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Quantum Theory of Many-Particle Systems. II. Study of the Ordinary Hartree-Fock Approximation*

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A system of N antisymmetric particles, moving under the influence of a fixed potential and their mutual many-particle interactions, is investigated in the ordinary Hartree-Fock scheme, having the total wave function approximated by a single Slater determinant. It is shown that all the density matrices of various orders, the wave function, and the entire physical situation depends only on a fundamental invariant $\rho(x_1,x_2)$, which is identical with the first-order density matrix. The Hartree-Fock equations are expressed in terms of this quantity.

The Hartree-Fock equations are also solved by expanding the eigenfunctions in a given complete set, and applications to the MO-LCAO theory of the electronic structure of molecules, and crystals are given. It is shown that, in this scheme, the entire physical situation depends on a charge- and bond-order matrix $R(\nu\mu)$ with respect to the ordinary atomic spin-orbitals involved. The Hartree-Fock equations for this matrix are investigated.

Finally, the ionized and excited states are investigated, and it is shown that the Hartree-Fock scheme has a high degree of physical visuality also in case of many-particle interactions. The excitation energy of the system is the difference $(\omega_j'-\omega_i)$ between two "spin-orbital energies," being eigenvalues to the effective Hamiltonians associated with the two states under consideration.

In a preceding paper,[1] we have investigated the possibilities for expressing the total wave function Ψ for a system of N antisymmetric particles by a series of Slater determinants over all configurations of order N, formed from a basic complete set ψ_k of one-particle functions or spin-orbitals. This basic set may have been arbitrarily chosen, and the convergence of the configuration expansion is then correspondingly slow. However, if we introduce the *natural spin-orbitals* χ_k diagonalizing the first order density matrix $\gamma(\mathbf{x}_1'|\mathbf{x}_1)$, we obtain the configuration expansion of most rapid convergence, which is directly connected with the convergency of the series

$$\textstyle\sum_k n_k=N, \tag{1}$$

where the occupation numbers n_k fulfill the condition $0\leq n_k\leq 1$. The N particles are therefore always distributed over more than N spin-orbitals, but, mathematically, there is a limiting case when exactly N natural spin-orbitals are fully occupied, and the configuration expansion is then reduced to a *single* Slater determinant:

$$\Psi=(N!)^{-\frac{1}{2}}\det\{\chi_1,\chi_2,\cdots\chi_N\}. \tag{2}$$

Physically, this wave function would have a particular importance since it is the simplest wave function based on the "independent-particle model" which has the correct antisymmetry property. However, in constructing this wave function by antisymmetrizing a simple product, the *mutual interaction* between the particles is usually only partly taken into account, and this means that the limiting case cannot have a physical reality and that the wave function cannot be exact.

The many-particle theory based on the approximate wave function (2) is usually called the Hartree-Fock scheme,[2] and it represents the first important step towards a more exact theory of antisymmetric particles. The scheme has been developed in great detail for the electronic structure of the atoms by Hartree[3] and his collaborators, and a large part of the periodic system is now covered in their applications. It will certainly take a rather long time, before a theory of similar accuracy has been developed for molecules and crystals, but the basic principles are well known and have been discussed by several authors; recent contributions to this field have been given by Mulliken,[4] Roothaan,[5] Slater,[6] and others.

In the previous discussions of the Hartree-Fock approximation, one has usually started from a basic set of N individual Hartree-Fock functions or spin-orbitals, but we will here emphasize another aspect of the scheme, namely that the properties of the system are dependent only on the first-order density matrix

$$\gamma(\mathbf{x}_1'|\mathbf{x}_1) \tag{3}$$

but independent on the individual spin-orbitals, which are used in forming this matrix. All the higher-order density matrices may be expressed in (3), and, in order

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[1] P. O. Löwdin, preceding paper [Phys. Rev. 96, 1474 (1954)], in the following referred to as Part I.

[2] D. R. Hartree, Proc. Cambridge Phil. Soc. 24, 89 (1928); V. Fock, Z. Physik 61, 126 (1930); J. C. Slater, Phys. Rev. 35, 210 (1930).

[3] For a survey, see D. R. Hartree, Repts. Progr. Phys. 11, 113 (1946).

[4] R. S. Mulliken, J. chim. phys. 46, 497, 675 (1949).

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

[6] J. C. Slater, Phys. Rev. 81, 385 (1951); 82, 538 (1951); see also his series of Technical Reports of the Solid-State and Molecular Theory Group at Massachusetts Institute of Technology 1951–1954 (unpublished).

to describe the entire physical situation of the system in the Hartree-Fock approximation, it is therefore *sufficient* to describe its first-order density matrix (3). The theory of electronic structure of molecules and crystals may consequently be reduced to a comparatively simple quantity.

Due to its connection with the "independent-particle model," the Hartree-Fock scheme has further a physical simplicity and visuality which is of importance in discussing, e.g., ionizations and excitations of the system. We will here investigate these properties in greater detail with the particular intention to find out whether, in some way, it would be possible to preserve this visuality also in a more exact theory based on configurational interaction. In this connection, we will consider physical quantities which are represented by operators of the form (I, 2), and we note that even many-particle operators may occur. This is of importance not only in the nuclear theory but also for the extension of the ordinary Hartree-Fock scheme to include degenerate systems and correlation effects, which will be discussed in a following paper.

1. DENSITY AND TRANSITION MATRICES IN THE HARTREE-FOCK SCHEME

In Part I, it was shown that all physical properties of a system of N antisymmetric particles may be characterized by means of a series of density matrices (I, 3) of various orders, and that a transition between two states of the system may be described by a similar series of transition matrices (I, 17). We will now investigate the special form of these fundamental quantities in the Hartree-Fock approximation.

(a) Density Matrix for a Single Slater Determinant

Let us start by considering a wave function of the form

$$U(\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N)=(N!)^{-\frac{1}{2}}\det\{u_1,u_2,\cdots u_N\},\tag{4}$$

which is built up of a set of N spin-orbitals u_1, u_2, $\cdots u_N$, being linearly independent but not necessarily orthogonal. The basic spin-orbitals may therefore have nonorthogonality integrals

$$\int u_k^*(\mathbf{x}_1)u_l(\mathbf{x}_1)dx_1=d(kl),\tag{5}$$

which are different from zero, if $k\neq l$. According to (I, 39), the normalization integral for U is then given by

$$\int U^*U(dx)=D=\det\{d(kl)\}.\tag{6}$$

The wave function (4) is characterized by the fact that, except for an unessential factor which vanishes in the normalization, it is *invariant* against linear transformations of the spin-orbitals involved. We will consider a transformation

$$\bar{u}_k=\sum_{\alpha=1}^{N}u_\alpha a_{\alpha k}.\tag{7}$$

According to the well-known theorem for determinant multiplication, we then obtain

$$\bar{U}=U\det\{a_{\alpha k}\},\tag{8}$$

$$\bar{d}(kl)=\sum_{\alpha\beta}a_{k\alpha}^\dagger d(\alpha\beta)a_{\beta l},\tag{9}$$

$$\bar{D}=\det\{a_{k\alpha}^\dagger\}\cdot D\cdot\det\{a_{\beta l}\}.\tag{10}$$

Since $D\neq 0$, the matrix $\mathbf{d}$ of the elements (5) has an inverse matrix $\mathbf{d}^{-1}$ having the elements $d^{-1}(lk)=D(kl)/D$. According to (9), the matrix $\mathbf{d}^{-1}$ has the transformation property

$$\bar{\mathbf{d}}^{-1}=\mathbf{a}^{-1}\mathbf{d}^{-1}(\mathbf{a}^\dagger)^{-1}.\tag{11}$$

In investigating the transformations, we may consider the basic set u_k ($k=1, 2, \cdots N$) as the components of a vector in a not necessarily orthogonal Hilbert space and the relation (7) as a vector transformation. The "length" of this vector, defined by the relation

$$\rho(\mathbf{x}_1,\mathbf{x}_2)=\sum_{kl}u_k^*(\mathbf{x}_1)u_l(\mathbf{x}_2)d^{-1}(lk),\tag{12}$$

is then the only fundamental *invariant* against (7), and, by using (7) and (11), this invariance is easily checked. A quantity of this type was first introduced by Fock[2] and investigated in detail by Dirac[7] for the orthogonal case ($d_{kl}=\delta_{kl}$), but, considering the applications to molecules and crystals with atomic orbitals having overlap integrals essentially different from zero, we have here carried out the generalization to the nonorthogonal case. By using (5) and (12), we find that $\boldsymbol{\rho}$ fulfills the two matrix relations

$$\boldsymbol{\rho}^2=\boldsymbol{\rho},\quad \mathrm{Tr}(\boldsymbol{\rho})=N,\tag{13}$$

and $\boldsymbol{\rho}$ is therefore a projection operator; see also (I, 85).

Since the general densities (3) of various orders are all invariant with respect to the transformation (7), we may expect that they must be functions of the fundamental invariant (12), and the explicit form for these functions is easily found. Since $D^{-1}=\det\{d^{-1}(lk)\}$, we get for the density matrix of order N:

$$\begin{aligned}\Gamma^{(N)}&(\mathbf{x}_1'\mathbf{x}_2'\cdots\mathbf{x}_N'|\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N)\\&=U^*(\mathbf{x}_1'\mathbf{x}_2'\cdots\mathbf{x}_N')U(\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N)D^{-1}\\&=(N!)^{-1}\det\{u_k^*(\mathbf{x}_i')\}\det\{u_l(\mathbf{x}_j)\}\det\{d^{-1}(lk)\}\\&=(N!)^{-1}\det\{\rho(\mathbf{x}_i',\mathbf{x}_j)\},\end{aligned}\tag{14}$$

where we have used (12) and the ordinary law of determinant multiplication. The higher densities may now be derived successively according to (I, 5) and

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

(13). Let us assume that the density of order p has the explicit form

$$\Gamma^{(p)}(\mathbf{x}_1'\mathbf{x}_2'\cdots\mathbf{x}_p'|\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_p) = (p!)^{-1}\begin{vmatrix} \rho(\mathbf{x}_1',\mathbf{x}_1) & \rho(\mathbf{x}_1',\mathbf{x}_2) & \cdots & \rho(\mathbf{x}_1',\mathbf{x}_p) \\ \rho(\mathbf{x}_2',\mathbf{x}_1) & \rho(\mathbf{x}_2',\mathbf{x}_2) & \cdots & \rho(\mathbf{x}_2',\mathbf{x}_p) \\ \cdots & \cdots & \cdots & \cdots \\ \rho(\mathbf{x}_p',\mathbf{x}_1) & \rho(\mathbf{x}_p',\mathbf{x}_2) & \cdots & \rho(\mathbf{x}_p',\mathbf{x}_p) \end{vmatrix}, \quad (15)$$

which apparently is true for $p=N$. By developing this density after its last column, putting $\mathbf{x}_p'=\mathbf{x}_p$, and integrating by using (13), we find that the density of order $(p-1)$ has exactly the same form, which proves our theorem. However, by reversing the arguments used in forming (14), we may now expand the density of order p by using the law for the determinant of the product of two rectangular matrices[8] in the following way:

$$\Gamma^{(p)}(\mathbf{x}_1'\mathbf{x}_2'\cdots\mathbf{x}_p'|\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_p) = (p!)^{-1}\sum_{\substack{k_1<k_2<\cdots k_p \\ l_1<l_2<\cdots l_p}} \begin{vmatrix} u^*_{k_1}(\mathbf{x}_1') & \cdots & u^*_{k_p}(\mathbf{x}_1') \\ \cdot & \cdot & \cdot \\ u^*_{k_1}(\mathbf{x}_p') & \cdots & u^*_{k_p}(\mathbf{x}_p') \end{vmatrix} \cdot \begin{vmatrix} u_{l_1}(\mathbf{x}_1) & \cdots & u_{l_p}(\mathbf{x}_1) \\ \cdot & \cdot & \cdot \\ u_{l_1}(\mathbf{x}_p) & \cdots & u_{l_p}(\mathbf{x}_p) \end{vmatrix} \cdot \begin{vmatrix} d^{-1}(l_1k_1) & \cdots & d^{-1}(l_1k_p) \\ \cdot & \cdot & \cdot \\ d^{-1}(l_pk_1) & \cdots & d^{-1}(l_pk_p) \end{vmatrix}$$

$$= (p!)^{-1}\sum_{\substack{k_1k_2\cdots k_p \\ l_1l_2\cdots l_p}} u^*_{k_1}(\mathbf{x}_1')\cdots u^*_{k_p}(\mathbf{x}_p')u_{l_1}(\mathbf{x}_1)\cdots u_{l_p}(\mathbf{x}_p) \begin{vmatrix} d^{-1}(l_1k_1) & \cdots & d^{-1}(l_1k_p) \\ \cdot & \cdot & \cdot \\ d^{-1}(l_pk_1) & \cdots & d^{-1}(l_pk_p) \end{vmatrix}. \quad (16)$$

According to (I, 47) and (I, 48), we hence obtain for the density matrix of order p in the space defined by the nonorthogonal basic set u_k $(k=1, 2, \cdots N)$:

$$\Gamma^{(p)}(l_1l_2\cdots l_p|k_1k_2\cdots k_p) = (p!)^{-1}\begin{vmatrix} d^{-1}(l_1k_1) & \cdots & d^{-1}(l_1k_p) \\ \cdot & \cdot & \cdot \\ d^{-1}(l_pk_1) & \cdots & d^{-1}(l_pk_p) \end{vmatrix}. \quad (17)$$

The charge- and bond-order matrix of order p is therefore entirely characterized by the components of the matrix $\mathbf{d}^{-1}$, and for $p=1$, we obtain in particular

$$\gamma(l|k)=d^{-1}(lk). \quad (18)$$

Let us now turn back to the x-space. According to (15) for $p=1$ and $p=2$, we have particularly

$$\gamma(\mathbf{x}_1'|\mathbf{x}_1)=\rho(\mathbf{x}_1',\mathbf{x}_1),$$
$$\Gamma(\mathbf{x}_1'\mathbf{x}_2'|\mathbf{x}_1\mathbf{x}_2)=\tfrac{1}{2}\begin{vmatrix} \rho(\mathbf{x}_1',\mathbf{x}_1) & \rho(\mathbf{x}_1',\mathbf{x}_2) \\ \rho(\mathbf{x}_2',\mathbf{x}_1) & \rho(\mathbf{x}_2',\mathbf{x}_2) \end{vmatrix}, \quad (19)$$

i.e., the first-order density matrix is identical with the fundamental invariant (12). This means that, if the total wave function is approximated by a single Slater determinant, the first-order density matrix determines also all the higher-order density matrices by (15), the normalized wave function by (14), and hence the entire physical situation. We can now also make a proper interpretation of the first relation $\boldsymbol{\rho}^2=\boldsymbol{\rho}$ in (13), which is equivalent with the relation $\boldsymbol{\gamma}^2=\boldsymbol{\gamma}$; it means that the eigenvalues of the matrix $\gamma(l|k)$ or the occupation numbers n_k must be either 0 or 1. This result is characteristic for the Hartree-Fock approximation, and, in connection with our results in part I (Sec. 4), we have then shown that the relation $\boldsymbol{\gamma}^2=\boldsymbol{\gamma}$ is the necessary and sufficient condition for reducing the total wave function Ψ to a single determinant.

In the Hartree-Fock approximation, it is hence not necessary to specify either the total wave function or the special set of spin-orbitals used in the calculations, since all information about the system in the specific state under consideration is contained in the fundamental invariant $\rho(\mathbf{x}_1,\mathbf{x}_2)$ given by (12). By using (15), the fundamental formula (I, 10) takes the form

$$\langle\Omega_{\mathrm{op}}\rangle_{\mathrm{Av}}=\Omega_{(0)}+\int\Omega_1\rho(1',1)dx_1+(2!)^{-1}\int\Omega_{12}\begin{vmatrix} \rho(1',1) & \rho(1',2) \\ \rho(2',1) & \rho(2',2) \end{vmatrix}dx_1dx_2$$
$$+(3!)^{-1}\int\Omega_{123}\begin{vmatrix} \rho(1',1) & \rho(1',2) & \rho(1',3) \\ \rho(2',1) & \rho(2',2) & \rho(2',3) \\ \rho(3',1) & \rho(3',2) & \rho(3',3) \end{vmatrix}dx_1dx_2dx_3+\cdots. \quad (21)$$

The corresponding formula for the orthogonal case and two-particle operators was first derived by Fock[2] in his pioneer work. The average value of the operator Ω_{op} may now also be expressed directly in terms of the basic set u_k.

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[8] See part I, reference 7.

Introducing the matrix notations

$$(k|\Omega_1|l)=\int u_k^*(1)\Omega_1 u_l(1)dx_1,$$

$$(k_1k_2|\Omega_{12}|l_1l_2)=\int u_{k_1}^*(1)u_{k_2}^*(2)\Omega_{12}u_{l_1}(1)u_{l_2}(2)dx_1dx_2, \tag{22}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

and putting expansion (16) into (I, 10), we obtain

$$\langle\Omega_{\mathrm{op}}\rangle_{\mathrm{Av}}=\Omega_{(0)}+\sum_{kl}(k|\Omega_1|l)d^{-1}(lk)+(2!)^{-1}\sum_{\substack{k_1k_2\\l_1l_2}}(k_1k_2|\Omega_{12}|l_1l_2)\begin{vmatrix}d^{-1}(l_1k_1) & d^{-1}(l_1k_2)\\ d^{-1}(l_2k_1) & d^{-1}(l_2k_2)\end{vmatrix}$$

$$+(3!)^{-1}\sum_{\substack{k_1k_2k_3\\l_1l_2l_3}}(k_1k_2k_3|\Omega_{123}|l_1l_2l_3)\begin{vmatrix}d^{-1}(l_1k_1) & \cdots & d^{-1}(l_1k_3)\\ \cdot & \cdots & \cdot\\ d^{-1}(l_3k_1) & \cdots & d^{-1}(l_3k_3)\end{vmatrix}+\cdots. \tag{23}$$

This is the general formula for the average value of an arbitrary physical quantity (I, 2), containing also many-particle operators, for a nonorthogonal basic set u_k. The nonorthogonality problem has been discussed rather extensively in the literature:[9] we note that the corresponding formula for two-particle operators, previously given by the author,[10] was derived in an entirely different way.

(b) Transition Matrices for Two Slater Determinants

Let us now consider two Slater determinants U and V, built up from two not necessarily orthogonal sets u_k ($k=1, 2, \cdots N$) and v_l ($l=1, 2, \cdots N$) according to (I, 36). If the mutual nonorthogonality integrals are given by

$$d_{uv}(kl)=\int u_k^*(1)v_l(1)dx_1, \tag{24}$$

we have in (I, 39) obtained

$$\int U^*V(dx)=D_{UV}=\det\{d_{uv}(kl)\}. \tag{25}$$

For the discussion in this paper, we will assume that the basic determinant D_{UV} is essentially different from zero: $D_{UV}\neq 0$. In this case, the matrix $\mathbf{d}_{uv}$ of the elements (24) has an inverse matrix $\mathbf{d}_{uv}^{-1}$ with the elements $d_{uv}^{-1}(lk)=D_{UV}(kl)/D$.

Except for unessential factors, each determinant U and V is invariant against linear transformations of the type (7):

$$\bar{u}_k=\sum\nolimits_\alpha u_\alpha a_{\alpha k},\quad \bar{v}_l=\sum\nolimits_\beta v_\beta b_{\beta l}, \tag{26}$$

and the matrices $\mathbf{d}_{uv}$ and $\mathbf{d}_{uv}^{-1}$ have then in matrix form the transformation properties

$$\bar{\mathbf{d}}_{uv}=\mathbf{a}^\dagger\mathbf{d}_{uv}\mathbf{b},\quad \bar{\mathbf{d}}_{uv}^{-1}=\mathbf{b}^{-1}\mathbf{d}_{uv}^{-1}(\mathbf{a}^\dagger)^{-1}. \tag{27}$$

Let us now consider u and v as vectors in two associated nonorthogonal Hilbert spaces, and the transformations (26) as vector transformations. Then the "scalar product" of these two vectors, defined by

$$\rho_{uv}(\mathbf{x}_1,\mathbf{x}_2)=\sum_{kl}u_k^*(\mathbf{x}_1)v_l(\mathbf{x}_2)d^{-1}(lk), \tag{28}$$

must be the only fundamental *invariant* against the transformations (26), and, by using (26) and (27), this invariance is easily checked. Using (24), we find that the matrix $\boldsymbol{\rho}_{uv}$ also fulfills the characteristic relations (13) for a projection operator.

The transition matrices of various orders may now be calculated in the same way as for $u=v$. Introducing the normalization constant

$$\kappa_{UV}=D_{UV}(D_{UU}D_{VV})^{-\frac{1}{2}}, \tag{29}$$

we find for $p=N$:

$$\Gamma_{UV}^{(N)}(\mathbf{x}_1'\mathbf{x}_2'\cdots\mathbf{x}_N'|\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N)$$
$$=\kappa_{UV}U^*(\mathbf{x}_1'\mathbf{x}_2'\cdots\mathbf{x}_N')V(\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N)\det\{d_{uv}^{-1}(lk)\}$$
$$=\kappa_{UV}(N!)^{-1}\det\{\rho_{uv}(\mathbf{x}_i',\mathbf{x}_j)\}. \tag{30}$$

The density matrices of lower orders may then be found successively by using (I, 5) and (13), and the form is the same as in (15), (16), and (17) with $\boldsymbol{\rho}$ and $\mathbf{d}^{-1}$ replaced by $\boldsymbol{\rho}_{uv}$ and $\mathbf{d}_{uv}^{-1}$, respectively, multiplied by the normalization constant (29).

In analogy to (21) and (23), we get therefore for the transition element of an operator Ω_{op} with respect to

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[9] See Part I, reference 10.

[10] See part I, reference 11.

two Slater determinants U and V with $D_{UV}\neq 0$:

$$\langle U|\Omega_{\rm op}|V\rangle=\int U^*\Omega_{\rm op}V(dx)/(D_{UU}D_{VV})^{\frac{1}{2}}$$

$$=\kappa_{UV}\left\{\Omega_{(0)}+\int\Omega_1\rho_{uv}(1',1)dx_1+(2!)^{-1}\int\Omega_{12}\begin{vmatrix}\rho_{uv}(1',1) & \rho_{uv}(1',2)\\ \rho_{uv}(2',1) & \rho_{uv}(2',2)\end{vmatrix}dx_1dx_2+\cdots\right\}$$

$$=\kappa_{UV}\left[\Omega_{(0)}+\sum_{kl}\{k|\Omega_1|l\}d_{uv}^{-1}(lk)+(2!)^{-1}\sum_{\substack{k_1k_2\\l_1l_2}}\{k_1k_2|\Omega_{12}|l_1l_2\}\begin{vmatrix}d_{uv}^{-1}(l_1k_1) & d_{uv}^{-1}(l_1k_2)\\ d_{uv}^{-1}(l_2k_1) & d_{uv}^{-1}(l_2k_2)\end{vmatrix}+\cdots\right],\quad(31)$$

where the matrix elements are now defined by (I, 50).

In the special case when $D_{UV}=0$, the invariant (28) no longer exists, and formula (31) looses its meaning. The general method developed in Part I, Sec. 2 b, covers also this case, but it remains to investigate whether the various transition matrices may be reduced to some simpler fundamental invariants also in this case. We will here leave this problem open.

2. HARTREE-FOCK EQUATIONS IN TERMS OF THE FUNDAMENTAL INVARIANT

(a) Variation of an Orthonormal Basic Set

Let us now determine the basic set $u_1, u_2, \cdots u_N$ in such a way that the Slater determinant (4) form as accurate an approximation as possible to a solution of the eigenvalue problem:

$$\Omega_{\rm op}\Psi=\mathcal{W}\Psi,\quad(32)$$

where $\Omega_{\rm op}$ given by (I, 2) may contain also many-particle terms. Up till now we have not imposed any particular condition on the set u_k, but, by a suitable linear transformation, this set may now be orthonormalized without changing the character of the total wave function. For this purpose, we will use the formula[11]:

$$\psi_k=\sum\nolimits_\alpha u_\alpha d^{-\frac{1}{2}}(\alpha k),\quad(33)$$

and we note that the set ψ_k ($k=1, 2, \cdots N$) has the required orthonormality property:

$$\int\psi_k^*\psi_l dx_1=\delta_{kl}.\quad(34)$$

Putting (33) into the fundamental invariant (12), we obtain

$$\rho(\mathbf{x}_1,\mathbf{x}_2)=\sum_{k=1}^{N}\psi_k^*(\mathbf{x}_1)\psi_k(\mathbf{x}_2),\quad(35)$$

which is just the Fock-Dirac density matrix with the spin functions explicitly included in accordance with the recommendations by Slater. This is also the diagonalized form (I, 74) of the first-order density matrix $\gamma(\mathbf{x}_1|\mathbf{x}_2)$, and, due to the degeneracy $n_1=n_2=\cdots n_N=1$, the set $\psi_k=\chi_k$ is still undetermined on a unitary transformation of spin-orbitals.

We will now determine the *best* choice of the set ψ_k, by applying the variation principle (I, 22). Using (21), varying the set ψ_k, and taking the orthornormality condition (34) into account by introducing a Hermitean matrix $\lambda(l|k)$ of Lagrangian multipliers, we obtain a set of conditions which, according to (I, 92), may be condensed in the form

$$\Omega_1\rho(\xi_1',\mathbf{x}_1)+\int\Omega_{12}\begin{vmatrix}\rho(\xi_1',\mathbf{x}_1) & \rho(\xi_1',\mathbf{x}_2)\\ \rho(\mathbf{x}_2',\mathbf{x}_1) & \rho(\mathbf{x}_2',\mathbf{x}_2)\end{vmatrix}dx_2$$

$$+(2!)^{-1}\int\Omega_{123}\begin{vmatrix}\rho(\xi_1',\mathbf{x}_1) & \rho(\xi_1',\mathbf{x}_2) & \rho(\xi_1',\mathbf{x}_3)\\ \rho(\mathbf{x}_2',\mathbf{x}_1) & \rho(\mathbf{x}_2',\mathbf{x}_2) & \rho(\mathbf{x}_2',\mathbf{x}_3)\\ \rho(\mathbf{x}_3',\mathbf{x}_1) & \rho(\mathbf{x}_3',\mathbf{x}_2) & \rho(\mathbf{x}_3',\mathbf{x}_3)\end{vmatrix}dx_2dx_3$$

$$+\cdots=\lambda(\xi_1'|\mathbf{x}_1),\quad(36)$$

where the operators Ω do not work on the primed variables and, after the operations in the integrands have been carried out, we have to put all $\mathbf{x}_i'=\mathbf{x}_i$. This is the Hartree-Fock equation for the fundamental invariant $\rho(\xi_1',\mathbf{x}_1)$. The function

$$\lambda(\xi_1'|\mathbf{x}_1)=\sum_{kl}\psi_k^*(\xi_1')\psi_l(\mathbf{x}_1)\lambda(l|k),\quad(37)$$

in the right-hand member was here derived by using the orthonormality condition (34) for the individual spin-orbitals ψ_k, but we will later see that we can formulate this auxiliary condition also in terms of the invariant $\boldsymbol{\rho}$ without reference to any orthonormality property.

Since the density matrix (35) is already on diagonal form, we may now use the remaining unitary transformation of the set ψ_k for diagonalizing the matrix $\lambda(l|k)$ in the function (37), and we will denote the eigenvalues by ω_k. Applying (I, 96), we may now rewrite (36) in the form

$$\Omega_1\psi_k(\mathbf{x}_1)+\int\Omega_{12}\begin{vmatrix}\psi_k(\mathbf{x}_1) & \psi_k(\mathbf{x}_2)\\ \rho(\mathbf{x}_2',\mathbf{x}_1) & \rho(\mathbf{x}_2',\mathbf{x}_2)\end{vmatrix}dx_2$$

$$+(2!)^{-1}\int\Omega_{123}\begin{vmatrix}\psi_k(\mathbf{x}_1) & \psi_k(\mathbf{x}_2) & \psi_k(\mathbf{x}_3)\\ \rho(\mathbf{x}_2',\mathbf{x}_1) & \rho(\mathbf{x}_2',\mathbf{x}_2) & \rho(\mathbf{x}_2',\mathbf{x}_3)\\ \rho(\mathbf{x}_3',\mathbf{x}_1) & \rho(\mathbf{x}_3',\mathbf{x}_2) & \rho(\mathbf{x}_3',\mathbf{x}_2)\end{vmatrix}dx_2dx_3$$

$$+\cdots=\omega_k\psi_k(\mathbf{x}_1),\quad(38)$$

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[11] See part I, reference 11. The matrix $d^{-\frac{1}{2}}$ may here be constructed by transforming the Hermitean matrix d to diagonal form by a unitary transformation U, taking the inverse of the square root out of the diagonal elements (which are all positive), and going back to the original representation by the unitary transformation $U^\dagger$.

which is just the set of ordinary Hartree-Fock equations for the individual functions ψ_k ($k=1, 2, \cdots N$) generalized to many-particle operators. Introducing the operator P_{ij} for permuting the variables $\mathbf{x}_i$ and $\mathbf{x}_j$, we may instead write (38) in the form of an eigenvalue problem

$$\Omega_{\mathrm{eff}}(1)\psi_k(\mathbf{x}_1)=\omega_k\psi_k(\mathbf{x}_1), \tag{39}$$

where the "effective" one-particle operator Ω_{eff} corresponding to (I, 2) has the explicit form

$$\Omega_{\mathrm{eff}}(1)=\Omega_1+\int\Omega_{12}\begin{vmatrix}1 & P_{12}\\ \rho(\mathbf{x}_2',\mathbf{x}_1) & \rho(\mathbf{x}_2',\mathbf{x}_2)\end{vmatrix}dx_2+(2!)^{-1}\int\Omega_{123}\begin{vmatrix}1 & P_{12} & P_{13}\\ \rho(\mathbf{x}_2',\mathbf{x}_1) & \rho(\mathbf{x}_2',\mathbf{x}_2) & \rho(\mathbf{x}_2',\mathbf{x}_3)\\ \rho(\mathbf{x}_3',\mathbf{x}_1) & \rho(\mathbf{x}_3',\mathbf{x}_2) & \rho(\mathbf{x}_3',\mathbf{x}_3)\end{vmatrix}dx_2dx_3+\cdots, \tag{40}$$

where the permutation operators P_{1j} should work directly on the wave function, i.e., should be written to the *right* of the ρ-factors in expanding the determinants. In this operator, the elements $P_{11}=1$ give rise to ordinary potentials, whereas the elements P_{1j} for $j\neq 1$ give rise to *exchange potentials.* Expanding the determinants after their first rows, we can rewrite the effective Ω-operator in the form

$$\Omega_{\mathrm{eff}}(1)=\Omega_1+V_{\mathrm{op}}(1), \tag{41}$$

where

$$V_{\mathrm{op}}(1)=\int\Omega_{12}(1-P_{12})\rho(2',2)dx_2+(2!)^{-1}\int\Omega_{123}(1-P_{12}-P_{13})\begin{vmatrix}\rho(2',2) & \rho(2',3)\\ \rho(3',2) & \rho(3',3)\end{vmatrix}dx_2dx_3+\cdots. \tag{42}$$

As before we have here used the convention that, after the operations have been carried out, we have to put all $\mathbf{x}_i'=\mathbf{x}_i$. It is easily shown that Ω_{eff} is an Hermitean operator, and this implies that the eigenfunctions ψ_k to (39) belonging to different eigenvalues ω_k are automatically orthogonal in consistency with the fact that we have here transformed away all nondiagonal Lagrangian multipliers, which otherwise could be used for preserving the orthogonality.

(b) Spin-Orbital Interaction

By means of the variation principle (I, 22) and the simplifying assumption about the form (4) of the wave function, the original eigenvalue problem (32) in configuration space for the many-particle operator (I, 2) has now been reduced to an eigenvalue problem for *one* particle in the ordinary **x**-space. The effective Ω operator in (39) has the advantage of a certain degree of physical visuality: it consists of the one-particle term in the original operator plus an "average potential" on the particle, depending on its interaction with all the other particles. This visuality may be emphasized by introducing the individual spin-orbitals ψ_k or the density matrices $\rho_k(\mathbf{x}_1,\mathbf{x}_2)=\psi_k^*(\mathbf{x}_1)\psi_k(\mathbf{x}_2)$ associated with them.

Expanding the density matrix (35) in the form

$$\rho(\mathbf{x}_1,\mathbf{x}_2)=\sum_{k=1}^{N}\rho_k(\mathbf{x}_1,\mathbf{x}_2), \tag{43}$$

and substituting this expression into (42), we obtain

$$V_{\mathrm{op}}(1)=\sum_l V^l(1)+(2!)^{-1}\sum_{lm}V^{lm}(1)+\cdots, \tag{44}$$

where

$$V^l(1)=\int\Omega_{12}(1-P_{12})\rho_l(2',2)dx_2,$$

$$V^{lm}(1)=V^{ml}(1)=\int\Omega_{123}(1-P_{12}-P_{13})\times\begin{vmatrix}\rho_l(2',2) & \rho_l(2',3)\\ \rho_m(3',2) & \rho_m(3',3)\end{vmatrix}dx_2dx_3; \tag{45}$$

. . . .

Here each term has a specific physical meaning: $V^l(1)$ is the potential on particle 1 arising from another particle in spin-orbital l due to the two-particle interaction operator Ω_{12}; $V^{lm}(1)$ is the potential on particle 1 arising from a pair of particles in the spin-orbitals l and m due to the three-particle interaction operator Ω_{123}; etc. The effect of these operators on an arbitrary function $f(\mathbf{x}_1)$ is demonstrated by the formulas

$$V^l(1)f(\mathbf{x}_1)=\int\Omega_{12}\begin{vmatrix}f(1) & f(2)\\ \rho_l(2',1) & \rho_l(2',2)\end{vmatrix}dx_2,$$

$$V^{lm}(1)f(\mathbf{x}_1)=\int\Omega_{123}\begin{vmatrix}f(1) & f(2) & f(3)\\ \rho_l(2',1) & \rho_l(2',2) & \rho_l(2',3)\\ \rho_m(3',1) & \rho_m(3',2) & \rho_m(3',3)\end{vmatrix}dx_2dx_3; \tag{46}$$

. . . .

In discussing the physical interpretation of the potentials (45), we note that the first term in each of them has an almost "classical" meaning, whereas the terms containing the permutation operators P_{1j} depend on the antisymmetry requirement (I, 1) and therefore correspond to typical quantum-mechanical effects. We have seen that, in the **x**-space, the antisymmetry leads to the relation (I, 8) and the existence of the "Fermi hole," and we observe now another consequence, namely:

$$V^k(1)\psi_k(\mathbf{x}_1)\equiv 0,\quad V^{kl}(1)\psi_k(\mathbf{x}_1)\equiv 0,\quad\cdots \tag{47}$$

which means that the particle in spin-orbital k does not interact with itself. This important result is not limited to the ordinary Hartree-Fock approximation, for, in considering the extended Hartree-Fock equations (I, 89), (I, 90), (I, 92), and (I, 96) for limited configurational interaction, we find that the coefficients for the interactions of various orders are given by the matrix elements

$$\Gamma^{(p)}(l_1l_2\cdots l_p|k_1k_2\cdots k_p), \tag{48}$$

which are antisymmetric in each set of their indices, and which therefore vanish identically if two indices in a set happen to be the same. In the nonrelativistic quantum theory of antisymmetric particles with static interaction, there is consequently no self-energy problem, but, unfortunately, one has so far not been able to generalize this result to relativistic theories and time-dependent interactions.

In this connection, we will also introduce the total quantities:

$$\begin{aligned}
V_k{}^l&=\int V^l(1)\rho_k(1',1)dx_1=\int\Omega_{12}\begin{vmatrix}\rho_k(1',1) & \rho_k(1',2)\\ \rho_l(2',1) & \rho_l(2',2)\end{vmatrix}dx_1dx_2,\\
V_k{}^{lm}&=\int V^{lm}(1)\rho_k(1',1)dx_1=\int\Omega_{123}\begin{vmatrix}\rho_k(1',1) & \rho_k(1',2) & \rho_k(1',3)\\ \rho_l(2',1) & \rho_l(2',2) & \rho_l(2',3)\\ \rho_m(3',1) & \rho_m(3',2) & \rho_m(3',3)\end{vmatrix}dx_1dx_2dx_3;\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots
\end{aligned} \tag{49}$$

where $V_k{}^l=V_l{}^k$ is the total potential between the spin-orbitals k and l due to the two-particle interaction Ω_{12}, $V_k{}^{lm}=V_l{}^{mk}=V_m{}^{kl}$ is the total potential between the spin-orbitals k, l, and m due to the three-particle interaction Ω_{123}, etc. Using (39), (44), and (49), we now obtain for the "spin-orbital eigenvalue" ω_k:

$$\begin{aligned}
\omega_k&=\int\psi_k{}^*(1)\Omega_{\text{eff}}(1)\psi_k(1)dx_1\\
&=\int\Omega_1\rho_k(1',1)dx_1+\sum_l V_k{}^l+(2!)^{-1}\sum_{lm}V_k{}^{lm}+\cdots,
\end{aligned} \tag{50}$$

giving a simple physical interpretation of this quantity. We may also express $\langle\Omega_{\text{op}}\rangle_{\text{Av}}$ in terms of the total spin-orbital interaction potentials (49), and, according to (21) and (43), we obtain

$$\begin{aligned}
\langle\Omega_{\text{op}}\rangle_{\text{Av}}=\Omega_{(0)}&+\sum_k\int\Omega_1\rho_k(1',1)dx_1\\
&+(2!)^{-1}\sum_{kl}{}'V_k{}^l+(3!)^{-1}\sum_{klm}{}'V_k{}^{lm}+\cdots,
\end{aligned} \tag{51}$$

where, due to the factorial coefficients, each interaction term $V_k{}^l$, $V_k{}^{lm}$, etc. will be counted only once. Comparing (50) and (51), we get also

$$\langle\Omega_{\text{op}}\rangle_{\text{Av}}=\Omega_{(0)}+\sum_{k=1}^N\omega_k-\tfrac{1}{2}\sum_{kl}{}'V_k{}^l-\tfrac{1}{3}\sum_{klm}{}'V_k{}^{lm}-\cdots, \tag{52}$$

showing that $\langle\Omega_{\text{op}}\rangle_{\text{Av}}$ is different from the sum of the eigenvalues, since the interaction potentials are counted in different ways in these two quantities.

(c) Average Exchange Potentials

The exchange potentials in (42) are of a rather complicated character, and Slater[12] has therefore proposed that they should be approximately replaced by "average exchange potentials" being ordinary functions of $\mathbf{x}_1$. In Part I, we have shown that this can be strictly done by minimizing the weighted "error sum" (I, 100), and, according to the general formula (I, 103), we then obtain in the Hartree-Fock approximation:

$$V(\mathbf{x}_1)=\int\Omega_{12}\begin{vmatrix}\rho(1',1) & \rho(1',2)\\ \rho(2',1) & \rho(2',2)\end{vmatrix}dx_2/\rho(1,1)+(2!)^{-1}\int\Omega_{123}\begin{vmatrix}\rho(1',1) & \rho(1',2) & \rho(1',3)\\ \rho(2',1) & \rho(2',2) & \rho(2',3)\\ \rho(3',1) & \rho(3',2) & \rho(3',3)\end{vmatrix}dx_2dx_3/\rho(1,1)+\cdots. \tag{53}$$

For $\Omega_{ij}=e^2/r_{ij}$, $\Omega_{ijk}=0$, this is just the potential introduced and investigated in detail by Slater.[13] However, an essential difference between (42) and (53) will later be pointed out in connection with the treatment of the "virtual" solutions to the eigenvalue problem (39).

(d) Variation of the Fundamental Invariant

In considering the problem how to determine the Slater determinant (4) in order to get as accurate approximation as possible to an eigenfunction of the operator Ω_{op}, we have in the previous section applied the variation principle by varying the basic orthonormal set ψ_k. In connection with the orthonormality condition

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

[13] See also J. C. Slater, Phys. Rev. 82, 538 (1951); G. W. Pratt, Jr., Phys. Rev. 88, 1217 (1952).

(34), we have then introduced a matrix $\lambda(l|k)$ of Lagrangian multipliers having the eigenvalues ω_k. However, according to (14), the total wave function (4) is dependent only on the fundamental invariant ϱ defined by (12), and we will now instead treat the same problem by varying this quantity as a whole. Since ϱ fulfills the relations (13), we get for its variation $\delta\varrho=\delta\rho(x_1,x_2)$:

$$\delta\varrho=\varrho\delta\varrho+\delta\varrho\cdot\varrho;\quad \mathrm{Tr}(\delta\varrho)=0. \tag{54}$$

Varying expression (21), and using (40) and the first relation (54), we then obtain

$$\delta\langle\Omega_{\mathrm{op}}\rangle_{\mathrm{Av}}=\int\Omega_{\mathrm{eff}}(1)\delta\rho(1',1)dx_1=\int\delta\rho(1,2)\Omega_{\mathrm{eff}}(1)\times\rho(2,1)dx_1dx_2+\text{complex conj.} \tag{55}$$

The auxiliary conditions for the variation of ϱ are contained in (54), and the problem is now to express them in convenient form.[14] Combining the first relation (13) with the first relation (54), we get

$$\varrho\cdot\delta\varrho\cdot\varrho=0. \tag{56}$$

In the terminology of Part I, Sec. 5, this means that $\delta\rho$ is without orthogonal projection within the subspace of the Hilbert space defined by the matrix ϱ. If $\boldsymbol{\Lambda}=\Lambda(\mathbf{x}_2,\mathbf{x}_1)$ is an *arbitrary* function and $\boldsymbol{\lambda}=\lambda(\mathbf{x}_2,\mathbf{x}_1)$ its orthogonal projection within the same subspace, defined by the matrix relation

$$\boldsymbol{\lambda}=\varrho\boldsymbol{\Lambda}\varrho, \tag{57}$$

then the "scalar product" of $\delta\varrho$ and $\boldsymbol{\lambda}$ must be zero, and the direct proof is simple:

$$\mathrm{Tr}(\delta\varrho\cdot\boldsymbol{\lambda})=\mathrm{Tr}(\delta\varrho\cdot\varrho\boldsymbol{\Lambda}\varrho)=\mathrm{Tr}(\varrho\delta\varrho\varrho\cdot\boldsymbol{\Lambda})=0. \tag{58}$$

This is the auxiliary condition desired, and it can be expressed in the same form as (55), if we assume that $\boldsymbol{\lambda}$ is an Hermitean matrix and we further add the complex conjugate to (58):

$$\int\delta\rho(1,2)\lambda(2,1)dx_1dx_2+\text{complex conj.}=0. \tag{59}$$

Combining (55) and (59), we obtain

$$\Omega_{\mathrm{eff}}(1)\rho(\mathbf{x}_2,\mathbf{x}_1)=\lambda(\mathbf{x}_2,\mathbf{x}_1), \tag{60}$$

which is the Hartree-Fock equation for the fundamental invariant ϱ. This equation is, of course, identical with (36), but we note that the function $\lambda(\mathbf{x}_2,\mathbf{x}_1)$ in the right-hand member is here expressed directly in terms of ϱ according to (57). If the basic set is chosen orthonormal, $\lambda(\mathbf{x}_2,\mathbf{x}_1)$ may then be expanded in the form (37), see (I, 82) and (I, 86), and we obtain the connection with the previous theory.

Instead of solving a set of N Hartree-Fock equations for functions $\psi_k(\mathbf{x}_1)$ $(k=1, 2, \cdots N)$ of a single variable, we can therefore principally treat the same problem by solving a single equation (60) for a function $\rho(\mathbf{x}_1,\mathbf{x}_2)$ of two variables, fulfilling the auxiliary conditions

$$\varrho^2=\varrho,\quad \mathrm{Tr}(\varrho)=N. \tag{61}$$

From the practical point view, we do not know any convenient *direct* numerical method for solving equations like (60) and (61), but, with the development of the modern electronic computers, the situation may be changed. For the moment, Eq. (60) has mainly principal interest, and it may serve as starting point for theories based on approximate forms of the matrix $\rho(\mathbf{x}_1,\mathbf{x}_2)$, as the statistical approximation.

3. SOLUTION OF THE HARTREE-FOCK EQUATIONS BY EXPANDING THE EIGENFUNCTIONS IN A FIXED COMPLETE SET

(a) General Theory

The essential problem in the Hartree-Fock method, where the total wave function is approximated by a single Slater determinant, is the solution of the one-particle equation

$$\Omega_{\mathrm{eff}}(1)\psi_k(\mathbf{x}_1)=\omega_k\psi_k(\mathbf{x}_1), \tag{62}$$

for the basic spin-orbitals ψ_k $(k=1, 2, \cdots N)$, where $\Omega_{\mathrm{eff}}(1)$ is given by (40). The Hartree-Fock equations (62) form together a system of coupled nonlinear integro-differential equations connected with an eigenvalue problem, and, since they therefore have a rather complicated character, we will discuss the methods for solving them in greater detail.

Hartree[2,3] has shown that, for a single atom or ion, Eq. (62) is separable in polar coordinates, and that, after elimination of the angular part, it remains to solve a system of nonlinear radial integro-differential equations. Hartree and his collaborators have solved this system numerically by a method of successive approximation: one starts from trial values of the spin-orbitals, calculates ϱ and the corresponding potentials (45), and introduces them in the effective Ω operator. For this fixed operator, one then determines the first N eigenvalues and eigenfunctions by numerical integration, which then may be used for a new evaluation of ϱ and the potentials, etc. The process is carried on until it becomes self-consistent, i.e., until two successive approximations agree within the accuracy desired, and the procedure is therefore called the "self-consistent-field" method.

In molecular and crystals problems, it is usually not possible to separate Eq. (62) by using any particular form of coordinates.[15] In such cases, one may try another approach, namely to expand the eigenfunctions

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[14] See also J. Frenkel, *Wave Mechanics, Advanced General Theory* (Clarendon Press, Oxford, 1934), p. 435.

[15] The only exceptions would be systems of extremely high symmetry; compare the "cellular" method for crystals and its modifications.

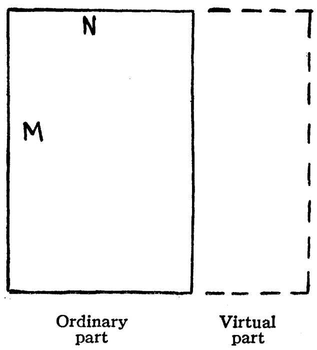

FIG. 1. The form of the rectangular matrix **c**, which has unitary properties at least in the vertical direction.

to (62) in terms of a fixed complete orthonormal set φ_μ ($\mu=1, 2, \cdots$):

$$\psi_k(\mathbf{x}_1)=\sum_{\mu=1}^{\infty} \varphi_\mu(\mathbf{x}_1)c_{\mu k}. \tag{63}$$

For the following general discussion, it is not necessary to specify the detailed character of our many-particle system, which may be an atom,[16] molecule, crystal, or atomic nucleus. For the sake of simplicity, we may formally assume that the set has only finite order M, and afterwards we will then let $M\rightarrow\infty$.

Since the operator Ω_{eff} is Hermitean, its eigenfunctions ψ_k ($k=1, 2, \cdots N$) are automatically orthogonal, and we will further assume that they are normalized to fulfill (34). We note that, in addition to the N eigenfunctions which are used in constructing the density matrix $\boldsymbol{\rho}$, there may be also higher solutions for $k=N+1, N+2, \cdots$, but, for the moment, we are not interested in these "virtual spin-orbitals." The main problem is now to determine the coefficients $c_{\mu k}$ in (63), which form a *rectangular matrix* of order $M\times N$ with $M>N$. It is here understood that (63) is momentarily replaced by the approximate expansion

$$\psi_k(\mathbf{x}_1)=\sum_{\mu=1}^{M} \varphi_\mu(\mathbf{x}_1)c_{\mu k}. \tag{64}$$

Substituting (64) into the orthonormality condition (34), we obtain

$$\sum_{\mu=1}^{M} c_{k\mu}{}^{\dagger}c_{\mu l}=\delta_{kl}, \tag{65}$$

which may be condensed in matrix form to $\mathbf{c}^{\dagger}\mathbf{c}=\mathbf{1}$, if we strictly observe that the symbols $\mathbf{c}$ and $\mathbf{c}^{\dagger}$ indicate rectangular matrices. We note that the matrix $\mathbf{c}$ has *unitary* properties at least in the vertical direction, but that we cannot prove the complementary relation $\mathbf{c}\mathbf{c}^{\dagger}=\mathbf{1}$ without completing the matrix to square form by investigating the character of the virtual orbitals. The properties of c are indicated in Fig. 1.

In Sec. 1 we have shown that, in the Hartree-Fock approximation, the entire physical situation of the many-particle system may be described by the fundamental invariant $\boldsymbol{\rho}$ defined by (12) or (35). Putting (64) into (35), we obtain

$$\rho(\mathbf{x}_1,\mathbf{x}_2)=\sum_{k=1}^{N} \psi_k{}^*(\mathbf{x}_1)\psi_k(\mathbf{x}_2)=\sum_{\mu,\nu=1}^{M} \varphi_\mu{}^*(\mathbf{x}_1)\varphi_\nu(\mathbf{x}_2)Q(\nu\mu), \tag{66}$$

where we have introduced the symbol

$$Q(\nu\mu)=\sum_{k=1}^{N} c_{\nu k}c_{k\mu}{}^{\dagger}. \tag{67}$$

The entire physical situation is now instead determined by the quadratic matrix $\mathbf{Q}$ of order $M\times M$.

Relation (66) gives also the first-order density matrix $\boldsymbol{\gamma}$ of the system. In Part I, the matrix of the coefficients $\gamma(\nu|\mu)$ in the expansion of this density matrix with respect to a particular basic set φ_μ has generally been called the *charge- and bond-order matrix* with respect to this set. We will here use the special notation

$$\gamma(\nu|\mu)\equiv Q(\nu\mu), \tag{68}$$

in order to indicate that we are considering the Hartree-Fock approximation. The physical interpretation of the elements is given in Part I, Sec. 2. We note also that, in forming (66), we are carrying out the reverse to the procedure used in forming (I, 74), since we are here going from natural spin-orbitals to an arbitrarily chosen basic set φ_μ.

Since $\boldsymbol{\rho}$ fulfills the relations (13), the same must be true also for the matrix $\mathbf{Q}$:

$$\mathbf{Q}^2=\mathbf{Q}, \quad \mathrm{Tr}(\mathbf{Q})=N, \tag{69}$$

and we can easily check these relations by using (67). The Hermitean matrix $\mathbf{Q}$ is therefore a "projection operator" in the sense of Part I, Sec. 5. It has N eigenvalues equal to 1 and $(M-N)$ eigenvalues equal to zero, and the eigenvectors associated with the eigenvalue 1 form together the rectangular matrix $\mathbf{c}$. Hence we have

$$\mathbf{Q}\mathbf{c}=\mathbf{c}, \quad \mathbf{c}^{\dagger}\mathbf{Q}\mathbf{c}=\mathbf{1}, \tag{70}$$

where the unit matrix of the last relation is a square matrix of order N. These relations are easily checked by using (65) and (67).

Let us now consider the density matrices in the μ space. Putting (66) into (15) and using the law for forming the determinant of a product of matrices, we

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[16] We note that, for atoms, the method may be used alternatively with Hartree's conventional treatment applying numerical integration.

obtain

$$\gamma(\mathbf{x}_1'|\mathbf{x}_1)=\sum_{\mu\nu}\varphi_\mu^*(\mathbf{x}_1')\varphi_\nu(\mathbf{x}_1)Q(\nu\mu),$$

$$\begin{aligned}\Gamma^{(p)}&(\mathbf{x}_1'\mathbf{x}_2'\cdots\mathbf{x}_p'|\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_p)\\ &=(p!)^{-1}\sum_{\substack{\mu_1<\mu_2<\cdots\mu_p\\ \nu_1<\nu_2<\cdots\nu_p}}\begin{vmatrix}\varphi_{\mu_1}^*(\mathbf{x}_1') & \cdots & \varphi_{\mu_p}^*(\mathbf{x}_1')\\ \cdot & \cdot & \cdot\\ \varphi_{\mu_1}^*(\mathbf{x}_p') & \cdots & \varphi_{\mu_p}^*(\mathbf{x}_p')\end{vmatrix}\cdot\begin{vmatrix}\varphi_{\nu_1}(\mathbf{x}_1) & \cdots & \varphi_{\nu_p}(\mathbf{x}_1)\\ \cdot & \cdot & \cdot\\ \varphi_{\nu_1}(\mathbf{x}_p) & \cdots & \varphi_{\nu_p}(\mathbf{x}_p)\end{vmatrix}\cdot\begin{vmatrix}Q(\nu_1\mu_1) & \cdots & Q(\nu_1\mu_p)\\ \cdot & \cdot & \cdot\\ Q(\nu_p\mu_1) & \cdots & Q(\nu_p\mu_p)\end{vmatrix}\\ &=(p!)^{-1}\sum_{\substack{\mu_1\mu_2\cdots\mu_p\\ \nu_1\nu_2\cdots\nu_p}}\varphi_{\mu_1}^*(\mathbf{x}_1')\cdots\varphi_{\mu_p}^*(\mathbf{x}_p')\varphi_{\nu_1}(\mathbf{x}_1)\cdots\varphi_{\nu_p}(\mathbf{x}_p)\begin{vmatrix}Q(\nu_1\mu_1) & \cdots & Q(\nu_1\mu_p)\\ \cdot & \cdot & \cdot\\ Q(\nu_p\mu_1) & \cdots & Q(\nu_p\mu_p)\end{vmatrix},\end{aligned}\tag{71}$$

which gives

$$\Gamma^{(p)}(\nu_1\nu_2\cdots\nu_p|\mu_1\mu_2\cdots\mu_p)=(p!)^{-1}\begin{vmatrix}Q(\nu_1\mu_1) & Q(\nu_1\mu_2) & \cdots & Q(\nu_1\mu_p)\\ \cdot & \cdot & \cdot & \cdot\\ Q(\nu_p\mu_1) & Q(\nu_p\mu_2) & \cdots & Q(\nu_p\mu_p)\end{vmatrix}.\tag{72}$$

All charge- and bond-order matrices of higher orders may therefore be expressed in the fundamental matrix $\mathbf{Q}$, and this is true also for $p=N$, i.e., for the wave function itself. Introducing the matrix elements with respect to the set φ_μ:

$$\begin{aligned}[\mu|\Omega_1|\nu]&=\int\varphi_\mu^*(1)\Omega_1\varphi_\nu(1)dx_1,\\ [\mu_1\mu_2|\Omega_{12}|\nu_1\nu_2]&=\int\varphi_{\mu_1}^*(1)\varphi_{\mu_2}^*(2)\Omega_{12}\varphi_{\nu_1}(1)\varphi_{\nu_2}(2)dx_1dx_2,\\ &\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\end{aligned}\tag{73}$$

and applying (I, 10), we get the fundamental formula

$$\begin{aligned}\langle\Omega_{\mathrm{op}}\rangle_{\mathrm{Av}}=\Omega_{(0)}&+\sum_{\mu\nu}[\mu|\Omega_1|\nu]Q(\nu\mu)+(2!)^{-1}\sum_{\substack{\mu_1\mu_2\\ \nu_1\nu_2}}[\mu_1\mu_2|\Omega_{12}|\nu_1\nu_2]\begin{vmatrix}Q(\nu_1\mu_1) & Q(\nu_1\mu_2)\\ Q(\nu_2\mu_1) & Q(\nu_2\mu_2)\end{vmatrix}\\ &+(3!)^{-1}\sum_{\substack{\mu_1\mu_2\mu_3\\ \nu_1\nu_2\nu_3}}[\mu_1\mu_2\mu_3|\Omega_{123}|\nu_1\nu_2\nu_3]\begin{vmatrix}Q(\nu_1\mu_1) & \cdots & Q(\nu_1\mu_3)\\ \cdot & \cdot & \cdot\\ Q(\nu_3\mu_1) & \cdots & Q(\nu_3\mu_3)\end{vmatrix}+\cdots,\end{aligned}\tag{74}$$

showing that the average value of a physical quantity Ω_{op} may be expressed in terms of the matrix elements (73) and the charge- and bond-order matrix $\mathbf{Q}$.

The essential problem is now to solve the Hartree-Fock equation (62) and determine the matrix $\mathbf{Q}$. Since (62) for a *fixed* Ω_{eff} operator represents a linear eigenvalue problem in the ordinary $\mathbf{x}$-space, we may again apply the variation principle (I, 22). Forming the average value of Ω_{eff} by using expansion (64) and omitting the index k, we obtain

$$\omega=\int\psi^*(1)\Omega_{\mathrm{eff}}(1)\psi(1)dx_1\Big/\int\psi^*(1)\psi(1)dx_1=\sum_{\mu\nu}c_\mu^*[\mu|\Omega_{\mathrm{eff}}|\nu]c_\nu/\sum_{\mu\nu}c_\mu^*\delta_{\mu\nu}c_\nu,\tag{75}$$

where

$$\begin{aligned}[\mu|\Omega_{\mathrm{eff}}|\nu]&=\int\varphi_\mu^*(1)\Omega_{\mathrm{eff}}(1)\varphi_\nu(1)dx_1\\ &=[\mu|\Omega_1|\nu]+\int\varphi_\mu^*(1)\Omega_{12}\begin{vmatrix}\varphi_\nu(1) & \varphi_\nu(2)\\ \rho(2',1) & \rho(2',2)\end{vmatrix}dx_1dx_2\\ &\qquad+(2!)^{-1}\int\varphi_\mu^*(1)\Omega_{123}\begin{vmatrix}\varphi_\nu(1) & \varphi_\nu(2) & \varphi_\nu(3)\\ \rho(2',1) & \rho(2',2) & \rho(2',3)\\ \rho(3',1) & \rho(3',2) & \rho(3',3)\end{vmatrix}dx_1dx_2dx_3+\cdots\\ &=[\mu|\Omega_1|\nu]+\sum_{\mu_2\nu_2}Q(\nu_2\mu_2)(1-P_{\nu\nu_2})[\mu\mu_2|\Omega_{12}|\nu\nu_2]\\ &\qquad+(2!)^{-1}\sum_{\substack{\mu_2\mu_3\\ \nu_2\nu_3}}\begin{vmatrix}Q(\nu_2\mu_2) & Q(\nu_2\mu_3)\\ Q(\nu_3\mu_2) & Q(\nu_3\mu_3)\end{vmatrix}(1-P_{\nu\nu_2}-P_{\nu\nu_3})[\mu\mu_2\mu_3|\Omega_{123}|\nu\nu_2\nu_3]+\cdots.\end{aligned}\tag{76}$$

As in (44)–(52), the operator $\Omega_{\rm eff}$ may here be expanded in terms of potentials from the densities $\varphi_\mu{}^*\varphi_\nu Q(\nu\mu)$, and the matrix elements (76) may then be interpreted analogously.

Keeping $\Omega_{\rm eff}$ fixed, varying the coefficients c in (75), and putting $\delta\omega=0$, we obtain a system of linear equations

$$\sum_\nu\{[\mu|\Omega_{\rm eff}|\nu]-\omega\delta_{\mu\nu}\}c_\nu=0, \tag{77}$$

which is soluble only if

$$\det\{[\mu|\Omega_{\rm eff}|\nu]-\omega\delta_{\mu\nu}\}=0. \tag{78}$$

This secular equation is an algebraic equation in ω of the order M, and it has therefore M eigenvalues ω_k $(k=1, 2, \cdots M)$ which are all real. After the eigenvalues have been determined, we may solve the M systems (77) giving a quadratic matrix $c_{\mu k}$ of order M. In addition to the N ordinary solutions, in which we were originally interested, we have therefore also obtained $(M-N)$ "virtual" solutions, which will be discussed later.

The whole nonlinear problem may now be solved by a process of successive approximations which is analogous to Hartree's "self-consistent-field" method for atoms. One starts from trial values $\mathbf{Q}^{(0)}$ of the fundamental charge- and bond-order matrix, evaluates the matrix elements (76), solves the secular equation (78), and thereafter the linear system (77). From the rectangular matrix $c_{\mu k}$ corresponding to the N ordinary solutions of (78), one may then form a new approximation of the matrix $\mathbf{Q}$ by using the definition (67), and the procedure is then repeated until it becomes "self-consistent," i.e., until two successive approximations agree within the accuracy desired.

The method of expanding the Hartree-Fock functions in terms of a fixed given set was first used in the molecular orbital theory in investigating the electronic structure of molecules and crystals. However, a first systematic treatment of the variation problem, emphasizing its nonlinear character, was first given by Roothaan,[5] who varied the coefficients $c_{\mu k}$ directly in the total quantity $\langle\Omega_{\rm op}\rangle_{\rm Av}$. The derivation given here follows more Hartree's conventional scheme and, in addition, we have pointed out the essential simplifications of the calculations which may be obtained by introducing the charge- and bond-order matrix $\mathbf{Q}$.

(b) Direct Variation of the Matrix *Q*

One could also consider the matrix $\mathbf{Q}$ as the fundamental variable in the problem and vary this quantity as a whole instead of the coefficients $c_{\mu k}$. By varying expression (74) and using (76), we obtain

$$\delta\langle\Omega_{\rm op}\rangle_{\rm Av}=\sum_{\mu\nu}[\mu|\Omega_{\rm eff}|\nu]\delta Q(\nu\mu)={\rm Tr}(\boldsymbol{\Omega}_{\rm eff}\cdot\delta\mathbf{Q}). \tag{79}$$

The auxiliary conditions may be treated analogously to Sec. 2 (d). Since $\mathbf{Q}$ fulfills the relations (69), we get for its variation:

$$\delta\mathbf{Q}=\mathbf{Q}\delta\mathbf{Q}+\delta\mathbf{Q}\cdot\mathbf{Q},\quad {\rm Tr}(\delta\mathbf{Q})=0, \tag{80}$$

and further

$$\mathbf{Q}\delta\mathbf{Q}\cdot\mathbf{Q}=0, \tag{81}$$

showing that $\delta\mathbf{Q}$ is without orthogonal projection within the subspace of the general Hilbert space defined by the projection operator $\mathbf{Q}$. If $\boldsymbol{\Lambda}$ is an arbitrary matrix of order M and $\boldsymbol{\lambda}$ its orthogonal projection within this subspace defined by

$$\boldsymbol{\lambda}=\mathbf{Q}\boldsymbol{\Lambda}\mathbf{Q}, \tag{82}$$

$$\lambda_{\mu\nu}=\sum_{k,l=1}^{N}c_{\mu k}\lambda_{kj}c_{j\nu}{}^\dagger,\quad \lambda_{kj}=\sum_{\mu,\nu=1}^{M}c_{k\mu}{}^\dagger\Lambda_{\mu\nu}c_{\nu j},$$

then the "scalar product" of $\delta\mathbf{Q}$ and $\boldsymbol{\lambda}$ is vanishing;

$${\rm Tr}(\delta\mathbf{Q}\cdot\boldsymbol{\lambda})=0. \tag{83}$$

This relation presents the auxiliary conditions in a convenient form, and, by combining (79) and (83), we obtain

$$[\mu|\Omega_{\rm eff}|\nu]=\lambda_{\mu\nu}. \tag{84}$$

This is the Hartree-Fock condition for the charge- and bond-order matrix $\mathbf{Q}$, and it says simply that the matrix $[\mu|\Omega_{\rm eff}|\nu]$ should belong to the subspace defined by $\mathbf{Q}$. Togther with (69), this condition is sufficient for determining $\mathbf{Q}$. It may also be expressed in the form

$$\boldsymbol{\Omega}_{\rm eff}=\mathbf{Q}\boldsymbol{\Omega}_{\rm eff}\mathbf{Q}, \tag{85}$$

where $\boldsymbol{\Omega}_{\rm eff}$ as in (79) is the matrix formed by the elements $[\mu|\Omega_{\rm eff}|\nu]$.

(c) Applications to the MO-LCAO-Method in the Theory of the Electronic Structure of Molecules and Crystals

In the molecular-orbital theory of molecules and crystals introduced by Lennard-Jones, Hund, Mulliken, Bloch, and others, the molecular orbitals for the electrons were assumed to be solutions to a one-particle Schrödinger equation, where the "effective" Hamiltonian consisted of the kinetic energy of the electron, its potential energy in the nuclear framework, and its potential energy in the field of all the other electrons. As in the original Hartree scheme, the exclusion of the interaction between a particle and itself caused mathematical as well as physical difficulties, until this problem was successfully solved by the introduction of the antisymmetry requirement in the Hartree-Fock scheme, which automatically eliminated the self-interaction; see (47). The effective Hamiltonian of a molecule or a crystal may therefore now be properly represented by the one-particle operator (40) corresponding to a total Hamiltonian of the form (I, 11):

$$\mathcal{H}_{\rm eff}(1)=\frac{\mathbf{p}_1{}^2}{2m}-e^2\sum_g\frac{Z_g}{r_{1g}}+e^2\int\frac{\rho(\mathbf{x}_2,\mathbf{x}_2)-\rho(\mathbf{x}_2,\mathbf{x}_1)P_{12}}{r_{12}}dx_2, \tag{86}$$

but we note that we here have neglected relativistic effects (including all spin couplings) as well as the zero-point vibrations of the nuclei g, having the atomic numbers Z_g.

(d) Fundamental Charge and Bond Order Matrix R with Respect to the Ordinary Atomic Orbitals

In the MSO-LCASO method of treating the electronic structure of molecules and crystals, the molecular spin-orbitals (MSO) are assumed to be formed by linear combinations of atomic spin-orbitals (ASO) ϕ_μ, which may be the ordinary or hybridized $1s$, $2s$, $2p$, $3s$, $\cdots$ spin-orbitals associated with the atomic constituents of the system. In comparison to (a), this assumption leads to a complication, since atomic spin-orbitals ϕ_μ and ϕ_ν belonging to neighboring atoms are usually overlapping, and they have therefore nonorthogonality or *overlap integrals*

$$\int \phi_\mu^*(1)\phi_\nu(1)dx_1=\Delta_{\mu\nu}=\delta_{\mu\nu}+S_{\mu\nu}, \tag{87}$$

which may be essentially different from zero. However, by a suitable linear transformations as (33):

$$\varphi_\mu=\sum_\alpha \phi_\alpha(\Delta^{-\frac{1}{2}})_{\alpha\mu}=\sum_\alpha \phi_\alpha[(1+\mathbf{S})^{-\frac{1}{2}}]_{\alpha\mu}, \tag{88}$$

the basic set may be orthonormalized, $\int \varphi_\mu^*\varphi_\nu dx=\delta_{\mu\nu}$, and the general theory developed in (a) may then be directly applied to the set φ_μ of orthonormalized atomic spin-orbitals (ON-ASO).

Let us consider a molecule or crystal in the Hartree-Fock approximation having a total wave function approximated by a single Slater determinant, built up from N molecular spin-orbitals $\psi_1, \psi_2, \cdots \psi_N$. Expanding ψ_k in the form (64) and using (88), we now obtain for the fundamental invariant $\boldsymbol{\rho}$ defined by (35):

$$\begin{aligned}\rho(\mathbf{x}_1,\mathbf{x}_2)&=\sum_{k=1}^{N}\psi_k^*(\mathbf{x}_1)\psi_k(\mathbf{x}_2)\\&=\sum_{\mu\nu}\varphi_\mu^*(\mathbf{x}_1)\varphi_\nu(\mathbf{x}_2)Q(\nu\mu)\\&=\sum_{\alpha\beta}\phi_\alpha^*(\mathbf{x}_1)\phi_\beta(\mathbf{x}_2)R(\beta\alpha),\end{aligned} \tag{89}$$

where

$$\mathbf{R}=\mathbf{\Delta}^{-\frac{1}{2}}\mathbf{Q}\mathbf{\Delta}^{-\frac{1}{2}}=(1+\mathbf{S})^{-\frac{1}{2}}\mathbf{Q}(1+\mathbf{S})^{-\frac{1}{2}}. \tag{90}$$

We note that the matrix $\mathbf{R}$ may also be introduced directly without the help of the ON-ASO, if we instead start from the expansion

$$\psi_k=\sum_\alpha \phi_\alpha r_{\alpha k} \tag{91}$$

and introduce R by the definition

$$R(\beta\alpha)=\sum_{k=1}^{N} r_{\beta k}r_{k\alpha}{}^\dagger, \tag{92}$$

Since the set ψ_k is orthonormalized according to (34), we get further

$$\mathbf{r}^\dagger\mathbf{\Delta}\mathbf{r}=\mathbf{1}, \tag{93}$$

for the rectangular matrix $r_{\alpha k}$ of order $M\times N$. By using (92) and (93), it is easily shown that, instead of (69), the matrix $\mathbf{R}$ fulfills the relations

$$\mathbf{R\Delta R}=\mathbf{R},\quad \mathrm{Tr}(\mathbf{\Delta}\cdot\mathbf{R})=N, \tag{94}$$

corresponding to (13). We note that the "overlapping" matrix $\mathbf{\Delta}$ occurs in (93) and (94), since it describes the "geometry" of the nonorthogonal space, defined by the basic set ϕ_μ, and $\mathbf{R}$ may then be interpreted as a "projection operator" in this space.

In a previous paper,[17] we have called the $\mathbf{Q}$ the charge- and bond-order matrix of the system and $\mathbf{R}$ the "bonding-overlapping" matrix, but, according to the general terminology introduced in Part I, Sec. 2, we are now going to change our nomenclature and call $\mathbf{Q}$ and $\mathbf{R}$ the charge- and bond-order matrices with respect to the orthonormalized and ordinary atomic spin-orbitals, respectively. Let us now discuss the relation between $\mathbf{Q}$ and $\mathbf{R}$ in greater detail, particularly from the chemical point of view.

As an example, we will consider the interaction between "closed-shell" ions. This case is nondegenerate, and, if we choose $M=N$, it follows from the complementary relation to (65) that

$$Q(\nu\mu)=\delta_{\mu\nu}. \tag{95}$$

Since the bond orders vanish for $\mu\neq\nu$, this relation corresponds to the nonexistence of valence bonds between closed-shell systems. However, if the ions are put together in, e.g., *an ionic crystal*, the circumstances will be changed. In previous papers,[18] we have shown that the existence of such a crystal depends on the equilibrium between the electrostatic attraction between the ions and the *repulsion* due to the overlapping between the ions at closer distances. It should be possible to express these repulsive properties also in the valency language, and we note that, in this special case, the matrix $\mathbf{R}$ is defined by

$$\mathbf{R}=\mathbf{\Delta}^{-1}=(1+\mathbf{S})^{-1},$$

giving charge and bond orders essentially depending on the overlapping between the ions. Numerical applications may be found in reference 11 of Part I, and we will here only illustrate the result by some recent data on LiH by Lundqvist,[19] who has found the first elements of the charge- and bond-order matrix associated with the $1s$-orbitals of Li^+ and H^- to be:

$R_{\mu\mu}=1.419$ for H^-, $R_{\nu\nu}=1.021$ for Li^+,
$R_{\nu\mu}=-0.052$ for $\mathrm{Li}^+\mathrm{H}^-$ (nearest neighbors),
$R_{\nu\mu}=-0.165$ for $\mathrm{H}^-\mathrm{H}^-$ (next nearest neighbors).

We note the negative signs and repulsive character of the bond orders for nearest and next nearest neighbors.

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[17] P. O. Löwdin, J. Chem. Phys. **19**, 1570 (1951).

[18] See Part I, reference 11.

[19] S. O. Lundqvist, Arkiv Fysik **8**, 177 (1954). Compare also I. Waller and S. O. Lundqvist, Arkiv Fysik **7**, 121 (1953), where, as Lundqvist has kindly pointed out to me, there are some misprints in the signs of the bond orders.

Lundqvist has used these and higher elements for investigating the diagonal element $\rho(\mathbf{x},\mathbf{x})$ of the density matrix, and, in this connection, he has been able to draw interesting conclusions concerning the amount of "covalent" character of LiH. It should here further be remarked that, in investigating the properties of ionic crystals, the complete density-matrix formalism has previously been used also by Fröman[20] and by Montet, Keller, and Mayer.[21]

Another example may be found in a paper by Sponer[22] and the author, where the matrices **Q** and **R** for the $\pi\pi$ bond in ethylene have been compared.

Our comparison between **Q** and **R** shows that, from the chemical point of view, **Q** is the charge- and bond-order matrix for separated atoms with nondiagonal elements representing the *formal* valency of the atoms, whereas **R** is the charge- and bond-order matrix associated with the atoms in the molecule or crystal under consideration with nondiagonal elements representing the *actual* bond strengths. This result seems to be in agreement with the new definition of "relative bond strengths" introduced by Mulliken.[23]

In discussing molecules and crystals, we have previously[17] also introduced so-called "combined atomic spin-orbitals" by the relation

$$\phi_\mu{}^C=\textstyle\sum_\alpha \phi_\alpha R(\alpha\mu). \tag{96}$$

Using the fact that **R** is a "projection operator" fulfilling (94), we now obtain for the fundamental invariant

$$\begin{aligned}\rho(\mathbf{x}_1,\mathbf{x}_2)&=\textstyle\sum_{\alpha\beta} \phi_\alpha{}^*(\mathbf{x}_1)\phi_\beta(\mathbf{x}_2)R(\beta\alpha)\\&=\textstyle\sum_{\mu\nu} \phi_\mu{}^{C*}(\mathbf{x}_1)\phi_\nu{}^C(\mathbf{x}_2)\Delta_{\nu\mu}.\end{aligned} \tag{97}$$

Since this quantity depends only on the set $\phi_\mu{}^C$ and the overlapping matrix Δ, all our previous asymmetric formulas in reference 15 are now easily symmetrized. Using (94), we obtain further

$$\int \phi_\mu{}^{C*}(1)\phi_\nu{}^C(1)dx_1=R(\mu\nu). \tag{98}$$

This is therefore a case where the overlap integral between two one-particle functions really measures the charge and bond orders of the system.

From the fundamental theorem derived in Sec. 1, it is clear that if, in any way, we could determine or measure the first-order density matrix $\gamma(\mathbf{x}_1'|\mathbf{x}_1)$ or the charge- and bond-order matrix **R**, then we would have all information needed for describing the properties of the system with an accuracy corresponding at least to the Hartree-Fock approximation. It is possible, e.g., by diffraction experiments to determine the average particle distribution in the ordinary **x**-space, corresponding to the diagonal element, $\gamma(\mathbf{x}_1|\mathbf{x}_1)$, but, so far, none has been able to devise any experiments for measuring the entire matrix $\gamma(\mathbf{x}_1'|\mathbf{x}_1)$. This quantity offers, in fact, a rather intricate problem, since it gives the description of the same physical situation in two complementary spaces, and, like the complex wave function,[24] it has therefore only a *symbolic* character and can never be measured directly. How $\gamma(\mathbf{x}_1'|\mathbf{x}_1)$ may be determined from two diagonal distributions $\gamma(\mathbf{x}|\mathbf{x})$ and $\gamma(k|k)$ in complementary spaces is a particular problem.[24]

We will finally give the expression of the average value of a physical quantity Ω_{op} defined by (I, 2) in terms of the fundamental matrix **R**. The charge- and bond-order matrices of higher orders are expressed by formula (72) with **Q** replaced by **R**, and, according to (I, 10), we then obtain

$$\begin{aligned}\langle\Omega_{\text{op}}\rangle_{\text{Av}}=\Omega_{(0)}+\sum_{\mu\nu}(\mu|\Omega_1|\nu)R(\nu\mu)+(2!)^{-1}\sum_{\substack{\mu_1\mu_2\\\nu_1\nu_2}}(\mu_1\mu_2|\Omega_{12}|\nu_1\nu_2)\begin{vmatrix}R(\nu_1\mu_1) & R(\nu_1\mu_2)\\R(\nu_2\mu_1) & R(\nu_2\mu_2)\end{vmatrix}\\+(3!)^{-1}\sum_{\substack{\mu_1\mu_2\mu_3\\\nu_1\nu_2\nu_3}}(\mu_1\mu_2\mu_3|\Omega_{123}|\nu_1\nu_2\nu_3)\begin{vmatrix}R(\nu_1\mu_1) & \cdots & R(\nu_1\mu_3)\\\cdot & \cdot\;\cdot\;\cdot & \cdot\\R(\nu_3\mu_1) & \cdots & R(\nu_3\mu_3)\end{vmatrix}+\cdots,\end{aligned} \tag{99}$$

where the matrix elements are given by (73) with the functions φ_μ replaced by the functions ϕ_μ. A special case of this formula was previously derived by the author[17] in another way.

(e) Hartree-Fock Equations in the MO-LCAO-Theory

Let us turn now to the question of determining the molecular spin-orbitals ψ_k, i.e., the coefficients $r_{\alpha k}$ in expansion (91). They are solutions to the eigenvalue problem (62), and, for a fixed operator Ω_{eff}, they may therefore be found from the variation principle. Using (91), we obtain

$$\begin{aligned}\omega=\int\psi^*(1)\Omega_{\text{eff}}(1)\psi(1)dx_1\Big/\int\psi^*(1)\psi(1)dx_1\\=\sum_{\mu\nu} r_\mu{}^*(\mu|\Omega_{\text{eff}}|\nu)r_\nu\Big/\sum_{\mu\nu} r_\mu{}^*\Delta_{\mu\nu}r_\nu,\end{aligned} \tag{100}$$

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[20] P. O. Fröman, Arkiv Fysik **5**, 135 (1952); **9**, 93 (1954).

[21] Montet, Keller, and Mayer, J. Chem. Phys. **20**, 1057 (1952).

[22] H. Sponer and P. O. Löwdin, J. phys. radium **15**, 607 (1954).

[23] R. S. Mulliken (private communication).

[24] See, for instance, W. Pauli, *Handbuch der Physik* (Julius Springer, Berlin, 1933), Vol. **24**, No. 1, particularly p. 98.

where

$$(\mu|\Omega_{\text{eff}}|\nu)$$
$$=(\mu|\Omega_1|\nu)+\sum_{\mu_2\nu_2}R(\nu_2\mu_2)(1-P_{\nu\nu_2})(\mu\mu_2|\Omega_{12}|\nu\nu_2)$$
$$+(2!)^{-1}\sum_{\substack{\mu_2\mu_3\\ \nu_2\nu_3}}\begin{vmatrix}R(\nu_2\mu_2) & R(\nu_2\mu_3)\\ R(\nu_3\mu_2) & R(\nu_3\mu_3)\end{vmatrix}$$
$$\times(1-P_{\nu\nu_2}-P_{\nu\nu_3})(\mu\mu_2\mu_3|\Omega_{123}|\nu\nu_2\nu_3)+\cdots. \quad (101)$$

All matrix elements are here to be taken with respect to the functions ϕ_μ. Keeping Ω_{eff} fix, varying the coefficients r_μ in (100), and putting $\delta\omega=0$, we obtain a system of linear equations

$$\sum_\nu\{(\mu|\Omega_{\text{eff}}|\nu)-\omega\Delta_{\mu\nu}\}r_\nu=0, \quad (102)$$

which is soluble only if

$$\det\{(\mu|\Omega_{\text{eff}}|\nu)-\omega\Delta_{\mu\nu}\}=0. \quad (103)$$

These relations are identical with (77) and (78), if the Kronecker symbol $\delta_{\mu\nu}$ in them is replaced by the overlapping matrix $\Delta_{\mu\nu}$. The nonlinear problem of finding the coefficients r_μ may therefore again be solved by a method of "self-consistent fields," starting from trial values $\mathbf{R}^{(0)}$ of the matrix $\mathbf{R}$, solving the secular equation (103), evaluating the coefficients $r_{\mu k}$ from (102), and recomputing a new approximation of $\mathbf{R}$ according to (92), etc.

If the numerical program for solving the secular equation (78) may be adapted to the case $\Delta_{\mu\nu}\neq 0$ for $\mu\neq\nu$, the occurrence of the overlapping matrix does not cause any particular difficulties. The rectangular matrix $r_{\mu k}$ has to fulfill the relation (93), but we note that, for $\mu\neq\nu$, the relation $(\mathbf{r}^\dagger\boldsymbol{\Delta}\mathbf{r})_{\mu\nu}=0$ is automatically fulfilled and that the solutions to (102) only have to be properly "normalized" by a constant coefficient to satisfy $(\mathbf{r}^\dagger\boldsymbol{\Delta}\mathbf{r})_{\mu\mu}=1$.

The MO-LCAO method in its "self-consistent field" form was first discussed in detail by Roothaan,[5] but we note the essential simplification of the procedure here obtained by introducing the charge- and bond-order matrix $\mathbf{R}$. The first numerical application of Roothaan's scheme was carried out by Parr and Mulliken.[25]

In analogy to (79)–(85), we may also derive the Hartree-Fock equations by varying the matrix $\mathbf{R}$ as a whole. According to (94), we obtain

$$\mathbf{R}\boldsymbol{\Delta}\cdot\delta\mathbf{R}\cdot\boldsymbol{\Delta}\mathbf{R}=0, \quad (104)$$

which leads to the following auxiliary condition:

$$\text{Tr}(\delta\mathbf{R}\cdot\boldsymbol{\Delta}\mathbf{R}\boldsymbol{\Lambda}\mathbf{R}\boldsymbol{\Delta})=0, \quad (105)$$

where $\boldsymbol{\Lambda}$ is an arbitrary matrix of the order M. The Hartree-Fock equations may then be condensed in a single relation

$$(\mu|\Omega_{\text{eff}}|\nu)=\lambda_{\mu\nu}, \quad (106)$$

where

$$\boldsymbol{\lambda}=\boldsymbol{\Delta}\mathbf{R}\boldsymbol{\Lambda}\mathbf{R}\boldsymbol{\Delta}. \quad (107)$$

(f) The Coulomb and Exchange Integrals in the MO-LCAO Theory of Conjugated Systems

In the theory of conjugated organic compounds, there are particularly two types of quantities which are considered to be of importance, namely the "Coulomb integrals" α_μ and the "exchange integrals" $\beta_{\mu\nu}$ $(\mu\neq\nu)$ defined as the matrix elements of the effecttive Hamiltonian[4] but usually determined by fitting some theoretical quantities containing them to experimental data. In the Hartree-Fock scheme, the effective Hamiltonian is now given by the simple expression (86), and its matrix elements may then be determined on a purely theoretical basis. For the elements of $\mathcal{H}_{\text{eff}}$ with respect to the ordinary atomic spin-orbitals ϕ_μ, we obtain

$$(\mu|\mathcal{H}_{\text{eff}}|\nu)=\int\phi_\mu^*(1)\left\{\frac{\mathbf{p}_1^2}{2m}-e^2\sum_g\frac{Z_g}{r_{1g}}\right\}\phi_\nu(1)dx_1$$
$$+e^2\sum_{\kappa\lambda}R(\lambda\kappa)\int\frac{\phi_\mu^*(1)\phi_\kappa^*(2)\phi_\nu(1)\phi_\lambda(2)-\phi_\mu^*(1)\phi_\kappa^*(2)\phi_\lambda(1)\phi_\nu(2)}{r_{12}}dx_1dx_2, \quad (108)$$

as a special case of (101). According to (76), the corresponding elements $[\mu|\mathcal{H}_{\text{eff}}|\nu]$ with respect to the orthonormalized set φ_μ may be obtained by replacing ϕ_μ and $\mathbf{R}$ in (108) by φ_μ and $\mathbf{Q}$, respectively. We note that the change of basic set is easily carried out by means of the formulas

$$\mathbf{r}=\boldsymbol{\Delta}^{-\frac{1}{2}}\mathbf{c}, \quad \mathbf{R}=\boldsymbol{\Delta}^{-\frac{1}{2}}\mathbf{Q}\boldsymbol{\Delta}^{-\frac{1}{2}},$$
$$[\mu|\mathcal{H}_{\text{eff}}|\nu]=\sum_{\alpha\beta}(\Delta^{-\frac{1}{2}})_{\mu\alpha}(\alpha|\mathcal{H}_{\text{eff}}|\beta)(\Delta^{-\frac{1}{2}})_{\beta\nu}. \quad (109)$$

A further discussion of these quantities for the aromatic compounds will be given in a following paper.

4. ORDINARY AND VIRTUAL HARTREE-FOCK FUNCTIONS

In treating the basic eigenvalue problem (39):

$$\Omega_{\text{eff}}(1)\psi_k(1)=\omega_k\psi_k(1), \quad (110)$$

by, e.g., the method of expanding the eigenfunctions in a fixed set φ_μ of order M, we have found that, in addition to the N ordinary solutions used in forming the density matrix (66), there are $(M-N)$ solutions to (77) and (78) which are also eigenfunctions to Ω_{eff}

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[25] R. G. Parr and R. S. Mulliken, J. Chem. Phys. **18**, 1338 (1950).

considered as a fixed operator. Hall and Lennard-Jones[26] have called these extra solutions *virtual* Hartree-Fock functions, and they have pointed out that they correspond to the existence of spin-orbitals containing "virtual" particles moving under the influence of the real particles of the system without influencing their motion in return; the "virtual" particles should therefore in some way behave like classical "test charges."

If $M\rightarrow\infty$ and the basic set φ_μ becomes complete, the number of virtual solutions becomes also infinite, but, without a detailed investigation, it is impossible to predict the character of the eigenvalue spectrum for ω_k, how large part of it will be discrete and how large part will be continuous, etc. It could happen that the ordinary and virtual solutions to (110) together would form a *complete* orthonormal set, and, in such cases, this set is of particular importance for discussing the properties of the system.

If the N ordinary solutions to (110) are used for describing the properties of the system in the Hartree-Fock scheme, the virtual spin-orbitals could be used for improving this approximation by, e.g., the method of configurational interaction based on (I, 70) and (I, 71). It is evident that, if the basic set satisfies (110), considerable simplifications can be carried out in the fundamental matrix elements (I, 68). Increasing the number of virtual spin-orbitals taken into account, one can in this way obtain a series of approximations, where the Hartree-Fock scheme represents the first step, as described by Møller and Plesset.[27]

The more or less complete set of ordinary and virtual solutions to (110) may be used also in the one-particle space for solving eigenvalue problems of the same type as (110) but for other effective operators. One can then apply the standard scheme developed in Sec. 3 (a), and the method is, of course, particularly convenient if the operator under consideration is only slightly different from the basic operator Ω_{eff}, in which case the procedure will be related to the "perturbation method" developed by Peng.[28]

In treating the virtual solutions to (110), one should observe the difference between the exact potential (42) containing also exchange operators and Slater's[12,13] average potential (53). In deriving (53), we have minimized the weighted "error sum" (I, 100) containing only the ordinary solutions, and this means that there might be considerable differences between (42) and its approximate form (53) when applied to the virtual spin-orbitals. For the sake of simplicity, let us consider the Coulomb potential, in which case (42) and (53) take the forms

$$V_{\text{op}}(1)=e^2\int\frac{\rho(2,2)-\rho(2,1)P_{12}}{r_{12}}dx_2, \quad (111)$$

$$V_{\text{Av}}(1)=e^2\int\frac{\rho(2,2)-\{\rho(2,1)\rho(1,2)\}/\rho(1,1)}{r_{12}}dx_2, \quad (112)$$

where the density matrix $\boldsymbol{\rho}$ has the character of a projection operator fulfilling (13). We have further

$$\int\rho(2,1)\psi_k(2)dx_2=\begin{cases}\psi_k(1), & k=1,\,2,\,\cdots N;\\ 0, & k=N+1,\,N+2,\,\cdots,\end{cases} \quad (113)$$

giving a characteristic difference between the ordinary spin-orbitals ($k=1,\ 2,\ \cdots N$) and the virtual spin-orbitals ($k=N+1,\ N+2,\ \cdots$). The potentials (111) and (112) are different particularly with respect to their asymptotic behavior when applied to virtual spin-orbitals, and, if x_1 is a point having a very large distance R_1 from the average position of the ordinary particles in the system, then we obtain

$$V_{\text{op}}(1)\psi_k(1)\sim\frac{e^2}{R_1}\psi_k(1)\times\begin{cases}N-1, & k=1,\,2,\,\cdots N;\\ N, & k=N+1,\,N+2,\,\cdots\end{cases} \quad (114)$$

and

$$V_{\text{Av}}(1)\psi_k(1)\sim\frac{e^2}{R}\psi_k(1)\times(N-1), \qquad \text{for all } k. \quad (115)$$

This result implies that the virtual spin-orbitals will be essentially different for the two potentials under consideration. We observe that the approximate form (112) corresponds to a screening of the nuclear framework which is one particle less than the screening corresponding to (111), and one can therefore expect that the virtual solutions associated with (112) would be more stable and have a more extended discrete eigenvalue spectrum than the virtual spin-orbitals belonging to the exact eigenvalue problem (110). From this point of view, the Slater potential would therefore be more convenient in constructing a complete set.[29]

In the MO-LCAO theory of molecules and crystals, sets of approximate virtual spin-orbitals have been evaluated in a few cases and used in configurational interaction, but, otherwise, the theory of the virtual Hartree-Fock solutions to (110) seems to be a field waiting for a closer investigation.

5. TREATMENT OF IONIZED AND EXCITED STATES

In considering the eigenvalue problem (32), we have applied the variation principle (I, 22) without any further restraining condition, and this means that we are actually investigating the state corresponding to the lowest eigenvalue of Ω_{op}, i.e., the ground state of this operator. In this section, we will now show how the

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[26] G. G. Hall and J. Lennard-Jones, Proc. Roy. Soc. (London) **A202**, 155 (1950).

[27] C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).

[28] H. W. Peng, Proc. Roy. Soc. (London) **A178**, 499 (1941).

[29] See also Part I, reference 17.

method may be extended to include also the treatment of ionized and excited states.

In Sec. 1, we have shown that, in the Hartree-Fock approximation, the entire physical situation of the system is determined by the first-order density matrix $\gamma(\mathbf{x}_1'|\mathbf{x}_1)=\rho(\mathbf{x}_1',\mathbf{x}_1)$, and we have not been able to give a particular physical importance to anyone of the basic sets of individual spin-orbitals ψ_k ($k=1, 2, \cdots N$) being connected with each other by unitary transformations. However, in considering also the ionized states, Koopmans[30] has shown that a special physical meaning could be attached to the set representing the *eigenfunctions* to the effective operator (40), i.e., to the set for which the matrix $\lambda(l|k)$ of the Lagrangian multipliers is diagonalized, and, in this connection, he gave also a specific interpretation of the corresponding eigenvalues.

In considering also other properties of the system, it could happen that another set of spin-orbitals will get a particular importance, and, as an example, we will mention the "equivalent" orbitals introduced by Lennard-Jones[31] in treating the problem of chemical valency.

Here we will show that it is possible to extend Koopman's theorem for ionized states to be valid even for many-particle operators Ω_{op} of the form (I, 2). However, the main purpose of the investigation is to try to give a thorough treatment also of the problem of the excited states.

Let us consider two different states of the same system having a fixed outer framework[32] and representing different eigenstates of the same operator (I, 2). In the Hartree-Fock approximation, these states may be described by two single-determinant wave functions Ψ' and Ψ, characterized by the invariants $\boldsymbol{\rho}'$ and $\boldsymbol{\rho}$, respectively, where

$$\boldsymbol{\rho}'=\boldsymbol{\rho}+\Delta\boldsymbol{\rho}. \tag{116}$$

In order to determine the differences

$$\Delta\langle\Omega_{\text{op}}\rangle=\langle\Omega_{\text{op}}'\rangle_{\text{Av}}-\langle\Omega_{\text{op}}\rangle_{\text{Av}},\quad \Delta\Omega_{\text{eff}}=\Omega_{\text{eff}}'-\Omega_{\text{eff}}, \tag{117}$$

we will put (116) into (21) and (40)–(42), and carry out the subtractions. We obtain the two basic formulas

$$\Delta\langle\Omega_{\text{op}}\rangle=\int\Omega_{\text{eff}}(1)\Delta\rho(1',1)dx_1+(2!)^{-1}\int\Omega_{12}\begin{vmatrix}\Delta\rho(1',1) & \Delta\rho(1',2)\\ \Delta\rho(2',1) & \Delta\rho(2',2)\end{vmatrix}dx_1dx_2$$
$$+(3!)^{-1}\int\Omega_{123}\left\{3\begin{vmatrix}\Delta\rho(1',1) & \Delta\rho(1',2) & \rho(1',3)\\ \Delta\rho(2',1) & \Delta\rho(2',2) & \rho(2',3)\\ \Delta\rho(3',1) & \Delta\rho(3',2) & \rho(3',3)\end{vmatrix}+\begin{vmatrix}\Delta\rho(1',1) & \Delta\rho(1',2) & \Delta\rho(1',3)\\ \Delta\rho(2',1) & \Delta\rho(2',2) & \Delta\rho(2',3)\\ \Delta\rho(3',1) & \Delta\rho(3',2) & \Delta\rho(3',3)\end{vmatrix}\right\}dx_1dx_2dx_3+\cdots, \tag{118}$$

and

$$\Delta\Omega_{\text{eff}}=\int\Omega_{12}(1-P_{12})\Delta\rho(2',2)dx_2$$
$$+(2!)^{-1}\int\Omega_{123}(1-P_{12}-P_{13})\left\{2\begin{vmatrix}\Delta\rho(2',2) & \rho(2',3)\\ \Delta\rho(3',2) & \rho(3',3)\end{vmatrix}+\begin{vmatrix}\Delta\rho(2',2) & \Delta\rho(2',3)\\ \Delta\rho(3',2) & \Delta\rho(3',3)\end{vmatrix}\right\}dx_2dx_3+\cdots. \tag{119}$$

(a) Ionized States

Let us first consider the singly ionized states, where the system has the operator (I, 2) but contains only $(N-1)$ particles. This means that one particle has been removed to infinity from the original system, and it seems therefore natural to assume that, at least in a first approximation, nothing new has been added to the system and that, in the terminology of Part I, Sec. 5, the *matrix* $\boldsymbol{\rho}'$ *for the ionized state belongs entirely to the subspace defined by the matrix* $\boldsymbol{\rho}$ *for the original state*, or $\boldsymbol{\rho}\boldsymbol{\rho}'\boldsymbol{\rho}=\boldsymbol{\rho}'$. The matrices $\boldsymbol{\rho}$ and $\boldsymbol{\rho}'$ are both "projection operators" fulfilling the relations $\boldsymbol{\rho}^2=\boldsymbol{\rho}$, $\text{Tr}(\boldsymbol{\rho})=N$, $(\boldsymbol{\rho}')^2=\boldsymbol{\rho}'$, $\text{Tr}(\boldsymbol{\rho}')=N-1$, and for their difference $\Delta\boldsymbol{\rho}=\boldsymbol{\rho}'-\boldsymbol{\rho}$, we then obtain

$$(\Delta\boldsymbol{\rho})^2=-\Delta\boldsymbol{\rho},\quad \text{Tr}(\Delta\boldsymbol{\rho})=-1. \tag{120}$$

In expanding $\Delta\boldsymbol{\rho}$ in a fixed basic set according to (I, 34), this implies that the matrix of the coefficients has a single eigenvalue equal to -1 and all the others 0. By transforming this expansion to "natural spin-orbitals" analogous to (I, 74), we then obtain

$$\Delta\rho(\mathbf{x}_1,\mathbf{x}_2)=-\psi^*(\mathbf{x}_1)\psi(\mathbf{x}_2), \tag{121}$$

where $\psi(\mathbf{x})$ is an undetermined spin-orbital. Our basic assumption leads therefore automatically to a factorization of the difference $\Delta\boldsymbol{\rho}$, which will essentially simplify the discussion, since all determinants in (118) which are of at least the second degree in $\Delta\boldsymbol{\rho}$ will now vanish identically.

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

[31] J. Lennard-Jones, Proc. Roy. Soc. (London) **A198**, 1, 14 (1949); G. G. Hall and J. Lennard-Jones, Proc. Roy. Soc. (London) **202**, 155 (1950); J. Lennard-Jones and J. A. Pople, Proc. Roy. Soc. (London) **202**, 166 (1950); J. A. Pople, Proc. Roy. Soc. (London) **202**, 323 (1950); G. G. Hall, Proc. Roy. Soc. (London) **202**, 336 (1950); G. G. Hall and J. Lennard-Jones, Proc. Roy. Soc. (London) **205**, 357 (1951); G. G. Hall, Proc. Roy. Soc. (London) **205**, 541 (1951); **213**, 113 (1952).

[32] In considering molecules and crystals, this means that we treat only "vertical" transitions with the nuclei fixed in the same positions in both states. If the nuclei are in equilibrium in one state, they are therefore usually outside their equilibrium positions in the other states; compare the Franck-Condon principle.

Combining (118) and (121), we obtain

$$\Delta\langle\Omega_{\mathrm{op}}\rangle=-\int\psi^*(1)\Omega_{\mathrm{eff}}(1)\psi(1)dx_1, \tag{122}$$

or

$$\langle\Omega_{\mathrm{op}}'\rangle_{\mathrm{Av}}=\langle\Omega_{\mathrm{op}}\rangle_{\mathrm{Av}}-\int\psi^*(1)\Omega_{\mathrm{eff}}(1)\psi(1)dx_1. \tag{123}$$

According to the variation principle (I, 22), the eigenstates of the ionized system are associated with the extreme values of $\langle\Omega_{\mathrm{op}}'\rangle_{\mathrm{Av}}$, and, since $\langle\Omega_{\mathrm{op}}\rangle_{\mathrm{Av}}$ is a constant, these occur simultaneously with the extreme values of the last term in the right-hand member of (123), i.e., for spin-orbitals satisfying the relation

$$\Omega_{\mathrm{eff}}(1)\psi(\mathbf{x}_1)=\omega\psi(\mathbf{x}_1), \tag{124}$$

where the variation principle is applied a second time to the one-particle space. The eigenfunctions ψ_k to Ω_{eff} are therefore of particular importance in constructing the ionized states, and, if the wave function for the original state is a determinant built up from the functions $\psi_1, \psi_2, \cdots\psi_N$, then the wave function for the ionized state (k) may be obtained by striking away the column containing the spin-orbital ψ_k together with an arbitrary particle row. Combination of (123) and (124) gives further

$$\langle\Omega_{\mathrm{op}}'\rangle_{\mathrm{Av}}=\langle\Omega_{\mathrm{op}}\rangle_{\mathrm{Av}}-\omega_k. \tag{125}$$

This is a generalization of Koopmans' theorem[30] to include also many-particle operators,[33] and it gives a rather visual interpretation of the eigenfunctions ψ_k $(k=1, 2, \cdots N)$ and the corresponding eigenvalues ω_k. We note that the result is not exact even within the Hartree-Fock approximation, since it is based on a simplifying assumption leading to (121). A proper treatment could be carried out by solving the Hartree-Fock equations for the system of $(N-1)$ particles by applying the methods in (3a) to, e.g., the basic set formed by the ordinary and virtual eigenfunctions of ψ_k for the system of N particles.[34] However, as Mullikan[4] has pointed out, due to cancellation of errors, it seems likely that the values of $\Delta\langle\Omega\rangle$ given in (125) will show better agreement with experimental data than the refined quantities.

(b) Excited States

Let us now turn to the problem of the excited states which, according to our opinion, has not been too satisfactorily treated in the literature. If $\boldsymbol{\rho}$ and $\boldsymbol{\rho}'$ are the invariants associated with the original and the excited state, respectively, we have

$$\boldsymbol{\rho}'=\boldsymbol{\rho}+\Delta\boldsymbol{\rho}=\boldsymbol{\rho}+\Delta\boldsymbol{\rho}_j-\Delta\boldsymbol{\rho}_i, \tag{126}$$

where the quantity $+\Delta\boldsymbol{\rho}_j$ indicates that something essentially new has been added in the excited state, whereas the quantity $-\Delta\boldsymbol{\rho}_i$ means that something previously existing in the original state has been taken away. In a first approximation, we will assume that the three matrices

$$\boldsymbol{\rho}-\Delta\boldsymbol{\rho}_i, \quad \boldsymbol{\rho}, \quad \boldsymbol{\rho}+\Delta\boldsymbol{\rho}_j, \tag{127}$$

are all idempotent $(\boldsymbol{\rho}^2=\boldsymbol{\rho}$, etc.), and that the first belongs to the subspace defined by the second, and the second to the subspace defined by the third; see (I, 88). It is then easily shown that the matrices $\Delta\boldsymbol{\rho}_i$ and $\Delta\boldsymbol{\rho}_j$ are also idempotent with 0 and 1 as their only eigenvalues, and their traces are then also integers. For a single excitation, their traces are 1, and the coefficient matrices in their expansions (I, 34) have therefore a single eigenvalue equal to 1 and the others equal to zero. By transforming $\Delta\boldsymbol{\rho}_i$ and $\Delta\boldsymbol{\rho}_j$ to diagonal form according to (I, 74), we then obtain

$$\Delta\rho_i(1,2)=\psi_i^*(1)\psi_i(2), \quad \Delta\rho_j(1,2)=\psi_j^*(1)\psi_j(2), \tag{128}$$

where ψ_i and ψ_j are natural spin-orbitals to be determined. Under these simplifying assumptions, $\Delta\boldsymbol{\rho}$ may therefore be written in the form

$$\Delta\rho(1,2)=\psi_j^*(1)\psi_j(2)-\psi_i^*(1)\psi_i(2) \tag{129}$$

for a single excitation, and we will now see that this special form for $\Delta\boldsymbol{\rho}$ leads to a considerable simplification of our discussion.

The basic quantities (118) and (119) are expressed in terms of determinants of the elements $\boldsymbol{\rho}$ and $\Delta\boldsymbol{\rho}$, and we note that all determinants of third or higher degree in $\Delta\boldsymbol{\rho}$ will vanish identically independent of their orders, since they may be expanded in determinants containing two or more columns of $\Delta\boldsymbol{\rho}_i$ or $\Delta\boldsymbol{\rho}_j$, which vanish due to the factorization in (128). By putting $\boldsymbol{\rho}=\boldsymbol{\rho}'-\Delta\boldsymbol{\rho}$ into (21) and repeating the subtraction, we may also obtain a new form for $\Delta\langle\Omega_{\mathrm{op}}\rangle$ expressed in Ω_{eff}', $\boldsymbol{\rho}'$, and $\Delta\boldsymbol{\rho}$, which is analogous to (118) but has minus signs for all the determinants of the second degree in $\Delta\boldsymbol{\rho}$. By adding the two expressions for $\Delta\langle\Omega\rangle$, the determinants of the second-order cancel, and the higher order determinants combine to determinants of the third degree in $\Delta\boldsymbol{\rho}$, which will then vanish identically due to the argument given above. In this way, we obtain the simple formula:†

$$\Delta\langle\Omega_{\mathrm{op}}\rangle=\tfrac{1}{2}\int\{\Omega_{\mathrm{eff}}'(1)+\Omega_{\mathrm{eff}}(1)\}\Delta\rho(1',1)dx_1. \tag{130}$$

By using (119) and (128), we may further derive the

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[33] It should be noted that, in several textbooks and surveys, Koopmans' theorem have been treated rather superficially, proving only the relation $\Delta\langle\Omega_{\mathrm{op}}\rangle=-\omega_k$ without considering the extreme value properties.

[34] See also G. G. Hall and J. Lennard-Jones, Proc. Roy. Soc. (London) **A202**, 155 (1950), where this problem is treated by using perturbation theory.

† We note that, in Eqs. (130)–(132) and (137)–(138), the "prime" has been used with two different meanings, which must not be confused: the prime on $\Omega_{\mathrm{eff}}'(1)$ indicates that the operator is associated with the excited state, whereas the prime on $\mathbf{x}_1'$ in the integrands indicates that the operators do not work on this coordinate, which afterwards has to be put equal to $\mathbf{x}_1$.

relation:

$$\int \Delta\Omega_{\mathrm{eff}}(1)\{\Delta\rho_i(1',1)+\Delta\rho_j(1',1)\}dx_1=0, \quad (131)$$

which, in combination with (130), gives

$$\Delta\langle\Omega_{\mathrm{op}}\rangle=\int \Omega_{\mathrm{eff}}'(1)\Delta\rho_j(1',1)dx_1 - \int \Omega_{\mathrm{eff}}(1)\Delta\rho_i(1',1)dx_1, \quad (132)$$

or finally

$$\langle\Omega_{\mathrm{op}}'\rangle_{\mathrm{Av}}=\langle\Omega_{\mathrm{op}}\rangle_{\mathrm{Av}}+\int \psi_j{}^*(1)\Omega_{\mathrm{eff}}'(1)\psi_j(1)dx_1 - \int \psi_i{}^*(1)\Omega_{\mathrm{eff}}(1)\psi_i(1)dx_1. \quad (133)$$

According to the variation principle (I, 22), the higher eigenvalues of Ω_{op} are associated with the extreme values of $\langle\Omega_{\mathrm{op}}'\rangle_{\mathrm{Av}}$, and since $\langle\Omega_{\mathrm{op}}\rangle_{\mathrm{Av}}$ is a constant, these occur simultaneously with the extreme values of the second and third terms of the right-hand member of (133), i.e., for functions ψ_j' and ψ_i satisfying

$$\Omega_{\mathrm{eff}}'\psi_j'=\omega_j'\psi_j', \quad \Omega_{\mathrm{eff}}\psi_i=\omega_i\psi_i. \quad (134)$$

For the excitation difference, we then obtain

$$\langle\Omega_{\mathrm{op}}'\rangle_{\mathrm{Av}}-\langle\Omega_{\mathrm{op}}\rangle_{\mathrm{Av}}=\omega_j'-\omega_i. \quad (135)$$

The process may therefore be described as an excitation $i\rightarrow j$ of an entire particle from an occupied spin-orbital ψ_i, being an eigenfunction to Ω_{eff}, to an unoccupied spin-orbital ψ_j', being an eigenfunction to Ω_{eff}'. We note particularly that, in (135), the quantity ω_j' is a spin-orbital eigenvalue associated with the operator Ω_{eff}' for the excited state, and that Ω_{eff}' may have an eigenvalue spectrum which is rather different from the corresponding spectrum for Ω_{eff}.[35] It is evident that the arguments leading to the naive form $(\omega_j-\omega_i)$ for the excitation difference $\Delta\langle\Omega_{\mathrm{op}}\rangle$ must be erroneous, but also that it is possible to preserve the visuality of the theory by introducing the operator Ω_{eff}'.[36]

Let us now construct the wave function Ψ' for the excited state by using (129) and (134). If the function Ψ for the ground state is a determinant built up from the eigenfunctions ψ_k $(k=1, 2, \cdots N)$ to the operator Ω_{eff}, then Ψ' is the determinant obtained from Ψ by replacing the column containing the spin-orbital ψ_i by a column containing the excited spin-orbital ψ_j'. Using (119) and (128), we may derive the relation

$$\int \psi_j'^*\Delta\Omega_{\mathrm{eff}}\psi_i dx=0, \quad (136)$$

which shows that the spin-orbitals ψ_j' and ψ_i satisfying (134) will still be *orthogonal*, and, according to (I, 39), the same is then true also for the total wave functions Ψ' and Ψ. The auxiliary condition to the variational principle (I, 22) is therefore fulfilled.

Even under the simplifying assumptions leading to (128), the treatment of the excited states is a rather complicated problem due to the unknown character of the operator Ω_{eff}'. According to (119), Ω_{eff}' is given by the formula

$$\Omega_{\mathrm{eff}}'(1)=\Omega_{\mathrm{eff}}(1)+\int \Omega_{12}(1-P_{12})\Delta\rho(2',2)dx_2 + (2!)^{-1}\int \Omega_{123}(1-P_{12}-P_{13})\left\{2\begin{vmatrix}\Delta\rho(2',2) & \rho(2',3)\\ \Delta\rho(3',2) & \rho(3',3)\end{vmatrix}+\begin{vmatrix}\Delta\rho(2',2) & \Delta\rho(2',3)\\ \Delta\rho(3',2) & \Delta\rho(3',3)\end{vmatrix}\right\}dx_2dx_3+\cdots, \quad (137)$$

but, as usual in the Hartree-Fock scheme, the problem of finding its eigenfunctions has a nonlinear character, since Ω_{eff}' depends on $\Delta\rho$ and consequently also on ψ_j'.

In principle, this problem could be solved by the general method developed in (3a) by expanding the eigenfunctions ψ_j' to Ω_{eff}' in the set formed by the ordinary and virtual eigenfunctions to Ω_{eff}. In a first very rough approximation, the eigenvalues to Ω_{eff}' are then given by first-order perturbation theory:

$$\omega_j'\approx\int \psi_j{}^*(1)\Omega_{\mathrm{eff}}'(1)\psi_j(1)dx_1=\omega_j-\int \Omega_{12}\begin{vmatrix}\Delta\rho_j(1',1) & \Delta\rho_j(1',2)\\ \Delta\rho_j(2',1) & \Delta\rho_j(2',2)\end{vmatrix}dx_1dx_2 - \int \Omega_{123}\begin{vmatrix}\Delta\rho_j(1',1) & \Delta\rho_j(1',2) & \Delta\rho_j(1',3)\\ \Delta\rho_i(2',1) & \Delta\rho_i(2',2) & \Delta\rho_i(2',3)\\ \rho(3',1) & \rho(3',2) & \rho(3',3)\end{vmatrix}dx_1dx_2dx_3-\cdots, \quad (138)$$

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[35] Compare, e.g., J. C. Slater, "Technical Report No. 6 of the Solid-State and Molecular Theory Group at M.I.T.," April 15, 1954 (unpublished).

[36] Compare C. C. J. Roothaan, Revs. Modern Phys. **23**, 69 (1951), p. 80.

where we have used (128). Using the notations (49), this may also be written

$$\omega_j' \approx \omega_j - V_j^i - \sum_k V_j^{ik} - \cdots, \tag{139}$$

which result corresponds to the formula for the two-particle case and average singlet-triplet state given by Roothaan.[36] However, first-order perturbation theory is probably not accurate enough for treating the question of the nature of the excited states, and a much more detailed study seems therefore to be necessary.[35] In a really accurate theory, one must finally remove the simplifying assumptions leading to the factorization in (128).

(c) Limitations of the Present Theory

Up till now we have assumed that the total wave function for the state and system under consideration may be represented by a *single* Slater determinant. We note that, in most cases, this means a rather hard restriction on the validity of the Hartree-Fock scheme; only in exceptional cases can we consider, e.g., pure spin states, since a single determinant will in general represent a mixture between several multiplets.

In order to treat this problem in greater detail, we will assume that the natural spin-orbitals involved have either plus or minus spin and write the fundamental density matrix $\boldsymbol{\rho}$, defined by (35), in the form

$$\rho(\mathbf{x}_1,\mathbf{x}_2) = \rho_+(\mathbf{r}_1,\mathbf{r}_2)\alpha(s_1)\alpha(s_2) + \rho_-(\mathbf{r}_1,\mathbf{r}_2)\beta(s_1)\beta(s_2), \tag{140}$$

where we have separated the two groups of orbitals having different spins. The matrices $\boldsymbol{\rho}_+$ and $\boldsymbol{\rho}_-$ are "projection operators" in the ordinary r-space satisfying the relations

$$\begin{aligned} \boldsymbol{\rho}_+^2 &= \boldsymbol{\rho}_+ \qquad \mathrm{Tr}(\boldsymbol{\rho}_+) = N_+, \\ \boldsymbol{\rho}_-^2 &= \boldsymbol{\rho}_- \qquad \mathrm{Tr}(\boldsymbol{\rho}_-) = N_-, \end{aligned} \tag{141}$$

where N_+ and N_- are the number of orbitals associated with plus and minus spin, respectively. Independent of the way in which we have chosen our two sets of orbitals, we will further let ν denote the number of "doubly occupied orbitals," defined by the integral

$$\nu = \int \rho_+(r_1,r_2)\rho_-(r_2,r_1)dv_1dv_2. \tag{142}$$

The average value of the total spin S^2 (measured in units of $\hbar$) with respect to a single determinant, characterized by the invariant (140), is given by the general formula (I, 14), and, since the second-order density is represented by the determinant (19), we obtain after some elementary calculations:

$$\langle S^2 \rangle_{\text{Av}} = \tfrac{1}{4}(N_+ - N_-)^2 + (\tfrac{1}{2}N - \nu). \tag{143}$$

Only in the special cases $N_+ = N_- = \nu = N/2$ and $N_+ = N$, $N_- = \nu = 0$, we have, respectively,

$$\langle S^2 \rangle_{\text{Av}} = 0, \quad \langle S^2 \rangle_{\text{Av}} = \tfrac{1}{2}N(\tfrac{1}{2}N+1), \tag{144}$$

corresponding to the pure spin states of lowest and highest multiplicity.

It is therefore evident that the ordinary Hartree-Fock scheme cannot properly treat states and systems showing spin or orbital degeneracies, since, in such cases, the wave function cannot be represented by a single determinant. It is also well known that correlation effects associated with particles having different spins are not taken into account in constructing the single-determinant wave function (2). These weaknesses in the present theory may be removed only by considering wave functions to be sums of Slater determinants, i.e., by using the method of "configurational interaction" described in Part I. However, between the ordinary Hartree-Fock scheme and the exact method of configurational interaction, there seems to exist also an intermediate stage of "fixed" configurational interaction, where it is possible to preserve part of the physical simplicity and visuality characteristic of the Hartree-Fock method. This problem will be treated in a following paper of this series.