any quantity A, with operator $\mathcal{A}$, becomes

$$\begin{aligned}(\Psi_K|\mathcal{A}|\Psi_K)&=\int\Psi_K^*(q)\mathcal{A}\Psi_K(q)dq\\&=\int[\mathcal{A}\rho(KK|q;q')]_{q'\to q}dq,\end{aligned} \tag{15}$$

where $\mathcal{A}$ works on the unprimed variables and the prime is removed *after* the operation. This procedure is analogous to taking the trace of a matrix and may be abbreviated to

$$(\Psi_K|\mathcal{A}|\Psi_K)=\operatorname{tr}\mathcal{A}\rho(KK|q;q'). \tag{16}$$

An *off*-diagonal element of $\mathcal{A}$, between states K and L, may similarly be written

$$(\Psi_L|\mathcal{A}|\Psi_K)=\operatorname{tr}\mathcal{A}\rho(KL|q;q'), \tag{17}$$

where

$$\rho(KL|q;q')=\Psi_K(q)\Psi_L^*(q') \tag{18}$$

is a *transition* density matrix for the two states.

When $\Phi_K(q)$ is expanded according to (3), it follows that

$$\rho^{KK}\to\rho(KK|q;q')=\sum_{\kappa,\lambda}\rho^{KK}{}_{\kappa\lambda}\Phi_\kappa(q)\Phi_\lambda^*(q'),$$

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[5] P. A. M. Dirac, *The Principles of Quantum Mechanics* (Oxford University Press, New York, 1947), third edition.

[6] The term "density *kernal*" would be preferable.

where (19)

$$\boldsymbol{\varrho}^{KK}=\mathbf{C}^K\mathbf{C}^{K\dagger},$$

and in this case the expectation value, Eq. (15), becomes

$$(\Psi_\kappa|\mathcal{A}|\Psi_\kappa)=\sum_{\kappa,\lambda} A_{\lambda\kappa}\rho_{\kappa\lambda}{}^{KK}=\text{tr}\,\mathbf{A}\boldsymbol{\varrho}, \qquad (20)$$

a trace in the usual matrix sense. Similarly, the matrix element of $\mathcal{A}$ between states K and L is (note the order of K, L)

$$(\Psi_L|\mathcal{A}|\Psi_K)=\text{tr}\,\mathbf{A}\boldsymbol{\varrho}^{KL},$$

where (21)

$$\boldsymbol{\varrho}^{KL}=\mathbf{C}^K\mathbf{C}^{L\dagger}.$$

The density matrix $\boldsymbol{\varrho}^{KK}$, referred to the Φ basis, is obviously idempotent:

$$\mathbf{C}^{KK}\mathbf{C}^{KK}=\mathbf{C}^K\mathbf{C}^{K\dagger}\mathbf{C}^K\mathbf{C}^{K\dagger}=\mathbf{C}^K\mathbf{C}^{K\dagger}=\boldsymbol{\varrho}^{KK},$$

since $\mathbf{C}^{K\dagger}\mathbf{C}^K=\mathbf{1}$ when Ψ_K is normalized. For states which are orthogonal (i.e., mutually exclusive), $\boldsymbol{\varrho}^{KK}\boldsymbol{\varrho}^{LL}=\mathbf{0}$, since $\mathbf{C}^{K\dagger}\mathbf{C}^L=\mathbf{0}$ expresses the orthogonality. For a system in a definite *stationary* state K, Eq. (7) can evidently be written

$$\mathbf{H}\boldsymbol{\varrho}^{KK}=E_K\boldsymbol{\varrho}^{KK}, \quad \boldsymbol{\varrho}^{KK}\boldsymbol{\varrho}^{KK}=\boldsymbol{\varrho}^{KK} \quad (\text{tr}\,\boldsymbol{\varrho}^{KK}=1). \qquad (22)$$

We show later that this is also *sufficient* to define a stationary state.

1.3. *Ensembles. Thermodynamics*

Suppose now that we have incomplete knowledge of a dynamical system, the probabilities of finding it in states Ψ_A, Ψ_B, $\cdots\Psi_K$, $\cdots$ (which need not even be stationary states, though they must be orthogonal in order to be mutually exclusive) being p_A, p_B, $\cdots p_K$, $\cdots$. This situation (a "mixed" state) is described by an associated "ensemble" of identical systems of which a fraction p_K are definitely in state K. The expectation value of A in this "mixed state" is then an ensemble average

$$\langle A\rangle_{\text{av}}=\sum_K p_K(\Psi_K|\mathcal{A}|\Psi_K).$$

This is neatly expressed by defining the density operator for a mixed state by

$$\rho=\sum_K p_K\rho^{KK}$$

or (23)

$$\rho(q;q')=\sum_K p_K\rho(KK|q;q');$$

for then

$$\langle A\rangle_{\text{av}}=\sum_K p_K\int[\mathcal{A}\rho(KK|q;q')]_{q'\to q}dq$$

$$=\int[\mathcal{A}\rho(q;q')]_{q'\to q}dq=\text{tr}\,\mathcal{A}\rho(q;q'). \qquad (24)$$

In a matrix representation,

$$\langle A\rangle_{\text{av}}=\text{tr}\,\mathbf{A}\boldsymbol{\varrho}, \quad \boldsymbol{\varrho}=\sum_K p_K\boldsymbol{\varrho}^{KK}. \qquad (25)$$

The original formulation of quantum mechanics is in this way extended to admit incompletely specified states and ensemble averaging.

The time development of the density matrix (23), where the ρ^{KK} may, in general, refer to arbitrary nonstationary states, is easily determined by using the matrix form (25): for

$$\rho_{\kappa\lambda}=\sum_K p_K\rho^{KK}{}_{\kappa\lambda}=\sum_K p_K C^K{}_\kappa C^K{}_\lambda{}^*$$

and thus

$$\rho(q;q')=\sum_{\kappa,\lambda}\rho_{\kappa\lambda}\Phi_\kappa(q)\Phi_\lambda{}^*(q'),$$

where (26)

$$\boldsymbol{\varrho}=\mathbf{CpC}^\dagger,$$

in which $\mathbf{C}$ is the matrix whose Kth column is $\mathbf{C}^K$ and $\mathbf{p}$ is a diagonal matrix of ensemble weights p_K. From (6) we then have

$$\mathbf{HC}=-(\hbar/i)(d\mathbf{C}/dt) \quad\text{and}\quad \mathbf{C}^\dagger\mathbf{H}=+(\hbar/i)(d\mathbf{C}^\dagger/dt),$$

while the p_K are simply constants defining the initial condition of the ensemble; and hence the density matrix at any subsequent time is determined by

$$d\boldsymbol{\varrho}/dt=-(i/\hbar)(\mathbf{H}\boldsymbol{\varrho}-\boldsymbol{\varrho}\mathbf{H}). \qquad (27)$$

Thus, *ensemble* stationary states, in which the initial degree of uncertainty in all quantities persists without change, can occur provided $\boldsymbol{\varrho}$ and $\mathbf{H}$ commute. The condition that the ensemble be *pure* [i.e., described by $p_K=1$, $p_L=0$ $(L\neq K)$], as well as stationary, is

$$\boldsymbol{\varrho}^2=\boldsymbol{\varrho} \quad (\text{tr}\,\boldsymbol{\varrho}=1).$$

It is easily shown (Appendix) that this is the necessary and sufficient condition that $\boldsymbol{\varrho}$ can be written in the form $\mathbf{C}^K\mathbf{C}^{K\dagger}$, where $\mathbf{C}^K$ is a *column* matrix; and this means that $\mathbf{p}$ has a single nonvanishing element (unity) in the Kth place. The necessary and sufficient conditions that a system be in energy eigenstate Ψ_K are thus

$$\mathbf{H}\boldsymbol{\varrho}-\boldsymbol{\varrho}\mathbf{H}=\mathbf{0}, \quad \boldsymbol{\varrho}^2=\boldsymbol{\varrho} \quad (\text{tr}\,\boldsymbol{\varrho}=1). \qquad (28)$$

The solution $\boldsymbol{\varrho}=\boldsymbol{\varrho}^{KK}$ then satisfies (22) in which, since $E=\text{tr}\,\mathbf{H}\boldsymbol{\varrho}$,

$$E_K=\text{tr}\,\mathbf{H}\boldsymbol{\varrho}^{KK}.$$

In thermodynamic applications it is useful to consider ensembles in which the states Ψ_K are energy eigenstates, so that $\mathbf{HC}^K=E_K\mathbf{C}^K$. The ensemble is then stationary for any choice of the p_K, K indicating the constants of the motion in state K. One such choice is

$$p_K=\exp(\alpha-\beta E_K), \qquad (29)$$

which defines the "canonical" ensemble, and this turns out to be appropriate for the description of a system in thermal equilibrium. The argument is well known and is not reproduced in detail (see, for example, Tolman,[7] ter Haar[8,9]). By considering a quasi-static change in the system parameters (volume, etc.) which occur in $\mathcal{H}$, it is possible to devise a quantum mechanical analog of the empirical laws of thermodynamics, in which the ensemble expectation value of $\mathcal{H}$ is identified with the mean internal energy U in thermal equilibrium. The parameter β is found to be an integrating factor of the quantity $dQ=dU-dW$, where W is the work done on the system during the change, and may thus be identified with $1/kT$, where T is the absolute thermodynamic temperature and k is a constant (the Boltzmann constant). It is also found that the quantity, S say, whose differential is dQ/T may be expressed as

$$S=-k\sum_K p_K \log p_K, \tag{30}$$

and, by simple rearrangement, that

$$F=U-TS=-kT\log(\sum_K \exp -E_K/kT)$$
$$=-kT\log Z,\quad\text{say.} \tag{31}$$

Since the trace of a matrix is invariant under a unitary transformation, the sum may be expressed alternatively as

$$Z=\sum_K \exp -E_K/kT=\operatorname{tr}\exp(-\mathbf{H}/kT), \tag{32}$$

where $\mathbf{H}$ is the matrix associated with $\mathcal{H}$ in *any* basis $\boldsymbol{\Phi}$, and the function is interpreted as the series. This also may be written

$$Z=\sum_\kappa (\Phi_\kappa|\exp(-\mathcal{H}/kT)|\Phi_\kappa), \tag{33}$$

the basis again being arbitrary. The operator form of the partition function has been used extensively in statistical mechanics (for an example, see Wilson[10]).

For a thorough discussion of the basis of ensemble theory, with an extensive bibliography, see a recent review by ter Haar.[9]

2. N-Particle Systems

In dealing with systems of noninteracting particles, it is possible to replace the virtual ensemble by a real ensemble which is stationary when the N particles occupy N of the one-particle eigenstates. When no two states are the same (Fermi-Dirac case), the condition for a pure state, $\boldsymbol{\varrho}^2=\boldsymbol{\varrho}$ (tr $\boldsymbol{\varrho}=1$), is replaced by

$$\boldsymbol{\varrho}^2=\boldsymbol{\varrho}\quad(\operatorname{tr}\boldsymbol{\varrho}=N), \tag{34}$$

for this means that $\mathbf{p}$ has N unit elements (new normalization), since it is the condition that $\boldsymbol{\varrho}$ can be written in the form $\mathbf{CC}^\dagger$ where $\mathbf{C}$ consists of N orthonormal columns—each representing a different eigenstate. $E=\operatorname{tr}\mathbf{H}\boldsymbol{\varrho}$ (where $\mathbf{H}$ is the 1-particle Hamiltonian) is then the *total* energy of the N particles, and the ensemble is completely characterized by

$$\mathbf{H}\boldsymbol{\varrho}-\boldsymbol{\varrho}\mathbf{H}=\mathbf{0},\quad \boldsymbol{\varrho}^2=\boldsymbol{\varrho}\quad(\operatorname{tr}\boldsymbol{\varrho}=N). \tag{35}$$

For strongly interacting particles, this description is not legitimate: we must deal with the system *as a whole.* To obtain information about its constituent parts (particles), it is necessary to introduce *reduced* density matrices. Husimi[3] has treated systems of bosons and fermions at an arbitrary temperature, ensemble weights being given by (29) from this point of view; but only in the case of weak interaction, where each Ψ_K is assumed to be a *single* symmetrized or antisymmetrized product function. We are interested mainly in the pure energy eigenstates of an N-electron system where the interactions are strong and a single antisymmetrized product is not a satisfactory description of the state.

2.1. Reduced Density Matrices

We consider the case of an N-electron system in a stationary state $\Psi=\Psi_K$, where the label K is now suppressed. Similar considerations can be applied to mixed states, corresponding to a macroscopic system in thermal equilibrium at an arbitrary temperature (see, e.g., M. Born and H. S. Green,[11] but are not required in the present context. The density operator is now defined by (13) and (14): abbreviating the N sets of variables describing the N particles to 1, 2, $\cdots N$, we write

$$\rho(q;q')=\rho(1,\cdots N;1',\cdots N')$$
$$=\Psi(1,\cdots N)\Psi^*(1',\cdots N'). \tag{36}$$

The diagonal element, for which $1'=1, 2'=2, \cdots N'=N$, then determines the probability that the variables of the first particle lie in volume element $d\tau_1$, those of the second simultaneously in $d\tau_2$, etc. Now, for indistinguishable particles,

$$\mathcal{P}\rho(1,\cdots N;1',\cdots N')=\rho(1,\cdots N;1',\cdots N'),$$

where $\mathcal{P}$ permutes the sets 1, 2, $\cdots N$ (primed and unprimed) and, for instance, $\rho(2,1,\cdots N;2,1,\cdots N)$ means that the variables of the first particle take the values previously associated with the second, etc. Consequently, the symbols 1, $\cdots N$ refer merely to N different volume elements while their places, which in principle indicate the particles referred to, are arbitrary owing to the symmetry. The probability that the N particles will occupy simultaneously N selected volume elements $d\tau_1$, $d\tau_2$, $\cdots d\tau_N$ at points 1, 2, $\cdots N$, *in any order*, is then

$$[\rho(1,2,\cdots N;1,2,\cdots N)+\rho(2,1,\cdots N;2,1,\cdots N)$$
$$+\cdots]d\tau_1 d\tau_2\cdots d\tau_N=N!\rho(1,2,\cdots N;1,2,\cdots N).$$

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[7] R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, New York, 1938).

[8] D. ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, Inc., New York, 1954).

[9] D. ter Haar, Revs. Modern Phys. 27, 289 (1955).

[10] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1953), second edition, p. 160.

[11] M. Born and H. S. Green, Proc. Roy. Soc. (London) **A191**, 168 (1947).

It is convenient to introduce an *N-particle* density matrix, whose diagonal element is this quantity, simply by renormalizing the *system* density matrix. We define

$$\rho_N(1,2,\cdots N;1',2',\cdots N') = N!\Psi(1,2,\cdots N)\Psi^*(1',2',\cdots N'). \quad (37)$$

Similarly, it is possible to define[3,12–14] a *reduced* density matrix whose diagonal element determines the probability of finding any n of the N particles, in any order, at n selected points 1, 2, $\cdots n$ of configuration space. The n-particle density matrix is

$$\rho_n(1,2,\cdots n;1',2',\cdots n') = N(N-1)\cdots(N-n+1)\int\Psi(1,\cdots N) \times\Psi^*(1',\cdots n',n+1,\cdots N)d\tau_{n+1}\cdots d\tau_N. \quad (38)$$

On removing the primes, the integral is seen to give the probability of the first n sets of variables having specific values; but the n sets can be selected in $N(N-1)\cdots\times(N-n+1)$ different ways, corresponding to the occupation of the same points by different particles, and each gives the same result by symmetry. Only the aggregate is physically significant. The 1- and 2-particle density matrices

$$\rho_1(1;1') = N\int\Psi(1,2,\cdots N) \times\Psi^*(1',2,\cdots N)d\tau_2 d\tau_3\cdots d\tau_N, \quad (39)$$

$$\rho_2(1,2;1',2') = N(N-1)\int\Psi(1,2,3,\cdots N) \times\Psi^*(1',2',3,\cdots N)d\tau_3\cdots d\tau_N \quad (40)$$

are of particular importance; thus $\rho_1(1;1)d\tau_1$ is the probability of finding a particle with variables in the range $d\tau_1$ at point 1 in configuration space. It should be noted that $\rho_1(1;1)$ integrates to N (not 1), and that it is therefore the "number density." The relationship between successive density matrices is seen to be

$$(N-n)\rho_n(1,2,\cdots n;1',2',\cdots n') = \int\rho_{n+1}(1,2,\cdots n,n+1; \times 1',2',\cdots n',n+1)d\tau_{n+1}. \quad (41)$$

The calculation of matrix elements of operators which involve all particles symmetrically is immediate once the density matrices have been determined. Thus, the expectation value of any n-electron operator $\mathcal{A}(1,2,\cdots n)$ is independent of the names of the variables, and any symmetrical sum

$$\sum_{(n)}^{N}{}'\,\mathcal{A} = \sum_{i,j,\cdots=1}^{N}{}'\,\mathcal{A}(i,j,\cdots) \quad (42)$$

in which there are $N(N-1)\cdots(N-n+1)$ selections of the n different[15] variables i, j, $\cdots$, has an expectation value

$$(\Psi|\sum_{(n)}^{N}{}'\,\mathcal{A}|\Psi) = \int[\mathcal{A}(1,\cdots n)\rho_n(1,\cdots n;1',\cdots n')]_{1'\to1,\ldots n'\to n}d\tau_1\cdots d\tau_n = \mathrm{tr}\,\mathcal{A}\rho_n(1,\cdots n;1',\cdots n'). \quad (43)$$

The usual Hamiltonian operator

$$\mathcal{H}(1,\cdots N) = \sum_{i=1}^{N}\mathfrak{h}(i) + \tfrac{1}{2}\sum_{i,j=1}^{N}{}'\,g(i,j),$$

where (44)

$$\mathfrak{h}(i) = -(\hbar^2/2m)\nabla^2(i) + V(i), \quad g(i,j) = e^2/r_{ij},$$

contains two such sums and, accordingly, in state Ψ,

$$E = (\Psi|\mathcal{H}|\Psi) = \mathrm{tr}\,\mathfrak{h}(1)\rho_1(1;1') + \tfrac{1}{2}\,\mathrm{tr}\,g(1,2)\rho_2(1,2;1',2'). \quad (45)$$

Here g and V are simply multipliers and the script notation is accordingly discarded.

It is possible to reduce transition density matrices, defined by any two N-electron functions, in exactly the same way. When Ψ is given by (8), the energy follows from (20) as

$$E = \mathrm{tr}\,\mathbf{H}\boldsymbol{\varrho} = \sum_{\kappa,\lambda} H_{\lambda\kappa}\rho_{\kappa\lambda} \quad (\boldsymbol{\varrho} = \mathbf{C}\mathbf{C}^\dagger), \quad (46)$$

and if, by comparison with (17) and (18), a formal transition density matrix is defined for any pair of functions Φ_κ and Φ_λ by

$$\rho_N(\kappa\lambda|1,\cdots N;1',\cdots N') = N!\Phi_\kappa(1,\cdots N)\Phi_\lambda^*(1',\cdots N'), \quad (47)$$

with reduced transition matrices

$$\rho_n(\kappa\lambda|1,\cdots n;1',\cdots n') = N(N-1)\cdots(N-n+1)\int\Phi_\kappa(1,\cdots N) \times\Phi_\lambda^*(1',\cdots n',n+1,\cdots N)d\tau_{n+1}\cdots d\tau_N, \quad (48)$$

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[12] R. McWeeny, Tech. Rept. No. 7, Solid State and Molecular Theory Group, Massachusetts Institute of Technology (May 1, 1955).

[13] R. McWeeny, Proc. Roy. Soc. (London) **A232**, 114 (1954) (see also ibid. **A223**, 63 (1954)).

[14] P.-O. Löwdin, Phys.Rev. **97**, 1474 (1955). (It should be noted that Löwdin's reduced density matrices differ by a factor of $n!$ from those defined in the other papers.)

[15] Omission of terms for which $i=j$, etc. are indicated throughout by a prime on the summation sign. We use $\mathcal{A}(1,2,\cdots n)$ for an operator which works on the variables, 1, 2, $\cdots$; thus $\nabla^2(i)$ is used in preference to ∇_i^2.

then $H_{\lambda\kappa}$ itself is

$$H_{\lambda\kappa}=(\Phi_\lambda|\mathcal{H}|\Phi_\kappa)=\operatorname{tr}\mathfrak{h}(1)\rho_1(\kappa\lambda|1;1')+\tfrac{1}{2}\operatorname{tr}g(1,2)\rho_2(\kappa\lambda|1,2;1',2'). \quad (49)$$

The n-electron density matrix in state Ψ is then, from (38) [cf. (19)],

$$\rho_n(1,\cdots n;1',\cdots n')=\sum_{\kappa,\lambda}\rho_{\kappa\lambda}\rho_n(\kappa\lambda|1,\cdots n;1',\cdots n'). \quad (50)$$

The reduced density matrices are defined without reference to any specific operator but are conveniently calculated by evaluating the matrix element of a symmetrical operator such as $\sum'_{i,j=1}{}^N g(i,j)$. Thus $\rho_2(\kappa\lambda|1,2;1',2')$ is simply the coefficient of $g(1,2)$ in the integrand of

$$(\Phi_\lambda|\sum_{i,j=1}^{N}{}' g(i,j)|\Phi_\kappa)=\int\Phi_\lambda^*(1,\cdots N)[\sum_{i,j=1}^{N}{}' g(i,j)]\Phi_\kappa(1,\cdots N)d\tau_1\cdots d\tau_N$$

$$=\int g(1,2)\rho_2(\kappa\lambda|1,2;1,2)d\tau_1 d\tau_2, \quad (51)$$

with primes restored to the variables in those factors which come from $\Phi_\lambda^*(1,\cdots N)$.

2.2. *Spinless Density Matrices. Correlation*

For many purposes the simultaneous values of particle spins are of secondary importance, and it is convenient to introduce spinless density matrices. These are defined[12,13] simply by

$$P_n(1,\cdots n;1',\cdots n')=\int[\rho_n(1,\cdots n;1',\cdots n')]_{\omega_1'\to\omega_1,\cdots\omega_n'\to\omega_n}d\omega_1\cdots d\omega_n, \quad (52)$$

where $\int d\omega_i$ indicates integration over the ith spin variable and the arguments in P_n are now spatial variables only.

The diagonal elements $P_n(1,\cdots n;1,\cdots n)$, which are conveniently abbreviated to $P_n(1,\cdots n)$, are simply distribution functions:

$P_n(1,\cdots n)dv_1\cdots dv_n$
= probability of finding any n particles, in any order, in volume elements $dv_1\cdots dv_n$ at points $1,\cdots n$. (53)

Thus $P_1(1)$ is the charge (or "number") density function and integrates to N, while $P_2(1,2)$ is the pair function.

Provided all operators are spinless, the spin integrations are immediate and the results of the preceding section may be rewritten with ρ_n replaced by P_n and $d\tau_i$ by dv_i. Thus, (45) becomes

$$E=\operatorname{tr}\mathfrak{h}(1)P_1(1;1')+\tfrac{1}{2}\operatorname{tr}g(1,2)P_2(1,2;1',2')$$

$$=\int[-(\hbar^2/2m)\nabla^2(1)P_1(1;1')]_{1'\to1}dv_1+\int V(1)P_1(1)dv_1+\tfrac{1}{2}\int g(1,2)P_2(1,2)dv_1dv_2$$

$$=T+V_e+V_{ee}, \quad (54)$$

where T is the expectation value of the kinetic energy; V_e is the total potential energy of the individual electrons in the given potential field and is identical with that of a static "charge cloud" of density $P_1(1)$; and V_{ee} has a corresponding classical interpretation as the average interaction energy of particles distributed with pair function $P_2(1,2)$. This immediate pictorial interpretation, which admits considerable development, is characteristic of a density matrix approach.

2.3. *Correlation*

To a first approximation it would be expected that the motion of one electron would be independent of the *instantaneous* positions of the others, though the form of $P_1(1)$ would certainly reflect the *average* effect of $N-1$ other electrons. In this case, where the particles might be described as quasi-independent, we should have

$$P_2(1,2)=P_1(1)P_1(2),$$

the multiplicative law for the simultaneous occurrence of two independent events. No properly antisymmetric wave function can, however, give such a result. Generally,

$$P_2(1,2)=P_1(1)P_2(2)+C(1,2),$$

where $C(1,2)$ describes the departure from quasi-independence due to *correlation* between the motions of the two particles. It is convenient to write

$$P_2(1,2)=P_1(1)P_1(2)[1+f(1,2)], \quad (55)$$

where $f(1,2)$ is a correlation factor. The *conditional* probability of finding a particle at point 2, when one is known to be at point 1, is then, by elementary probability theory,

$$P_2(1,2)/P_1(1)=P_1(2)[1+f(1,2)]. \quad (56)$$

The presence of a particle at point 1 therefore changes the probability of finding a particle at a second point, 2, by a fractional amount $f(1,2)$ and an absolute amount $P_1(2)f(1,2)$. Mutual repulsion between the particles results in a correlation factor which is negative for $2\to1$, and which therefore makes a "hole" in the 1-particle probability function, surrounding any point at which a particle is already supposed to be and of depth $P_1(2)f(1,2)$. To examine the main properties of the correlation hole, it is necessary to resolve the spinless density matrices into parts associated with the various possible spin configurations.

The most general 1-particle density matrix may be written

$$\begin{aligned}\rho_1(1;1') &= P_1(\overset{\alpha}{1};\overset{\alpha}{1'})\alpha(1)\alpha^*(1')+P_1(\overset{\alpha}{1};\overset{\beta}{1'})\alpha(1)\beta^*(1')\\ &\quad +P_1(\overset{\beta}{1};\overset{\alpha}{1'})\beta(1)\alpha^*(1')+P_1(\overset{\beta}{1};\overset{\beta}{1'})\beta(1)\beta^*(1'),\end{aligned} \tag{57}$$

since any quantity which operates on the spins can be written in this form by suitable choice of the dyad coefficients—which depend on spatial coordinates alone. From (53) it then follows that

$$P_1(\overset{\alpha}{1};\overset{\alpha}{1})$$

must be interpreted as the probability of a particle being at point 1 in spin state α, and

$$P_1(\overset{\beta}{1};\overset{\beta}{1})$$

as the probability of its being there in spin state β. It is easily seen that in any state where the z component of total spin is definite, the other two components

$$P_1(\overset{\alpha}{1};\overset{\beta}{1'}) \quad \text{and} \quad P_1(\overset{\beta}{1};\overset{\alpha}{1'})$$

must vanish: for if the wave function is expanded in terms of spin products, each containing the same number of α and the same number of β factors, the $(N-1)$ spin integrations which lead to $\rho_1(1;\,1')$ introduce zeros (orthogonality) unless the products from Ψ and Ψ^* match in all spin factors. With the usual abbreviation for the diagonal elements,

$$P_1(1)=P_1(\overset{\alpha}{1})+P_1(\overset{\beta}{1}). \tag{58}$$

In the same way, the 2-particle density matrix may be written

$$\begin{aligned}\rho_2(1,2;1',2') &= P_2(\overset{\alpha}{1},\overset{\alpha}{2};\overset{\alpha}{1'},\overset{\alpha}{2'})\alpha(1)\alpha(2)\alpha^*(1')\alpha^*(2')\\ &\quad +P_2(\overset{\alpha}{1},\overset{\beta}{2};\overset{\alpha}{1'},\overset{\beta}{2'})\alpha(1)\beta(2)\alpha^*(1')\beta^*(2')\\ &\quad +P_2(\overset{\beta}{1},\overset{\alpha}{2};\overset{\beta}{1'},\overset{\alpha}{2'})\beta(1)\alpha(2)\beta^*(1')\alpha^*(2')\\ &\quad +P_2(\overset{\beta}{1},\overset{\beta}{2};\overset{\beta}{1'},\overset{\beta}{2'})\beta(1)\beta(2)\beta^*(1')\beta^*(2')\\ &\quad +\text{etc.},\end{aligned} \tag{59}$$

where the terms not shown, although present, give zero contributions to $P_2(1,2;1'2')$ and to the matrix elements of all spinless operators. Thus, integrating over spins, the pair function is

$$P_2(1,2)=P_2(\overset{\alpha}{1},\overset{\alpha}{2})+P_2(\overset{\alpha}{1},\overset{\beta}{2})+P_2(\overset{\beta}{1},\overset{\alpha}{2})+P_2(\overset{\beta}{1},\overset{\beta}{2}), \tag{60}$$

where, for instance

$$P_2(\overset{\alpha}{1},\overset{\beta}{2})$$

determines the probability of finding a particle in volume element at point 1, in spin state α, and another simultaneously at point 2, in spin state β. Again it is useful to introduce correlation factors, putting, for example,

$$P_2(\overset{\alpha}{1},\overset{\beta}{2})=P_1(\overset{\alpha}{1})P_1(\overset{\beta}{2})[1+f(\overset{\alpha}{1},\overset{\beta}{2})]. \tag{61}$$

The correlation factors then have two important general properties. In the first place, the antisymmetry of $\rho_2(1,2;1',2')$ in each separate pair of variables implies, from (59), that $P_2(1,2;1',2')$ and $P_2(1,2;1',2')$ each have a similar antisymmetry—owing to the symmetry of the spin products to which they are attached. This means that for $2\rightarrow 1$, the pair functions for particles of like spin both tend to zero and [cf. (61)]

$$2\rightarrow 1\colon\quad f(\overset{\alpha}{1},\overset{\alpha}{2})\rightarrow -1,\quad f(\overset{\beta}{1},\overset{\beta}{2})\rightarrow -1. \tag{62}$$

There is, therefore, a 100% negative correlation which prevents particles of like spin being found at the same point in space. This is the most general statement of the Pauli principle and is completely independent of the form of the wave function.

The second basic property arises from (41), which now yields

$$\begin{aligned}(N-1)P_1(\overset{\alpha}{1}) &= \int P_2(\overset{\alpha}{1},\overset{\alpha}{2})dv_2+\int P_2(\overset{\alpha}{1},\overset{\beta}{2})dv_2,\\ (N-1)P_1(\overset{\beta}{1}) &= \int P_2(\overset{\beta}{1},\overset{\alpha}{2})dv_2+\int P_2(\overset{\beta}{1},\overset{\beta}{2})dv_2.\end{aligned} \tag{63}$$

On writing the first equation in terms of correlation factors,

$$\begin{aligned}(N-1)P_1(\overset{\alpha}{1}) &= \int P_1(\overset{\alpha}{1})P_1(\overset{\alpha}{2})[1+f(\overset{\alpha}{1},\overset{\alpha}{2})]dv_2\\ &\quad +\int P_1(\overset{\alpha}{1})P_1(\overset{\beta}{2})[1+f(\overset{\alpha}{1},\overset{\beta}{2})]dv_2\\ &= P_1(\overset{\alpha}{1})\int P_1(2)dv_2\\ &\quad +P_1(\overset{\alpha}{1})\left\{\int P_1(\overset{\alpha}{2})f(\overset{\alpha}{1},\overset{\alpha}{2})dv_2\right.\\ &\qquad \left.+\int P_1(\overset{\beta}{2})f(\overset{\alpha}{1},\overset{\beta}{2})dv_2\right\}.\end{aligned}$$

Since $\int P_1(2)dv_2=N$, this gives

$$\int P_1(\overset{\alpha}{2})f(\overset{\alpha}{1},\overset{\alpha}{2})dv_2+\int P_1(\overset{\beta}{2})f(\overset{\alpha}{1},\overset{\beta}{2})dv_2=-1. \tag{64}$$

The two integrands describe the correlation holes for particles of α and β spin, respectively, in the vicinity of one of α spin at point 1: that they must together integrate to -1 is intuitively obvious—because when one particle has been located, the probability of finding a second particle somewhere must be reduced by unity. In fact, for definite z component of spin,

$$\int P_1(\overset{\alpha}{2})f(\overset{\alpha}{1},\overset{\alpha}{2})dv_2=-1,\quad \int P_1(\overset{\beta}{2})f(\overset{\alpha}{1},\overset{\beta}{2})dv_2=0. \tag{64a}$$

It appears later that for noninteracting particles the unlike-spin correlation factor vanishes, but the like-spin correlation hole still exists, arising merely from the antisymmetry of the wave function, and is called the "Fermi hole": when a particle is known to be at point 1 in spin state α, the probability of finding a *second* particle *somewhere* in the same spin state is consequently diminished by unity. One of the outstanding problems of quantum mechanics is the precise determination of the form of the correlation holes when strong interactions are admitted.

2.4. *Significance of Spin Densities*

Finally, we consider the physical significance and utility of the individual components,

$$P_1(\overset{\alpha}{1};\overset{\alpha}{1}') \quad\text{and}\quad P_1(\overset{\beta}{1};\overset{\beta}{1}'),$$

of the 1-electron density matrix; and more particularly of their diagonal elements, the α- and β-spin density functions,

$$P_1(\overset{\alpha}{1}) \quad\text{and}\quad P_1(\overset{\beta}{1}).$$

For any system in a state with $S_z=0$ (described by a wave function symmetrical between α's and β's), the two components are identical and, naturally,

$$\langle S_z\rangle_{\mathrm{av}}=\int[\mathcal{S}_z(1)\rho_1(1;1')]_{1'\rightarrow 1}d\tau_1$$

$$=\int[\tfrac{1}{2}P_1(\overset{\alpha}{1};\overset{\alpha}{1})-\tfrac{1}{2}P_1(\overset{\beta}{1};\overset{\beta}{1})]dv_1=0.$$

However, in states with $S_z\neq 0$ (e.g., in free radicals),

$$P_1(\overset{\alpha}{1})\neq P_1(\overset{\beta}{1}),$$

and we obtain instead

$$\langle S_z\rangle_{\mathrm{av}}=\tfrac{1}{2}\int[P_1(\overset{\alpha}{1})-P_1(\overset{\beta}{1})]dv_1=\tfrac{1}{2}\int Q_1(1)dv_1, \tag{65}$$

where

$$Q_1(1)=P_1(\overset{\alpha}{1})-P_1(\overset{\beta}{1}). \tag{66}$$

The quantity $Q_1(1)$ may be called the (resultant) *spin density*, since it gives the amount by which the probability of finding an electron at point 1 with plus spin outweighs that of finding it there with minus spin: when weighted with the *magnitude* of the spin ($\frac{1}{2}$) and integrated over all space, the result is $\langle S_z\rangle_{\mathrm{av}}$ or, for a definite spin state, S_z. Now, when spin terms are included in the Hamiltonian, the nuclear hyperfine splitting due to the Fermi contact interaction with a given nucleus is easily shown to be proportional to the value of $Q_1(1)$ at the nucleus. The spin density defined by (66) is therefore experimentally measurable at any point where a nuclear probe can be inserted. McConnell et al., in particular, have shown how the peripheral protons in an aromatic free radical can be used to detect the spin density associated with the π electrons. Our present definition of spin density is, however, more primitive than that adopted by McConnell, being defined without reference to the nature of the wave function. An application is sketched in Sec. III.

3. Configuration Interaction

Even without considering wave functions of specific form, it is possible to make some general progress simply on the assumption that Ψ is built up from some set of N-electron functions Φ_0, Φ_1, $\cdots\Phi_\kappa$, $\cdots$. In general, a single term of specific form (e.g., an antisymmetrized product of one-electron functions or "orbitals") can be so chosen as to give a fair approximation to the state of interest, Ψ. This approximation, which we call Φ_0, is then transcended by admitting the mixing of other functions, Φ_κ ($\kappa>0$). We borrow the terminology of orbital theories—which are studied in Sec. II and generalized in Sec. III—and refer to Φ_0 as the one-configuration approximation; the refinement of admitting Φ_κ ($\kappa>0$) is then described as configuration interaction. The significance of the terms need not be specified further at this point: the question which concerns us here is how the approximate density matrices associated with Φ_0 are affected when configuration interaction is admitted.

3.1. *Perturbation Method*

On writing

$$\Psi=\sum_\kappa C_\kappa\Phi_\kappa, \tag{67}$$

where $\kappa=0$ is reserved for the one-configuration approximation, the energy expression becomes [cf. (19), (20)]

$$E=\mathrm{tr}\,\mathbf{H}\boldsymbol{\varrho}(=\mathbf{C}^\dagger\mathbf{H}\mathbf{C}/\mathbf{C}^\dagger\mathbf{C}), \tag{68}$$

where $\boldsymbol{\varrho}=\mathbf{C}\mathbf{C}^\dagger/\mathbf{C}^\dagger\mathbf{C}$. By using this form we avoid the necessity for normalizing Ψ. The general element of $\mathbf{H}$ is given by (49) and upper bounds to the exact eigenvalues (see MacDonald[16]) are usually determined (along with corresponding optimum sets of coefficients $\mathbf{C}$) by solution of

$$\mathbf{H}\mathbf{C}=E\mathbf{C}. \tag{69}$$

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[16] J. K. L. MacDonald, Phys. Rev. 43, 830 (1933).

It is, however, useful to start from the one-configuration approximation, for which $C_0=1$, $C_\kappa=0$ $(\kappa>0)$, and to obtain the density matrix associated with the corresponding accurate solution of (69) in the form of a series. The standard Rayleigh-Schrödinger perturbation theory is unwieldy for this purpose and frequently diverges; we therefore use a method developed by Löwdin[17] which is free from these defects.

We write (69) in the partitioned form

$$\left(\begin{array}{c|c}\mathbf{H}^{AA} & \mathbf{H}^{AB}\\ \hline \mathbf{H}^{BA} & \mathbf{H}^{BB}\end{array}\right)\left(\begin{array}{c}\mathbf{A}\\ \hline \mathbf{B}\end{array}\right)=E\left(\begin{array}{c}\mathbf{A}\\ \hline \mathbf{B}\end{array}\right), \tag{70}$$

where A labels the initial approximation and B the functions whose effect is to be admitted as a perturbation. For a nondegenerate one-configuration approximation (which we assume—though generalization is not difficult), $\mathbf{H}^{AA}=H_{00}$, the unperturbed energy. Equation (70) is then equivalent to

$$E=\mathbf{H}^{AA}+\mathbf{H}^{AB}(E\mathbf{1}-\mathbf{H}^{BB})^{-1}\mathbf{H}^{BA}=f(E), \tag{71}$$

which gives the Brillouin-Wigner series (Wigner[18]; Brillouin[19]; see also Löwdin[17]) on expansion of the inverse matrix. If we take $C_0=1$ (normalization arbitrary), the coefficients C_κ $(\kappa>0)$ are contained in the column matrix $\mathbf{B}$,

$$\mathbf{B}=(E\mathbf{1}-\mathbf{H}^{BB})^{-1}\mathbf{H}^{BA}=\mathbf{B}(E). \tag{72}$$

Since E occurs on the right in (71) and (72), it is natural to solve by iteration: one iterative sequence would be $E^{(0)}$, $E_1{}^{(1)}$, $E^{(2)}$, $\cdots$, with

$$E^{(k)}=\mathbf{H}^{AA}+\mathbf{H}^{AB}\mathbf{B}^{(k)}, \tag{73}$$

$$\mathbf{B}^{(k+1)}=\mathbf{B}(E^{(k)})=(E^{(k)}\mathbf{1}-\mathbf{H}^{BB})^{-1}\mathbf{H}^{BA}. \tag{74}$$

But this represents a first-order process (see, for example, Hartree[20]) with poor convergence properties. Moreover, $E^{(k)}\neq\mathbf{C}^{(k)\dagger}\mathbf{H}\mathbf{C}^{(k)}/\mathbf{C}^{(k)\dagger}\mathbf{C}^{(k)}$, and the approximate energy and density matrix *in any given order of iteration* are not, therefore, compatible; $E^{(k)}$ is *not* an energy expectation value for state $\Psi=\sum_\kappa C_\kappa{}^{(k)}\Phi_\kappa$. These difficulties disappear on going over to a *second-order* process (Löwdin[21]); for when this is done, the sequence $E^{(0)}$, $E^{(1)}$, $E^{(2)}$, $\cdots$ is replaced by $E^{(0)}$, $\bar{E}^{(1)}$, $\bar{E}^{(2)}$, $\cdots$, where $\bar{E}^{(k)}$ is found to be just the expectation energy associated with the coefficients determined by (74). We therefore discard (73) and adopt the second-order process (dropping the bars), which leads immediately to

$$E^{(k)}=\operatorname{tr}\mathbf{H}\boldsymbol{\varrho}^{(k)},$$

$$\boldsymbol{\varrho}^{(k)}=[\mathbf{1}+\mathbf{B}^{(k)\dagger}\mathbf{B}^{(k)}]^{-1}\left(\begin{array}{c|c}1 & \mathbf{B}^{(k)\dagger}\\ \hline \mathbf{B}^{(k)} & \mathbf{B}^{(k)}\mathbf{B}^{(k)\dagger}\end{array}\right), \tag{75}$$

where $\mathbf{B}^{(k)}$ is defined by (74). The new sequence $E^{(0)}$, $E^{(1)}$, $E^{(2)}$, $\cdots$ nearly always converges rapidly (even when the first-order process diverges—Löwdin[21]) and its limit is an upper bound to an exact eigenvalue. Usually, taking $E^{(0)}=H_{00}$, the approximation $\boldsymbol{\varrho}=\boldsymbol{\varrho}^{(1)}$ is adequate and $E=E^{(1)}$ remains an upper bound for the *lowest* eigenvalue.

The Rayleigh-Schrödinger series can be obtained by iteration on expanding the inverse matrix in (74) in powers of its off-diagonal part, the expansion converging under certain well-defined conditions (e.g., Ferrar[22]). When the usual series diverges, it is generally because these conditions are not met. Equation (75) is, however, still valid and the inverse matrix in (74), which always exists, may be determined by other methods. When the usual series does converge, it is of considerable value and leads to corresponding series expansions of the density matrices. On putting $H_{\kappa\lambda}=\xi H_{\kappa\lambda}$ $(\xi\rightarrow 1)$ for $\kappa\neq\lambda$, it is a simple matter to show that the first iterate corresponds to the inclusion of the *exact* first- and second-order terms of the usual theory plus *parts* of all the higher-order terms. The results up to ξ^2 are

$$\begin{aligned}
\rho_{00}(=\rho^{AA}{}_{00})&=\left[1-\xi^2\sum_{\kappa>0}\frac{H_{0\kappa}H_{\kappa0}}{(H_{00}-H_{\kappa\kappa})^2}+\cdots\right],\\
\rho_{0\kappa}(=\rho^{AB}{}_{0\kappa})&=\left[\xi\frac{H_{0\kappa}}{(H_{00}-H_{\kappa\kappa})}\right.\\
&\qquad\left.+\xi^2\sum_{\lambda(\neq0,\kappa)}\frac{H_{0\lambda}H_{\lambda\kappa}}{(H_{00}-H_{\lambda\lambda})(H_{00}-H_{\kappa\kappa})}+\cdots\right]=\rho_{\kappa0}{}^*,\\
\rho_{\kappa\lambda}(=\rho^{BB}{}_{\kappa\lambda})&=\left[\xi^2\frac{H_{\kappa0}H_{0\lambda}}{(H_{00}-H_{\kappa\kappa})(H_{00}-H_{\lambda\lambda})}+\cdots\right].
\end{aligned} \tag{76}$$

The energy in this order may be found directly from (75):

$$\begin{aligned}
E=\operatorname{tr}\mathbf{H}\boldsymbol{\varrho}&=H_{00}\rho_{00}+\sum_{\kappa>0}H_{\kappa\kappa}\rho_{\kappa\kappa}+\sum_{\kappa>0}\xi H_{0\kappa}\rho_{\kappa0}\\
&\qquad+\sum_{\kappa>0}\xi H_{\kappa0}\rho_{0\kappa}+\sum_{\kappa,\lambda>0}{}'\,\xi H_{\lambda\kappa}\rho_{\kappa\lambda}\\
&=H_{00}\left[1-\xi^2\sum_{\kappa>0}\frac{H_{0\kappa}H_{\kappa0}}{(H_{00}-H_{\kappa\kappa})^2}\right]\\
&\qquad+\xi^2\sum_{\kappa>0}H_{\kappa\kappa}\frac{H_{\kappa0}H_{0\kappa}}{(H_{00}-H_{\kappa\kappa})^2}+2\xi^2\sum_{\kappa>0}\frac{H_{0\kappa}H_{\kappa0}}{(H_{00}-H_{\kappa\kappa})}.
\end{aligned}$$

Thus

$$E=H_{00}+\xi^2\sum_{\kappa>0}\frac{H_{0\kappa}H_{\kappa0}}{(H_{00}-H_{\kappa\kappa})}+O(\xi^3)\quad \xi\rightarrow 1. \tag{77}$$

Evidently, the ξ^2 terms in the off-diagonal elements of $\boldsymbol{\varrho}$ have no effect on the *energy* in this order, for they occur

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[17] P.-O. Löwdin, J. Chem. Phys. **19**, 1396 (1951).

[18] E. P. Wigner, Math. u. naturw. Anz. ungar. Akad. Wiss. **53**, 477 (1934).

[19] L. Brillouin, J. phys. radium **3**, 373 (1951).

[20] D. R. Hartree, Proc. Cambridge Phil. Soc. **45**, 230 (1949).

[21] P.-O. Löwdin, *Advances in Chemical Physics* (Interscience Publishers, Inc., New York, 1959), Vol. II, p. 270.

[22] W. L. Ferrar, *Finite Matrices* (Oxford University Press, New York, 1952).

only with off-diagonal elements of **H**: but in discussing electron distribution functions and expectation values of operators other than the Hamiltonian, these terms cannot consistently be omitted.

II. ORBITAL APPROXIMATIONS

1. Slater Method

Wave functions are most commonly constructed from orbital products. In this section we use orbital approximations to illustrate in more detail the ideas developed in Sec. I and to prepare the way for a natural generalization of the product approximation (Sec. III).

1.1. Antisymmetrized Products

We start from a set of functions

$$\psi_A(i),\quad \psi_B(i),\quad \psi_C(i),\quad \cdots \tag{1}$$

(in principle infinite), which is complete in the sense that an arbitrary function of space and spin coordinates of one particle, symbolized by i, can be expressed with any desired accuracy in the form

$$f(i)=\sum_R c_R\psi_R(i). \tag{2}$$

These one-electron functions are *spin orbitals*. Then the totality of all N-electron products of the form

$$\psi_P(1)\psi_Q(2)\psi_R(3)\cdots,\psi_X(N),$$

in which ψ_P, ψ_Q, $\cdots\psi_X$ are drawn from the set (1) in all possible ways, is complete for functions of the variables of all N electrons. Repetitions and rearrangements are, at this stage, allowed; but, as Slater first pointed out, a great simplification arises from the essential antisymmetry of the wave function. It follows readily that, in the expansion of an antisymmetric function, the coefficients of all products which differ only by a permutation of the same selection of orbitals can differ in *sign* only—those which arise by odd permutations differing from those which arise by even. Consequently, the terms of the expansion can be collected into groups, each containing $N!$ products and expressible in the form $\sum_{\mathcal{P}}(-1)^p\mathcal{P}\psi_P(1)\psi_Q(2)\cdots\psi_X(N)$, where the sum is over all permutations of the variables $1, \cdots N$ and there is only one distinct antisymmetrized product for any given selection of spin orbitals ψ_P, ψ_Q, $\cdots\psi_X$. It follows that any wave function can be expanded in the form

$$\Psi(1,\cdots N)=\sum_{(PQ\cdots X)} C_{PQ\ldots X}\Phi_{PQ\ldots X}(1,\cdots N), \tag{3}$$

where

$$\Phi_{PQ\ldots X}(1,2,\cdots N)=M\sum_{\mathcal{P}}(-1)^p\mathcal{P}\psi_P(1)\psi_Q(2)\cdots\psi_X(N) \tag{4}$$

(M being chosen to normalize the function), and each selection of spin orbitals occurs only once—with, say, the orbitals in dictionary order. The function (4)—which may be written as a determinant—is specified by stating the spin-orbital configuration, and (3) may be abbreviated to

$$\Psi(1,\cdots N)=\sum_\kappa C_\kappa\Phi_\kappa(1,\cdots N), \tag{5}$$

where κ denotes the configuration $\kappa=(P,Q,\cdots X)$.

Systems in singlet ground states (e.g., most molecules) are most commonly represented by a *single* spin-orbital configuration, i.e., by one term in (5), Φ_0 say. The refinement of admitting other functions $\Phi_\kappa(\kappa>0)$ is described as configuration interaction and may be discussed along the lines of Sec. I.3. More generally (e.g., atoms with incomplete shells), the determinants in (5) appear in groups, dictated by space and spin symmetry requirements (see, e.g., Condon and Shortley[23]).

1.2. Matrix Elements and Density Matrices

The matrix elements of the Hamiltonian I(44)[24] between antisymmetrized products were first given by Slater.[25] The results have recently been extended to the case of nonorthogonal orbitals by Löwdin[26] but, in practice, the general results are somewhat unwieldy and we here consider only the orthogonal case. There are only three nonvanishing types of element $(\Phi_\lambda|\mathcal{H}|\Phi_\kappa)$:

(*a*) $\kappa=\lambda=(A,B,\cdots)$

$$(\Phi_\kappa|\mathcal{H}|\Phi_\kappa)=\sum_R(\psi_R|\mathfrak{h}|\psi_R)+\tfrac{1}{2}\sum_{R,S}{}'[(\psi_R\psi_S|g|\psi_R\psi_S)-(\psi_R\psi_S|g|\psi_S\psi_R)]. \tag{6a}$$

(*b*) $\kappa=(A,B,\cdots R,\cdots),\ \lambda=(A,B,\cdots R',\cdots)$

$$\begin{aligned}(\Phi_\lambda|\mathcal{H}|\Phi_\kappa)=(\psi_{R'}|\mathfrak{h}|\psi_R)&+\tfrac{1}{2}\sum_{S(\neq R)}[(\psi_{R'}\psi_S|g|\psi_R\psi_S)-(\psi_{R'}\psi_S|g|\psi_S\psi_R)]\\&+\tfrac{1}{2}\sum_{S(\neq R)}[(\psi_S\psi_{R'}|g|\psi_S\psi_R)-(\psi_S\psi_{R'}|g|\psi_R\psi_S)].\end{aligned} \tag{6b}$$

(*c*) $\kappa=(A,B,\cdots R,\cdots S,\cdots),\ \lambda=(A,B,\cdots R',\cdots S',\cdots)$

$$(\Phi_\lambda|\mathcal{H}|\Phi_\kappa)=\tfrac{1}{2}[(\psi_{R'}\psi_{S'}|g|\psi_R\psi_S)-(\psi_{R'}\psi_{S'}|g|\psi_S\psi_R)]+\tfrac{1}{2}[(\psi_{S'}\psi_{R'}|g|\psi_S\psi_R)-(\psi_{S'}\psi_{R'}|g|\psi_R\psi_S)]. \tag{6c}$$

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[23] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), Chap 8.

[24] Equation (44), Sec. I.

[25] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

[26] P.-O. Löwdin, Phys. Rev. **97**, 1474 (1955).

Here we have used the most symmetrical form of the expressions [which may be reduced since, for example, $(\psi_{R'}\psi_S|g|\psi_R\psi_S)=(\psi_S\psi_{R'}|g|\psi_S\psi_R)$] and the Dirac-type abbreviation for the 1- and 2-electron matrix elements:

$$(\psi_R|\mathfrak{h}|\psi_S)=\int\psi_R^*(1)\mathfrak{h}(1)\psi_S(1)d\tau_1,\quad(\psi_R\psi_S|g|\psi_T\psi_U)=\int\psi_R^*(1)\psi_S^*(2)g(1,2)\psi_T(1)\psi_U(2)d\tau_1d\tau_2.\tag{7}$$

From these results it is a simple matter to write down [e.g., using I(51)], the corresponding density matrices and transition density matrices. Thus,

<u>(*a*) $\kappa=\lambda=(A,B,\cdots)$</u>

$$\rho_2(\kappa\kappa|1,2;1',2')=\sum_{R,S}{}'\psi_R(1)\psi_S(2)\psi_R^*(1')\psi_S^*(2')-\sum_{R,S}{}'\psi_S(1)\psi_R(2)\psi_R^*(1')\psi_S^*(2')$$

and by use of I(41), this gives (8a)

$$\rho_1(\kappa\kappa|1;1')=(N-1)^{-1}\{\sum_{R,S}{}'\psi_R(1)\psi_R^*(1')\delta_{SS'}-\sum_{R,S}{}'\psi_S(1)\psi_R^*(1')\delta_{RS}\}=\sum_R\psi_R(1)\psi_R^*(1'),$$

which checks with the alternative derivation by inspection of the one-electron matrix elements. In the same way we find

<u>(*b*) $\kappa=(A,B,\cdots R,\cdots),\ \lambda=(A,B,\cdots R',\cdots)$</u>

$$\begin{aligned}\rho_2(\kappa\lambda|1,2;1',2')=&\sum_{S(\neq R)}\psi_R(1)\psi_S(2)\psi_{R'}^*(1')\psi_S^*(2')-\sum_{S(\neq R)}\psi_P(1)\psi_R(2)\psi_{R'}^*(1')\psi_S^*(2')\\&+\sum_{S(\neq R)}\psi_S(1)\psi_R(2)\psi_S^*(1')\psi_{R'}^*(2')-\sum_{S(\neq R)}\psi_R(1)\psi_S(2)\psi_S^*(1')\psi_{R'}^*(2').\end{aligned}\tag{8b}$$

<u>(*c*) $\kappa=(A,B,\cdots R,\cdots S,\cdots),\ \lambda=(A,B,\cdots R',\cdots S',\cdots)$</u>

$$\begin{aligned}\rho_2(\kappa\lambda|1,2;1',2')=&\psi_R(1)\psi_S(2)\psi_{R'}^*(1')\psi_{S'}^*(2')-\psi_S(1)\psi_R(2)\psi_{R'}^*(1')\psi_{S'}^*(2')\\&+\psi_S(1)\psi_R(2)\psi_{S'}^*(1')\psi_{R'}^*(2')-\psi_R(1)\psi_S(2)\psi_{S'}^*(1')\psi_{R'}^*(2').\end{aligned}\tag{8c}$$

In view of later developments it is useful to introduce an alternative form of these results. Instead of adding primes to denote substitution of new orbitals, we may use a second subscript, so that ψ_{A1}, ψ_{A2}, $\cdots$ are the various orbitals admitted as the A factor and, generally ψ_{R1}, ψ_{R2}, $\cdots$ are the orbitals admitted in the Rth place. All orbitals are drawn from the one complete set. In this case we note that $\psi_{Rr}(1)\psi_{Rr}^*(1')$ is the density matrix for the Rth 1-electron system described by the orbital ψ_{Rr}, while $\psi_{Rr}(1)\psi_{Rr'}^*(1')$ is a transition density matrix for this system corresponding to an electron jumping from ψ_{Rr} to $\psi_{Rr'}$. If we denote these quantities by $\rho_1^R(rr|1;1')$ and $\rho_1^R(rr'|1;1')$, respectively, Eq. (8) may be rewritten as

$$\begin{aligned}(a)\quad&\rho_2(\kappa\kappa|1,2;1',2')=\sum_{R,S}{}'P_1^R(rr|1;1')\rho_1^S(ss|2;2')-\sum_{R,S}\rho_1^R(rr|2;1')\rho_1^S(ss|1;2'),\\&\rho_1(\kappa\kappa|1;1')=\sum_R\rho_1^R(rr|1;1'),\end{aligned}\tag{9a}$$

$$\begin{aligned}(b)\quad&\rho_2(\kappa\lambda|1,2;1',2')=\sum_{S(\neq R)}\rho_1^R(rr'|1;1')\rho_1^S(ss|2;2')-\sum_{S(\neq R)}\rho_1^R(rr'|2;1')\rho_1^S(ss|1;2')\\&\qquad+\sum_{S(\neq R)}\rho_1^S(ss|1;1')\rho_1^R(rr'|2;2')-\sum_{S(\neq R)}\rho_1^S(ss|2;1')\rho_1^R(rr'|1;2'),\\&\rho_1(\kappa\lambda|1;1')=\rho_1^R(rr'|1;1'),\end{aligned}\tag{9b}$$

$$\begin{aligned}(c)\quad&\rho_2(\kappa\lambda|1,2;1',2')=\rho_1^R(rr'|1;1')\rho_1^S(ss'|2;2')-\rho_1^R(rr'|2;1')\rho_1^S(ss'|1;2')\\&\qquad+\rho_1^S(ss'|1;1')\rho_1^R(rr'|2;2')-\rho_1^S(ss'|2;1')\rho_1^R(rr'|1;2').\end{aligned}\tag{9c}$$

The reduced density matrices of the N-electron system can thus be expressed in terms of the density matrices of a set of one-electron systems. These results are not new and could have been obtained in other ways[27,28]; but the present form suggests a generalization, taken up in Sec. III, in which the one-electron systems

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[27] P. A. M. Dirac, Proc. Cambridge Phil. Soc. **27**, 240 (1931).

[28] J. E. Lennard-Jones, Proc. Cambridge Phil. Soc. **27**, 469 (1931); see also Löwdin, reference 26.

are replaced by electron groups, each comprising any number of electrons. It should also be noted that the restriction $R \neq S$ in (6) [and also in (9)] may be removed, since the $R=S$ terms cancel: this leads to a considerable simplification which is peculiar to the one-determinant approximation. We are, in fact, often concerned with the one-determinant approximation, in which $\Psi=\Phi_\kappa=\Phi_0$, the first term in (5). The energy associated with this particular spin-orbital configuration, $\kappa=(a,b,c,\cdots)$, is then given by (6a): it may be improved by admitting interaction with excited configurations [other terms in (5)] in which new spin orbitals $\psi_{Rr'}$ occur.

1.3. Coulomb and Exchange Operators

The matrix element expressions (6a) and (6b) may be put in an alternative form by introducing two new operators to represent the effect upon an electron in any orbital of the electrons in *another* orbital. Thus

$$(\psi_{Rr'}\psi_{Ss}|g|\psi_{Rr}\psi_{Ss})=\int \psi_{Rr'}^*(1)\psi_{Ss}(2)g(1,2)\psi_{Rr}(1)\psi_{Ss}(2)d\tau_1 d\tau_2=\int \psi_{Rr'}^*(1)\left[\int g(1,2)\psi_{Ss}(2)\psi_{Ss}^*(2)d\tau_2\right]\psi_{Rr}(1)d\tau_1$$

or

$$(\psi_{Rr'}\psi_{Ss}|g|\psi_{Rr}\psi_{Ss})=\mathrm{tr}\ \mathcal{J}^S(1)\rho_1^R(rr'|1;1')=(\psi_{Rr'}|\mathcal{J}^S|\psi_{Rr}), \tag{10}$$

where

$$\mathcal{J}^S(1)=J^S(1)=\int g(1,1')\rho_1^S(ss|1';1')d\tau_{1'}. \tag{11}$$

$\mathcal{J}^S(1)$ is a Coulomb operator, since it is simply a multiplier, giving the electrostatic field at point 1 due to a charge distribution whose density at point $1'$ is $\rho_1^S(ss|1';1')$—the electron density associated with orbital ψ_{Ss}. We use such operators only to describe the effect of an electron in one of the *unexcited* orbitals of Φ_0, a one-determinant approximation, and the "state" subscript s may therefore be suppressed. The exchange integral $(\psi_{Rr'}\psi_{Ss}|g|\psi_{Ss}\psi_{Rr})$ cannot be expressed quite so simply and requires the introduction of an *integral* operator (see, e.g., Seitz[29]). Thus

$$\begin{aligned}(\psi_{Rr'}\psi_{Ss}|g|\psi_{Ss}\psi_{Rs})&\\ &=\int K^S(1;2)\rho_1^R(rr'|2;1)d\tau_2 d\tau_1\\ &\qquad [\text{where } K^S(1;2)=g(1,2)\psi_{Ss}(1)\psi_{Ss}^*(2)]\\ &=\int [K^S(1;1'')\rho_1^R(rr'|1'';1')d\tau_{1''}]_{1'\to 1}d\tau_1\end{aligned}$$

or

$$\begin{aligned}(\psi_{Rr'}\psi_{Ss}|g|\psi_{Ss}\psi_{Rr})&=\mathrm{tr}\ \mathcal{K}^S(1)\rho_1^R(rr|1;1')\\ &=(\psi_{Rr'}|\mathcal{K}^S|\psi_{Rr}),\end{aligned} \tag{12}$$

where $\mathcal{K}^S(1)$ is the integral operator with kernel $K^S(1;1')$:

$$\mathcal{K}^S(1)\to K^S(1;1')=g(1,1')\rho_1^S(ss|1;1'). \tag{13}$$

$\mathcal{K}^S(1)$ is the "exchange operator," giving the "exchange field" at point 1 due to an electron in orbital ψ_{Ss}. We find later that it describes a spin-dependent correlation effect. We can now introduce sums of these operators to describe the *total* effect upon an electron in an R orbital of all the electrons in the other orbitals:

$$\mathcal{J}_{(R)}(1)=\sum_{S(\neq R)}\mathcal{J}^S(1),\quad \mathcal{K}_{(R)}(1)=\sum_{S(\neq R)}\mathcal{K}^S(1). \tag{14}$$

Finally, if we introduce an *effective Hamiltonian* for the electron in the R orbital,

$$\mathfrak{h}_{\mathrm{eff}}^R(1)=\mathfrak{h}(1)+\mathcal{J}_{(R)}(1)-\mathcal{K}_{(R)}(1), \tag{15}$$

we can rewrite the formulas (6a), (6b), (6c) as

$$\begin{aligned}(a)\quad H_{\kappa\kappa}&=\sum_R (\psi_{Rr}|\mathfrak{h}|\psi_{Rr})+\tfrac{1}{2}\sum_{R,S}{}' [(\psi_{Rr}\psi_{Ss}|g|\psi_{Rr}\psi_{Ss})-(\psi_{Rr}\psi_{Ss}|g|\psi_{Ss}\psi_{Rr})]\\ &=\sum_R (\psi_{Rr}|\mathfrak{h}_{\mathrm{eff}}^R|\psi_{Rr})-\tfrac{1}{2}\sum_{R,S}{}' [(\psi_{Rr}\psi_{Ss}|g|\psi_{Rr}\psi_{Ss})-(\psi_{Rr}\psi_{Ss}|g|\psi_{Ss}\psi_{Rr})],\end{aligned} \tag{16a}$$

$$\begin{aligned}(b)\quad H_{\lambda\kappa}&=(\psi_{Rr'}|\mathfrak{h}|\psi_{Rr})+\sum_{S(\neq R)} [(\psi_{Rr'}\psi_{Ss}|g|\psi_{Rr}\psi_{Ss})-(\psi_{Rs'}\psi_{Ss}|g|\psi_{Ss}\psi_{Rr})]\\ &=(\psi_{Rr'}|\mathfrak{h}_{\mathrm{eff}}^R|\psi_{Rr}),\end{aligned} \tag{16b}$$

$$(c)\quad H_{\lambda\kappa}=[(\psi_{Rr'}\psi_{Ss'}|g|\psi_{Rr}\psi_{Ss})-(\psi_{Rr'}\psi_{Ss'}|g|\psi_{Ss}\psi_{Rr})]. \tag{16c}$$

Since

$$(\psi_{Rr'}|\mathcal{J}^R-\mathcal{K}^R|\psi_{Rr})=(\psi_{Rr'}\psi_{Rr}|g|\psi_{Rr}\psi_{Rr})-(\psi_{Rr'}\psi_{Rr}|g|\psi_{Rr}\psi_{Rr})=0,$$

the restriction $S\neq R$ in (14) may be removed and the subscript R dropped. In a one-determinant approximation, each electron feels the *same* Coulomb-exchange field, described by the effective (Hartree-Fock) Hamiltonian

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[29] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 245.

$$\mathfrak{h}_{\text{eff}}{}^R(1)=\mathfrak{h}_{\text{eff}}(1)=\mathfrak{h}(1)+\mathcal{J}(1)-\mathcal{K}(1)\quad (\text{all } R)$$

where

$$\mathcal{J}(1)=\sum_S \mathcal{J}^S(1),\quad \mathcal{K}(1)=\sum_S \mathcal{K}^S(1). \tag{17}$$

The first term in the second form of (16a) is a sum of orbital energies—each being the energy expectation value of an electron in a given orbital in an effective field which recognizes the presence of all other electrons—corrected by *subtraction* of interaction terms which would otherwise be counted twice. We find that the same effective Hamiltonian has another significance, when other terms are admitted in (5)—an important class of excited configurations giving off-diagonal matrix elements of the *one*-electron type (16b).

2. Interpretation of the Wave Function

In this section we illustrate, using straightforward examples, the topics considered in Sec. I.2. As a first step, it is necessary to take spin into account explicitly and then to derive the spinless density matrices.

2.1. Elimination of the Spin

The complete set of spin orbitals (1) may be constructed by taking a complete set of functions of *space* coordinates

$$A(i),\ B(i),\ C(i),\ \cdots \tag{18}$$

and combining these with the spin factors $\alpha(i)$, $\beta(i)$. Thus, we may use

$$\psi_A(i),\ \bar{\psi}_A(i),\ \psi_B(i),\ \bar{\psi}_B(i),\ \cdots,$$

where

$$\psi_R(i)=R(i)\alpha(i),\quad \bar{\psi}_R(i)=R(i)\beta(i). \tag{19}$$

In this case, each (space) orbital $R(i)$ may appear twice in an antisymmetrized product—once with each spin factor. In the examples, the *one*-configuration approximation is used to describe the ground state of an even number of electrons—and there is no need to use a second subscript to distinguish a variety of orbitals admitted in each place. This is the approximation used in the simple Hartree-Fock theory which is considered in Secs. II.(3.1–3.3); the case where some orbitals are singly and others doubly occupied is dealt with later in Sec. II.(3.4). Assuming then that each orbital appears twice, and using the notation of (9) (omitting the unnecessary labels $a, b, \cdots r$, and dropping the κ, since there is only one configuration), we have

$$\rho_1{}^R(1;1')=P_1{}^R(1;1')\alpha(1)\alpha^*(1')\quad \text{for an electron in } \psi_R,$$

$$\rho_1{}^R(1;1')=P_1{}^R(1;1')\beta(1)\beta^*(1'),\quad \text{for an electron in } \bar{\psi}_R. \tag{20}$$

Consequently, the second equation in (9a) becomes

$$\rho_1(1;1')=\sum_{\text{occ}}\rho_1{}^R(1;1')$$

$$=P_1(\overset{\alpha}{1};\overset{\alpha}{1}{}')\alpha(1)\alpha^*(1')+P_1(\overset{\beta}{1};\overset{\beta}{1}{}')\beta(1)\beta^*(1'), \tag{21}$$

where

$$P_1(\overset{\alpha}{1};\overset{\alpha}{1}{}')=P_1(\overset{\beta}{1};\overset{\beta}{1}{}')=\tfrac{1}{2}P_1(1;1')=\sum_{R(\text{occ})}P_1{}^R(1;1'). \tag{22}$$

Since (9a) may be written without the prime on the $\sum$ (the $R=S$ terms canceling), we have

$$\rho_2(1,2;1',2')=\rho_1(1;1')\rho_1(2;2')-\rho_1(2;1')\rho_1(1;2'), \tag{23}$$

and on inserting (21) and integrating over the spins, we obtain [cf. I(52)]

$$P_2(\overset{\alpha}{1},\overset{\alpha}{2};\overset{\alpha}{1}{}',\overset{\alpha}{2}{}')=P_1(\overset{\alpha}{1};\overset{\alpha}{1}{}')P_1(\overset{\alpha}{2};\overset{\alpha}{2}{}')-P_1(\overset{\alpha}{2};\overset{\alpha}{1}{}')P_1(\overset{\alpha}{1};\overset{\alpha}{2}{}'), \tag{24}$$

$$P_2(\overset{\alpha}{1},\overset{\beta}{2};\overset{\alpha}{1}{}',\overset{\beta}{2}{}')=P_1(\overset{\alpha}{1};\overset{\alpha}{1}{}')P_1(\overset{\beta}{2};\overset{\beta}{2}{}'). \tag{25}$$

The pair function for particles of different spin is therefore of product form,

$$P_2(\overset{\alpha}{1},\overset{\beta}{2})=P_1(\overset{\alpha}{1})P_1(\overset{\beta}{2}), \tag{26}$$

and fails to describe any correlation. But the pair function for particles of like spin does contain a correlation term: thus

$$P_2(\overset{\alpha}{1},\overset{\alpha}{2})=P_1(\overset{\alpha}{1})P_1(\overset{\alpha}{2})-P_1(\overset{\alpha}{2};\overset{\alpha}{1})P_1(\overset{\alpha}{1};\overset{\alpha}{2}), \tag{27}$$

and the correlation factor defined in I(61) is

$$f(\overset{\alpha}{1},\overset{\alpha}{2})=-P_1(\overset{\alpha}{2};\overset{\alpha}{1})P_1(\overset{\alpha}{1};\overset{\alpha}{2})/P_1(\overset{\alpha}{1})P_1(\overset{\alpha}{2}). \tag{28}$$

This clearly fulfills the necessary conditions I(62) and I(64)—the latter holding because the integral operator with kernel

$$P_1(\overset{\alpha}{1};\overset{\alpha}{2})$$

is idempotent,

$$\int P_1(\overset{\alpha}{1};\overset{\alpha}{2})P_2(\overset{\alpha}{2};\overset{\alpha}{1})dv_2=P_1(\overset{\alpha}{1};\overset{\alpha}{1})=P_1(\overset{\alpha}{1}).$$

This particular correlation factor, which operates between particles of like spin, even when they are noninteracting, defines the Fermi hole [I(64) et seq.].

When spin states of the particles are of no interest, it is unnecessary to analyze the pair function into its parts. By addition of (24), (25), etc., it follows that

$$P_2(1,2;1',2')=P_1(1;1')P_1(2;2')-\tfrac{1}{2}P_1(2;1')P_1(1;2'), \tag{29}$$

where

$$P_1(1;1')=2\sum_{R(\text{occ})}R(1)R^*(1'). \tag{30}$$

2.2. Correlation: Like Spins

It is instructive to derive, from the present standpoint, the correlation factor for particles of like spin in a uniform electron gas of low density. This was first discussed by Wigner and Seitz.[30] Analysis of the high-density case recently has received much attention in connection with nuclear models (see, e.g., Gell-Mann and Brueckner[31]), but the corresponding form of the correlation hole has not yet been discussed.

We consider a cube of side G and volume $V(=G^3)$, with periodic boundary conditions on the 1-electron wave functions; these are then most conveniently denoted by ϕ_{k} where $\mathbf{k}$ specifies a triplet of quantum numbers. Thus

$$\phi_{\mathrm{k}}(j)=G^{-\frac{3}{2}}\exp 2\pi i\mathbf{k}\cdot\mathbf{r}_j, \tag{31}$$

where $\mathbf{r}_j$ is the position vector with components (x_j,y_j,z_j) and $\mathbf{k}=(k_x,k_y,k_z)$ indicates the electron momentum. The boundary conditions require $k_x=\kappa_x/G$, $k_y=\kappa_y/G$, $k_z=\kappa_z/G$, where $\kappa_x,\kappa_y,\kappa_z$ are integers, and the corresponding orbital energies are

$$\epsilon_{\mathrm{k}}=(\hbar^2/2m)|\mathbf{k}|^2=(\hbar^2/2m)(k_x^2+k_y^2+k_z^2). \tag{32}$$

To every orbital there corresponds a point in $\mathbf{k}$-space, one point per volume G^{-3} or $G^3(=V)$ per unit volume, and the points representing orbitals with energy less than ϵ lie within a sphere of radius k_F, where $k_F^2=2m\epsilon/\hbar^2$. If N electrons are described by a single determinant of doubly occupied orbitals, these being filled in ascending energy order, we must therefore have $2(\frac{4}{3})\pi k_F^3V=N$. The radius of the Fermi sphere of occupied orbitals is thus

$$k_F=(3N/8\pi V)^{\frac{1}{3}}, \tag{33}$$

and the occupied orbitals are determined by the condition

$$k_x^2+k_y^2+k_z^2\leqslant k_F^2.$$

The 1-particle spinless density matrix for particles of like spin follows from (22) on replacing $P_1{}^R(1;1')$ by $\phi_{\mathrm{k}}(1)\phi_{\mathrm{k}}{}^*(1')$ and the summation over R by an integration over $\mathbf{k}$-space:

$$\begin{aligned}P_1(\overset{\alpha}{1};\overset{\alpha}{1}{}')&=P_1(\overset{\beta}{1};\overset{\beta}{1}{}')\\&=V^{-1}\int_{|\mathbf{k}|\leqslant k_F}\exp\{2\pi i(\mathbf{r}_1-\mathbf{r}_1')\cdot\mathbf{k}\}\,Vd\mathbf{k},\end{aligned}$$

A straightforward integration in polar coordinates then gives

$$P_1(\overset{\alpha}{1};\overset{\alpha}{1}{}')=\tfrac{1}{2}\rho\left\{\frac{3[\sin 2\pi k_F\delta-2\pi k_F\delta\cos 2\pi k_F\delta]}{(2\pi k_F\delta)^3}\right\}, \tag{34}$$

where $\delta=|\mathbf{r}_1-\mathbf{r}_1'|$ and $\rho=N/V$ is the particle density. It is easily verified that, when $\mathbf{r}_1'\rightarrow\mathbf{r}_1$,

$$P_1(\overset{\alpha}{1};\overset{\alpha}{1}{}')\rightarrow\tfrac{1}{2}\rho,$$

as it should, since the density $P_1(\overset{\alpha}{1})$ of particles of given spin must be half the total density.

The correlation factor for particles of like spin then follows from (28):

$$f(\overset{\alpha}{1},\overset{\alpha}{2})=-\tfrac{1}{2}\rho\left\{\frac{3[\sin 2\pi k_Fr_{12}-2\pi k_Fr_{12}\cos 2\pi k_Fr_{12}]}{(2\pi k_Fr_{12})^3}\right\}^2. \tag{35}$$

The Fermi hole which it describes has been fully discussed by Slater.[32] The correlation factor has a simple analytical form only in the case of a free electron gas, where the electron density is uniform.

The shape of the Fermi hole for electrons in an atom has recently been discussed by Maslem,[33] who points out that it is no longer spherical and that the maximum depth no longer occurs at the electron which it surrounds. This is to be expected: the like-spin correlation factor certainly has its numerically greatest value (-1) for $2\rightarrow 1$, but the hole itself is described by the function

$$P(\overset{\alpha}{2})f(\overset{\alpha}{1},\overset{\alpha}{2})$$

and, if 1 lies in a region of low electron density, the depth of the hole is small for $2\rightarrow 1$; since, however, the hole function must *integrate* to -1, it must be of considerable depth elsewhere, namely, where the electron density is large. If point 1 is removed to infinity, the like-spin correlation factor in this expression must become independent of r_{12}, the hole function becoming proportional to $P(2)$: the integration condition I(64) then gives $f(1,2)\rightarrow 1/N$. Thus, if one electron is a long way outside the atom, the probability of finding a second at any point is reduced by $(1/N)$th of its original value, the actual form of the density being undisturbed: this is physically necessary.

2.3. Correlation: Unlike Spins

The main problem of N-particle quantum mechanics is that of introducing a correlation factor to describe the mutual repulsion of charged particles, irrespective of their spin states. This is not of crucial importance for particles of like spin because they stay apart anyway as a result of antisymmetry; but it is vital for particles of unlike spin, which in one-configuration approximation are described as being free to come arbitrarily close together. The simplest example of how this type of correlation is described in an orbital approach is provided by a comparison of two hydrogen molecule wave functions—the molecular orbital function,

$$\Psi_{\mathrm{MO}}(1,2)=A(1)A(2)(2)^{-\frac{1}{2}}[\alpha(1)\beta(2)-\beta(1)\alpha(2)]$$
$$\text{(1 spin-orbital configuration)}, \tag{36}$$

and the Heitler-London function

$$\begin{aligned}\Psi_{\mathrm{HL}}(1,2)=M[&a(1)b(2)+a(2)b(1)]\\&\times(2)^{-\frac{1}{2}}[\alpha(1)\beta(2)-\beta(1)\alpha(2)]\end{aligned}$$
$$\text{(2 spin-orbital configurations)}. \tag{37}$$

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[30] E. P. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); see also reference 29, p. 241.

[31] M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957).

[32] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[33] V. W. Maslem, Proc. Phys. Soc. (London) **A69**, 734 (1956).

Here a and b represent the 1s atomic orbitals on the two centers and the bonding molecular orbital is $A=m(a+b)$ where $m=(2+2S)^{-\frac{1}{2}}$ and S is the overlap integral between a and b. The normalizing factor in (37) is $M=(2+2S^2)^{-\frac{1}{2}}$. A simple calculation gives:

MO approximation

$$\begin{aligned} &P_2(\overset{\alpha}{1},\overset{\alpha}{2})=P_2(\overset{\beta}{1},\overset{\beta}{2})=0,\\ &P_2(\overset{\alpha}{1},\overset{\beta}{2})=P_2(\overset{\beta}{1},\overset{\alpha}{2})=m^4[a^2(1)+b^2(1)+2a(1)b(1)]\\ &\qquad\qquad\times[a^2(2)+b^2(2)+2a(2)b(2)],\\ &P_1(\overset{\alpha}{1})=P_1(\overset{\beta}{1})=m^2[a^2(1)+b^2(1)+2a(1)b(1)].\end{aligned} \tag{38}$$

HL approximation

$$\begin{aligned} &P_2(\overset{\alpha}{1},\overset{\alpha}{2})=P_2(\overset{\beta}{1},\overset{\beta}{2})=0,\\ &P_2(\overset{\alpha}{1},\overset{\beta}{2})=P_2(\overset{\beta}{1},\overset{\alpha}{2})=2M^2[a^2(1)b^2(2)+a^2(2)b^2(1)\\ &\qquad\qquad+2a(1)b(1)a(2)b(2)],\\ &P_1(\overset{\alpha}{1})=P_1(\overset{\beta}{1})=2M^2[a^2(1)+b^2(1)+2S_{ab}a(1)b(1)].\end{aligned} \tag{39}$$

Both approximations exhibit Fermi correlation in an extreme form, though this is not usually recognized: for

$$P_2(\overset{\alpha}{1},\overset{\alpha}{2})=P_2(\overset{\beta}{1},\overset{\beta}{2})=0$$

means, by comparison with I(61), that

$$f(\overset{\alpha}{1},\overset{\alpha}{2})=f(\overset{\beta}{1},\overset{\beta}{2})=-1$$

everywhere, and this means that the Fermi hole is identical in form with the electron density and subtracts exactly one electron. Again, this is intuitively necessary —given one electron in spin state α, there should be zero probability of the second being in the same spin state if the z component of total spin is to be zero. On the other hand, there is also a correlation between particles of *unlike* spin in the HL approximation;

$$P(\overset{\alpha}{1},\overset{\beta}{2})\neq P(\overset{\alpha}{1})P(\overset{\beta}{2}).$$

To see most clearly what is described, it is convenient to suppose the atoms are rather far apart. In this case $M\rightarrow\frac{1}{2}$ and

$$\begin{aligned} &P(\overset{\alpha}{1})\rightarrow\tfrac{1}{2}[a^2(1)+b^2(1)],\\ &P(\overset{\alpha}{1},\overset{\beta}{2})\rightarrow P_1(\overset{\alpha}{1})P_1(\overset{\beta}{2})-\tfrac{1}{4}[a^2(1)a^2(2)+b^2(1)b^2(2)\\ &\qquad\qquad-a^2(1)b^2(2)-b^2(1)a^2(2)].\end{aligned}$$

If points 1 and 2 lie in the vicinity of one nucleus (where a is large, b small), it is clear that

$$P_1(\overset{\alpha}{1})\rightarrow\tfrac{1}{2}a^2(1)$$

and

$$P_1(\overset{\alpha}{1},\overset{\beta}{2})\rightarrow\tfrac{1}{4}a^2(1)a^2(2)-\tfrac{1}{4}[a^2(1)a^2(2)]=0.$$

For large internuclear distances, the two electrons are therefore forbidden from coming onto the same nucleus. At smaller internuclear distances, the probability of their being near the same nucleus is simply reduced below the value

$$P_1(\overset{\alpha}{1})P_1(\overset{\beta}{1}).$$

If the hole function defined in I(56) et seq. is plotted for an electron at point 1, near one nucleus, the hole ($-ve$ values) is confined to that nucleus, while there is a peak on the other nucleus indicating that the second electron is most likely to be found there. Like the Fermi correlation, however, this effect depends upon a special form of the wave function and is not in any way conditioned by the *actual repulsion* between the electrons. At the same time it is in harmony with the fact that the electrons like to keep apart and therefore simulates the kind of correlation which would arise from electron repulsion—though very crudely. The hole can be properly fitted to describe the actual repulsion only by adding more and more configurations, determining their mixing by variational methods in which the *energy* of repulsion plays its part. It is, however, clear that an orbital approach, with a severely limited number of configurations, can give only a crude description of the correlation hole owing to the clumsy nature of the orbitals with which it is approximated. The correctly localized character of the hole can be introduced by admitting functions which contain the variable r_{12}, but this generally leads to insuperable computational difficulties. This is the present dilemma in molecular theory: its nature suggests that the only way of dealing with complicated systems is to shift the emphasis from *a priori* calculations onto the general elucidation of molecular properties in terms of the density matrices of the molecule and its constituent parts, leaving the detailed mathematical form of these functions unspecified wherever possible. We find in Sec. III that it is possible to make considerable progress in this direction.

2.4. *Population Analysis*

We have seen that in an orbital approach the density matrices are approximated in the form

$$P_1(1;1')=\sum_{R,S}R(1)P_{1RS}S^*(1'), \tag{40}$$

$$P_2(1,2;1',2')=\sum_{R,S,T,U}R(1)S(2)P_{2RS,TU}T^*(1')U^*(2'), \tag{41}$$

where the coefficients of the different orbital products may be collected into square matrices $\mathbf{P}_1$ and $\mathbf{P}_2$. Thus, in the molecular orbital approximation (single antisymmetrized product), the elements of $\mathbf{P}_1$ and of $\mathbf{P}_2$ (rows and columns labeled by index *pairs*) follow from (29) and (30):

$$P_{1RS}=2\delta_{RS}, \tag{42}$$

$$P_{2RS,TU}=2[2\delta_{RT}\delta_{SU}-\delta_{RU}\delta_{ST}]. \tag{43}$$

Here R, S, T, U run over the set of $n(=\frac{1}{2}N)$ doubly occupied orbitals of the one-configuration approximation: $\mathbf{P}_1$ is thus twice the $n\times n$ unit matrix, while $\mathbf{P}_2$ is $n^2\times n^2$. It is now necessary to discuss the physical significance of the matrices $\mathbf{P}_1$ and $\mathbf{P}_2$. Matrices $\boldsymbol{\rho}_1$ and $\boldsymbol{\rho}_2$ can be defined and discussed in a formally identical way, but for present purposes it is necessary to take spin into account explicitly and then to proceed to the spinless quantities.

If $\mathbf{P}_1$ and $\mathbf{P}_2$ are unrestricted in dimensions and form, the quantities $P_1(1;1')$ and $P_2(1,2;1',2')$ define general operators P_1 and P_2 [34] in the representation spaces for one and two particles, respectively. For example,

$$P_1\phi(1)=\int P_1(1;1')\phi(1')dv_{1'}, \qquad (44)$$

and the elements of $\mathbf{P}_1$ are simply the matrix elements of the operator P_1, in the usual sense, relative to the basis $A(1)$, $B(1)$, $\cdots R(1)$, $\cdots$ in terms of which any 1-electron function $\phi(1)$ can be expanded. Thus [cf. I(12) et seq.]

$$(A|P_1|B)=\int A(1)P_1(1;1')B^*(1')dv_1dv_{1'}$$
$$=\sum_{R,S}\delta_{AR}P_{1RS}\delta_{RB}=P_{1AB}.$$

In the same way, the elements of $\mathbf{P}_2$ are just the matrix elements of an operator P_2, relative to the basis of 2-electron products $A(1)A(2)$, $A(1)B(2)$, $\cdots B(1)A(2)$, $B(1)B(2)$, $\cdots R(1)S(2)$, $\cdots$ in terms of which any 2-electron function $\Phi(1,2)$ can be expanded. Thus, if matrices are associated with 1- and 2-electron operators in the usual way, results such as I(43) may be transcribed:

$$\int[\mathfrak{h}(1)P_1(1;1')]_{1'\rightarrow 1}dv_1=\int\sum_{R,S}S^*(1)\mathfrak{h}(1)R(1)P_{1RS}dv_1$$
$$=\sum_{R,S}h_{SR}P_{1RS}=\mathrm{tr}\,\mathbf{hP}_1. \qquad (45)$$

This transcription is valid even when the basis functions are nonorthogonal. The energy expression I(54) may thus be written

$$E=\mathrm{tr}\,\mathbf{hP}_1+\tfrac{1}{2}\,\mathrm{tr}\,\mathbf{gP}_2, \qquad (46)$$

where $\mathbf{P}_1$ and $\mathbf{P}_2$ are defined in the preceding and

$$h_{RS}=(R|\mathfrak{h}|S), \quad g_{RS,TU}=(RS|g|TU).$$

With an approximate wave function, restrictions are placed upon the forms of $\mathbf{P}_1$ and $\mathbf{P}_2$ [cf. (42) and (43)] and (46) then gives the corresponding *approximate* energy.

The elements of the density matrices have another significance in so far as they define a resolution of the distribution functions into terms associated with orbitals. The charge density is of particular importance. Thus $P_1(1)=\sum_{R,S}R(1)P_{1RS}S^*(1)$, and on integrating over all space, it is clear that P_{1RR} electrons are contributed from the orbital density $R(1)R^*(1)$. The diagonal elements of $\mathbf{P}_1$ are thus the *populations* of the corresponding orbitals. This picture is confused, however, by the presence of off-diagonal terms—for overlap densities such as $R(1)S^*(1)$, although contributing no *net* charge when R and S are orthogonal, profoundly modify the distribution defined by the diagonal terms. Moreover, the populations are in no sense unique. Both objections may be met by introducing a new basis. For on putting $(\bar{A}\bar{B}\cdots)=(AB\cdots)\mathbf{U}$ ($\mathbf{U}$ a unitary matrix), $\mathbf{P}_1$ must be replaced by $\bar{\mathbf{P}}_1=\mathbf{U}^\dagger\mathbf{P}_1\mathbf{U}$, and $\mathbf{U}$ may be chosen so that $\mathbf{P}_1$ is diagonal. In this case, then,

$$P(1)=\sum_R\bar{R}(1)\bar{P}_{1RR}\bar{R}^*(1), \qquad (47)$$

and the charge density is simply a sum of orbital contributions, both orbitals and populations being uniquely determined by the diagonalization (the columns of $\mathbf{U}$ being the eigenvectors of $\mathbf{P}_1$). The new orbitals are the spinless counterparts of the natural *spin* orbitals introduced by Löwdin[35]: by considering

$$P_1(\overset{\alpha}{1}) \quad \text{and} \quad P_1(\overset{\beta}{1})$$

separately, the natural orbitals may be defined for electrons in each spin state. In molecular orbital theory, for example,

$$\mathbf{P}_1=\overset{\alpha}{\mathbf{P}}_1+\overset{\beta}{\mathbf{P}}_1, \quad \text{where} \quad \overset{\alpha}{\mathbf{P}}_1=\overset{\beta}{\mathbf{P}}_1=\mathbf{1}_n$$

(the n-dimensional unit matrix), and the MO's are thus approximate natural orbitals of unit population for each spin. In this very special case (n-fold degeneracy of the populations), the orbitals are arbitrary to within a unitary transformation: more generally, the populations are nonintegral and distinct, and the arbitrariness disappears. Interesting examples of this kind of analysis have been given by Shull and Löwdin.[36,37]

In spite of these simplifications, the natural orbitals are not always convenient for descriptive purposes: they generally extend over the whole molecule and are therefore superimposed in the same region of space, and their forms are characteristic of the molecule considered. Usually, the occupied orbitals are all expressed in terms of a basis of *atomic* orbitals, which are localized in different regions of space and are characteristic of the *atoms* in the molecule. In such cases, transformation to the atomic orbital basis gives a charge density expression which contains terms referring to localized

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[34] Script is not required for the *density operators* since there are no corresponding dynamical variables: This leaves $\mathcal{P}$ free to represent a permutation operator.

[35] Reference 26, p. 1474 (see in particular p. 1483).

[36] P.-O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956).

[37] H. Shull and P.-O. Löwdin, J. Chem. Phys. **25**, 1035 (1956).

regions which are easily visualized: this is the basis of population analysis (Mulliken[38]; see also McWeeny[12,39]).

Let us denote the primitive set of 1-electron basis functions by a, b, c, $\cdots$, these being certain atomic orbitals (including more generally Slater functions, Gaussians, etc.) centered on the various nuclei. The orbitals employed so far [Eq. (18)] are linear combinations of these functions:

$$R(1)=\sum_{s} s(1)T_{sR} \tag{48}$$

or, with the abbreviation $(ABC\cdots)=\mathbf{A}$, $(abc\cdots)=\mathbf{a}$,

$$\mathbf{A}=\mathbf{a}\mathbf{T}. \tag{49}$$

It is convenient to refer loosely to the orbitals of $\mathbf{A}$ and $\mathbf{a}$ as MO's (molecular orbitals) and AO's (atomic orbitals).[40] The density matrices (40), (41) may then be written in terms of the AO basis:

$$P_1(1;1')=\sum_{r,s} r(1)\mathbf{P}_{1rs}s^*(1'), \tag{50}$$

$$P_2(1,2;1',2')=\sum_{r,s,t,u} r(1)s(2)\mathbf{P}_{2rs,tu}t^*(1')u^*(2') \tag{51}$$

where, in terms of MO quantities,

$$\mathbf{P}_1=\mathbf{T}_1\overline{\mathbf{P}}\mathbf{T}^\dagger \quad (m\times m \text{ matrix}), \tag{52}$$

$$\mathbf{P}_2=\mathbf{T}^{(2)}\overline{\mathbf{P}}_2\mathbf{T}^{(2)\dagger} \quad (m^2\times m^2 \text{ matrix}), \tag{53}$$

and $\mathbf{T}^{(2)}=\mathbf{T}\times\mathbf{T}$, the outer product[41] of $\mathbf{T}$ with itself. If there are n MO's and m AO's, $\mathbf{T}$ is $m\times n$ and $\mathbf{T}^{(2)}$ is $m^2\times n^2$. The matrices $\overline{\mathbf{P}}_1$ and $\overline{\mathbf{P}}_2$ may be resolved into components corresponding to I(57) and I(59). Thus, for example,

$$P_1(\overset{\alpha}{1};\overset{\alpha}{1}')=\sum_{R,S} R(1)\bar{P}_1{}^{\alpha,\alpha}{}_{RS}S^*(1')=\sum_{r,s} r(1)P_1{}^{\alpha,\alpha}{}_{rs}s^*(1')$$

where [cf. (52)]

$$\mathbf{P}_1{}^{\alpha,\alpha}=\mathbf{T}\overline{\mathbf{P}}_1{}^{\alpha,\alpha}\mathbf{T}^\dagger$$

and in this case

$$\mathbf{P}_1=\mathbf{P}_1{}^{\alpha,\alpha}+\mathbf{P}_1{}^{\alpha,\beta}+\mathbf{P}_1{}^{\beta,\alpha}+\mathbf{P}_1{}^{\beta,\beta}. \tag{54}$$

The elements of $\mathbf{P}_1{}^{\alpha,\alpha}$, for instance, then determine the density of electrons of α spin in corresponding regions of space: they have an intrinsic physical importance which is revealed in magnetic resonance experiments [see Sec. III.(4.3)].

This procedure has in effect been followed in Sec. II.(2.3). To illustrate a more general case, we consider the usual one-determinant approximation, with n doubly occupied MO's and m AO's. In this case $\mathbf{T}$ is a rectangular $m\times n$ matrix whose Rth column contains the AO coefficients in the Rth MO. From (42) and (43) it follows readily that

$$P_{1rs}=2R_{rs}, \tag{55}$$

$$P_{2rs,tu}=2[2R_{rt}R_{su}-R_{ru}R_{st}], \tag{56}$$

where

$$\mathbf{R}=\mathbf{T}\mathbf{T}^\dagger. \tag{57}$$

It is characteristic of the Hartree-Fock approximation that all the density matrices are determined by a single matrix $\mathbf{R}$. In higher approximation the density matrices would be determined from I(50), contributions arising from the mixing of a number of determinants according to Eq. (8) with weights determined by the mixing coefficients calculated by variational methods or by the perturbation method of Sec. I. The number of MO's employed then exceeds n, and in the transformation to the AO basis, (52) and (53), $\mathbf{T}$ contains more than n columns —being $m\times m$ in the limiting case of full configuration interaction.

Information about the electron distribution is most readily obtained from the matrices $\mathbf{P}_1$ and $\mathbf{P}_2$ by introducing normalized orbital and overlap densities. Assuming real basis functions, these are

$$\rho_r(1)=r^2(1), \quad \rho_{rs}(1)=r(1)s(1)/S_{rs}, \tag{58}$$

and in this case the electron density is

$$P_1(1)=q_r\rho_r(1)+\sum_{r<s} q_{rs}\rho_{rs}(1), \tag{59}$$

where

$$q_r=P_{1rr}, \quad q_{rs}=2S_{rs}P_{1rs}. \tag{60}$$

These latter quantities are the *orbital* and *overlap populations*[39] and give the amounts of charge distributed according to density functions ρ_r and ρ_{rs}, respectively. The analysis is formal since the density functions overlap considerably, but if the basis orbitals are reasonably well localized, the q's can give a useful picture of the general disposition of charge in the molecule. Broadly speaking, chemical binding is to be attributed to the charge density which has left the valence orbitals of the free atoms and accumulated in the overlap regions. For this reason the off-diagonal elements of $\mathbf{P}_1$ are, in an appropriate context, bond orders, and $\mathbf{P}_1$ is sometimes called the charge and bond order matrix. It is sometimes convenient to introduce normalized populations, replacing $\mathbf{P}_1$ by $\mathbf{P}_1/N$, in order to show where any one electron is likely to be found. Thus, in the example of Sec. II.(2.3), the normalized populations of the orbital and overlap regions are estimated as follows:

		Electron in a or in b	Electron in ab
Normalized population	MO	$1/(1+S)$	$S/(1+S)$
	HL	$1/(1+S^2)$	$S^2/(1+S^2)$.

Thus, with $S=\frac{1}{2}$ the HL function would predict a 20% probability of an electron being found in the bond

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[38] R. S. Mulliken, J. Phys. Chem. **23**, 1833, 2346 (1955).

[39] R. McWeeny, J. Chem. Phys. **19**, 1614 (1951); **20**, 920 (1951).

[40] Henceforth, a bar will be used to distinguish matrices referred to MO's from those referred to AO's.

[41] $(\mathbf{A}\times\mathbf{B})_{ij,kl}=A_{ik}B_{jl}$.

region, while the MO function would give 33%. Conflicting estimates are brought into agreement as configuration interaction is admitted (see, e.g., McWeeny[42]), and population values provide a sensitive wave function criterion.

Pair populations may be defined analogously[12] and are of value in discussing electron correlation. Thus, if

$$P_2(\overset{\alpha}{1},\overset{\beta}{2})$$

includes a term which may be written $q_{ab,cd}\rho_{ab}(1)\rho_{cd}(2)$, then the pair population $q_{ab,cd}$ is the contribution to the integrated two-electron probability arising from electron 1 in ρ_{ab} (with α spin) and electron 2 in ρ_{cd} (with β spin). Division by $N(N-1)$ yields a normalized pair population which gives the probability of two electrons (in this case with opposite spins) simultaneously occupying the two regions. Thus, in the example of Sec. II.(2.3), we obtain

		Both electrons in *a* or in *b*	One in *a*, one in *b*	One in *a* or *b*, one in *ab*	Both in *ab*
Normalized pair population	MO	$1/2(1+S)^2$	$1/2(1+S)^2$	$2S/(1+S)^2$	$S^2/(1+S)^2$
	HL	0	$1/(1+S)^2$	0	$S^2/(1+S)^2$

Thus, with $S=\frac{1}{2}$ say, there is, according to HL theory, zero probability of both electrons in the same orbital or of one in an orbital and the other in an overlap region, 80% probability of the electrons in different orbitals, and 20% probability of both in the overlap region. These figures give a simple and precise description of the strong correlation described by a HL approximation [cf. Sec. II.(2.3)].

2.5. *Status of Hybridization*

There are many instances in which the description of a molecular system is facilitated by introducing in place of the primitive AO's a new set in which functions belonging to the same center have been allowed to mix: the mixtures are *hybrid* AO's. Usually, hybrids are chosen on intuitive grounds, bonds between atoms being conveniently described in terms of hybrids which point towards each other so as to give large overlap in the bond regions. But from a knowledge of the 1-electron density matrix, it is possible to uniquely define certain *natural hybrids*.[12]

Suppose the primitive AO's are $a_1, a_2, \cdots$ (on atom a), $b_1, b_2, \cdots$ (on atom b), etc. Then the charge density in this basis is

$$P_1(1)=\sum_{i,j}\sum_{r,s} r_i(1)\mathbf{P}_{1r_is_j}s_j^*(1), \qquad (61)$$

where $\mathbf{P}_1$ has the form

$$\mathbf{P}_1=\left[\begin{array}{c|c|c} \mathbf{P}_1{}^a & \mathbf{P}_1{}^{ab} & \cdots \\ \hline \mathbf{P}_1{}^{ba} & \mathbf{P}_1{}^{b} & \cdots \\ \hline \cdot & \cdot\;\cdot\;\cdot & \cdot\;\cdot \end{array}\right].$$

Formally, since $\mathbf{P}_1{}^r$ is not generally diagonal, there are bond orders between different orbitals on the same atom and the intra-atomic density is not a simple sum of orbital contributions. But each block of the density matrix may be brought to diagonal form by a unitary transformation, exactly as in (47). The new basis orbitals on any atom r are then mixtures of the original set: the mixing coefficients are the eigenvectors of $\mathbf{P}_1{}^r$ and the populations of the new orbitals are the eigenvalues. The orbitals

$$(a_1'a_2'\cdots b_1'b_2'\cdots)=(a_1a_2\cdots b_1b_2\cdots)\mathbf{U}, \qquad (62)$$

where $\mathbf{U}$ contains the diagonal blocks $\mathbf{U}^a$; and $\mathbf{U}^b\cdots$ are the natural hybrids. Nonvanishing bond orders then occur only between hybrids on *different* atoms, and these are determined by the off-diagonal blocks

$$\mathbf{P}_1{}'^{ab}=\mathbf{U}^{a\dagger}\mathbf{P}_1{}^{ab}\mathbf{U}^b \qquad (63)$$

giving the bond orders between the various hybrids on a and b.

To give an example, consider an atom r in a linear molecule. The valence orbitals invoked might be $r_1=\phi_{2s}$, $r_2=\phi_{2p}$ (along the axis), and the charge density given by a configuration interaction calculation might turn out to be

$$\mathbf{P}_1{}^r=\begin{pmatrix}0.9 & 0.2\\ 0.2 & 1.1\end{pmatrix},$$

$$P_1(1)=\cdots+0.9r_1{}^2(1)+0.4r_1(1)r_2(1)+1.1r_2{}^2(1)+\cdots.$$

In this case

$$\mathbf{P}_1{}^r=\begin{pmatrix}0.9 & 0.2\\ 0.2 & 1.1\end{pmatrix},$$

with eigenvectors

$$\begin{pmatrix}0.526\\ 0.851\end{pmatrix} \text{ and } \begin{pmatrix}0.851\\ -0.526\end{pmatrix}$$

and eigenvalues 1.224, 0.776. The natural hybrids are then

$$(r_1'r_2')=(r_1r_2)\begin{pmatrix}0.526 & 0.851\\ 0.851 & -0.526\end{pmatrix},$$

and the charge density becomes

$$P_1(1)=\cdots+1.224\,r_1'^2(1)+0.776\,r_2'^2+\cdots.$$

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[42] R. McWeeny, Proc. Roy. Soc. (London) **A227**, 288 (1955).

The hybrids are obviously of *sp* type, pointing in opposite directions along the molecular axis, but are not equivalent in the particular example owing to the asymmetry of the charge distribution. In cases of symmetry, the $\mathbf{P}_1{}^r$ have degenerate eigenvalues and the hybrids lose their uniqueness: this may be restored, however, by imposing a symmetry requirement.

Hybrid AO's are introduced essentially for conceptual reasons. If each hybrid has a large bond order with only *one* other hybrid so that a number of different *pairs* may be distinguished, the system contains *localized bonds*, and a good approximate wave function can be set up most simply by using the hybrids. The departure from zero of the remaining bond orders indicates the degree of *de*localization resulting from incipient bonding between hybrids which overlap less strongly.

3. Hartree-Fock Approximation

Hartree-Fock theory starts from a single antisymmetrized spin-orbital product, an approximation which has so far dominated molecular theory. Usually, the best orbitals (MO's) to use in such wave functions are determined variationally by the self-consistent field method. It is, however, unnecessary to determine the orbitals themselves since in this approximation the wave function is completely determined by the 1-electron density matrix and this may be calculated directly by a suitable iterative method. Here we give a brief account of some present trends, in which *analytical* approximations are obtained by expansion over a set of *m* basis orbitals (AO's) and the numerical integration techniques of Hartree[43] are replaced by matrix methods.

3.1. Matrix Formulation

When the density matrices are expressed in terms of the occupied MO's A, B, $\cdots$ according to (40) and (41), (46) becomes (with bars added—see footnote 40)

$$E = \operatorname{tr} \bar{\mathbf{h}}\bar{\mathbf{P}}_1 + \tfrac{1}{2} \operatorname{tr} \bar{\mathbf{g}}\bar{\mathbf{P}}_2. \tag{64}$$

When the MO's are expressed in terms of the AO's a, b, $\cdots$, according to (50) and (51), the corresponding form is

$$E = \operatorname{tr} \mathbf{h}\mathbf{P}_1 + \tfrac{1}{2} \operatorname{tr} \mathbf{g}\mathbf{P}_2, \tag{65}$$

where $\mathbf{P}_1 = \mathbf{T}\bar{\mathbf{P}}_1\mathbf{T}^\dagger$ and $\mathbf{P}_2 = \mathbf{T}^{(2)}\bar{\mathbf{P}}_2\mathbf{T}^{(2)\dagger}$ are the density matrices referred to, the AO basis and $\mathbf{h}$, $\mathbf{g}$ are the corresponding matrices of the 1- and 2-electron operators, $\mathbf{h}_{rs} = (r|\mathfrak{h}|s)$, $\mathbf{g}_{rs,tu} = (rs|g|tu)$. This is quite general; but in the usual Hartree-Fock case there are $n = \frac{1}{2}N$ doubly occupied MO's expressed in terms of, say, m AO's, and $\mathbf{P}_1$, $\mathbf{P}_2$ have already been expressed in terms of a single matrix $\mathbf{R} = \mathbf{T}\mathbf{T}^\dagger$. On inserting the expressions (55) and (56) into (65), the electron interaction term (which contains $m^2 \times m^2$ matrices) may be simplified:

$$\tfrac{1}{2} \operatorname{tr} \mathbf{g}\mathbf{P}_2 = \sum_{r,s,t,u} [2(tu|g|rs)R_{su} - (tu|g|sr)R_{su}]R_{rt},$$

where the dummy indices r, s are interchanged in the second term. Thus,

$$E = 2 \operatorname{tr} \mathbf{h}\mathbf{R} + \operatorname{tr} \mathbf{G}\mathbf{R}, \tag{66}$$

where

$$G_{tr} = \sum_{s,u} R_{su}[2(tu|g|rs) - (tu|g|sr)] \tag{67}$$

is the $(m \times m)$ electron interaction matrix of Roothaan.[44]

It is convenient to assume that the basis $\mathbf{a}$ is orthonormal (though the extension to the nonorthogonal case is not difficult[45]), and in this case the assumption that the *occupied* orbitals $\mathbf{A}$ are orthonormal takes the simple form

$$\sum_r T_{rR}{}^* T_{rS} = \sum_r \mathbf{T}^\dagger{}_{Rr}\mathbf{T}_{rS} = (\mathbf{T}^\dagger\mathbf{T})_{RS} = \delta_{RS}$$

or

$$\mathbf{T}^\dagger\mathbf{T} = \mathbf{1}_n. \tag{68}$$

This is equivalent (Appendix) to the statement that $\mathbf{R}$ is idempotent:

$$\mathbf{R}\mathbf{R} = \mathbf{T}\mathbf{T}^\dagger\mathbf{T}\mathbf{T}^\dagger = \mathbf{T}\mathbf{T}^\dagger = \mathbf{R}. \tag{69}$$

The variational problem of determining the best orbitals is thus equivalent to

$$E = 2 \operatorname{tr} \mathbf{h}\mathbf{R} + \operatorname{tr} \mathbf{G}\mathbf{R} = \text{stationary value},$$

subject to

$$\mathbf{R}^2 = \mathbf{R} \quad (\operatorname{tr} \mathbf{R} = n). \tag{70}$$

Interest is generally first centered on the ground state, and in this case the stationary value is a *minimum*. Since $\mathbf{P} = 2\mathbf{R}$, $\mathbf{R}$ is the 1-electron density matrix for particles of given spin, $\mathbf{P}^{\alpha,\alpha} = \mathbf{P}^{\beta,\beta} = \mathbf{R}$, and since only $\mathbf{R}$ appears in the present formulation the orbitals themselves clearly have no unique physical significance.

3.2. Hartree-Fock Hamiltonian

The stationary condition (70) may be expressed otherwise by considering a first-order variation $\delta\mathbf{R}$ and noting that

$$\delta E = 2 \operatorname{tr} \mathbf{h}\delta\mathbf{R} + \operatorname{tr} \mathbf{G}\delta\mathbf{R} + \operatorname{tr} \delta\mathbf{G}\mathbf{R} + \text{(higher-order terms)}.$$

Now $\mathbf{G} = \mathbf{G}(\mathbf{R})$,[46] and by (67) it follows easily that

$$\operatorname{tr} \delta\mathbf{G} \cdot \mathbf{P} = \operatorname{tr} \mathbf{G}(\delta\mathbf{R}) \cdot \mathbf{R} = \operatorname{tr} \mathbf{G}(\mathbf{R}) \cdot \delta\mathbf{R}, \tag{71}$$

which allows us to eliminate the first-order variation in $\mathbf{G}$. The stationary energy condition $\delta E = 0$ then becomes $2 \operatorname{tr} \mathbf{h}\delta\mathbf{R} + 2 \operatorname{tr} \mathbf{G}\delta\mathbf{R} = 0$, and (70) may be replaced by

$$\mathcal{E} = 2 \operatorname{tr} \mathbf{h}^F\mathbf{R} = \text{stationary value},$$

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[43] D. R. Hartree, *Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

[44] C. C. J. Roothaan, Revs. Modern Phys. **23**, 69 (1951).

[45] R. McWeeny, Phys. Rev. **114**, 1528 (1959).

[46] It is convenient to use a functional notation for the dependence of the *matrix* **G** upon the *matrix* **R**.

subject to

$$\mathbf{R}^2=\mathbf{R}\ (\mathrm{tr}\ \mathbf{R}=n), \tag{72}$$

in which

$$\mathbf{h}^F=\mathbf{h}+\mathbf{G} \tag{73}$$

is regarded as a fixed matrix during the variation and is the matrix of the *(Hartree-)Fock Hamiltonian.* $\mathbf{h}^F$ depends, through $\mathbf{G}(\mathbf{R})$, on the matrix $\mathbf{R}$ appropriate to the stationary point (i.e., upon the approximate electron density), and the problem must therefore be solved iteratively. Before considering the method of solution, we verify that the conditions (72) are formally equivalent to those for a stationary ensemble describing a 1-electron system equally likely to be in any of n states [see Sec. I.(2.3)].

To this end, the auxiliary condition $\mathbf{R}^2=\mathbf{R}$, which is somewhat troublesome, may be incorporated at the outset: in fact (Appendix), any variation compatible with this condition may be expressed as a power series involving the matrix

$$\mathbf{v}=(\mathbf{1}-\mathbf{R})\boldsymbol{\Delta}\mathbf{R}, \tag{74}$$

where $\boldsymbol{\Delta}$ is an arbitrary nonsingular $m\times m$ matrix. To second order,

$$\delta\mathbf{R}=(\mathbf{v}+\mathbf{v}^\dagger)+(\mathbf{v}\mathbf{v}^\dagger-\mathbf{v}^\dagger\mathbf{v})+\cdots, \tag{75}$$

and on substituting this result in (72), we obtain the first-order condition

$$\delta\mathcal{E}=\mathrm{tr}\ \mathbf{h}^F\delta\mathbf{R}=\mathrm{tr}\ \mathbf{h}^F(\mathbf{v}+\mathbf{v}^\dagger)=2\ \mathrm{tr}\ \mathbf{h}^F\mathbf{v}$$
$$=2\ \mathrm{tr}\ \boldsymbol{\Delta}\mathbf{R}\mathbf{h}^F(\mathbf{1}-\mathbf{R})=0$$

for arbitrary $\boldsymbol{\Delta}$. This implies that $\mathbf{R}\mathbf{h}^F(\mathbf{1}-\mathbf{R})=\mathbf{0}$, and by taking the difference of this equation and its Hermitian conjugate, it follows that $\mathbf{R}\mathbf{h}^F-\mathbf{h}^F\mathbf{R}=\mathbf{0}$, which is easily shown to be sufficient as well as necessary. Equation (72) is thus equivalent to [cf. I(35)]

$$\mathbf{R}\mathbf{h}^F-\mathbf{h}^F\mathbf{R}=\mathbf{0},\quad \mathbf{R}^2=\mathbf{R}\quad (\mathrm{tr}\ \mathbf{R}=n). \tag{76}$$

The system thus formally resembles a collection of *weakly coupled* 1-electron systems, the 1-electron Hamiltonian being replaced by one with matrix $\mathbf{h}^F$, which contains a $\mathbf{G}$ term to describe the "average" effect of strong interactions.

We may also verify that the occupied orbitals are determined (to within a unitary transformation) as eigenfunctions of the same 1-electron problem with Hamiltonian matrix $\mathbf{h}^F$. This leads to the traditional self-consistent field method, which involves the factorization $\mathbf{R}=\mathbf{T}\mathbf{T}^\dagger$ and the explicit determination of $\mathbf{T}$, whose columns represent the n occupied orbitals. On using $\mathbf{c}_R$ to denote the R column of $\mathbf{T}$ and putting $\epsilon_R=\mathbf{c}_R{}^\dagger\mathbf{h}^F\mathbf{c}_R$, (72) becomes

$$\mathcal{E}=2\sum_R\epsilon_R=\text{stationary value},$$

subject to

$$\mathbf{c}_R{}^\dagger\mathbf{c}_S=\delta_{RS}. \tag{77}$$

Here ϵ_R is the expectation value of a certain *one*-electron Hamiltonian, with matrix $\mathbf{h}^F$, for an electron in orbital $\mathbf{R}$. It is a straightforward matter to show (cf. Roothaan[44]) that the solution occurs when

$$\mathbf{h}^F\mathbf{T}=\mathbf{T}\boldsymbol{\varepsilon}, \tag{78}$$

where the symmetric matrix $\boldsymbol{\varepsilon}$ contains undetermined multipliers which may be eliminated by using $\epsilon_{RS}=\mathbf{c}_R{}^\dagger\mathbf{h}^F\mathbf{c}_S$. Moreover, $\mathbf{R}$ and hence the energy, is invariant against a change to new (orthonormal) orbitals, $\mathbf{T}=\tilde{\mathbf{T}}\mathbf{U}$ ($\mathbf{U}$ unitary), and it is therefore convenient to make the particular choice which reduces $\boldsymbol{\varepsilon}$ to *diagonal* form. In this case, $\mathbf{h}^F\tilde{\mathbf{T}}=\tilde{\mathbf{T}}\tilde{\boldsymbol{\varepsilon}}$ ($\tilde{\boldsymbol{\varepsilon}}=\mathbf{U}\boldsymbol{\varepsilon}\mathbf{U}^\dagger$), and the elements of $\tilde{\boldsymbol{\varepsilon}}$ and columns of $\tilde{\mathbf{T}}$ are then the eigenvalues and eigenvectors of (dropping the tilde)

$$\mathbf{h}^F\mathbf{c}=\epsilon\mathbf{c}. \tag{79}$$

A particular solution is thus uniquely defined in a mathematical sense, although the physical situation is described equally well by any other orthonormal mixtures of the orbitals so defined. This freedom of choice of occupied orbitals has been utilized by Lennard-Jones and others,[47] nonlocalized orbitals being replaced where possible by linear combinations which describe more strongly localized pairs of electrons: this possibility is considered from a more general standpoint in Sec. III. The advantages of using MO's determined by (79) (which may be adopted as the *strict* definition of a true molecular orbital) appear only in discussing excited and ionized states; thus, to first order, $-\epsilon_R$ is an ionization energy (Koopmans' theorem[48]).

Generally, there are m distinct solutions of (79), but in the ground state only the lowest n of these are occupied, determining $\mathbf{T}$, $\mathbf{R}$, and hence $\mathbf{h}^F$. Traditionally, Eqs. (78) are regarded as quasi-linear in the elements of $\mathbf{T}$, these being determined by repeated solution of (79) with a corresponding iterative revision of $\mathbf{h}^F$ until self-consistency is established. The $m-n$ remaining solutions are often referred to as *virtual orbitals* and their use in improving the wave function by configuration interaction is well known.[49]

3.3. Direct Determination of the Density Matrix

It is evident that the 1-electron eigenvalue equation (79) has a purely formal significance and is without meaning except *at the stationary point* where it expresses alternatively the conditions (70) or (72). During the iterative process, $\mathbf{h}^F$ is merely an approximation to the desired SCF Hamiltonian, and (79) is solved not because its solutions have any intrinsic value but because they suggest the direction in which $\mathbf{h}^F$ should be revised. There is no guarantee whatever that this process converges and it seems preferable to solve (70) *directly* by systematically changing $\mathbf{R}$ in such a way as to reduce E most rapidly to a minimum. There are other quan-

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[47] J. E. Lennard-Jones, Proc. Roy. Soc. (London) **A198**, 1 (Pt. I), 14 (Pt. II) (1946), and subsequent papers.

[48] T. Koopmans, Physica **1**, 104 (1933).

[49] R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1952).

tities which take a minimum value when (70) is satisfied [e.g., $\Omega = \mathrm{tr}\,\mathbf{CC}^\dagger$, where $\mathbf{C} = \mathbf{Rh}^F - \mathbf{h}^F\mathbf{R}$; cf. (76)] and a corresponding variety of *steepest descent* processes with various convergence properties: we outline only the process based on (70), since this is related most closely to the conventional SCF method.

Starting from an arbitrary idempotent matrix $\mathbf{R}$ (e.g., the density matrix for an approximate set of n orbitals), we consider a first-order change (75), preserving idempotency, and find from (66) and (71),

$$\delta E_{\text{first order}} = \delta\mathcal{E} = 4\,\mathrm{tr}\,\mathbf{Rh}^F(\mathbf{1}-\mathbf{R})\mathbf{\Delta} = 4\,\mathrm{tr}\,[(\mathbf{1}-\mathbf{R})\mathbf{h}^F\mathbf{R}]^\dagger\mathbf{\Delta}. \quad (80)$$

We now wish to choose $\mathbf{\Delta}$ in order to descend the energy surface as quickly as possible. It is useful to associate a *vector* with the m^2 elements of an $m\times m$ matrix and to define a scalar product

$$\mathbf{A}\cdot\mathbf{B} = \sum_{r,s} A_{rs}{}^* B_{rs} = \sum_{r,s} A^\dagger{}_{sr} B_{rs} = \mathrm{tr}\,\mathbf{A}^\dagger\mathbf{B}. \quad (81)$$

In this case $\mathrm{tr}\,\mathbf{A}^\dagger\mathbf{A}$ is the squared modulus of $\mathbf{A}$, and for fixed $\mathbf{B}$ the scalar product takes its greatest negative value when $\mathbf{A}$ is rotated into the antiparallel position $\mathbf{A} = -\lambda\mathbf{B}$. Thus, for a step $\delta\mathbf{R}$ of given size, (80) gives the greatest reduction in E when $\mathbf{\Delta} = -\lambda(\mathbf{1}-\mathbf{R})\mathbf{h}^F\mathbf{R}$ and $\mathbf{v} = -(\mathbf{1}-\mathbf{R})\mathbf{\Delta R} = -\lambda(\mathbf{1}-\mathbf{R})\mathbf{h}^F\mathbf{R}$ [$\mathbf{R}$ and $(\mathbf{1}-\mathbf{R})$ both being idempotent]. The change corresponding to steepest descent of the energy surface is thus

$$\delta\mathbf{R} = -\lambda(\mathbf{s}+\mathbf{s}^\dagger) + \lambda^2(\mathbf{ss}^\dagger - \mathbf{s}^\dagger\mathbf{s}) + \cdots, \quad (82)$$

where

$$\mathbf{s} = (\mathbf{1}-\mathbf{R})\mathbf{h}^F\mathbf{R}. \quad (83)$$

On introducing

$$\mathbf{L} = \mathbf{s}+\mathbf{s}^\dagger, \quad \mathbf{M} = \mathbf{s}-\mathbf{s}^\dagger, \quad (84)$$

Eq. (82) may be written [observing that $(\mathbf{1}-\mathbf{R})\mathbf{R} = \mathbf{0}$]

$$\delta\mathbf{R} = -\lambda\mathbf{L} - \lambda^2\mathbf{LM} + \cdots. \quad (85)$$

Now this correction satisfies the auxiliary condition to *second* order and therefore determines not only the slope of the E surface in the direction of increasing λ but also its curvature; and it is therefore possible to determine a value λ_{opt} which corresponds to a minimum in the direction of steepest descent (Fig. 1). From (70), (71), and (85), the energy change to second order is

$$\delta E = 2\,\mathrm{tr}\,(-\lambda\mathbf{L} - \lambda^2\mathbf{LM})\mathbf{h}^F + \mathrm{tr}\,\lambda^2\mathbf{LG}(\mathbf{L}), \quad (86)$$

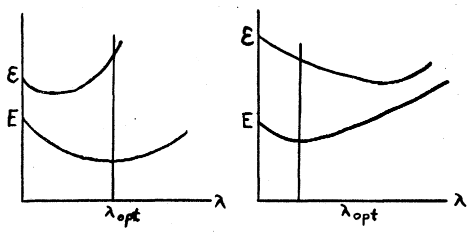
where[46] $\mathbf{G}(\mathbf{L})$ is defined by (67), the elements of $\mathbf{R}$ being replaced by those of $\mathbf{L}$. On putting

$$\mathrm{tr}\,\mathbf{h}^F\mathbf{L} = l, \quad \mathrm{tr}\,\mathbf{h}^F\mathbf{LM} = m, \quad \mathrm{tr}\,\mathbf{LG}(\mathbf{L}) = m', \quad (87)$$

and setting $\partial(\delta E)/\partial\lambda = 0$, it follows that

$$\lambda_{\text{opt}} = -[l/(2m-m')]. \quad (88)$$

The correction (85) leads to the best 1-descent approximation to $\mathbf{R}$ and E. The process is then repeated as often as required.[50] A sensitive test of accuracy of the solution is provided by the matrix $\mathbf{h}^F\mathbf{R}$, which is calculated in each cycle and which, according to (76), ultimately must become symmetric. The quantity m' in (87) is important in estimating λ_{opt}: it arises from the dependence of $\mathbf{h}^F$ upon $\mathbf{R}$, a dependence which is ignored in the traditional method until the end of each cycle when the initial $\mathbf{h}^F$ is revised using the new eigenvectors. In fact, the standard technique seeks a local minimum on an $\mathcal{E}$ surface, defined by (72) (correspondto *fixed* $\mathbf{h}^F$). This procedure usually gives some improvement because both the $\mathcal{E}$ and E surfaces have the same slope at the initial point ($\delta E_{\text{first order}} = \delta\mathcal{E}$), but their curvatures may differ greatly and it is easy to see from Fig. 1(b) how the usual process may diverge.



(a) (b)

FIG. 1. Section through the energy surfaces: (a) The simple Hartree-Fock procedure predicts too small a change; (b) it leads to divergence.

It has been shown[50] that the orbitals themselves (contained in the matrix $\mathbf{T}$) may easily be obtained from the self-consistent $\mathbf{R}$ matrix by using its projection operator property. These may then be used in configuration interaction studies.

In this way, it is possible to obtain analytical self-consistent solutions of the Hartree-Fock equations of arbitrarily high accuracy, since the dimensionality of the basis m is unrestricted. In practice, the basis is finite and the solution is a best approximation in the usual sense of variation theory. Nevertheless, recent work[51] suggests that matrix methods are often more powerful, besides being more widely applicable, than the original Hartree method.

3.4. *Many-Shell Systems*

In most quantum mechanical systems it is possible to distinguish different weakly coupled electron groups or shells: it is then advantageous to formulate the SCF method so that each group may be dealt with individually. It is also possible to admit both *closed* shells, in which the orbitals are doubly occupied, and *open* shells, in which they are singly occupied. In this way it is possible to deal with, for example, a transition metal atom with a shell of singly occupied orbitals outside a core consisting of several closed shells. The method already developed can be taken over with trivial modifications.

A density matrix must now be defined for the orbitals

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[50] Small but cumulative departures from idempotency may be eliminated at any stage by a simple iterative method: R. McWeeny, Proc. Roy. Soc. (London) A235, 496 (1957) (see also Appendix).

[51] R. E. Watson, Tech. Rept. No. 12, Solid State and Molecular Theory Group, Massachusetts Institute of Technology (June 15, 1959).

of each shell, and if these are denoted by $\mathbf{R}_1$, $\mathbf{R}_2$, $\cdots$, it is easily shown that the one-determinant energy expression can be written

$$E=\sum_i \operatorname{tr} \nu_i\mathbf{R}_i\mathbf{h}+\tfrac{1}{2}\sum_i \operatorname{tr} \nu_i\mathbf{R}_i\mathbf{G}_i, \qquad (89)$$

where $\nu_i=1$ or 2 according as the orbitals of group 1 are singly or doubly occupied and $\mathbf{G}_i$ is an electron interaction matrix appropriate to the ith shell. If we define Coulomb and exchange matrices by

$$\begin{aligned}[\mathbf{J}(\mathbf{R})]_{rs}&=\sum_{t,u} R_{tu}(ru|g|st),\\ [\mathbf{K}(\mathbf{R})]_{rs}&=\sum_{t,u} R_{tu}(ru|g|ts),\end{aligned} \qquad (90)$$

then

$$\mathbf{G}_i=\sum_j G_{i,j}(\nu_j\mathbf{R}_j), \qquad (91)$$

where

$$\begin{aligned}\mathbf{G}_{i,j}(\mathbf{R})&=\mathbf{J}(\mathbf{R})-\mathbf{K}(\mathbf{R}) \quad \nu_i=\nu_j=1\\ &=\mathbf{J}(\mathbf{R})-\tfrac{1}{2}\mathbf{K}(\mathbf{R}) \quad \text{otherwise.}\end{aligned} \qquad (92)$$

The first-order variation may then be written

$$(\delta E)_{\text{first order}}=\delta\mathcal{E},$$

where [cf. (72)]

$$\mathcal{E}=\sum_i \nu_i \operatorname{tr} \mathbf{R}_i\mathbf{h}_i^F, \qquad (93)$$

where

$$\mathbf{h}_i^F=\mathbf{h}+\mathbf{G}_i \qquad (94)$$

is a Hamiltonian for shell i, and is again regarded as *fixed* during the variation. But two types of auxiliary condition are now necessary to express the orthonormality of all orbitals:

$$\mathbf{R}_i^2=\mathbf{R}_i, \quad \mathbf{R}_i\mathbf{R}_j=\mathbf{0} \quad (i\neq j). \qquad (95)$$

For a best one-determinant approximation E must be stationary against any variation $\mathbf{R}_i\rightarrow\mathbf{R}_i+\delta\mathbf{R}_i$, in each shell i, subject to (95). This condition may be achieved by solving for each shell in turn, in the Coulomb-exchange field of the others, and repeating the cycle until over-all self-consistency is obtained. If, then, we consider the ith shell, a general variation satisfying (95) is readily found to be [cf. (74) and (75)]

$$\delta\mathbf{R}_i=(\mathbf{v}_i+\mathbf{v}_i^\dagger)+(\mathbf{v}_i\mathbf{v}_i^\dagger-\mathbf{v}_i^\dagger\mathbf{v}_i), \qquad (96)$$

$$\mathbf{v}_i=(\mathbf{1}-\sum_j \mathbf{R}_j)\boldsymbol{\Delta}_i\mathbf{R}_i, \qquad (97)$$

where $\boldsymbol{\Delta}_i$ is an arbitrary square matrix and (96) is valid to second order. That both conditions (95) are satisfied to this order is easily confirmed by substitution and use of the properties $\mathbf{R}_i^2=\mathbf{R}_i$, $\mathbf{R}_i\mathbf{R}_j=\mathbf{0}$ $(i\neq j)$.

The first-order energy change for a variation (96) in the ith shell alone is then

$$\delta\mathcal{E}_{(i)}=\nu_i \operatorname{tr} \delta\mathbf{R}_i\mathbf{h}_i^F,$$

and the analysis of Sec. II.(3.3) may be taken over directly. The steepest descent occurs for

$$\delta\mathbf{R}_i=-\lambda_i\mathbf{L}_i-\lambda_i^2\mathbf{L}_i\mathbf{M}_i, \qquad (98)$$

where

$$\mathbf{L}_i=\mathbf{s}_i+\mathbf{s}_i^\dagger, \quad \mathbf{M}_i=\mathbf{s}_i-\mathbf{s}_i^\dagger \qquad (99)$$

and

$$\mathbf{s}_i=(\mathbf{1}-\sum_j \mathbf{R}_j)\mathbf{h}_i^F\mathbf{R}_i. \qquad (100)$$

The optimum value of λ_i is determined by considering the second-order energy change, and it follows readily that

$$\lambda_{i\ \text{opt}}=-[l_i/(2m_i-m_i')], \qquad (101)$$

where [cf. (87)]

$$l_i=\operatorname{tr} \mathbf{L}_i\mathbf{h}_i^F, \quad m_i=\operatorname{tr} \mathbf{L}_i\mathbf{M}_i\mathbf{h}_i^F, \quad m_i'=\operatorname{tr} \mathbf{L}_i\mathbf{G}_{i,i}(\nu_i\mathbf{L}_i). \qquad (102)$$

For a closed shell $\mathbf{G}_{i,i}(\nu_i\mathbf{L}_i)=2\mathbf{J}(\mathbf{L}_i)-\mathbf{K}(\mathbf{L}_i)=\mathbf{G}(\mathbf{L}_i)$ [cf. the Roothaan $\mathbf{G}$ matrix of (67)]. The result is then analogous to that of the one-shell theory, but the effect of all other shells is allowed for in the new definition of $\mathbf{h}_i^F$ by (94).

This method has been used in obtaining approximate SCF functions for two-shell systems consisting of a single electron outside a closed shell.[52] Convergence has been found entirely satisfactory.

4. Configuration Interaction

Brillouin[53] first pointed out that the configuration interaction problem, discussed in general terms in Sec. I.(3), is to some extent simplified by the use of SCF orbitals satisfying an eigenvalue equation of the type (79). Here we discuss the converse problem, showing that when only single excitations are admitted, a sufficient condition for vanishing of the second-order energy corrections is that the orbitals satisfy an SCF eigenvalue equation. This approach proves particularly appropriate in the more general situation of Sec. III.

4.1. Second-Order Energy Formula

If Φ_0 is a one-determinant approximation to the ground state, the effect of configuration interaction may be incorporated up to second order by the method of Sec. I.(3.1). We split the summation in I(77) into parts referring to single and double excitations and use the matrix element expressions (16), taking the second form of (16b). The energy expression I(77) then becomes

$$E=E^{(0)}+E^{(1)}+E^{(2)}, \qquad (103)$$

where

$$E^{(0)}=H_{00}, \qquad (104)$$

$$E^{(1)}=-\sum_R \sum_{r'(\neq r)} \frac{|(\psi_{Rr'}|\mathfrak{h}_{\text{eff}}|\psi_{Rr})|^2}{E(Rr\rightarrow Rr')}, \qquad (105)$$

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[52] R. McWeeny (unpublished) (1956).

[53] L. Brillouin, Actualités sci et ind. No. 71 (1933).

$$E^{(2)}=-\sum_{R,S}{}' \sum_{\substack{r'(\neq r)\\ s'(\neq s)}} \frac{|(\psi_{Rr'}\psi_{Ss'}|g|\psi_{Rr}\psi_{Ss})-(\psi_{Rr'}\psi_{Ss'}|g|\psi_{Ss}\psi_{Rr})|^2}{E(Rr\rightarrow Rr',\, Ss\rightarrow Ss')}, \tag{106}$$

and the excitation energies are

$$\begin{aligned} &E(Rr\rightarrow Rr')=H_{\kappa\kappa}-H_{00}, \quad \kappa=(a,\,b,\,\cdots r',\,\cdots),\\ &E(Rr\rightarrow Rr',\, Ss\rightarrow Ss')=H_{\kappa\kappa}-H_{00},\\ &\qquad\qquad \kappa=(a,\,b,\,\cdots r',\,\cdots s',\,\cdots). \end{aligned} \tag{107}$$

It is apparent that if each spin orbital in Φ_0 is an exact eigenfunction of $\mathfrak{h}_{\text{eff}}$, then all matrix elements

$$(\psi_{Rr'}|\mathfrak{h}_{\text{eff}}|\psi_{Rr}) \quad (r'\neq r)$$

vanish identically, there is *no* single-excitation energy contribution (105), and H_{00} is stationary against $\psi_{Rr}\rightarrow\psi_{Rr}+\delta\psi_{Rr}$ (all R). We must now show that this result also holds when the spin orbitals in Φ_0 are *approximate* eigenfunctions of $\mathfrak{h}_{\text{eff}}$ and must elucidate the connection between $\mathfrak{h}_{\text{eff}}$ and the operator with matrix $\mathbf{h}^F$.

4.2. *Connection with Approximate Hartree-Fock Theory*

In practice, ψ_{Rr} is seldom an *exact* eigenfunction of the one-electron operator $\mathfrak{h}_{\text{eff}}$, but the vanishing of (105) is ensured provided

$$(\psi_{Rr'}|\mathfrak{h}_{\text{eff}}|\psi_{Rr})=0 \quad (\text{all } r'\neq r), \tag{108}$$

and this condition is sufficient to characterize a certain optimum set of spin orbitals. Generally, the $\psi_{Rr'}$ $(r'\neq r)$ are unspecified except in that, together with ψ_{Rr}, they form a complete orthonormal set. The condition (108) is then equivalent to

$$(\psi|\mathfrak{h}_{\text{eff}}|\psi_{Rr})=0, \quad \psi=\sum_{r'(\neq r)} C_{Rr'}\psi_{Rr'}, \tag{109}$$

and this in turn is equivalent to

$$\begin{aligned} &(\psi_{Rr}|\mathfrak{h}_{\text{eff}}|\psi_{Rr})=\text{stationary value}\\ \text{for}\quad &\psi_{Rr}\rightarrow\psi_{Rr}+\sum_{r'(\neq r)} C_{Rr'}\psi_{Rr'}. \end{aligned} \tag{110}$$

A more familiar form of (110), which arises when the constraint is normalization to unity rather than to $C_{Rr}=1$, is

$$(\psi_{Rr}|\mathfrak{h}_{\text{eff}}|\psi_{Rr})/(\psi_{Rr}|\psi_{Rr})=\text{stationary value}. \tag{111}$$

If therefore, ψ_{Rr} is an *approximate* eigenfunction of $\mathfrak{h}_{\text{eff}}$ in the sense of variation theory, Brillouin's result continues to hold: the optimum spin orbitals, *at any level of approximation*, are those which lead to vanishing single-excitation configuration interaction or, equivalently, are best variational solutions of the *one*-electron problem

$$\mathfrak{h}_{\text{eff}}(1)\psi(1)=\epsilon\psi(1). \tag{112}$$

It must be stressed that $\mathfrak{h}_{\text{eff}}$, defined by (17), (11), and (13), is *not* the Hamiltonian usually employed in SCF theory, for it contains *spin terms*. Accordingly, (112) has as its solution *general spin orbitals* of the form

$$\psi(1)=\phi_\alpha(1)\alpha(1)+\phi_\beta(1)\beta(1), \tag{113}$$

where $\phi_\alpha(1)$ and $\phi_\beta(1)$ are independent spatial functions. Moreover, this form is tacitly assumed in the preceding variational considerations (although this is not usually recognized), where formal constraints are not envisaged. In practice, however, the variational process is usually applied to a determinantal function in which the spin orbitals are *constrained*, n_α having the form $\psi_R(i)=R_\alpha(i)\alpha(i)$ and n_β having the form $\bar{\psi}_R(i)=R_\beta(i)\beta(i)$.[54] When $n_\alpha=n_\beta$, it is further assumed that $R_\alpha(i)=R_\beta(i)$, so that the spin orbitals occur in degenerate pairs ψ_R, $\bar{\psi}_R$ with a common orbital part. In such cases the *spatial* factor alone is varied and the flexibility implied in the preceding formal discussion (and elsewhere—for example, Löwdin[26]) is lost. The justification for these special forms, assumed in Secs. II.(3.3) and (3.4), is not trivial and must now be considered.

We show that (112) has, in fact, self-consistent solutions provided only degenerate *pairs* of spin orbitals are occupied, these being of the form $\psi_R=R_\alpha\alpha$ and $\bar{\psi}_R=R_\beta\beta$ with $R_\alpha=R_\beta=R$ and that the occupied orbitals A, B, $\cdots R$, $\cdots$ must then satisfy the *spinless* equation

$$\mathfrak{h}^F(1)\phi(1)=\epsilon\phi(1), \tag{114}$$

where $\mathfrak{h}^F$ is the operator whose matrix form is employed in Sec. II.(3.3). This means that on solving (112), allowing ψ to be a *general* spin orbital (113), the assumed special forms must again emerge.

We use the definitions (11), (13), and (17), observing that

$$\begin{aligned} &\mathcal{J}(1)\psi(1)=\left(\int g(1,1')\rho_1(1';1')d\tau_{1'}\right)\psi(1),\\ &\mathcal{K}(1)\psi(1)=\int g(1,1')\rho_1(1;1')\psi(1')d\tau_{1'}, \end{aligned} \tag{115}$$

and insert the special form (21), (22). The effect of each part of $\mathfrak{h}_{\text{eff}}(1)$ upon a general spin orbital (113) is then easily determined. $\mathfrak{h}(1)$ and $\mathcal{J}(1)$ are spinless and immediately give

$$\begin{aligned} &\mathfrak{h}(1)[\phi_\alpha(1)\alpha(1)+\phi_\beta(1)\beta(1)]\\ &\qquad=[\mathfrak{h}(1)\phi_\alpha(1)]\alpha(1)+[\mathfrak{h}(1)\phi_\beta(1)]\beta(1), \end{aligned} \tag{116}$$

$$\begin{aligned} &\mathcal{J}(1)[\phi_\alpha(1)\alpha(1)+\phi_\beta(1)\beta(1)]\\ &\qquad=[\mathcal{J}(1)\phi_\alpha(1)]\alpha(1)+[\mathcal{J}(1)\phi_\beta(1)]\beta(1), \end{aligned} \tag{117}$$

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[54] This form has been used in the case $n_\alpha\neq n_\beta$ by J. A. Pople and R. K. Nesbet [J. Chem. Phys. 22, 571 (1954)] and by Berthier [Compt. rend. 238, 91 (1952)] in the "unrestricted" Hartree-Fock method. Restrictions are still present and the term unrestricted would be more appropriate with spin orbitals of the form (113).

where, carrying out the spin integrations, the Coulomb operator amounts to multiplication by

$$j(1)=\int g(1,1')P_1(1';1')dv_{1'}. \tag{118}$$

The exchange operator has an explicit spin dependence:

$$\begin{aligned}\mathcal{K}(1)[\phi_\alpha(1)\alpha(1)+\phi_\beta(1)\beta(1)]\\ &=\int g(1,1')\tfrac{1}{2}P_1(1;1')[\alpha(1)\alpha^*(1')+\beta(1)\beta^*(1')]\\ &\qquad\times[\phi_\alpha(1')\alpha(1')+\phi_\beta(1')\beta(1')]d\tau_{1'}\\ &=\left[\tfrac{1}{2}\int g(1,1')P_1(1;1')\phi_\alpha(1')dv_{1'}\right]\alpha(1)\\ &\quad+\left[\tfrac{1}{2}\int g(1,1')P_1(1;1')\phi_\beta(1')dv_1'\right]\beta(1)\\ &=[\mathfrak{k}(1)\phi_\alpha(1)]\alpha(1)+[\mathfrak{k}(1)\phi_\beta(1)]\beta(1),\end{aligned} \tag{119}$$

where $\mathfrak{k}(1)$ is the *spinless* exchange operator whose effect on a function of space variables is given by

$$\mathfrak{k}(1)\phi(1)=\tfrac{1}{2}\int g(1,1')P_1(1;1')\phi(1')dv_1. \tag{120}$$

On inserting (116), (117), and (119) in (112), the linear independence of the spin factors allows us to separate the equation into two spinless equations

$$\begin{aligned}[\mathfrak{h}(1)+\mathfrak{j}(1)-\mathfrak{k}(1)]\phi_\alpha(1)=\epsilon\phi_\alpha(1),\\ [\mathfrak{h}(1)+\mathfrak{j}(1)-\mathfrak{k}(1)]\phi_\beta(1)=\epsilon\phi_\beta(1).\end{aligned} \tag{121}$$

The independent components ϕ_α and ϕ_β must therefore satisfy the *same* spinless eigenvalue equation

$$\mathfrak{h}^F(1)\phi(1)=\epsilon\phi(1),\quad [\mathfrak{h}^F(1)=\mathfrak{h}(1)+\mathfrak{j}(1)-\mathfrak{k}(1)], \tag{122}$$

and if the solutions are denoted by $A(1)$, $B(1)$, $\cdots R(1)$, $\cdots$, then the simplest orthogonal spin-orbital solutions of (112) are the pairs $A(1)\alpha(1)$, $A(1)\beta(1)$, etc.

It remains only to show that $\mathfrak{h}^F(1)$ is the operator which appears in matrix form in Sec. II.(3.3). On referring $P_1(1;1')$ to the arbitrary basis $\mathbf{a}=(a\ b\ c\cdots)$, using (50) and (55), and evaluating the general matrix element of $\mathfrak{h}^F(1)$, this result follows at once.

There is no parallel reduction in the case of an *odd* number of electrons because in this case [cf. I(57) et seq.]

$$P_1(\overset{\alpha}{1};\overset{\alpha}{1'})\neq P_1(\overset{\beta}{1};\overset{\beta}{1'})$$

and the ϕ_α and ϕ_β equations [cf. (121)] then turn out to be *coupled*. It is possible to solve the coupled equations to obtain a set of optimum spin orbitals of the form (113), but it is more usual to simplify the problem by introducing constraints. Taking n_α orbitals of the form $R_\alpha(i)\alpha(i)$ and n_β of the form $R_\beta(i)\beta(i)$ (Nesbet and Pople[54]) ensures that the single determinant is an eigenfunction of $\mathcal{S}_z$ (the z component of total spin)—a requirement ignored in using optimum orbitals—but does *not* insure that it is an eigenfunction of $\mathcal{S}^2$ (the squared total spin). The second requirement is, however, satisfied if we choose $R_\alpha=R_\beta$ for certain pairs of spin orbitals (i.e., introduce doubly occupied orbitals) and give the remaining (singly occupied) orbitals a common spin factor. Both requirements are therefore met by the functions employed in Secs. II.(3.3) and (3.4), which probably represent the best one-determinant compromise between high accuracy—according to the energy criterion—and the proper representation of a definite spin eigenstate. A much more general approach, in which different groups of electrons (e.g., those in the doubly and singly occupied orbitals, respectively) are described by different vector-coupled functions so as to give any required spectroscopic state, is developed in Sec. III.

APPENDIX. IDEMPOTENT MATRICES

1. Factorization Property

We consider an idempotent $m\times m$ matrix $\mathbf{R}$, which is Hermitian symmetric and of rank n, and show first that $\mathbf{R}$ may always be written

$$\mathbf{R}=\mathbf{T}\mathbf{T}^\dagger, \tag{A1}$$

where $\mathbf{T}$ is an $m\times n$ matrix whose columns ($\mathbf{t}_i$) are orthonormal in the sense $\mathbf{t}_i^\dagger\mathbf{t}_j=\delta_{ij}$. We use the theorem that any Hermitian symmetric matrix can be brought to diagonal form by some unitary transformation, i.e., there exists a unitary matrix $\mathbf{U}$ such that

$$\overline{\mathbf{R}}=\mathbf{U}^\dagger\mathbf{R}\mathbf{U}=\text{diagonal matrix}. \tag{A2}$$

The property $\mathbf{R}^2=\mathbf{R}$ then means $\bar{R}_{ii}^2=\bar{R}_{ii}$, so that each diagonal element is either 0 or 1. But the rank of $\mathbf{R}$, which (like the trace) is unchanged by a unitary transformation, is n; and $\overline{\mathbf{R}}$ has rank n only if its diagonal contains n 1's and $m-n$ 0's. In this case, "rank $\mathbf{R}=n$" is equivalent to "tr $\mathbf{R}=n$," and (A2) yields (A1), in which $\mathbf{T}$ is an $m\times n$ rectangular matrix whose n columns are selected from those of $\mathbf{U}$. These columns have the required orthonormality from the unitary property, and the proof is complete.

2. Variations Preserving Idempotency

We require an expression for the most general change which an $m\times m$ matrix of rank n can suffer, consistent with preservation of idempotency. Since we can write $\mathbf{R}=\mathbf{T}\mathbf{T}^\dagger$, it is sufficient to consider a change $\mathbf{T}\rightarrow\mathbf{T}+\delta\mathbf{T}$, and quite generally

$$\delta\mathbf{T}=\mathbf{\Delta}\mathbf{T}, \tag{A3}$$

where $\mathbf{\Delta}$ is an arbitrary (nonsingular) $m\times m$ matrix. Now $\mathbf{R}$ is a projection operator, uniquely associated with the n-dimensional subspace (Γ_R) spanned by the columns of $\mathbf{T}$. There is a unique decomposition of any vector $\mathbf{c}$ into its projections on Γ_R and on the complementary subspace Γ_{1-R}:

$$\mathbf{c}=\mathbf{c}_R+\mathbf{c}_{1-R},$$

where

$$\mathbf{c}_R=\mathbf{R}\mathbf{c},\quad \mathbf{c}_{1-R}=(\mathbf{1}-\mathbf{R})\mathbf{c}. \tag{A4}$$

To define a new $\mathbf{R}$ it is sufficient to define a new n-dimen-subspace. But since any vector, including those represented by the columns of $\mathbf{T}$, can be decomposed according to (A4), any new ray (i.e., vector of arbitrary length) can be formed by adding a vector which lies *wholly outside* Γ_R. Now, n completely arbitrary linearly independent vectors of this kind are represented by the columns of

$$\delta\mathbf{T}=(\mathbf{1}-\mathbf{R})\mathbf{\Delta}\mathbf{T}, \tag{A5}$$

$(\mathbf{1}-\mathbf{R})$ projecting out the part of (A3) which lies in Γ_R. Hence $\mathbf{T}+\delta\mathbf{T}$, with $\delta\mathbf{T}$ defined by (A5), suffices to specify a new subspace in a completely general way. The columns of

$$\mathbf{T}'=\mathbf{T}+\delta\mathbf{T} \tag{A6}$$

do not, however, represent an orthonormal basis; and to define the associated projection operator in the standard form (A1), it is therefore necessary to orthonormalize the columns of $\mathbf{T}'$ to obtain a new set $\tilde{\mathbf{T}}$, in terms of which the new projection operator, $\mathbf{R}+\delta\mathbf{R}$ is given by

$$(\mathbf{R}+\delta\mathbf{R})=\tilde{\mathbf{T}}\tilde{\mathbf{T}}^{\dagger}. \tag{A7}$$

Now the metric associated with the vectors of $\mathbf{T}'$ is defined by the $m\times m$ matrix $\mathbf{M}=\mathbf{T}'^{\dagger}\mathbf{T}'$, and a convenient orthonormalization is

$$\tilde{\mathbf{T}}=\mathbf{T}'\mathbf{M}^{-\frac{1}{2}}. \tag{A8}$$

It remains only to evaluate (A7) in terms of $\mathbf{\Delta}$ and $\mathbf{R}$ using (A8), (A6), and (A5). A straightforward analysis, using the properties of the idempotent matrices $\mathbf{R}$ and $(\mathbf{1}-\mathbf{R})$, gives

$$\mathbf{R}=\delta\mathbf{R}=(\mathbf{R}+\mathbf{v})(\mathbf{1}+\mathbf{v}^{\dagger}\mathbf{v})^{-1}(\mathbf{R}+\mathbf{v}^{\dagger}),$$

where

$$\mathbf{v}=(\mathbf{1}-\mathbf{R})\mathbf{\Delta}\mathbf{R}. \tag{A9}$$

When $\mathbf{\Delta}$ represents a small change, the expansion

$$(\mathbf{1}+\mathbf{v}^{\dagger}\mathbf{v})^{-1}=\sum_{n=0}^{\infty}(-1)^n(\mathbf{v}^{\dagger}\mathbf{v})^n$$

is convergent and $\delta\mathbf{R}$ may be easily written down to any order. Thus,

$$\begin{aligned}\delta\mathbf{R}&=(\mathbf{v}+\mathbf{v}^{\dagger})\quad\text{(first order)},\\ \delta\mathbf{R}&=(\mathbf{v}+\mathbf{v}^{\dagger})+(\mathbf{v}\mathbf{v}^{\dagger}+\mathbf{v}^{\dagger}\mathbf{v})\quad\text{(second order)}.\end{aligned} \tag{A10}$$

3. Purification of an Almost Idempotent Matrix

It is necessary to be able to construct a (Hermitian symmetric) idempotent matrix from one which is only approximately so. If $\mathbf{R}_0^2\neq\mathbf{R}_0$, the problem is to reduce the matrix $(\mathbf{R}_0^2-\mathbf{R}_0)$ to zero, and this is equivalent to reducing to zero the (scalar) quantity $\Omega=\operatorname{tr}(\mathbf{R}_0^2-\mathbf{R}_0)^2$. This may be accomplished by the steepest descent method [Sec. II.(3.3)] which yields the rapidly convergent (second order) sequence $\mathbf{R}_0$, $\mathbf{R}_1$, $\mathbf{R}_2$ in which

$$\mathbf{R}_{n+1}=\mathbf{R}_n^2(3\mathbf{1}-2\mathbf{R}_n),$$

and the limit $\mathbf{R}$ is a strictly idempotent matrix close to $\mathbf{R}_0$ in the sense that the separation

$$\operatorname{tr}(\mathbf{R}-\mathbf{R}_0)^2\ll\operatorname{tr}\mathbf{R}(=n).$$

III. GENERALIZED PRODUCT APPROXIMATIONS

1. Electron Groups and Generalized Product Functions

In most many-electron systems it is possible to distinguish various groups of electrons. In the orbital approach, discussed in Sec. II, this analysis is carried to its formal limit, the electrons being assigned *one* at a time to different spin orbitals. It is physically more realistic to deal with larger groups of electrons. In an atom, for example, the natural groups to consider are the K, L, M, $\cdots$ shells; in a molecule they might be the electron pairs of various bonds; in a crystal, core electrons, valence electrons, and conduction electrons. Then again, since it is usually impossible to deal adequately with *all* the electrons in a system, molecular and solid-state theory often utilizes a model in which only *one group*, containing a relatively small number of electrons, is considered. It is clearly important to examine rigorously the basis for this kind of analysis and to deal generally with wave functions which explicitly recognize a separation into electron groups. Important steps in this direction have recently been made by Parr et al.[55–57] Here we extend the analysis from the stand point of density matrix theory.

1.1. Definitions and Aims

The natural generalization of the antisymmetrized orbital product II(4), namely,

$$\Phi_{Aa,Bb,\ldots}(1,\cdots N)=M\sum_{\mathcal{P}}(-1)^p\mathcal{P}\psi_{Aa}(1)\psi_{Bb}(2)\cdots, \tag{1}$$

is the antisymmetrized product

$$\Phi_{Aa,Bb,\ldots}(1,\cdots N)=M\sum_{\mathcal{P}}(-1)^p\mathcal{P}\Phi_{Aa}(1,\cdots N_A)\times\Phi_{Bb}(N_A+1,\cdots N_A+N_B)\cdots. \tag{2}$$

We call $\Phi_{Aa}(1,\cdots N_A)$ a group function for the N_A electrons of group A and use the subscript a to indicate the particular state of this group. Similarly, Φ_{Bb} describes a second electron group in state b, and M is

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[55] R. G. Parr, F. O. Ellison, and P. G. Lykes, J. Chem. Phys. 24, 1106 (1956).

[56] P. G. Lykos and R. G. Parr, J. Chem. Phys. 24, 1166 (1956).

[57] J. M. Parks and R. G. Parr, J. Chem. Phys. 28, 335 (1958).

simply a normalizing factor for the totally antisymmetrical sum. The function (2) is called a *generalized* product function. Wave functions of this form have already received some attention.[55–59] We also use linear combinations of such functions, a variety of states being permitted for each electron group to give a wave function

$$\Psi(1,\cdots N)=\sum_{a,b,\cdots} C_{ab\cdots}\Phi_{Aa,Bb,\cdots}(1,\cdots N). \qquad (3)$$

This mixing—again analogous to that employed in orbital theories—is referred to as configuration interaction, where now any specification of group states $(a,b,\cdots)$ defines a configuration. We are concerned with approximate solutions of the wave equation of type (2)—the one-configuration approximation—and more generally of type (3).

It is further assumed that the group functions are individually antisymmetric in the (space-spin) variables of the particles to which they refer; and in this case a completely antisymmetrical function results when the summation in (2) excludes the subgroup of permutations which leave every electron in its original group. If there are ν permutations in the remaining distinct cosets, the normalizing factor is then $\nu^{-\frac{1}{2}}$ *provided* the group functions are orthogonal in the sense

$$\int \Phi_{Rr}{}^{*}(1,i,j,\cdots)\Phi_{Ss}(1,k,l,\cdots)d\tau_1=0$$

$$(R\neq S,\ \text{or}\ r\neq s,\ \text{or both}), \qquad (4)$$

where the functions contain at least one common set of variables, indicated by 1 (and written in the first place, since—owing to antisymmetry—any set may be brought to this place with at most a sign change) and $\int d\tau_1$ indicates integration over these variables. This condition, which resembles those proposed by Hurley, Lennard-Jones, and Pople[59] and by Parr et al.[55] is a natural generalization of that usually assumed for orbitals and is adopted in what follows. With $R\neq S$, the functions are orthogonal because they belong to *different groups*, while for $R=S$ but $r\neq s$, they are orthogonal because they represent *different states* of the same group.

In Sec. III we examine quite generally the mathematical and physical implications of using wave functions of type (3) without any restriction on the individual group functions other than that implied by (4). We find that the density matrix approach of Sec. I then leads to a complete generalization of all the equations in Sec. II, the whole formal structure of the orbital approach being preserved.

It should be noted that an *exact* wave function cannot be expressed in the form (3), since the set of functions of type (2) cannot be complete unless all partitions of $N=N_A+N_B+\cdots$ are allowed (cf. Lykos and Parr[56]). Nevertheless, (2) and (3) appear to provide the most promising generalization of the Hartree-Fock approximation and are fully consistent with the need for a simple physical picture in which loosely coupled electron groups are distinguished.

1.2 Generalization of the Slater Method

Matrix elements of the Hamiltonian between antisymmetrized *orbital* products such as (1), first given by Slater,[25] appear in Sec. II along with corresponding contributions to the 1- and 2-electron density matrices. In this case, each group comprises a single electron described by a spin orbital. We now generalize these results to functions of type (2), in which each group comprises any number of electrons described by one of a variety of antisymmetrical group functions, the latter being subject to the requirement (4) but otherwise unspecified.

This may be done by the method indicated in I(51) et seq. We simply determine

$$(\Phi_\lambda|\sum_{i,j=1}^{N}{}' g(i,j)|\Phi_\kappa)$$

by standard methods (e.g., Slater,[25] Condon and Shortley[23]), remembering that each group function is individually antisymmetric and that the number of permutations which lead to nonvanishing contributions is severely limited by (4). The results take their neatest form on introducing the density matrices for each separate group, these being defined in the usual way [cf. I(38)]:

$$\rho_n{}^R(rr'|1,\cdots n;1',\cdots n')$$
$$=N_R(N_R-1)\cdots(N_R-n+1)\int\Phi_{Rr}{}^{*}(1,\cdots N_R)$$
$$\times\Phi_{Rr'}(1',\cdots n',n+1,\cdots N_R)d\tau_{n+1}\cdots d\tau_{N_R}, \qquad (5)$$

where the labeling of the variables is arbitrary.

To give one example, when $\kappa=(a,b,\cdots)$—giving the function (2)—it is found that

$$(\Phi_\kappa|\sum_{i,j=1}^{N}{}' g(i,j)|\Phi_\kappa)$$
$$=\sum_R\int g(1,2)\rho_2{}^R(rr|1,2;1,2)d\tau_1 d\tau_2$$
$$+\sum_{R,S}{}'\int g(1,2)\rho_1{}^R(rr|1;1)\rho_1{}^S(ss|2;2)d\tau_1 d\tau_2$$
$$-\sum_{R,S}{}'\int g(1,2)\rho_1{}^R(rr|2;1)\rho_1{}^S(ss|1;2)d\tau_1 d\tau_2,$$

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[58] W. Moffitt, Proc. Roy. Soc. (London) **A210**, 224, 245 (1951).

[59] A. C. Hurley, J. E. Lennard-Jones, and J. A. Pople, Proc. Roy. Soc. (London) **A220**, 446 (1953).

and, from I(51), this implies that

$$\rho_2(\kappa\kappa|1,2;1',2')=\sum_R \rho_2^R(rr|1,2;1',2') +\sum_{R,S}{}' \rho_1^R(rr|1;1')\rho_1^S(ss|2;2') -\sum_{R,S}{}' \rho_1^R(rr|2;1')\rho_1^S(ss|1;2').$$

The two-particle density matrix for an antisymmetrized product of orthogonal group functions can be expressed in terms of the one- and two-particle density matrices of the individual groups. This is a fundamental result and is an obvious generalization of II(9a)—to which it reduces when each group contains only one electron. From it, by using I(41) and remembering (4), it follows without difficulty that

$$\rho_1(\kappa\kappa|1;1')=\sum_R \rho_1^R(rr|1;1').$$

This means, in particular, that the electron densities of the separate groups are additive.

The general results are summarized in the following. As in Slater's analysis, nonvanishing terms arise only for configurations κ and λ, which differ in not more than *two* group functions. There are thus three distinct cases:

(*a*) $\kappa=\lambda=(a,b,\cdots r,\cdots s,\cdots)$

$$\begin{aligned}\rho_2(\kappa\kappa|1,2;1',2')&=\sum_R \rho_2^R(rr|1,2;1',2') +\sum_{R,S}{}' \rho_1^R(rr|1;1')\rho_1^S(ss|2;2') -\sum_{R,S}{}' \rho_1^R(rr|2;1')\rho_1^S(ss|1;2'),\\ \rho_1(\kappa\kappa|1;1')&=\sum_R \rho_1^R(rr|1;1').\end{aligned}\tag{6a}$$

(*b*) $\kappa=(a,b,\cdots r,\cdots),\ \lambda=(a,b,\cdots r',\cdots)$

$$\begin{aligned}\rho_2(\kappa\lambda|1,2;1',2')&=\rho_2^R(rr'|1,2;1',2') + \sum_{S(\neq R)} \rho_1^R(rr'|1;1')\rho_1^S(ss|2;2') - \sum_{S(\neq R)} \rho_1^R(rr'|2;1')\rho_1^S(ss|1;2')\\ &\quad+ \sum_{S(\neq R)} \rho_1^S(ss|1;1')\rho_1^R(rr'|2;2') - \sum_{S(\neq R)} \rho_1^S(ss|2;1')\rho_1^R(rr'|1;2'),\\ \rho_1(\kappa\lambda|1;1')&=\rho_1^R(rr'|1;1').\end{aligned}\tag{6b}$$

(*c*) $\kappa=(a,b,\cdots r,\cdots s,\cdots),\ \lambda=(a,b,\cdots r',\cdots s',\cdots)$

$$\begin{aligned}\rho_2(\kappa\lambda|1,2;1',2')&=\rho_1^R(rr'|1;1')\rho_1^S(ss'|2;2') -\rho_1^R(rr'|2;1')\rho_1^S(ss'|1;2')\\ &\quad+\rho_1^S(ss'|1;1')\rho_1^R(rr'|2;2') -\rho_1^S(ss'|2;1')\rho_1^R(rr'|1;2').\end{aligned}\tag{6c}$$

These results should be compared with those of II(9). The formal similarity with Slater's results is clearest in the actual matrix element expressions, I(41) giving [with the usual Hamiltonian of I(44)]

$$(a)\quad H_{\kappa\kappa}=\sum_R H^R(rr)+\tfrac{1}{2}\sum_{R,S}{}'[J^{RS}(rr,ss)-K^{RS}(rr,ss)],\tag{7a}$$

$$(b)\quad H_{\lambda\kappa}=H^R(rr')+\sum_{S(\neq R)}[J^{RS}(rr',ss)-K^{RS}(rr',ss)],\tag{7b}$$

$$(c)\quad H_{\lambda\kappa}=J^{RS}(rr',ss')-K^{RS}(rr',ss'),\tag{7c}$$

where

$$H^R(rr')=\operatorname{tr}\mathfrak{h}(1)\rho_1^R(rr'|1;1') +\tfrac{1}{2}\operatorname{tr} g(1,2)\rho_2^R(rr'|1,2;1',2'),\tag{8}$$

$$J^{RS}(rr',ss')=\operatorname{tr} g(1,2)\rho_1^R(rr'|1;1')\rho_1^S(ss'|2;2') =\int g(1,2)\rho_1^R(rr'|1;1)\rho_1^S(ss'|2;2)d\tau_1d\tau_2,\tag{9}$$

$$K^{RS}(rr',ss')=\operatorname{tr} g(1,2)\rho_1^R(rr'|2;1')\rho_1^S(ss'|1;2') =\int g(1,2)\rho_1^R(rr'|2;1)\rho_1^S(ss'|1;2)d\tau_1d\tau_2.\tag{10}$$

These results generalize those of II(16). The quantities (8)–(10) are the analogs of the one-electron, two-electron Coulomb, and two-electron exchange integrals, respectively; but they contain density matrices instead of orbitals, and the matrix element notation employed in II(16) would therefore be inappropriate. The analog of the one-electron integral $H^R(rr')$ can, however, be regarded as a matrix element of a *many*-electron Hamiltonian for group R *alone* in the field of the nuclei. Comparison of (8) with I(49) shows that

$$H^R(rr')=(\Phi_{Rr'}|\mathcal{H}^R|\Phi_{Rr}),\tag{11}$$

where

$$\mathcal{H}^R(1,\cdots N_R)=\sum_{i=1}^{N_R}\mathfrak{h}(i)+\tfrac{1}{2}\sum_{i,j=1}^{N_R}{}' g(i,j).\tag{12}$$

Clearly, (11) reduces to $(\psi_{Rr'}|\mathfrak{h}|\psi_{Rr})$ in the spin-orbital product approximation where $N_R=1$. In particular, $H^R(rr)$ is a group energy of the electrons described by Φ_{Rr}, with all other electrons removed.

It is clear from (9) that $J^{RS}(rr',ss')$ is simply the mutual repulsion of two electron distributions, whose densities—at points 1 and 2, respectively—are $\rho_1^R(rr'|1;1)$ and $\rho_1^S(ss'|2;2)$. This interpretation is not affected by elimination of the spin, for the spin integrations are immediate and give, by using I(52),

$$J^{RS}(rr',ss')=\int g(1,2)P_1^R(rr'|1;1) \times P_1^S(ss'|2;2)dv_1dv_2,\tag{13}$$

in which the two density factors are now ordinary three-dimensional charge densities associated with the transition $r\rightarrow r'$ in group R and $s\rightarrow s'$ in group S, respectively. Transition densities of this kind play an important part in the theory of radiation, their moments determining the transition probabilities. The interpretation of $K^{RS}(rr',ss')$ is less obvious and depends on the spin states of the two groups: it appears later that when these each correspond to zero total spin z component

$$K^{RS}(rr',ss')=\tfrac{1}{2}\int g(1,2)P_1{}^R(rr'|2;1)\times P_1{}^S(ss'|1;2)dv_1dv_2, \quad (14)$$

where the integrand is small unless groups R and S overlap considerably.

Generally, we start from a one-configuration approximation Φ_0, corresponding to $\kappa(=0)=(a,b,c,\cdots)$, and subsequently admit excited configurations, Φ_κ $(\kappa>0)$, in which one or more groups are in excited states $(\Phi_{Rr}\rightarrow\Phi_{Rr'})$. The expression (7a) thus gives the one-configuration approximation to the energy, while (7b) and (7c) are the off-diagonal matrix elements required in configuration interacting studies.

1.3. Coulomb and Exchange Operators for General Electron Groups

In Sec. II.(1.3) it was shown that Slater's results could be written in an alternative form by introducing Coulomb and exchange operators. Exactly similar one-electron operators can be defined in the more general case by using the natural interpretation of $\rho_1{}^R(rr|1;1')$ as the kernel of an integral operator. If $\sum_{i=1}{}^{N_R}\mathcal{A}(i)$ is any symmetrical sum [cf. $\sum_{i=1}{}^{N_R}\mathfrak{h}(i)$] of one-electron *integral* operators, $\mathcal{A}(1)$ having kernel $A(1;1')$, we can write [cf. I(43)]

$$(\Phi_{Rr'}|\sum_{i=1}^{N_R}\mathcal{A}(i)|\Phi_{Rr})=\mathrm{tr}\,\mathcal{A}(1)\rho_1{}^R(rr'|1;1')$$

$$=\int A(1;1')\rho_1{}^R(rr'|1'';1)d\tau_{1''}d\tau_1. \quad (15)$$

This enables us to express $K^{RS}(rr',ss)$ in (7) as the matrix element of a sum of one-electron operators associated with group S. For, from (10),

$$K^{RS}(rr',ss)=\int g(1,1'')\rho_1{}^S(ss|1;1'')\times\rho_1{}^R(rr'|1'';1)d\tau_{1''}d\tau_1,$$

and therefore, by (15),

$$K^{RS}(rr',ss)=\int K^S(1;1')\rho_1{}^R(rr'|1';1)d\tau_1d\tau_{1'}$$

$$=(\Phi_{Rr'}|\sum_{i=1}^{N_R}\mathcal{K}^S(i)|\Phi_{Rr}), \quad (16)$$

where the typical operator is $\mathcal{K}^S(1)$ with kernel $K^S(1;1')$:

$$\mathcal{K}^S(1)\rightarrow K^S(1;1')=g(1,1')\rho_1{}^S(ss|1;1'). \quad (17)$$

The state symbol s is dropped because we normally use $\mathcal{K}^S$ only to describe a group in the state indicated in the basic configuration Φ_0. On the other hand, $J^{RS}(rr',ss)$ can be regarded as the matrix element of an operator sum whose terms are merely multipliers: from (9),

$$J^{RS}(rr',ss)=\mathrm{tr}\,J^S(1)\rho_1{}^R(rr'|1;1')$$

$$=(\Phi_{Rr'}|\sum_{i=1}^{N_R}\mathcal{J}^S(1)|\Phi_{Rr}), \quad (18)$$

where the typical operator is $\mathcal{J}^S(1)=J^S(1)$, a simple multiplier;

$$\mathcal{J}^S(1)\rightarrow J^S(1)=\int g(1,1')\rho_1{}^S(ss|1';1')d\tau_{1'}. \quad (19)$$

We refer to $\mathcal{J}^S(1)$ and $\mathcal{K}^S(1)$, defined by (19) and (17), as the Coulomb and exchange operators for an electron in the field of the electrons of group S. $J^{RS}(rr',ss)$ and $K^{RS}(rr',ss)$ are therefore the matrix elements of the interaction between the N_R electrons of group R and the field produced by the electrons of group S. The Coulomb and exchange operators for an electron in the field of group S apparently have the following effect upon an arbitrary function:

$$\mathcal{J}^S(1)\psi(1)=J^S(1)\psi(1)$$

$$=\left\{\int g(1,1')\rho_1{}^S(ss|1';1')d\tau_{1'}\right\}\psi(1), \quad (20)$$

$$\mathcal{K}^S(1)\psi(1)=\int K^S(1;1')\psi(1')d\tau_{1'}$$

$$=\int g(1,1')\rho_1{}^S(ss|1;1')\psi(1')d\tau_{1'}. \quad (21)$$

The exchange operator is seen from (17) to be simply the one-electron density operator weighted with an inverse distance factor. It is also useful to introduce a *total* Coulomb operator and a *total* exchange operator to describe the Coulomb-exchange field felt by an electron of group R at point 1 in the presence of *all* groups *except* R—these are simply

$$\mathcal{J}_{(R)}(1)=\sum_{S(\neq R)}\mathcal{J}^S(1),\quad \mathcal{K}_{(R)}(1)=\sum_{S(\neq R)}\mathcal{K}^S(1). \quad (22)$$

The effective one-electron Hamiltonian for an electron of group R in the field of the nuclei and all other groups may then be defined as

$$\mathfrak{h}_{\mathrm{eff}}{}^R(1)=\mathfrak{h}(1)+\mathcal{J}_{(R)}(1)-\mathcal{K}_{(R)}(1), \quad (23)$$

and the effective total Hamiltonian for group R as [cf. (12)]

$$\mathcal{H}_{\text{eff}}{}^{R}(1,\cdots N_R)=\sum_{i=1}^{N_R}\mathfrak{h}_{\text{eff}}{}^{R}(i)+\tfrac{1}{2}\sum_{i,j=1}^{N_R}{}' g(i,j). \tag{24}$$

The matrix elements of $\mathcal{H}_{\text{eff}}{}^{R}$ are written, by analogy with (11),

$$\begin{aligned}H_{\text{eff}}{}^{R}(rr')=(\Phi_{Rr'}|\mathcal{H}_{\text{eff}}{}^{R}|\Phi_{Rr})&=H^{R}(rr')\\&+\sum_{S(\neq R)}[J^{RS}(rr',ss)-K^{RS}(rr',ss)],\end{aligned} \tag{25}$$

and it then follows easily that (7a) and (7b) may be written in the alternative forms

$$\text{(a)}\quad H_{\kappa\kappa}=\sum_{R}H_{\text{eff}}{}^{R}(rr)-\tfrac{1}{2}\sum_{R,S}{}'[J^{RS}(rr,ss)-K^{RS}(rr,ss)], \tag{26}$$

$$\text{(b)}\quad H_{\lambda\kappa}=H_{\text{eff}}{}^{R}(rr')\quad(\textit{one}\text{ difference}, \Phi_{Rr'}\neq\Phi_{Rr}). \tag{27}$$

These forms correspond closely to II(16a) and II(16b). It should, however, be noted that, in spite of the close analogy with the development of Sec. II.(1.3), each group is acted on by *different* effective field. This is because, in general, $K^{RR}(rr',rr)\neq J^{RR}(rr',rr)$ and the restriction $S\neq R$ in (22) cannot therefore be relaxed in defining $\mathfrak{h}_{\text{eff}}{}^{R}$ by (23).

2. Energy Expression

It is now necessary to obtain and interpret an energy expression corresponding to the wave function (3). It is possible to do this by starting from a one-configuration approximation Φ_0 and admitting configuration interaction by the method of Sec. I.3: the system density matrix may be obtained by iteration, the distribution functions calculated from I(50), and the energy expression interpreted along the lines of I(54). But it is more instructive to analyze the energy into terms associated with the separate electron groups, provided the interaction between them is not too strong. The natural tool for making this analysis is the perturbation expansion I(76), and this leads to an immediate generalization of Sec. II.4.

2.1. Perturbation Series

We repeat the analysis of Sec. II.(4.1), replacing orbitals by group functions. Equations II(103)–II(107) are then replaced by

$$E=E^{(0)}+E^{(1)}+E^{(2)}, \tag{28}$$

where

$$E^{(0)}=H_{00}=\sum_{R}H^{R}(rr)+\sum_{R<S}[J^{RS}(rr,ss)-K^{RS}(rr,ss)], \tag{29}$$

$$E^{(1)}=-\sum_{R}\sum_{r'(\neq r)}\frac{|H_{\text{eff}}{}^{R}(rr')|^{2}}{E(Rr\rightarrow Rr')}, \tag{30}$$

$$E^{(2)}=-\sum_{R,S}\sum_{\substack{r'(\neq r)\\ s'(\neq s)}}\frac{|J^{RS}(rr',ss')-K^{RS}(rr',ss')|^{2}}{E(Rr\rightarrow Rr',\,Ss\rightarrow Ss')}, \tag{31}$$

and the excitation energies in the denominators are

$$\begin{aligned}E(Rr\rightarrow Rr')&=H_{\kappa\kappa}-H_{00},\\&\qquad\kappa=(a,b,\cdots r',\cdots),\\E(Rr\rightarrow Rr',\,Ss\rightarrow Ss')&=H_{\kappa\kappa}-H_{00},\\&\qquad\kappa=(a,b,\cdots r',\cdots s',\cdots).\end{aligned} \tag{32}$$

It should be recalled that (since matrix elements vanish for Φ's differing in more than two group functions) *only* singly and doubly excited configurations occur in the second-order energy expression. Each term in (28) is now considered in detail.

2.2. First Approximation. Correlation

$E^{(0)}(=H_{00})$ is simply the energy in the one-configuration approximation and, as such, has a special importance. Although the terms in (29) admit an immediate description in terms of the charge densities of the separate groups [cf. (13) and (14)], it is important to remember that they originate in the reduction of $\rho_1(00|1;1')$ and $\rho_2(00|1,2;1',2')$ according to (6a) and that $E^{(0)}$ results when these one-configuration approximations are substituted in the general expression [I(45)]. It is then useful to obtain the corresponding spinless quantities which appear in I(54), but to do this some assumption about spin states is necessary. The most widely useful assumption is that each electron group has zero z component of total spin and for illustration we consider this case. It has been noted in I(57) et seq. that the 1-electron density matrices must then have the form

$$\begin{aligned}\rho_1{}^{R}(rr|1;1')=P_1{}^{R}(rr|\overset{\alpha}{1};\overset{\alpha}{1'})\alpha(1)\alpha^{*}(1')&\\+P_1{}^{R}(rr|\overset{\beta}{1};\overset{\beta}{1'})\beta(1)\beta^{*}(1'),&\end{aligned} \tag{33}$$

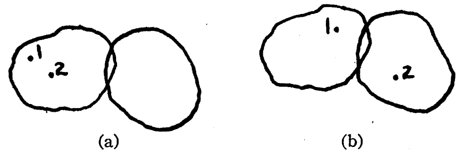
where

$$P_1{}^{R}(rr|\overset{\alpha}{1};\overset{\alpha}{1'})=P_1{}^{R}(rr|\overset{\beta}{1};\overset{\beta}{1'})=\tfrac{1}{2}P_1(rr|1;1').$$

Consequently, when the spin integrations are performed in (6a), we obtain (with $\kappa=0$)

$$\begin{aligned}P_2(00|1,2;1',2')=\sum_{R}P_2{}^{R}(rr|1,2;1',2')&\\+\sum_{R,S}{}'P_1{}^{R}(rr|1;1')P_1{}^{S}(ss|2;2')&\\-\tfrac{1}{2}\sum_{R,S}{}'P_1{}^{R}(rr|2;1')P_1{}^{S}(ss|1;2'),&\\P_1(00|1;1')=\sum_{R}P_1{}^{R}(rr|1;1').&\end{aligned} \tag{34}$$

The distribution functions, which determine the potential energy terms in the energy expression I(54) follow on removing the primes in (34).



(a) (b)

FIG. 2. Localized electron groups: Full correlation is admitted for electrons at 1 and 2 in (a); partial (Fermi) correlation is admitted in (b).

The charge density is simply a sum of the charge densities associated with the separate groups, irrespective of the forms of the group functions. But the pair function has the simplest interpretation when each Φ_{Rr}—and hence $P_n{}^R(rr|1,\cdots n;1',\cdots n')$, is *localized*, becoming small when any of the variables $1, \cdots n, 1', \cdots n'$ refer to a point outside some fairly definite region (Fig. 2). For in this case,

$$\begin{aligned} P_2(00|1,2;1,2) &\simeq P_2{}^R(rr|1,2;1,2) \\ &\qquad \text{for points 1 and 2 within region } R \\ &\simeq P_1{}^R(rr|1;1)P_1{}^S(ss|2;2) \\ &\qquad \text{for 1 in region } R, \text{ 2 in region } S. \end{aligned} \tag{35}$$

In other words, when two particles are close together in the same group region [Fig. 2(a)], they are described by the pair function for that group—which is capable of describing correlation effects since the group function has not been specified. In principle, it is only for two particles in *different* group regions [Fig. 2(b)] that the pair function must fail to admit full correlation, reducing to the product of two 1-electron probability functions. The wave function is thus flexible enough to admit correlation in regions where it is most important and yet recognizes in a simple way the independence of parts of the system which are remote from one another.

On inserting (34) in I(54), we retrieve (29) with the interaction terms reduced according to (13) and (14). But now it is clear that taking J^{RS} alone corresponds to neglecting *correlation* between the particles in group R and those in group S, each group being regarded as a *static* charge cloud; while admitting K^{RS} allows for some degree of *inter*group correlation (arising from the intergroup terms in (34) which are not of simple product form). Closer investigation shows that the associated correlation terms in $P_2(00|1,2;1,2)$ are completely analogous to those which, in one-determinant theory, represent the Fermi hole of Sec. II.(2.2), describing the reduced probability of approach of particles with the *same spin*. This exchange correction is fairly small even in Hartree-Fock theory, where the group functions (orbitals) are superimposed in the same region of space; it is expected to be exceedingly small when the functions are localized in the sense just discussed.

To summarize, $E^{(0)}$ is a sum of the energies of the different groups (each taken separately in the field of all nuclei), supplemented by the electrostatic interactions between their separate unperturbed charge clouds. There remains a correlation correction which is very small if the separate groups are substantially localized in different regions of space. In many applications, e.g., Sec. III.(4.1), it is reasonable to refer to $E^{(0)}$, given by (29), as the *electrostatic* approximation. We now find the $E^{(1)}$ and $E^{(2)}$ may be described in terms of the *perturbation* of each group by the presence of the others. For convenience, they may be referred to as *polarization* and *dispersion* energies—a terminology which we must now justify.

2.3. Polarization Energy

$E^{(1)}$ arises from admixture of singly excited configurations, those in which the R group is described by $\Phi_{Rr'}$ being incorporated with a weight depending on $H_{\text{eff}}{}^R(rr')$ and giving rise, by (76), to a change of *electron density* within group R. Since $H_{\text{eff}}{}^R(rr')$ is a matrix element of $\mathcal{H}_{\text{eff}}{}^R$, which contains the effective field produced by the nuclei and all electron groups other than R (each group in the state indicated in Φ_0), this modification of charge density results largely from the presence of other electron groups and is aptly described as a *polarization*. A given one-configuration approximation may thus be improved by admitting the polarization of each group in the Coulomb-exchange field of the others—the latter being calculated by using the group functions assigned in the one-configuration approximation. It is clear from (25) and (13) that the dominant potential energy terms in $H_{\text{eff}}{}^R(rr')$ may be visualized in terms of a transition charge cloud of density $P_1{}^R(rr'|1;1)$ in the field of the nuclei and other electron groups. The exchange effect is again of secondary importance, being associated with a correlation correction.

2.4. Dispersion Energy

$E^{(2)}$ involves double excitations and clearly represents the effect of mixing due to electrostatic interaction between *pairs* of transition densities; for that part which refers to groups R and S depends upon $J^{RS}(rr',ss')$ and $K^{RS}(rr',ss')$, the first being the interaction energy between charge clouds whose densities at points 1 and 2 are $P_1{}^R(rr'|1;1)$ and $P_1{}^S(ss'|2;2)$, respectively, and the second being the associated correlation correction. When the electron groups R and S belong to distant molecules, $K^{RS}(rr',ss')$ becomes quite negligible; and the Coulomb interaction of the two transition densities is then the well-known dispersion energy in London's theory of intermolecular forces.[60]

3. Generalization of the Self-Consistent Field Method

Since even a single generalized product is potentially far superior to a one-determinant orbital function, it is

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[60] F. London, Z. Physik 63, 245 (1930) (see also reference 63).

of interest to formulate conditions which determine the best group-group functions, just as the Hartree-Fock equations determine best orbitals. Lykos and Parr[56] have proposed on intuitive grounds that each group function should be determined by solving an eigenvalue problem, in which the Hamiltonian contains terms depending on the wave functions of the other groups; and that the whole set of group functions should be systematically adjusted until self-consistency results. We now investigate this possibility from the standpoint of variation theory, in close analogy with Sec. II.(4.2).

3.1. *Conditions for Best Group Functions*

From (30) it is clear that the polarization energy, which arises from admixture of singly excited configurations, vanishes when

$$(\Phi_{Rr'}|\mathcal{H}_{\text{eff}}{}^{R}|\Phi_{Rr})=0 \qquad \text{(all groups } R\text{, all excitations } r'\neq r\text{)}. \tag{36}$$

This condition, which implies the vanishing of the first-order variation of the one-configuration energy, would obviously be fulfilled if Φ_{Rr} were an exact eigenfunction of $\mathcal{H}_{\text{eff}}{}^{R}$, defined by (23) and (24). But in the present case this is not possible; for, while $\mathcal{H}_{\text{eff}}{}^{R}$ is a general N_R-electron operator, Φ_{Rr} is *constrained* to lie in a subspace orthogonal to all other group functions Φ_{Ss} $(S\neq R)$. It is, therefore, *not* strictly true that the best group functions satisfy eigenvalue equations [cf. II(112)]

$$\mathcal{H}_{\text{eff}}{}^{R}\Phi=\lambda\Phi. \tag{37}$$

The condition (36) may still be utilized, however, exactly as in Sec. II.(4.2). It is equivalent to

$$(\Phi_R|\mathcal{H}_{\text{eff}}{}^{R}|\Phi_{Rr})=0 \quad \text{(all } R\text{)},$$

where Φ_R is any function in the subspace spanned by the functions of group R and orthogonal to Φ_{Rr}. This, in turn, implies that

$$(\Phi_{Rr}|\mathcal{H}_{\text{eff}}{}^{R}|\Phi_{Rr})=\text{stationary value} \quad \text{(all } R\text{)}$$

against (38)

$$\Phi_{Rr}\rightarrow\Phi_{Rr}+\sum_{r'(\neq r)}C_{Rr'}\Phi_{Rr'}$$

which is equivalent to

$$(\Phi_{Rr}|\mathcal{H}_{\text{eff}}{}^{R}|\Phi_{Rr})/(\Phi_{Rr}|\Phi_{Rr}) =\text{stationary value} \quad \text{(all } R\text{)}, \tag{39}$$

for arbitrary variation of Φ_{Rr} *within* the R-group subspace. This means that Φ_{Rr} is an *approximate* eigenfunction of (37) in the usual sense of variation theory, the variation being constrained to the R-group subspace —which is orthogonal to those of all other groups according to (4). The simplest way of introducing such a constraint is to build the functions of different groups from different orthogonal sets of one-electron functions.

Since $\mathcal{H}_{\text{eff}}{}^{R}$ contains the density operators of all groups other than R, it is necessary to solve the set of equations (39) by an iterative method. Each effective Hamiltonian is calculated from an assumed approximate wave function; each group function is then revised by solution of (39), and the revised functions are employed in recalculating the effective Hamiltonians; the cycle is then repeated until self-consistency is achieved.

3.2. *Connection with the Theory of Lykos and Parr*

It is useful to give a specific example of the generalized product approach in order to bring out the connection with previous work in this field. We discuss the case of an atom with an *inner shell* (A) and an *outer shell* (B). Normally, the inner shell—which in orbital theories comprise filled groups of doubly occupied orbitals—is in a ^1S state, but the outer shell of valence electrons may be vector coupled to a state of higher (orbital and spin) angular momentum. In contrast, however, with the development of Sec. II.(3.4), it is unnecessary to restrict the functions Φ_{Aa} and Φ_{Bb} to particular states or orbital approximations. Nor is there any restriction upon the number of shells, although for convenience of exposition we consider only two.

The one-configuration energy is, from (29),

$$E^{(0)}=H^A(aa)+H^B(bb)+J^{AB}(aa,bb)-K^{AB}(aa,bb). \tag{40}$$

But from (25), this may be written alternatively as

$$E^{(0)}=H^A(aa)+H_{\text{eff}}{}^{B}(bb)=H_{\text{eff}}{}^{A}(aa)+H^B(bb). \tag{41}$$

In the first form, the energy is that of the A group described by Φ_{Aa}, *alone* in the field of the nucleus, plus that of the B group, alone in the field of the nucleus *and* its inner shell: in the second form, it is that of the B group described by Φ_{Bb}, alone in the field of the nucleus, plus that of the A group, alone in the field of the nucleus and the outer shell. Self-consistency is achieved when $H_{\text{eff}}{}^{A}(aa)$, the only part of the energy depending on Φ_{Aa}, is stationary against variation of Φ_{Aa}, and when $H_{\text{eff}}{}^{B}(bb)$ is stationary against variation of Φ_{Bb}. From (25), these are clearly the conditions derived more formally in Sec. III.(3.1). One form of the effective Hamiltonian $\mathcal{H}_{\text{eff}}{}^{R}$ $(R=A, B)$ has been given by Lykos and Parr: in the general definitions (23) and (24), this Hamiltonian has been reduced to its simplest possible form, the effect of all other groups being represented entirely by means of *one*-electron density operators.

The higher-order terms in the energy expression (28) have not been given previously. If the group functions are self-consistent, the polarization energy vanishes and the only remaining contribution, to second order, is the *dispersion* energy

$$E^{(2)}=-\sum_{\substack{a'(\neq b)\\ b'(\neq b)}}\frac{|J^{AB}(aa',bb')-K^{AB}(aa',bb')|^2}{E(Aa\rightarrow Aa',\, Bb\rightarrow Bb')}. \tag{42}$$

Suitable excited functions $\Phi_{Aa'}$ and $\Phi_{Bb'}$ arise incidentally in the determination of Φ_{Aa} and Φ_{Bb} (cf. the virtual orbitals of Hartree-Fock theory, Sec. II).

Finally, when the inner shell is tightly bound, and relatively insensitive to variations in the outer shell, the whole problem may formally be reduced to one of N_B electrons in the effective field defined by $\mathfrak{h}_{\text{eff}}{}^B$, energies being reckoned above that of the inner shell, namely, $H^A(aa)$. The only constraint on the outer shell function is that implied by (4). This observation (cf. McWeeny[61]; Parr et al.[55,56]) provides a rigorous basis for the common practice—in atomic, molecular, and solid-state theory—of confining attention to the valence electrons. In this case, where only the outer shell function is determined variationally, the polarization of the core by the valence electrons is represented by the extra term

$$E^{(1)}=-\sum_{a'(\neq a)}\frac{|H_{\text{eff}}{}^A(aa')|^2}{E(Aa\rightarrow Aa')}. \tag{43}$$

It seems likely that such terms may be of considerable importance in the theory of atomic spectra.

4. Remarks on Applications

It has now been established that whenever a system contains a number of orthogonal electron groups, it is possible to discuss each one separately in the field of the others, and that it is useful to distinguish interaction terms analogous to those recognized in the theory of intermolecular forces. It is, for example, meaningful—at a certain level of approximation—to speak of polarization and dispersion interactions between, say, two CH_3 groups in the same molecule; between the σ and π electrons of a conjugated system; and even between the K and shells of a single atom. In conclusion we briefly discuss one or two immediate applications of this analysis.

4.1. Separate Systems. Intermolecular Forces

Systems may be described as separate if the *nuclei* fall into groups, each with its own complement of electrons described by a substantially localized group function. Van der Waals forces and the cohesive energies of ionic and molecular crystals would be amenable to discussion using this model. For such a system we put

$$V(1)=V_A(1)+V_B(1)+\cdots, \tag{44}$$

a sum of contributions from the separate groups of nuclei, and define a one-electron Hamiltonian for group R in the field of its *own nuclei alone:*

$$\mathfrak{h}^R(1)=-(\hbar^2/2m)\nabla^2(1)+V_R(1), \tag{45}$$

and an associated N_R-electron Hamiltonian for system R,

$$\mathcal{H}_0{}^R(1,\cdots N_R)=\sum_{i=1}^{N_R}\mathfrak{h}^R(1)+\tfrac{1}{2}\sum_{i,j=1}^{N_R}{}' g(i,j). \tag{46}$$

If matrix elements of this Hamiltonian are distinguished by subscript zero, the one-configuration energy (29) takes the explicit form

$$\begin{aligned}E^{(0)}=\sum_R H_0{}^R(rr)+\sum_{R<S}\bigg\{&\int V_S(1)\rho_1{}^R(rr|1;1)d\tau_1\\&+\int V_R(1)\rho_1{}^S(ss|1;1)d\tau_1\\&+\int g(1,2)\rho_1{}^R(rr|1;1)\rho_1{}^S(ss|2;2)d\tau_1d\tau_2\\&-\int g(1,2)\rho_1{}^R(rr|2;1)\rho_1{}^S(ss|1;2)d\tau_1d\tau_2\bigg\}.\end{aligned} \tag{47}$$

If the functions Φ_{Rr} were exact wave functions for the separate systems, the first sum would be the total electronic energy at infinite separation: generally, it is the total electronic energy of separate systems whose wave functions are suitably deformed by their mutual approach. If the exchange correlation is neglected, the typical interaction term in (47) reduces, on eliminating spin, to

(energy of R-group charge distribution in field
of nuclei of system S)
+(energy of S-group charge distribution in
field of nuclei of system R)
+(interaction energy of charge densities of
group R and group S). (48)

The first-order interactions between all pairs of groups are thus basically Coulombic until their electron distributions begin to overlap—in which case the exchange terms can no longer be neglected.

The polarization and dispersion terms follow from (30) and (31). In particular, the polarization of system R by the other systems is now determined by the matrix element

$$\begin{aligned}H_{\text{eff}}{}^R(rr')=H_0{}^R(rr')+\sum_{S(\neq R)}\bigg\{&\int V_S(1)\rho_1{}^R(rr'|1;1)d\tau_1\\&+\int g(1,2)\rho_1{}^R(rr'|1;1)\rho_1{}^S(ss|2;2)d\tau_1d\tau_2\\&-\int g(1,2)\rho_1{}^R(rr'|2;1)\rho_1{}^S(ss|1;2|d\tau_1d\tau_2\bigg\}.\end{aligned} \tag{49}$$

The first term vanishes if Φ_{Rr} and $\Phi_{Rr'}$ are exact wave functions for the isolated system R but not otherwise. The second term is mainly the energy of a transition charge cloud $P_1{}^R(rr'|1;1)$ in the field of all other systems in their ground states.

Electrostatic and polarization forces are clearly large if the systems bear a net charge (ionic crystals), small if they are neutral (molecular crystals), and very small

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[61] R. McWeeny, Proc. Roy. Soc. (London) **A223**, 306 (1954) (in particular, Sec. 4).

if they possess high symmetry and small multipole moments (inert gases). As Longuet-Higgins[62] has pointed out, however, multipole expansions are neither an integral part of the London theory nor, at short distances, appropriate.

By exploiting the density matrix formulation, it is possible conveniently to redevelop the whole theory of intermolecular forces (for a review, see Margenau[63]) without making the multipole expansions which are characteristic of the older work in this field. The basic physical picture can in this way be preserved in all situations and with wave functions of great generality.

4.2. *Split-Orbital Wave Functions*

Various authors have pointed out the desirability of recognizing correlations between electrons of different spin by abandoning the idea of doubly occupied orbitals. Wave functions for pairs of electrons have been discussed by Lennard-Jones,[59,64] and by Löwdin,[65] Shull and Löwdin,[66] and Matsen et al.,[67] who develop the idea of split orbitals. The present methods are very conveniently applied in such work.

The wave function associated with a set of doubly occupied orbitals may be written as the generalized product

$$\Phi_0(1,\cdots N)=M\sum_{\mathcal{P}}(-1)^p\mathcal{P}\Phi_{Aa}(1,2)\Phi_{Bb}(3,4)\cdots, \tag{50}$$

where

$$\Phi_{Rr}(i,j)=R(i)R(j)\Theta_{00}(i,j), \tag{51}$$

and

$$\Theta_{00}(i,j)=2^{-\frac{1}{2}}[\alpha(i)\beta(j)-\beta(i)\alpha(j)]. \tag{52}$$

$\Phi_{Rr}(i,j)$ is thus a properly antisymmetric singlet function ($S=0$, $S_z=0$) describing the pair of electrons in orbital R. The simplest improvement on (51) is suggested by Eckart's[68] calculation on helium and consists of redefining $\Phi_{Rr}(1,2)$ as

$$\Phi_{Rr}(1,2)=m_R[R_+(1)R_-(2)+R_-(1)R_+(2)]\Theta_{00}(1,2). \tag{53}$$

This is the singlet function for an open-shell configuration in which electrons of different spin occupy different orbitals. Formally, this function resembles the Heitler-London function II(37) and the correlation which it admits may be discussed along similar lines. In an atom or ion (see, e.g., Matsen et al.[67]), R_+ and R_- might be inner and outer orbitals. In an alternant conjugated molecule (see, e.g., Löwdin[65]), they might be π-electron orbitals localized preferentially on different sets of carbon atoms. Perhaps the simplest way of constructing functions of the type (53) is to allow *two* orthogonal orbitals, R_1 and R_2, for each pair of electrons and to take

$$\begin{aligned} R_+(1)&=\lambda_R R_1(1)+\mu_R R_2(1),\\ R_-(1)&=\lambda_R R_1(1)-\mu_R R_2(1), \end{aligned} \tag{54}$$

so that R_1 is augmented in one region of space by addition of R_2 and diminished elsewhere, subtraction of R_2 having the reverse effect. In the limiting case $\mu_R\rightarrow 0$, (53) then reduces to a doubly occupied orbital, but for $\mu_R\neq 0$ the orbital is split, enabling the electrons to avoid one another. With the orbitals (54), (53) may be rewritten as

$$\Phi_{Rr}(1,2)=[c_{R1}R_1(1)R_1(2)+c_{R2}R_2(1)R_2(2)]\Theta(1,2)$$
$$(c_{R1}=2\lambda_R{}^2m_R,\quad c_{R2}=-2\mu_R{}^2m_R). \tag{55}$$

The parameters c_{R1} and c_{R2} may then be varied, in each group in turn, until self-consistency is achieved in the sense of Sec. III.(3.1). Any number of functions could be admitted in each group and a convenient generalization of (55) would be

$$\begin{aligned} \Phi_{Rr}(1,2)&=\sum_i c_{Ri}R_i(1)R_i(2)\Theta_{00}(1,2)\\ &=\sum_i c_{Ri}\Phi_{Rr_i}(1,2), \end{aligned} \tag{56}$$

where it is convenient to regard $R_i(1)R_i(2)\Theta_{00}(1,2)$ formally as the ith 2-electron state used in defining Φ_{Rr}. The spinless density matrices are readily seen to be

$$\begin{aligned} &P_2(rr|1,2;1',2')\\ &\quad=2\sum_{i,j}c_{Ri}c_{Rj}{}^*R_i(1)R_i(2)R_j{}^*(1')R_j{}^*(2')\\ &\qquad\qquad=\sum_{i,j}c_{Ri}c_{Rj}{}^*P_2{}^R(r_ir_j|1,2;1',2'),\\ &P_1(rr|1;1')\\ &\quad=2\sum_{i,j}c_{Ri}c_{Rj}{}^*\delta_{ij}R_i(1)R_j{}^*(1')\\ &\qquad\qquad=\sum_{i,j}c_{Ri}c_{Rj}{}^*P_1{}^R(r_ir_j|1;1'), \end{aligned} \tag{57}$$

and the analysis of Sec. III.(3.1) applies immediately. The best R-group fuction is determined by solving the secular problem

$$\det|(Rr_j|\mathcal{H}_{\text{eff}}{}^R|Rr_i)-\lambda\delta_{r_jr_i}|=0, \tag{58}$$

where $\mathcal{H}_{\text{eff}}{}^R$ has matrix elements given by (25), namely,

$$\begin{aligned} (\Phi_{Rr_j}|\mathcal{H}_{\text{eff}}{}^R|\Phi_{Rr_i})&=H_{\text{eff}}{}^R(r_ir_j)\\ &=H^R(r_ir_j)+\sum_{S(\neq R)}[J^{RS}(r_ir_j,ss)-K^{RS}(r_ir_j,ss)]. \end{aligned} \tag{59}$$

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[62] H. C. Longuet-Higgins, Proc. Roy. Soc. (London) **A235**, 537 (1956).

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[67] G. H. Brigman and F. A. Matsen, J. Chem. Phys. **27**, 829 (1957); R. P. Hurst, J. D. Gray, G. H. Brigman, and F. A. Matsen, J. Mol. Phys. **1**, 189 (1958).

[68] C. Eckart, Phys. Rev. **36**, 878 (1930).

Here, after integrating over spins and using (57), Eqs. (8), (9), and (10) give

$$H_{\mathrm{eff}}{}^{R}(r_ir_j)=2\delta_{ij}(R_j|\mathfrak{h}|R_i)+(R_jR_j|g|R_iR_i),$$

$$J^{RS}(r_ir_j,ss)=4\delta_{ij}\sum_k(R_jS_k|g|R_iS_k)|c_{Sk}|^2, \qquad (60)$$

$$K^{RS}(r_ir_j,ss)=2\delta_{ij}\sum_k(R_jS_k|g|S_kR_i)|c_{Sk}|^2.$$

The natural method of achieving self-consistency is to start from an assumed set of coefficients [e.g., $c_{R1}=1$, $c_{Ri}=0$ $(i>1)$] and to solve (58) for each group in turn to obtain new estimates of the coefficients. The parts of $H_{\mathrm{eff}}{}^{R}(r_ir_j)$ which depend on the coefficients may then be revised and the cycle repeated. The total energy is finally given by (26), in which

$$H_{\mathrm{eff}}{}^{R}(rr)=\sum_{i,j}c_{Ri}c_{Rj}{}^{*}H_{\mathrm{eff}}{}^{R}(r_ir_j). \qquad (61)$$

Various applications of this approach are at present in progress and will be reported fully elsewhere. Preliminary calculations indicate excellent convergence.

4.3. Applications Involving Spin Dependence

In conclusion, we illustrate the calculation of spin densities [Sec. I.(2.4)] for systems in states with $S_z\neq 0$. We take for illustration the aromatic free radicals discussed by McConnell and Chestnut,[69] in which the A group is a single π electron spread over a certain set of carbon atoms and the other groups B, C, $\cdots$ include electron pairs describing C—H bonds attached to these atoms. Proton magnetic resonance experiments indicate that the balance of α- and β-spin densities [Sec. I.(2.4)] in each C—H bond is disturbed by the presence of the odd π electron, giving a nonzero resultant spin density at the proton. To explain this effect theoretically, we start from a one-configuration approximation

$$\begin{aligned}\Phi_0(1,\cdots N)&=\Phi_{A1,B1,\ldots}(1,\cdots N)\\&=M\sum_{\mathcal{P}}(-1)^p\mathcal{P}\Phi_{A1}(1)\Phi_{B1}(2,3)\cdots,\end{aligned} \qquad (62)$$

in which

$$\Phi_{A1}(1)=A(1)\alpha(1),\ \Phi_{B1}(2,3)=B(2,3)\Theta_{00}(2,3),\ \text{etc.} \qquad (63)$$

This function gives zero spin density at the protons because A has a node in the molecular plane and the contributions from the other groups vanish for singlet states. We must therefore admit excited group functions with spin factors $\Theta_{S,\,S_z}(S\neq 0)$. But generalized products containing a triplet group function must appear in prescribed combinations to give a doublet state $(S=S_z=\frac{1}{2})$ of the whole molecule (see, e.g., Condon and Shortley,[23] p. 73). Thus, the combination in which the B group is excited into its first triplet state is

$$\Phi_\kappa=-(3)^{-\frac{1}{2}}\Phi_{A1,B3,C1\cdots}+(\tfrac{2}{3})^{\frac{1}{2}}\Phi_{A2,\,B2,\,C1,\cdots}=\Phi_B,\ \text{say}, \qquad (64)$$

where

$$\begin{aligned}\Phi_{A2}(1)&=A(1)\beta(1), &&(S=\tfrac{1}{2},\ S_z=-\tfrac{1}{2}),\\ \Phi_{B2}(2,3)&=B'(2,3)\Theta_{11}(2,3), &&(S=1,\ S_z=1),\\ \Phi_{B3}(2,3)&=B'(2,3)\Theta_{10}(2,3), &&(S=1,\ S_z=0).\end{aligned} \qquad (65)$$

If one such function is admitted for each pair, the perturbed density becomes, by I(50),

$$\begin{aligned}\rho_1(1;1')=\rho_{00}\rho_1(00|1;1)&+\sum_{R(\neq A)}\rho_{0R}\rho_1(0R|1;1')\\&+\sum_{R(\neq A)}\rho_{R0}\rho_1(R0|1;1')\\&+\sum_{R,S(\neq A)}\rho_{RS}\rho_1(RS|1;1'),\end{aligned} \qquad (66)$$

where, to first order, I(76) gives

$$\rho_{00}=1,\quad \rho_{0R}=\rho_{R0}{}^{*}=H_{0R}/(H_{00}-H_{RR}),\quad \rho_{RS}=0. \qquad (67)$$

The density and transition density matrices which occur are seen from (6) to be

$$\begin{aligned}\rho_1(00|1;1')&=P_1{}^{A}(11|1;1')+\sum_{R(\neq A)}\rho_1{}^{R}(11|1;1'),\\ \rho_1(0R|1;1')&=-(1/\sqrt{3})\rho_1{}^{R}(13|1;1'),\end{aligned} \qquad (68)$$

where for typical groups, A and B,

$$\begin{aligned}\rho_1{}^{A}(11|1;1)&=P_1{}^{A}(11|1;1')\alpha(1)\alpha^{*}(1'),\\ \rho_1{}^{B}(13|1;1')&=\tfrac{1}{2}Q_1{}^{B}(13|1;1')[\alpha(1)\alpha^{*}(1')-\beta(1)\beta^{*}(1')],\end{aligned} \qquad (69)$$

and we introduce a *transition* spin density [cf. Sec. I.(2.4)]

$$Q_1{}^{B}(13|1;1')=2\int B(1,2)B'^{*}(1,2)dv_2. \qquad (70)$$

On inserting these results in (66), the spin density I(66) is found to be

$$\begin{aligned}Q_1(1)&=\sum\frac{2H_{0R}}{\sqrt{3}E(R_1\rightarrow R_3)}Q_1{}^{R}(13|1;1)\\&\simeq\frac{2H_{0B}Q_1{}^{B}(13|1;1)}{\sqrt{3}E(B_1\rightarrow B_3)}\ \text{(near the proton of group } B\text{)}.\end{aligned} \qquad (71)$$

This result is perfectly general and independent of the precise form of the wave function or the number of electron groups distinguished. But it is of considerable interest to discuss the sign of the spin polarization, which depends on that of H_{0B}. A straightforward calculation shows that H_{0B} reduces to a single exchange

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[69] H. M. McConnell and D. B. Chestnut, J. Chem. Phys. 28, 107 (1958).

term,

$$H_{0B}=\sqrt{3}K^{AB}(11,13), \tag{72}$$

where

$$K^{AB}(11,13)=\tfrac{1}{2}\int g(1,2)P_1{}^A(11|2;1)\times Q_1{}^B(13|1;2)dv_1dv_2. \tag{73}$$

Even using the crudest orbital approximations to the singlet and triplet functions, B (symmetric) and B' (antisymmetric), it is then possible to infer by inspection that the spin density at a C—H proton is negative, i.e., that the electron spin at this end of the bond is most likely to be antiparallel to that of the π electron.

An exactly similar analysis can be used to show that the odd electron polarizes the other pairs of π electrons to give negative spin densities on the atoms where the odd electron is unlikely to be found. These negative π-electron spin densities are, in turn, revealed by their effect on the attached protons. It seems entirely possible that the analysis of hyperfine coupling constants, following McConnell and Chestnut,[69] can in this way be made accurately quantitative.