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Quantum Theory of Many-Particle Systems. III. Extension of the Hartree-Fock Scheme to Include Degenerate Systems and Correlation Effects*

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In treating a system of N antisymmetric particles, it is shown that, if the total Hamiltonian $\mathcal{H}_{op}$ is degenerate, the eigenstates of the operator used for classifying the corresponding degenerate states may be selected by means of a "projection operator" $\mathcal{O}$. If the total wave function is approximated by such a projection of a single determinant, the description of the system may be reduced to the ordinary Hartree-Fock scheme treating this determinant, if the original Hamiltonian is replaced by a complete Hamiltonian $\Omega_{op}=\mathcal{O}^\dagger\mathcal{H}_{op}\mathcal{O}$ containing also many-particle interactions. This approach corresponds to a "fixed" configurational interaction, but the scheme has preserved the physical simplicity and visuality of the Hartree-Fock approximation. The idea of "doubly filled" orbitals is abandoned, and the orbitals associated with different spins will automatically try to arrange themselves in such a way that particles having antiparallel spins will tend to avoid each other due to their mutual repulsion.

THE Hartree-Fock scheme for treating a system of N antisymmetric particles has a physical simplicity and visuality due to the fact that a single determinant is the simplest wave function based on the "independent-particle" model with the correct symmetry. However, it is well known that this scheme cannot properly treat states and systems having spin or orbital degeneracies and that further "correlation effects" associated with particles having different spins are not taken into account in constructing the single-determinant wave function. The purpose of this paper is to show that there exists a form of "fixed" configurational interaction, based on the use of "projection operators," which may be considered as an extension of the ordinary Hartree-Fock scheme to include degenerate systems and correlation effects, since it preserves the physical simplicity and visuality of the original scheme. This extended scheme is an intermediate stage between the ordinary Hartree-Fock approximation and the exact method of complete configurational interaction, treated in Parts II and I, respectively.[1]

1. TREATMENT OF SPIN AND ORBITAL DEGENERACIES BY PROJECTION OPERATORS

Let us consider a system of N antisymmetric particles having a Hamiltonian operator in configurational space of the form

$$\mathcal{H}_{op}=\mathcal{H}_{(0)}+\sum_i \mathcal{H}_i+\frac{1}{2!}\sum_{ij}{}'\,\mathcal{H}_{ij}+\frac{1}{3!}\sum_{ijk}{}'\,\mathcal{H}_{ijk}+\cdots, \quad (1)$$

analogous to (I, 2). If its eigenstates are *degenerate*, we will assume that they may be classified by an operator Λ having a finite number of discrete eigenvalues $\lambda_1, \lambda_2, \cdots \lambda_n$. We let further Ψ be an arbitrary wave function associated with the space of degeneracy, having an expansion of the form

$$\Psi=\sum_{k=1}^{n} A_k\Psi_k, \quad (2)$$

where Ψ_k is an eigenfunction to Λ belonging to the eigenvalue λ_k. We note that, since the factor $(\Lambda-\lambda_p)$ annihilates the term for $k=p$ in this expansion, the operator

$$\mathcal{O}_l=\prod_{k=1,n}^{k\neq l}(\Lambda-\lambda_k)/(\lambda_l-\lambda_k) \quad (3)$$

takes out only the term for $k=l$, i.e., it gives the "orthogonal projection" of Ψ on the eigenstate of Λ having the eigenvalue λ_l:

$$\mathcal{O}_l\Psi=A_l\Psi_l, \quad (4)$$

where we have used the terminology of Part I, Sec. 5. The operator $\mathcal{O}_l$ is therefore also a *projection operator*,[2] which, in matrix representation, fulfills the Cayley-Hamilton equation $(\Lambda-\lambda_l)\mathcal{O}_l\equiv 0$. Since the factors in (3) may be written in the form

$$(\Lambda-\lambda_k)/(\lambda_l-\lambda_k)=1+(\Lambda-\lambda_l)/(\lambda_l-\lambda_k), \quad (5)$$

we can then easily derive the relation

$$\mathcal{O}_l^2=\mathcal{O}_l, \quad (6)$$

characteristic for the projection operators.

Spin Degeneracies

As an example, we will now consider the projection operators associated with the spin degeneracy of N antisymmetric particles having spin one half, as electrons, or nucleons. Measuring the spin in units of

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[1] P. O. Löwdin, preceding paper [Phys. Rev. 97, 1474 and 1490 (1955)]. These papers are in the following referred to as Parts I and II, respectively.

[2] J. v. Neumann, *Math. Grundlagen der Quantenmechanik* (Dover Publications, New York, 1943), p. 41.

$\hbar$, we know that S^2 has the eigenvalues $l(l+1)$, where $l=N/2$, $(N/2)-1$, $(N/2)-2$, $\cdots 0$ or $\frac{1}{2}$ depending on whether N is even or odd. According to (3), the operator for selecting a state of multiplicity $(2l+1)$ is then

$$^{(2l+1)}\mathcal{O}=\prod_{k}^{k\neq l}\{S^2-k(k+1)\}/\{l(l+1)-k(k+1)\}, \quad (7)$$

where the product is to be taken over all $k\neq l$ from 0 or $\frac{1}{2}$ to $N/2$. For S^2 we may here use one of the expressions

$$\begin{aligned} S^2&=\sum_{ij}\mathbf{S}_i\cdot\mathbf{S}_j \\ &=S^+S^-+S_z^2-S_z & (8) \\ &=-\tfrac{1}{4}N(N-4)+\tfrac{1}{2}\sum_{i<j}(1+\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j) & \\ &=-\tfrac{1}{4}N(N-4)+\sum_{i<j}P_{ij}{}^{\sigma}. & (9) \end{aligned}$$

We will now investigate the effect of the spin projection operator (7) on a single determinant built up from N spin-orbitals. For the sake of simplicity, let us assume that N is even ($N=2n$) and that we are interested in states with $S_z=0$, i.e., having an equal number of α and β spins. Let us further assume that we have N orbitals $a_1, a_2, \cdots a_n, b_1, b_2, \cdots b_n$ at our disposal, and that the first n orbitals are occupied by particles with plus spin and the last n orbitals are occupied by particles with minus spin. The corresponding Slater determinant

$$(N!)^{-\frac{1}{2}}\det\{a_1\alpha,a_2\alpha,\cdots a_n\alpha\,|\,b_1\beta,b_2\beta,\cdots b_n\beta\} \quad (10)$$

may then be denoted by the abbreviated symbol

$$\{\alpha\alpha\cdots\alpha\,|\,\beta\beta\cdots\beta\} \quad (11)$$

showing the spin distribution over the N orbitals taken in their given order.

Pratt[3] has recently described a spin-operator formalism for constructing *singlets*, but, since he has not used the projection operator idea, his treatment is considerably more complicated than here. Using his notations, we will now introduce the quantities

$$\begin{aligned} T_0&=\{\alpha\alpha\cdots\alpha\,|\,\beta\beta\cdots\beta\}, \\ T_1&=\{(\beta\alpha\alpha\cdots)+(\alpha\beta\alpha\cdots)+\cdots\,|\,(\alpha\beta\beta\cdots) \\ &\qquad +(\beta\alpha\beta\cdots)+\cdots\}, \\ T_2&=\{(\beta\beta\alpha\cdots)+(\beta\alpha\beta\cdots)+\cdots\,|\,(\alpha\alpha\beta\cdots) \\ &\qquad +(\alpha\beta\alpha\cdots)+\cdots\}, \qquad (12) \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ T_n&=\{\beta\beta\cdots\beta\,|\,\alpha\alpha\cdots\alpha\}, \end{aligned}$$

where T_k is the sum of all different determinants, obtained by k interchanges of the spin functions between the two originally given groups (a) and (b) of orbitals; T_0 is identical with the given determinant (10). In (12), we have used Pratt's symbolic way of "multiplying" determinants: T_k is the "product" of two factors, each containing $\binom{n}{k}$ terms, and T_k consists therefore of a sum of $\binom{n}{k}^2$ determinants.

In order to evaluate S^2T_k, we will use the form (9), where we observe that $\sum_{i<j}P_{ij}{}^{\sigma}$ commutes with the antisymmetrization operator used in forming the determinant (10) from a simple product. Counting the possible spin interchanges, we find that S^2T_k may be expressed in T_{k-1}, T_k, and T_{k+1} with the following coefficients:

$$\begin{aligned} T_{k-1}&: \quad k^2\binom{n}{k}^2\Big/\binom{n}{k-1}^2=(n-k+1)^2, \\ T_k&: \quad -\tfrac{1}{4}N(N-4)+n(n-1)+2k(n-k) \\ &\qquad\qquad =n(2k+1)-2k^2, \qquad (13) \\ T_{k+1}&: \quad (n-k)^2\binom{n}{k}^2\Big/\binom{n}{k+1}^2=(k+1)^2, \end{aligned}$$

which gives the basic formula

$$\begin{aligned} S^2T_k=(n-k+1)^2T_{k-1} \\ +[n(2k+1)-2k^2]T_k+(k+1)^2T_{k+1}, \quad (14) \end{aligned}$$

with the definition $T_{-1}=T_{n+1}=0$ understood. Since the projection operator (7) is a polynomial in S^2, we have then proved that there exists an expansion of the form

$$^{(2l+1)}\mathcal{O}T_0=\sum_{k=0}^{n}c_k{}^{(l)}T_k. \quad (15)$$

The coefficients in this expansion may be determined by using (14) and the relation

$$S^2(\sum_k c_kT_k)=l(l+1)\sum_k c_kT_k, \quad (16)$$

which leads to the recurrence formula

$$\begin{aligned} (n-k)^2c_{k+1}+[n(2k+1)-2k^2-l(l+1)]c_k \\ +k^2c_{k-1}=0. \quad (17) \end{aligned}$$

For the important cases of lowest and highest multiplicity ($l=0$ and $l=n$), we obtain particularly

$$^{1}\mathcal{O}T_0=c_0{}^{(0)}\sum_{k=0}^{n}(-1)^k\binom{n}{k}^{-1}T_k, \quad (18)$$

$$^{(2n+1)}\mathcal{O}T_0=c_0{}^{(n)}\sum_{k=0}^{n}T_k, \quad (19)$$

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[3] G. W. Pratt, Jr., Phys. Rev. 92, 278 (1953).

and, in general, we have for the first coefficients

$$\begin{aligned} c_1^{(l)}/c_0^{(l)} &= [l(l+1)-n]/n^2, \\ c_2^{(l)}/c_0^{(l)} &= [l^2(l+1)^2-(4n-2)l(l+1) \\ &\qquad +2n(n-1)]/n^2(n-1)^2, \\ &\cdots\cdots\cdots\cdots\cdots \end{aligned} \tag{20}$$

The explicit form of the higher coefficients for an arbitrary l will be omitted, since they are rather complicated.

For the applications, the value of c_0 is usually unessential, but, by considering a system with doubly occupied orbitals, i.e., $a_k=b_k$, the value of c_0 for the singlet operator is easily determined: $c_0^{(0)}=(n+1)^{-1}$.

We note that (18) is just the Clebsch-Gordan expansion from which Pratt[3] started his investigations, and we have then shown that our projection operator for constructing singlets

$$^1\mathcal{O}=(1-S^2/1\cdot 2)(1-S^2/2\cdot 3)\cdots[1-S^2/n(n+1)], \tag{21}$$

gives the same expansion as Pratt's rather complicated spin-operator; except for a constant factor, the two operators must therefore be identical.

The Energy Formula for Various Multiplets

As an example of the applications of the projection operator formalism, we will calculate the energy of a spin state of multiplicity $(2l+1)$ having a wave function obtained by projection of a single determinant

$$\Psi={}^{(2l+1)}\mathcal{O}T_0, \tag{22}$$

for a spin-free Hamiltonian of the special form (I, 11) with $\mathcal{H}_{ij}=e^2/r_{ij}$. Since $\mathcal{O}$ is an Hermitean operator in our configurational space, we obtain by using (7) and (15):

$$\begin{aligned} \int \Psi^*\mathcal{H}_{\mathrm{op}}\Psi(dx) &= \int T_0^*(\mathcal{O}^\dagger\mathcal{H}_{\mathrm{op}}\mathcal{O})T_0(dx) \\ &= \sum_{k=0}^{n} c_k^{(l)}\int T_0^*\mathcal{H}_{\mathrm{op}}T_k(dx), \end{aligned} \tag{23}$$

and similarly:

$$\int \Psi^*\Psi(dx)=\sum_{k=0}^{n} c_k^{(l)}\int T_0^*T_k(dx). \tag{24}$$

In the simple case when all orbitals $a_1, a_2, \cdots a_n$, $b_1, b_2, \cdots b_n$ involved are strictly *orthogonal* (as they would be for singly filled molecular orbitals), there will be contributions to the energy only for $k=0$ and $k=1$ and to the normalization integral only for $k=0$ according to (I, 49). By using the first relation (20), we therefore obtain

$$\begin{aligned} \langle\mathcal{H}_{\mathrm{op}}\rangle_{\mathrm{Av}} &= \int T_0^*\mathcal{H}_{\mathrm{op}}T_0(dx)+\frac{l(l+1)-n}{n^2} \\ &\qquad \times\int T_0^*\mathcal{H}_{\mathrm{op}}T_1(dx) \\ &= \mathcal{H}_{(0)}+\sum_{\mu}(\mu|\mathcal{H}_1|\mu)+\tfrac{1}{2}\sum_{\mu\nu}(\mu\nu|\mathcal{H}_{12}|\mu\nu) \\ &\qquad -\tfrac{1}{2}\sum_{\mu\nu}^{\parallel\,\mathrm{spins}}(\mu\nu|\mathcal{H}_{12}|\nu\mu) \\ &\qquad -\frac{l(l+1)-n}{n^2}\sum_{i,j=1}^{n}(a_ib_j|\mathcal{H}_{12}|b_ja_i), \end{aligned} \tag{25}$$

where the spin is eliminated in the matrix elements, and μ and ν are to be summed independently over all orbitals a_i, b_j.

Since the exchange integrals for Coulomb forces are always positive as "self-potentials," formula (25) shows that, under our specific assumption of orthogonality, the state with the highest multiplicity will always have the lowest energy. This extension of Hund's rule was recently proved in a still more complete form by Koster[4] by using Dirac's vector model.

Spin degeneracy problems have previously been treated by either Slater's determinant method[5] or Dirac's vector model.[6] We note that, even if we have taken over some elements, as the spin permutation operators in (9), from Dirac's theory, our approach is firmly based on Slater's determinant idea with the wave function (22) expressed as a sum of determinants. However, there is also a connection with the vector model, and, if we form the mean value of the energy (25) for all possible distributions of α and β electrons over the orbitals $a_1, a_2, \cdots a_n, b_1, b_2, \cdots b_n$, we obtain

$$\begin{aligned} \langle\langle\mathcal{H}_{\mathrm{op}}\rangle_{\mathrm{Av}}\rangle_{\mathrm{Av}} &= \mathcal{H}_{(0)}+\textstyle\sum_{\mu}(\mu|\mathcal{H}_1|\mu) \\ &\qquad +\tfrac{1}{2}\textstyle\sum_{\mu\nu}'(\mu\nu|\mathcal{H}_{12}|\mu\nu) \\ &\qquad -\frac{1}{4}\left\{1+\frac{4l(l+1)-3N}{N(N-1)}\right\}\sum_{\mu\nu}'(\mu\nu|\mathcal{H}_{12}|\mu\nu), \end{aligned} \tag{26}$$

which is just the average energy given by the vector model.[7]

Let us now consider all pure spin states which may be constructed according to formula (22). We note that

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[4] G. F. Koster, Quarterly Progress Report of Solid-State and Molecular Theory Group at M.I.T., July 15, 1953 (unpublished), p. 37.

[5] J. C. Slater, Phys. Rev. **34,** 1293 (1929).

[6] P. A. M. Dirac, Proc. Roy. Soc. (London) **A123, 714** (1929); *Principles of Quantum Mechanics* (Oxford University Press, Oxford, 1935); see also references in E. M. Corson, *Perturbation Methods in the Quantum Mechanics of n-Electron Systems* (Blackie, London, 1951).

[7] See also F. Bloch, Z. Physik **57**, 545 (1929), p. 550; and W. Heitler, Z. Physik **47**, 835 (1928).

there are $\binom{N}{n}$ different ways of distributing the equal number of α and β electrons over the given orbitals, and each distribution corresponds to a determinant T_0, from which a series of pure spin states may be constructed by using (22). On the other hand, Bloch[7] has shown that the *independent* number of spin states of multiplicity $(2l+1)$ is only

$$\binom{N}{n-l}-\binom{N}{n-l-1}=(2l+1)N!/(n-l)!(n+l+1)!, \tag{27}$$

and this means that the $\binom{N}{n}$ states given by (22) cannot be linearly independent. In the general method of "configurational interaction," it is important that the basic functions form a linearly independent orthonormalized set, and this leads to the problem how to form such a set from the functions given by (22). For the singlets, Pratt[3] has solved this problem by using the "branching diagram," and his formulas may also be translated into the projection operator formalism. However, a more general approach may be obtained by treating all the functions given by (22) on an equal basis and to construct the independent orthonormalized set by a slight generalization of the orthonormalization procedure previously described by the author.[8]

We will later see that part of the degeneracy problem mentioned above will disappear when we start to take "correlation effects" into account; see Sec. 3. The orbitals at our disposal will then be naturally divided into two groups (a_i) and (b_j), associated with different spins, since the particles with different spins try to avoid each other. In this connection, it is also necessary to generalize formulas (23) and (24) to basic sets having nonorthogonality integrals essentially different from zero.

Applications to Systems Having Cyclic Symmetry

As another example of the projection operator formalism, we will consider the problem of the form of the total wave functions and the corresponding spin-orbitals in a system having a certain cyclic symmetry of order m, like a crystal or a benzene ring. Let us assume that Θ is the basic symmetry operation, which fulfills the condition

$$\Theta^m=1. \tag{28}$$

This may be considered as a Cayley-Hamilton equation in a certain matrix representation, and it is then clear that, in such a representation, the only possible eigenvalues of Θ are given by the roots of unity:

$$\theta_j=\exp(2\pi ij/m),\quad j=0,1,2,\cdots m-1. \tag{29}$$

According to (3), the corresponding projection operator is then given by

$$\begin{aligned}\mathcal{O}_l&=m^{-1}(1-\Theta^m)/(1-\theta_l^{-1}\Theta)\\&=m^{-1}\sum_{k=0}^{m-1}\theta_l^{-k}\Theta^k.\end{aligned} \tag{30}$$

If φ_0 is an arbitrary spin-orbital without any particular symmetry properties, its projection defined by

$$\psi_l=\mathcal{O}_l\varphi_0=m^{-1}\sum_{k=0}^{m-1}\theta_l^{-k}\Theta^k\varphi_0=m^{-1}\sum_{k=0}^{m-1}e^{-2\pi ikl/m}\varphi_k, \tag{31}$$

has the correct cyclic symmetry and fulfills the relation

$$\Theta\psi_l=e^{2\pi il/m}\psi_l. \tag{32}$$

The spin-orbital (31) is, of course, nothing but the function constructed by Bloch[9] by solving a secular equation, and (32) is the so-called Bloch condition. The same arguments may also be applied to the total wave functions.

We note finally that, in treating wave functions formed by projection operators, we may use the basic formula for adjoint matrices:

$$\int\Psi_1\mathcal{O}^*\Psi_2(dx)=\int\Psi_2\mathcal{O}^\dagger\Psi_1(dx), \tag{33}$$

only if the operator $\mathcal{O}$ is defined in the coordinates of the configuration space (dx) under consideration. The simplifications rendered by (33) in combination with (6) may therefore be obtained only if $\mathcal{O}$ is operating in the ordinary configurational space, or, if by some formal arguments, this space may be extended to include also the variables contained in $\mathcal{O}$.

The method described in this section is of a quite general character, and it may be used for treating degeneracies associated with the isotopic spin, the angular momentum, etc. Further applications will be given in a following paper.

2. AN EXTENSION OF THE HARTREE-FOCK METHOD TO DEGENERATE SYSTEMS

The importance of the ordinary Hartree-Fock scheme depends partly on the fact that a single Slater determinant,

$$\Psi_0=(N!)^{-\frac{1}{2}}\det\{\psi_1,\psi_2,\cdots\psi_N\}, \tag{34}$$

is the simplest wave function having the correct antisymmetry property which corresponds to the idea that N particles are moving independently of each other in the N spin-orbitals $\psi_1, \psi_2, \cdots\psi_N$. As shown in Part II, this scheme has therefore a physical visuality which is useful in the interpretations and in constructing ionized and excited states. However, if the system has spin or orbital degeneracies, there is a difficulty connected with

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[8] See Part II, footnote 11; more details will be given in a forthcoming paper.

[9] F. Bloch, Z. Physik 52, 555 (1928).

the fact that the total wave function must be expressed as a *sum* of Slater determinants, and part of the visuality seems then to be lost. We will here show that this problem may be solved by treating the degeneracy by the projection operators introduced in the preceding section.

Let Λ be the operator which is used for classifying the degenerate states (at least in a first approximation), and let $\mathcal{O}_l$ be the projection operator (3) for selecting an eigenfunction belonging to the eigenvalue λ_l. For the sake of simplicity, we will further assume that Λ is operating only in the ordinary configuration space, described by the coordinates $\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_N$. The wave function

$$\Psi = \mathcal{O}_l \Psi_0, \tag{35}$$

is then usually a sum of Slater determinants, but we note that it is still invariant with respect to unitary transformations of the two groups of orbitals associated with the two types of spin. It must therefore be possible to describe the properties of the system by means of the fundamental invariant

$$\rho(\mathbf{x}_1,\mathbf{x}_2) = \sum_{k=1}^{N} \psi_k^*(\mathbf{x}_1)\psi_k(\mathbf{x}_2), \tag{36}$$

defined by (II, 12 and 35) and fulfilling the relations $\boldsymbol{\rho}^2 = \boldsymbol{\rho}$ and $\mathrm{Tr}(\boldsymbol{\rho}) = N$. Forming the average energy and using (33), we obtain

$$\begin{aligned} \int \Psi^* \mathcal{H}_{\mathrm{op}} \Psi (dx) &= \int \Psi_0^* (\mathcal{O}^\dagger \mathcal{H}_{\mathrm{op}} \mathcal{O}) \Psi_0 (dx), \\ \int \Psi^* \Psi (dx) &= \int \Psi_0^* (\mathcal{O}^\dagger \mathcal{O}) \Psi_0 (dx), \end{aligned} \tag{37}$$

i.e., the same expression as for a single determinant and a "composite" Hamiltonian of the form

$$\Omega_{\mathrm{op}} = \mathcal{O}^\dagger \mathcal{H}_{\mathrm{op}} \mathcal{O}, \tag{38}$$

where one has also to take the normalization condition into proper account. If the operators $\mathcal{H}_{\mathrm{op}}$ and Λ strictly commute, the composite Hamiltonian is reduced to the form $\Omega_{\mathrm{op}} = \mathcal{H}_{\mathrm{op}} \mathcal{O}$, because of the relation (6).

The physical situation of the degenerate system may therefore be described by either the ordinary Hamiltonian $\mathcal{H}_{\mathrm{op}}$ and a wave function Ψ being a sum of determinants, or a composite Hamiltonian Ω_{op} and a wave function Ψ_0 being a single determinant. The formalism is parallel to the basic description of time dependence in quantum mechanics: in the Schrödinger representation, we are considering a fixed Hamiltonian and a time-dependent wave function, but, in the Heisenberg representation, we are instead using a time-dependent Hamiltonian and a fixed wave function. Both descriptions are entirely equivalent.

However, the formalism using the composite Hamiltonian has a certain advantage, since we may directly take over the mathematical apparatus of the ordinary Hartree-Fock scheme. The projection operators are symmetric with respect to the coordinates of the particles involved, and, if their explicit form (3) is known, the composite Hamiltonian (38) may be expanded in the form

$$\Omega_{\mathrm{op}} = \Omega_{(0)} + \sum_i \Omega_i + \frac{1}{2!} \sum_{ij}{}' \Omega_{ij} + \frac{1}{3!} \sum_{ijk}{}' \Omega_{ijk} + \cdots, \tag{39}$$

containing also many-particle operators. However, in Parts I and II, we have already extended the theory to include such many-particle interactions.

Under specific assumptions about the spin-orbitals in (34) the expansion (39) may sometimes be reduced to comparatively simple forms. As an example, we will mention that, if all basic orbitals in (34) are strictly orthogonal, the combination of the equation $T_1 = (S^2 - n) T_0$ and the first relation in (25) leads to a composite Hamiltonian of the form

$$\Omega_{\mathrm{op}} = \mathcal{H}_{(0)} + \sum_i \mathcal{H}_i + \frac{1}{2} \left\{ 1 + \frac{l(l+1) - n}{n^2} (S^2 - n) \right\} \sum_{ij}{}' \mathcal{H}_{ij}. \tag{40}$$

Since S^2 is given by (9), it contains many-particle operators up to the order 4; the normalization of Ψ is here taken into proper account.

The investigation in Part II tells us now that it is possible to extend the ordinary Hartree-Fock method to operators containing also many-particle terms and consequently also to include treatment of degenerate system by using the composite Hamiltonian (38). We will give here a summary only of the most important results. For a single determinant Ψ_0, all higher-order density matrices may be expressed as determinants of the first-order density matrix (36), and, according to (II, 21), we then obtain for the average energy

$$\begin{aligned} \langle \mathcal{H}_{\mathrm{op}} \rangle_{\mathrm{Av}} &= \int \Psi_0^* \Omega_{\mathrm{op}} \Psi_0 (dx) \\ &= \Omega_{(0)} + \int \Omega_1 \rho(1',1) dx_1 + \tfrac{1}{2} \int \Omega_{12} \begin{vmatrix} \rho(1',1) & \rho(1',2) \\ \rho(2',1) & \rho(2',2) \end{vmatrix} dx_1 dx_2 \\ &\qquad + \tfrac{1}{6} \int \Omega_{123} \begin{vmatrix} \rho(1',1) & \cdots & \rho(1',3) \\ \cdot & \cdot & \cdot \\ \rho(3',1) & \cdots & \rho(3',3) \end{vmatrix} dx_1 dx_2 dx_3 + \cdots, \end{aligned} \tag{41}$$

where, after the operations in the integrands have been carried out, we have to put all $\mathbf{x}_i'=\mathbf{x}_i$. The variation principle $\delta\langle\mathcal{H}_{\mathrm{op}}\rangle_{\mathrm{Av}}=0$ leads then to extended Hartree-Fock equations (II, 40–42) of the form

$$\Omega_{\mathrm{eff}}(1)\psi_k(\mathbf{x}_1)=\sum_{l=1}^{N}\psi_l(\mathbf{x}_1)\lambda(l|k), \tag{42}$$

where the one-particle operator Ω_{eff} is given by

$$\Omega_{\mathrm{eff}}(1)=\Omega_1+\int\Omega_{12}(1-P_{12})\rho(2',2)dx_2+\tfrac{1}{2}\int\Omega_{123}(1-P_{12}-P_{13})\begin{vmatrix}\rho(2',2) & \rho(2',3)\\ \rho(3',2) & \rho(3',3)\end{vmatrix}dx_2dx_3+\cdots, \tag{43}$$

and P_{ij} is the ordinary permutation operator for interchanging the coordinates $\mathbf{x}_i$ and $\mathbf{x}_j$. Due to the invariance of (36), we may carry out a unitary transformation of the two groups of orbitals associated with different spins in the basic set of spin-orbitals ψ_k, which brings the Hermitean matrix of the Lagrangian multipliers $\lambda(l|k)$ to diagonal form, and, in this special case, we obtain the eigenvalue problem

$$\Omega_{\mathrm{eff}}(1)\psi_k(\mathbf{x}_1)=\epsilon_k\psi_k(\mathbf{x}_1). \tag{44}$$

In forming (41) and (43), we have assumed that the normalization integral in the second relation (37) is equal to 1, but we note that there are no principal difficulties in treating also the general case when this integral has another constant value or is represented by an expansion of the form (41) for the operator $\mathcal{O}$. The expectation value of the energy, $E=\langle\mathcal{H}_{\mathrm{op}}\rangle_{\mathrm{Av}}$, is then given as the quotient between the two quantities (37), and, in applying the variation principle, one has to vary also the denominator; the auxiliary condition may be expressed in the form (II, 58). It is easily shown that the best spin-orbitals ψ_k are again determined by an eigenvalue problem of the form (44) but with $\Omega_{\mathrm{eff}}(1)$ replaced by the slightly more complicated one-particle operator

$$\{\Omega_{\mathrm{eff}}(1)-E\mathcal{O}_{\mathrm{eff}}(1)\}\Big/\int\Psi_0^*\mathcal{O}\Psi_0(dx),$$

where $\mathcal{O}_{\mathrm{eff}}(1)$ is formed from the expansion of the projection operator $\mathcal{O}$ in the same way as (43) is formed from (39). The mathematical details of this more general case will be further discussed in a forthcoming paper.

Since the operator Ω_{eff} is Hermitean, the eigenfunctions belonging to different "orbital energies" in (44) are automatically orthogonal. This simple result depends on the fact that we are here considering spin-orbitals without restraining conditions on the two groups of orbitals involved and that, in this connection, we have made us free from the idea of "doubly occupied" orbitals. Our result should also be compared with a previous discussion by Hartree and Hartree,[10] where, in investigating the first excited states ^3P and ^1P of beryllium, they were forced to keep a nondiagonal element $\lambda(1s|2s)\neq0$, since they assumed the $1s$-orbital to be doubly filled. However, Hartree and Hartree suggested also that it would be both physically and analytically significant to introduce different $1s$-orbitals for the two spins involved, and this extension of the theory has here been performed in a quite general way. We will later see that this distinction is of great importance for discussing also the correlation effects.

Our results show that, even for a degenerate system, we may keep the idea of the existence of an "effective" Hamiltonian, but, due to the degeneracy, all terms in this Hamiltonian may now contain couplings between several spin-orbitals corresponding to the occurrence of many-particle forces. In the "independent-particle" model, a degeneracy may therefore be described by replacing the ordinary effective Hamiltonian $\mathcal{H}_{\mathrm{eff}}$ by a composite effective Hamiltonian Ω_{eff} containing "degeneracy couplings" of many-particle character.

The composite effective Hamiltonian Ω_{eff} given by (38), (39), and (43) has not only a formal character but also an essential physical meaning, which becomes clear when investigating excited and ionized states. Let us consider two states associated with the same eigenvalue of the classifying operator Λ and therefore having wave functions Ψ' and Ψ which are obtained from single determinants by the same projection operator:

$$\Psi'=\mathcal{O}\Psi_0', \quad \Psi=\mathcal{O}\Psi_0, \tag{45}$$

where the determinants are characterized by the invariants ρ' and ρ, respectively. In a first approximation, we will then assume that, according to (II, 128), the difference $\Delta\rho=\rho'-\rho$ may be expressed as the sum of two factorized terms:

$$\Delta\rho(1,2)=\psi_j^*(1)\psi_j(2)-\psi_i^*(1)\psi_i(2). \tag{46}$$

Using (II, 133) and assuming that all basic orbitals are strictly orthogonal, we then obtain

$$\langle\mathcal{H}_{\mathrm{op}}'\rangle_{\mathrm{Av}}=\langle\mathcal{H}_{\mathrm{op}}\rangle_{\mathrm{Av}}+\int\psi_j^*(1)\Omega_{\mathrm{eff}}'(1)\psi_j(1)dx_1 -\int\psi_i^*(1)\Omega_{\mathrm{eff}}(1)\psi_i(1)dx_1, \tag{47}$$

showing that the system has eigenstates Ψ' of the total Hamiltonian $\mathcal{H}_{\mathrm{op}}$ when ψ_j and ψ_i fulfill the relations

$$\Omega_{\mathrm{eff}}'\psi_j'=\epsilon_j'\psi_j', \quad \Omega_{\mathrm{eff}}\psi_i=\epsilon_i\psi_i. \tag{48}$$

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[10] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A154**, 588 (1936), particularly p. 594.

For the excitation energy, we get therefore

$$\langle \mathcal{H}_{\text{op}}'\rangle_{\text{Av}} - \langle \mathcal{H}_{\text{op}}\rangle_{\text{Av}} = \epsilon_j' - \epsilon_i, \tag{49}$$

giving a rather visual meaning to the spin-orbital energies ϵ_j' and ϵ_i. This theorem was in (II, 135) proved for single determinants, i.e., for the average energies of a series of multiplets, but it is here extended to be valid even for the energies of pure spin states built up from orthogonal orbitals. This result gives a preliminary solution of a problem in the molecular theory which has been discussed rather frequently in the literature.[11] We note that, if the basic orbitals are partly overlapping, the simple result (49) must be somewhat modified.

Let us now consider the total wave functions Ψ' and Ψ given by (45). If the determinant Ψ_0 for the "ground state" is built up from the ordinary eigenfunctions to the operator Ω_{eff}, then the determinant Ψ_0' for the "excited state" is obtained from Ψ_0 by replacing the column containing the spin-orbital ψ_i by a column containing the spin-orbital ψ_j'. According to (II, 136), the spin-orbitals ψ_i and ψ_j' are strictly orthogonal, and it may then be shown that, for rather general forms of the projection operator $\mathcal{O}$ (as for ordinary and isotopic spins), also the total wave functions Ψ and Ψ' fulfill the necessary orthogonality condition.

The essential problem in treating the excited states is to construct the corresponding effective operator Ω_{eff}' and to solve the nonlinear problem of finding its eigenfunctions ψ_j' and eigenvalues ϵ_j'. For a discussion of this problem, the reader is referred to Part II.

The projection operator formalism renders also a simple way of calculating transition moments, for, if $\mathbf{D} = e\sum_i \mathbf{r}_i$ is the operator of electric moment, we have

$$\int \Psi'^* \mathbf{D} \Psi (dx) = \int \Psi_0'^* (\mathcal{O}^\dagger \mathbf{D} \mathcal{O}) \Psi_0 (dx), \tag{50}$$

which expression may be expanded analogously to (41).

We have here treated the excited states before the ionized states, since, in the excitations, the total number of particles is kept constant, which is of importance for having a fixed form of the projection operator $\mathcal{O}$ in (45). However, since an ionization may be considered as the limiting case of an excitation to a spin-orbital ψ_j' at infinity with $\epsilon_j' = 0$, we obtain from (49)

$$\langle \mathcal{H}_{\text{op}}'\rangle_{\text{Av}} - \langle \mathcal{H}_{\text{op}}\rangle_{\text{Av}} = -\epsilon_i, \tag{51}$$

showing that $(-\epsilon_i)$ measures the ionization energy. This is an extension of Koopmans' theorem[12] to degenerate systems built up from orthogonal orbitals.

3. INCLUSION OF CORRELATION EFFECTS

One of the strongest arguments against the validity of the ordinary Hartree-Fock scheme is that it does not treat the "correlation" between particles of different spin types in a proper way, and we will now take up this problem to discussion.

The basic idea of the "independent-particle model" is that, in a first approximation, one can neglect the mutual interaction between the N particles in the system in constructing the total wave function, which then takes the simple product form

$$\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\cdots\psi_N(\mathbf{x}_N), \tag{52}$$

where ψ_k $(k=1, 2, \cdots N)$ is a set of N spin-orbitals determined essentially by the outer framework. However, between the particles i and j, there is in reality a potential $\mathcal{H}_{ij}$ which, particularly for small distances $r_{ij}\approx 0$, may be tremendously large. If this potential is repulsive, like the Coulomb potential $\mathcal{H}_{ij} = e^2/r_{ij}$, it tries naturally to keep the particles apart,[13] and, since this "correlation" between the movements of the particles is entirely neglected in forming (34), the corresponding energy is affected by an error which is usually called the "correlation energy."

The situation is somewhat changed by the antisymmetrization procedure, which transforms the product function (52) into a single Slater determinant. In Part I, we have shown that, for every antisymmetric wave function, the second order density matrix (I, 3) $\Gamma(\mathbf{x}_1'\mathbf{x}_2'|\mathbf{x}_1\mathbf{x}_2)$ is also antisymmetric in each set of its indices, and this implies that, if two indices in a set are the same ($\mathbf{x}_1' = \mathbf{x}_2'$ or $\mathbf{x}_1 = \mathbf{x}_2$), the corresponding element will vanish identically. For the diagonal element, we obtain in particular

$$\Gamma(\mathbf{x}_1\mathbf{x}_2|\mathbf{x}_1\mathbf{x}_2) = 0, \quad \text{for } \mathbf{x}_1 = \mathbf{x}_2 \tag{53}$$

showing that the probability density for two particles with the same spin to be in the same place is zero of at least the second order (the "Fermi hole"). This means that the antisymmetry itself acts as if there would be a rather strong repulsion[14] between particles with the same spin at small distances, and this consequence of the Pauli principle automatically diminishes the error due to the neglect of the $\mathcal{H}_{ij}$-correlation. The exchange energy will therefore take care of a rather large part of the original correlation energy, referring to particles with parallel spins. The corresponding effect of the antisymmetrization on the particle distribution has been investigated by Lennard-Jones.[15]

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[11] R. S. Mulliken, J. Chem. Phys. **46**, 497, 675 (1949); C. C. J. Roothaan, Revs. Modern Phys. **23**, 69 (1951), p. 80.

[12] See Part II, references 30 and 31.

[13] Compare also some recent results for nucleons by M. Levy and others.

[14] In analogy to (37) and (38), we may interpret the effect of the antisymmetrization as if we still considered simple product functions (52) but a "composite" Hamiltonian of the form

$$\Omega_{\text{op}} = \mathcal{H}_{\text{op}} A, \quad A = (N!)^{-1} \sum_P (-1)^p P,$$

where A is the antisymmetrization operator obtained by summing over all permutations P having the parity p.

[15] J. E. Lennard-Jones, J. Chem. Phys. **20**, 1024 (1952).

The main problem is apparently to take the correlation between particles having different spins into proper account, and a first estimate of this effect was given by Wigner.[16] His preliminary results seems to be confirmed by the recent work by Bohm and Pines[17] using the "plasma" model. Here we will instead use another approach, which is based on our extension of the ordinary Hartree-Fock method.

The importance of the Hartree-Fock scheme depends on its connection with the "independent-particle model" giving it a physical visuality, which is useful in the interpretations and in constructing the ionized and excited states. In the previous section, we have shown that this visuality is preserved also in our extended scheme, where the wave function Ψ is a projection of a single determinant Ψ_0:

$$\Psi = \mathcal{O}\Psi_0. \tag{55}$$

The basic determinant is here built up from spin-orbitals obtained from two more or less independent groups of orbitals by multiplying them by the spin functions α and β, respectively. We note that we have already made us free from the idea of "doubly filled orbitals," and that this distinction was of importance for transforming the Hartree-Fock equations (42) to the eigenvalue problem form (44). This new degree of freedom may now also be used for including correlation effects, since we may choose the two sets of orbitals associated with different spin functions in such a way that they let particles with different spins try to avoid each other.[18] In fact, there is no new basic assumption needed for including correlation in our extended Hartree-Fock scheme, since the best spin-orbitals are always represented by the eigenfunctions to Ω_{eff}.

As a first example, we may consider the two-electron problem and its applications to the helium atom, the hydrogen molecule, and the π electrons of ethylene. By starting from *two* basic orbitals $u(\mathbf{r})$ and $v(\mathbf{r})$, we may construct a total wave function $\Psi = \mathcal{O}\{u\alpha, v\beta\}$, which, for the singlet state, is reduced to the form

$$\Psi = \text{const.}\{u(\mathbf{r}_1)v(\mathbf{r}_2)+u(\mathbf{r}_2)v(\mathbf{r}_1)\} \times\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}. \tag{56}$$

This is one of the exceptional cases, where it is possible to separate the orbital part and the spin part of the total wave function into two factors. The orbitals u and v are neither identical nor orthogonal, and their best form is automatically found by solving the extended Hartree-Fock equations (44) for the special case $N=2$.

Correlation Effects in the Helium Atom

We note that, without further calculations, we may say a few words about the results we may expect, due to the connection between our method and previous investigations treating the two-electron problem from other points of view. Let us start by considering the ground state of the helium atom, having an energy experimentally determined to 2.9032 atomic units ($e^2/a_0 = 2$ Ry). The symbol $(1s)^2$ indicates an approximation with $u=v$, and Kellner[19] has shown that, if this orbital is approximated by a single exponential, the best result is obtained for an effective nuclear charge $Z=1.6875$ giving a total energy of 2.8476. If $u=v$ is represented by the best Hartree-function,[20] the energy value is improved to 2.8615. The symbol $(1s', 1s'')$ would indicate an approximation, with $u\neq v$, and Eckart[21] has shown that, if u and v are approximated by two exponentials, the best result will be obtained for $Z_1=1.19$ and $Z_2=2.184$, giving a total energy of 2.8756, i.e., a result considerably better than the Hartree-approximation. Eckart's simple result is of great interest to us, since it indicates that we may expect considerable improvements of the present Hartree-Fock scheme for the atoms of the periodic system by making us free from the idea of doubly filled orbitals.

Eckart's result on helium has recently been improved by Taylor and Parr[22] by using a method of configurational interaction based on a series of determinants of exponential functions of *s*-, *p*-, *d*-, and *f*-type. Their results have been analyzed by Lennard-Jones[23] who has shown that the spatial correlation in helium may occur in two ways: as an "in-out" effect, with one electron tending to be outside the other, and as an "angular" effect with the two electrons tending to be on opposite sides of the nucleus. However, Taylor and Parr pointed out that, even if they obtain about 97 percent of the angular correction, their method of ordinary configurational interaction between *s*-functions showed a slow convergency with respect to the radial correlation. This phenomenon is also reflected by the fact that their

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[16] E. P. Wigner, Phys. Rev. **46**, 1002 (1934); Trans. Faraday Soc. **34**, 678 (1938).

[17] D. Bohm and D. Pines, Phys. Rev. **82**, 625 (1951); **85**, 338 (1952); **92**, 609 (1953); D. Pines, Phys. Rev. **92**, 626 (1953); Proc. 10th Solvay Conference (1953) (to be published).

[18] The possibility of having different orbitals for different spins was first mentioned by Hartree and Hartree in reference 10 in connection with the diagonalization of the matrix of Lagrangian multipliers, but it was never used by them. The importance of this possibility for the proper description of ferromagnetic and antiferromagnetic materials has several times been pointed out by J. C. Slater, Phys. Rev. **82**, 538 (1951). However, as far as we know, it has not been explicitly pointed out in the literature that this new degree of freedom may be used for including correlation effects in a simple way; compare reference 24.

[19] G. Kellner, Z. Physik **44**, 91 (1927).

[20] D. R. Hartree, Proc. Cambridge Phil. Soc. **24**, 111 (1928); for the energy value, see H. Bethe, Handbuch der Physik (Julius Springer, Berlin, 1933), Vol. 24, No. 1, p. 370. See also W. S. Wilson, Phys. Rev. **48**, 536 (1935).

[21] C. Eckart, Phys. Rev. **36**, 878 (1930). It seems to be less well known that this result was already obtained by E. H. Hylleraas in his pioneer work, Z. Physik **54**, 347 (1929). The author is indebted to Dr. Harrison Shull for some discussions of Hylleraas' paper.

[22] G. R. Taylor and R. G. Parr, Proc. Nat. Acad. Sci. U. S. **38**, 154 (1952).

[23] J. E. Lennard-Jones, Phil. Mag. **43**, 581 (1952).

best wave function contained only 64 percent of the radial correlation energy.

The helium problem was discussed at the Shelter Island Conference in 1951, and the situation was analyzed by Mulliken,[24] denoting $(1s)^2$ and $(1s', 1s'')$ as closed-shell and open-shell electron configurations. It is possible that the extended Hartree-Fock scheme proposed here is the "generalization of the SCF procedure" required by Mulliken. In all events, it will be interesting to see how good approximation of the energy one can obtain by solving the extended Hartree-equations (44) for $N=2$ and $u \neq v$ with the normalization integral taken into account, and how closely one can approach Hylleraas' classical result in the unrelativistic approximation. In a first approximation, we will assume that u and v are s-functions depending only on the distance to the nucleus, which will describe the main part of the "in-out" effect. In the next step, u and v may depend on the angles, but, in such case, we must introduce a projection operator containing also the total angular momentum operator in order to select an S state for the total wave function. Numerical calculations on the helium problem along these lines are now in progress.

Correlation Effects for Diatomic Molecules

The wave function (56) may also be applied to the hydrogen molecule problem. It would probably be very hard to solve the exact extended Hartree-Fock equations (44) for such a problem, but significative results could be obtained by using the variation principle. In such a case, it is therefore important to know something *a priori* about the general form of the orbitals involved, and, according to the previously mentioned "correlation principle," we will assume that u and v may be of such a type that the electrons in them (having different spins) tend to avoid each other. This is mainly established by two effects: the "alternant" effect, trying to keep the two electrons on separate atoms, and the "in-out" effect, trying to keep one electron outside the other, when they happen to be on the same atom. The form of these orbitals is indicated in Fig. 1. Semilocalized molecular orbitals were first constructed for the hydrogen molecule by Coulson and Fischer,[25] who pointed out that they lead to the same result as the ordinary method of configurational interaction using two determinants.

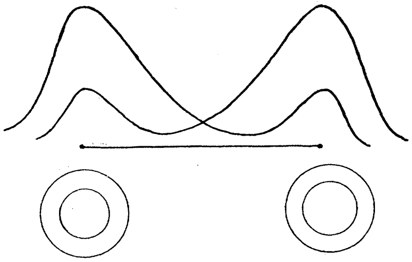

FIG. 1. The two orbitals u and v showing "alternant" and "in-out" effect for a two-electron problem in a diatomic molecule.

As far as we know, the "in-out" effect has not previously been used in the theory of molecules or crystals. It seems to be rather important, since the Coulomb integrals associated with two electrons concentrated in the same orbital on one atom are certainly too large, because of the neglect of the electronic correlation. The problem of these "ionic" Coulomb integrals have been particularly emphasized by Moffitt[26] in treating the oxygen molecule and by Pariser and Parr[27] in investigating some conjugated organic compounds, and these authors proposed that the values of the ionic integrals should be corrected by comparison with experimental data. Sponer[28] and the present author found similarly that, in a π-electron theory of ethylene based on the atomic Hartree-Fock functions for carbon, the singlet-triplet separation came out much too large, and that the error could be localized mainly to the ionic $(\pi\pi|\pi\pi)$-integral.[29] By introducing the "in-out" effect for the electrons condensed on the same atom, the value of the ionic Coulomb integrals will now be essentially diminished, and we note that this correction may be carried out in a purely theoretical way by using the variational principle for the total energy. Numerical applications to the hydrogen molecule and to ethylene are now being prepared.

4. THE METHOD OF ALTERNANT MOLECULAR ORBITALS

In a theory of molecules and crystals, where the total wave function is approximated by a single determinant constructed from molecular spin-orbitals, there is a certain difficulty connected with the fact that the cohesive energy shows a wrong asymptotic behavior for separated atoms.[30] This depends on the fact that such a wave function permits electrons of different spins to accumulate on the same atom and give rise to negative and positive ions, having higher energy together than the ordinary dissociation products; see Fig. 2. One way of removing this defect is by configurational interaction, but, except for the simplest

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[24] R. S. Mulliken, Proc. Nat. Acad. Sci. U. S. **38**, 160 (1952).

[25] C. A. Coulson and I. Fischer, Phil. Mag. **40**, 386 (1949). The "best orbital" problem for the hydrogen molecule was formulated in a complete form by M. Kotani, Proceedings of the Shelter Island Conference on Quantum Mechanical Methods in Valence Theory, 139 (1951), where he also discusses the solution in elliptical coordinates. See also J. Lennard-Jones and J. A. Pople, Proc. Roy. Soc. (London) **A210**, 190 (1951).

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

[27] R. Pariser, J. Chem. Phys. **21**, 568 L (1953); R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 767 (1953).

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

[29] See also the remarks by R. S. Mulliken and P. O. Löwdin at the Nikko symposium 1953, Proceedings of the Japanese Conference on Theoretical Physics, 1953 (to be published).

[30] See, e.g., J. H. Van Vleck and A. Sherman, Revs. Modern Phys. **7**, 167 (1930), p. 170; and J. C. Slater, Quarterly Progress Report of Solid-State and Molecular Theory Group, M.I.T., p. 26, January 15, 1952 (unpublished).

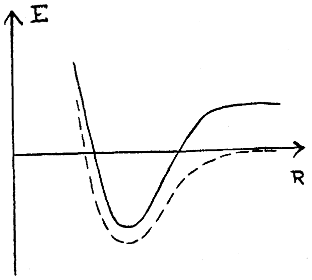

FIG. 2. The energy E as a function of interatomic distance R. The upper curve refers to a single determinant, and the lower curve represents the correct behavior.

molecules, this approach leads usually to secular equations of such a high order that they are extremely hard to solve.

Fortunately, there seems to be also another possibility for solving this problem. Slater[31] has several times pointed out that, in an antiferromagnetic material, there must be a tendency for a certain spin alignment with the crystal divided into two sublattices with the valence electrons having either plus or minus spin. Slater is accordingly looking for a crystal theory which would be similar to a valence bond method for separated atoms and similar to a molecular orbital method for small and intermediate distances between the atoms. The essential point is apparently to find a modification of the ordinary molecular orbital method which, for separated atoms, automatically would lead to a spin alignment of the type proposed by Slater, for then there would be no possibility for excessive occurrence of ions. However, in order to avoid a real antiferromagnetic behavior of the system, the total wave function must be invariant with respect to an interchange of the two spins.

An attempt to translate these ideas into mathematical form has been made by the author[32] by using the method of "alternant molecular orbitals," and we will here give a short survey of its main result in order to discuss its connection with the general theory developed in this paper.

Let us say that, by solving the Hartree-Fock equations by, e.g., the MO-LCAO method, we have found a set of MO's for the valence electrons belonging to the system. In the naive MO theory, the orbitals for the valence electrons are only partly filled. By using *all* the MO's available, we may now try to construct combinations which tend to be localized on two interpenetrating subsystems, I and II, for separated atoms. For the sake of simplicity, let us consider an *alternant* system, for instance a crystal constituted of two equivalent sublattices I and II, as the body-centered cubic structure, or an alternant hydrocarbon,[33] where the atom, if one moves along a chain of unsaturated carbon atoms, belong alternately to set I and to set II.

As in Part II, Sec. 3 (b), we let ϕ_μ be the ordinary or hybridized atomic orbitals associated with the system, and φ_μ the corresponding set of ON-AO's. It is a characteristic feature of the alternant systems that the MO's occur in pairs, j' and j'', with orbital energies $\epsilon_{j'}$ and $\epsilon_{j''}$ belonging to symmetric places in the lower and the upper half of the "energy band," respectively. The excited orbital $\psi_{j''}$ is obtained from the lower orbital $\psi_{j'}$ by changing the sign of the coefficients of the AO's of one of the subsystems, let us say II:

$$\begin{aligned}\psi_{j'}&=\sum_\mu^{\mathrm{I}}\varphi_\mu c_{\mu j}+\sum_\mu^{\mathrm{II}}\varphi_\mu c_{\mu j},\\ \psi_{j''}&=\sum_\mu^{\mathrm{I}}\varphi_\mu c_{\mu j}-\sum_\mu^{\mathrm{II}}\varphi_\mu c_{\mu j}.\end{aligned}\tag{57}$$

Let us then form the combinations

$$\begin{aligned}\psi_{j\mathrm{I}}&=a\psi_{j'}+b\psi_{j''}=(a+b)\sum_\mu^{\mathrm{I}}\varphi_\mu c_{\mu j}+(a-b)\sum_\mu^{\mathrm{II}}\varphi_\mu c_{\mu j},\\ \psi_{j\mathrm{II}}&=a\psi_{j'}-b\psi_{j''}=(a-b)\sum_\mu^{\mathrm{I}}\varphi_\mu c_{\mu j}+(a+b)\sum_\mu^{\mathrm{II}}\varphi_\mu c_{\mu j}.\end{aligned}\tag{58}$$

Since the normalization condition takes the form $a^2+b^2=1$, we may put $a=\cos\theta$ and $b=\sin\theta$ and describe the mixing between the MO's by an angle θ. We note the special cases:

$\theta=0°$, ordinary lower half MO's;

$\theta=45°$, purely alternant MO's;

$\theta=90°$, ordinary upper half MO's.

The MO's belonging to the lower half of the "energy band" are *bonding* orbitals, whereas the MO's belonging to the upper half are *antibonding*.[33] For $0<\theta<90°$, the orbitals $\psi_{j\mathrm{I}}$ are semilocalized on system I and the orbitals $\psi_{j\mathrm{II}}$ on system II, and we will therefore call them *alternant* molecular orbitals. For $\theta=45°$, this localization is complete. We note further that orbitals belonging to different indices j are still orthogonal, whereas

$$\lambda=\int\psi_{j\mathrm{I}}\psi_{j\mathrm{II}}dx=\cos2\theta.\tag{59}$$

As a simple example, we may consider the lowest orbitals for a linear chain; see Fig. 3.

In order to construct a wave function for the system, which leads to the correct asymptotic behavior of the

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[31] J. C. Slater, Phys. Rev. **35**, 509 (1930), see p. 527; Proceedings of the Shelter Island Conference on Quantum Mechanical Methods in Valence Theory, 121 (1951); Phys. Rev. **82**, 538 (1951).

[32] P. O. Löwdin, Proceedings of the Japanese Conference on Theoretical Physics, 1953, Nikko Symposium (to be published). It should be noted that our method is applicable to both mobile and localized electrons. Systems containing only localized single bonds have also been treated by L. A. Schmid, Phys. Rev. **92**, 1373 (1953) and Hurley, Lennard-Jones, and Pople, Proc. Roy. Soc. (London) **A220**, 446 (1953).

[33] C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) **A192**, 16 (1948).

energy for separated atoms, we will now consider a Slater determinant

$$T_0=\{\underset{\text{I}}{\alpha\alpha\cdots}\,|\,\underset{\text{II}}{\beta\beta\beta\cdots}\},\tag{60}$$

where we have used the notation (11); each orbital of type I is therefore occupied by an electron with plus spin and each orbital of type II by an electron with minus spin. The various spin multiplets may then be obtained by using the projection operator (7):

$$\Psi={}^{(2l+1)}\mathcal{O}T_0.\tag{61}$$

If, for separated atoms, we let θ tend to the value $\theta=45°$, there will be a spin alinement of the type proposed by Slater, and the wave function (60) will then have the correct asymptotic behavior. We will now check that the various spin multiplets of the wave function (60) also have preserved this property. For $\theta=45°$, the discussion is simplified by the fact that all the alternant MO's become strictly orthogonal, see (59), and the energy is then given by formula (25):

$$\langle\mathcal{H}_{\text{op}}\rangle_{\text{Av}}=\int T_0{}^*\mathcal{H}_{\text{op}}T_0(dx)$$
$$-\frac{l(l+1)-n}{n^2}\sum_{j,k=1}^{n}(j\text{I},k\text{II}|\,\mathcal{H}_{12}|\,k\text{II},j\text{I}).\tag{62}$$

Since the exchange integrals in the last term in the right-hand member tend to zero for $\theta=45°$ and separated atoms, our theorem is proved.

For $\theta=0$ and $l=0$, the function (61) reduces to the well-known single-determinant wave function of the ordinary MO theory with the bonding orbitals doubly occupied. This means that, by varying θ, we may obtain a depression of the energy curve in Fig. 2 also for intermediate distances, and, in particular cases, the improvement of the energy minimum may be appreciable. The physical interpretation of this procedure will be discussed in the next section. The energy expression in the general case ($\theta\neq 45°$) is somewhat more involved than (62), due to the occurrence of the nonorthogonality integral $\lambda=\cos 2\theta$ in (59), but it may be derived by using (23), (24), and (I, 49). The mathematical details will be confined for a following paper.

Here we would only like to mention that, in an application of the alternant MO method to the ground state of the benzene molecule, Itoh and Yoshizumi[34] have obtained a depression of the energy minimum for $\theta\approx 23°$ of about 2.35 ev, which amounts to 85 percent of the depression obtained by Parr, Craig, and Ross[35] by using a method of configurational interaction containing nine determinants; an expansion of the wave function (61) shows that there is also a fairly good resemblance between the two total wave functions found in so different ways.

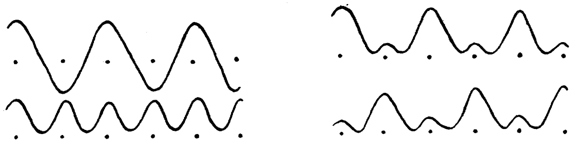

FIG. 3. Ordinary and alternant MO's.

5. GENERAL THEORY OF SPIN ALIGNMENT IN MOLECULES AND CRYSTALS

The principal investigation of "correlation effects," carried out in this paper, makes it now possible for us to build up the method of alternant MO's on a more general basis. It is clear that the erroneous asymptotic behavior of the upper energy curve in Fig. 2 depends mainly on the neglect of the Coulomb correlation between electrons with different spins, since it is just the Coulomb repulsion which prevents the excessive formation of negative ions with the electrons too closely condensed on the same atom. The solution provided by the method of alternant MO's must therefore in some way take this correlation into account, and, if we compare the form of the orbitals in Figs. 1 and 3, we find a striking similarity, and we see that the alternant MO's may be considered as being constructed according to the "correlation principle" so that electrons having different spins tend to avoid each other due to their mutual repulsion.

However, once we have put the method of alternant MO's in connection with our general theory, we see immediately that it may be improved in several ways, for instance by including the "in-out" effect for electrons which happen to be on the same atom. This can be performed by constructing the alternant MO's from two sets of atomic orbitals corresponding to different effective nuclear charges,[21] and the inclusion of this effect is certainly necessary in order to obtain good results in investigations of the ground state and lower excited states of, e.g., the conjugated systems.[27]

The theory of alternant MO's was originally built up on Slater's idea of the existence of a certain spin alinement in alternant systems, but we can now also make us free from this assumption as being unnecessary. The ordinary MO theory is firmly built on the idea of "doubly occupied orbitals," but, as soon as we have made us free from this restriction, there are two groups of orbitals associated with different spins at our disposal, and the "correlation" between them is automatically determined by the extended Hartree-Fock equations (44) and the composite effective Hamiltonian Ω_{eff} given by (38), (39), and (43), where, of course, we now have to take the total normalization integral given by (37) into full account. However, even if the

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[34] T. Itoh and H. Yoshizumi, J. Phys. Soc. Japan (to be published). The author is greatly indebted to them for kindly informing me about their results before publication.

[35] Parr, Craig, and Ross, J. Chem. Phys. 18, 1561 (1950).

form of the two groups of orbitals is fully determined by the eigenvalue problem (44), it is certainly extremely hard to solve this problem exactly for a molecule or crystal, and some ideas of the qualitative form of these orbitals will then be very useful in connection with the approximate solution of (44) by means of the variation principle.

This result is of importance, since it tells us that the extended Hartree-Fock equations (44) will give the answer to the question of the existence of a general spin arrangement in molecules and crystals. It gives a possibility for investigating the difference between the spin alignments in body-centered and face-centered cubic structures, and many other problems.

6. CONCLUSIONS

By using the idea of projection operators and wave functions being projections of single determinants, we have here given an extension of the ordinary Hartree-Fock scheme to include the treatment of degeneracies and correlation effects. From the very beginning, we have made us free from the idea of "doubly occupied" orbitals, and the two more or less independent groups of orbitals associated with different spins are then determined by extended Hartree-Fock equations, where the effective Hamiltonian is derived from a composite total Hamiltonian containing also the projection operator for the state under consideration. This effective Hamiltonian contains also many-particle interactions, but, otherwise, the extended scheme has preserved the simplicity and physical visuality characteristic for the theory based on a single Slater determinant. The two groups of orbitals are of such a type that particles having different spins tend to avoid each other, and the extended Hartree-Fock equations give therefore also a description of spin alignments in molecules and crystals.

In order to apply the theory developed in principle in this paper to practical problems, it is desirable to know also the reduced form of the basic energy (41) expressed only in terms of the two groups of basic orbitals, and the mathematical details of this problem will be treated in a forthcoming paper. Here we will only point out that, even if we have illustrated our extension of the "independent-particle model" by examples from the theory of electronic structure of atoms, molecules, and crystals, the general scheme may just as well be applied to nuclear theory after inclusion of the isotopic spin.

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