FIG. 20. $b_1 = a_1 \cos\theta + a_2 \sin\theta$;
$b_2 = -a_1 \sin\theta + a_2 \cos\theta$.

then one finds as the orientation coefficients

$$I' = b_1 b_1^* + b_2 b_2^* = a_1 a_1^* + a_2 a_2^* = I,$$

$$P_1' = b_1 b_1^* - b_2 b_2^* = P_2 \sin 2\theta + P_1 \cos 2\theta,$$

$$P_2' = b_1 b_2^* + b_2 b_1^* = -P_1 \sin 2\theta + P_2 \cos 2\theta,$$

$$P_3' = i(b_1 b_2^* - b_2 b_1^*) = i(a_1 a_2^* - a_2 a_1^*) = P_3.$$

Thus, for radiation (whose orthogonal state vectors correspond to orthogonal space vectors) we have for rotations about the axis corresponding to P_3

$$M_3 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos 2\theta & \sin 2\theta & 0 \\ 0 & -\sin 2\theta & \cos 2\theta & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}.$$

For particles, the orthogonal state vectors do not correspond to the space vectors (ψ_1 and ψ_2 representing spins in the $\pm z$ direction are orthogonal state vectors but the two space directions $\pm z$ are not orthogonal), so we cannot use the same expansion of b_1 and b_2; however, considering the meanings of P_1 and P_2, we see that the transformation matrix M is suitable if 2θ is replaced by θ; that is, a 90° rotation performs the transformations

$$P_1' = P_2, \quad P_2' = -P_1.$$

For particles we are mainly interested in rotations about the z axis, which is generally chosen as the direction of motion. The rotation matrix for this case can be obtained from that first given by a cyclic rotation of the rows and columns. Thus

$$M_1 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \cos\theta & \sin\theta \\ 0 & 0 & -\sin\theta & \cos\theta \end{bmatrix}.$$

Approximate Methods in the Quantum Theory of Many-Fermion Systems

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I. INTRODUCTION

THIS paper considers the Hartree-Fock approximation from two complementary points of view. In the first, the method is a convenient first step towards an *ab initio* solution of the many-particle Schrödinger equation for a system of fermions. It can be shown that the Hartree-Fock wave function satisfies mathematical conditions which ensure that a large class of matrix elements, in the perturbation solution of Schrödinger's equation, should vanish.[1,2] For this reason it is a useful zeroth-order wave function in a perturbation calculation. From this point of view, modifications to the Hartree-Fock method which simplify the details of calculations are desirable, if their effect on the perturbation calculation can easily be evaluated.

From the second point of view, the Hartree-Fock approximation is the last hand-hold for elementary physical intuition before it is forced to work directly in

terms of the superposition of wave amplitudes that depend on large numbers of independent variables. It can be argued that any attempt to think in terms of physical models, rather than pure mathematics, past this point is necessarily deceptive. In the Hartree-Fock approximation (or at least in the unrestricted Hartree-Fock approximation which is discussed in the following) there is a one-to-one correspondence between particles and one-particle wave functions (orbitals) which justifies the loose physical language used in talking about "an electron in an outer shell," for example, or "an electron moving through a lattice." Furthermore, in the Hartree-Fock approximation one is free to make up wave packets from the orbitals, and to localize them both conceptually and mathematically, so that it is not completely fallacious to talk about the force between two particles when mathematically this is described by the potential energy integral between density distributions made from the probability amplitudes denoted by two localized orbitals.

A modification of the Hartree-Fock method which

[1] L. Brillouin, *Actualités sci. et ind.* No. 159 (1934); R. Lefebvre, Compt. rend. **237**, 1158 (1953).
[2] R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955).

makes *ab initio* calculations easier might destroy the frame of reference within which physical intuition works most easily. Once a set of N particles is being described in terms of $N+1$ orbitals, the physical picture becomes unclear. New kinds of phenomena occur for which a system of independent particles is not a valid model. For this reason it is desirable to think of these phenomena as collective motion or correlation effects, and not try to include such effects in the independent particle model of the Hartree-Fock theory.

Three variants of the Hartree-Fock theory are considered. These are the unrestricted Hartree-Fock method, the traditional Hartree-Fock method,[3,4] and the method of symmetry and equivalence restrictions.[2] The latter two methods are identical in many cases, and the differences due to approximations are very small compared with approximations such as Hartree's method, the self-consistent field without exchange,[4] which neglects all exchange integrals, or Slater's methods[5] which replace exchange integrals by an average potential.

The Hartree-Fock approximate wave function is taken to be a single Slater determinant, a normalized antisymmetrized product

$$\det \phi_1(1)\phi_2(2)\cdots\phi_N(N),$$

constructed from orbitals $\{\phi_i\}$, $i \leqslant N$. The N-particle Hamiltonian is assumed to be of the form

$$H(1,2,\cdots,N) = \sum_j K(j) + \sum_{ij} Q(i,j), \qquad (1)$$

where $Q(i,j) = Q(j,i)$, the operators are Hermitian, and $i < j \leqslant N$.

A simple derivation of the integro-differential equations satisfied by the Hartree-Fock orbitals is given in Sec. II for all three methods, together with a proof that the method of symmetry and equivalence restrictions is identical with the traditional method in an important open-shell case, which includes the ground states of all second-row atoms except Li, and the atomic configurations $3d^n$. The method of symmetry and equivalence restrictions is designed to allow open-shell calculations that can always be put into the form of homogeneous eigenvalue equations, with a common effective one-particle Hamiltonian for all orbitals.[2]

Because all other variants of the Hartree-Fock method either include constraints introduced to simplify calculations, or deal with a trial wave function that cannot be expressed as a single Slater determinant, the physical model of a system of independent particles is strictly applicable only to the unrestricted Hartree-Fock method. The effects described in physical terms as collective motion or particle correlation are discussed in connection with the unrestricted Hartree-Fock method

[3] V. Fock, Z. Physik **61**, 126 (1930); **62**, 795 (1930); P. A. M. Dirac, Proc. Cambridge Phil. Soc. **27**, 240 (1931).
[4] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).
[5] J. C. Slater, Phys. Rev. **81**, 385 (1951); **91**, 528 (1953).

in Sec. III. These physical effects are closely related to the resolution of degeneracies and perturbation or variational solution of Schrödinger's equation, when the unrestricted Hartree-Fock wave function is taken as an initial approximation.

The relation between various generalizations of the Hartree-Fock method which have been proposed and those considered here in detail is discussed in Sec. VI.

II. DERIVATION OF THE HARTREE-FOCK EQUATIONS

Let Φ_0 be a single Slater determinant with occupied orbitals $\{\phi_i\}$, $i \leqslant N$, for a system of N fermions. Other orbitals orthogonal to the occupied orbitals which make up with them a complete orthonormal set are denoted by $\{\phi_a\}$, $a > N$.

In the unrestricted Hartree-Fock method[3] the mean value of total energy $(0|H|0)$ is to be made stationary with respect to any variation of the occupied orbitals of Φ_0 which preserves normalization. In particular, the energy must be stationary under all variations of the form

$$\delta\phi_i = \phi_a d\alpha, \qquad (2a)$$

$$\delta\Phi_0 = \Phi_i{}^a d\alpha, \qquad (2b)$$

where $d\alpha$ is an infinitesimal constant, ϕ_a is any normalized orbital orthogonal to all ϕ_i, and $\Phi_i{}^a$ is the determinant constructed from Φ_0 by replacing ϕ_i by ϕ_a. Since the Hamiltonian H of Eq. (1) is Hermitian, if $\delta(0|H|0)$ is to vanish for this variation it follows that

$$\text{Re}(_i{}^a|H|0)d\alpha^* = 0 \quad \text{for all } i \leqslant N < a. \qquad (3)$$

The complex phase of $d\alpha$ can be chosen so that $(_i{}^a|H|0)d\alpha^*$ is a real number, so this implies that

$$(_i{}^a|H|0) = 0 \quad \text{for all } i \leqslant N < a. \qquad (4)$$

But such a matrix element is identical with the matrix element $(a|\mathcal{K}_0|i)$ of an effective one-particle Hamiltonian[2]

$$\mathcal{K}_0 \equiv K + \sum_{j=1}^{N} (j|R|j). \qquad (5)$$

Here $(j|R|j)$ is a linear one-particle operator defined in terms of the two-particle operator Q of Eq. (1) by

$$(j|R|j)\phi_i \equiv (j|Q|j)\phi_i - (j|Q|i)\phi_j. \qquad (6)$$

The exchange term here results from the antisymmetry of the many-particle wave function.

From Eq. (4), the result of the variational calculation is

$$(\phi_a{}^*, \mathcal{K}_0\phi) = 0 \quad \text{for all } i \leqslant N < a. \qquad (7)$$

Since ϕ_a is arbitrary except for the condition of orthogonality to all of the occupied orbitals $\{\phi_i\}$, this implies

that $\mathcal{H}_0\phi_i$ is a linear combination of the orbitals $\{\phi_i\}$,

$$\mathcal{H}_0\phi_i=\sum_{j=1}^{N}\epsilon_{ji}\phi_j, \quad i\leqslant N. \tag{8}$$

Since any linear variation that preserves the normalization of Φ_0 can be expressed as a linear combination of the special variations considered previously, Eqs. (8) are equivalent to the statement that $(0|H|0)$ should be stationary under any variation of the orbitals, subject to normalization.

If the operators K and Q of Eq. (1) are Hermitian, the one-particle effective Hamiltonian $\mathcal{H}_0$ defined by Eq. (5) is Hermitian. $\mathcal{H}_0$ is also invariant under unitary transformation of the set of orbitals occupied in the determinant Φ_0, so a canonical form of Eqs. (8) can be obtained by diagonalizing the Hermitian matrix $[\epsilon_{ji}]$. This is

$$\mathcal{H}_0\phi_i=\epsilon_i\phi_i, \quad i\leqslant N. \tag{9}$$

Equations (9) are the (canonical) unrestricted Hartree-Fock equations for the occupied orbitals of Φ_0. Since $\mathcal{H}_0$ depends on its own eigenfunctions, by Eq. (5), these equations must be solved by an iterative process.[4]

In the traditional Hartree-Fock method,[3,4] as it would be applied to a trial wave function expressed as a single Slater determinant Φ_0, the orbitals would not be varied completely independently of one another. Since the principal application of the traditional method is to spherically symmetrical systems, it is sufficient to use the case of spherical symmetry to illustrate the general argument.

Irreducible representations of the transformation group in one-particle space that generates the transformation group of the many-particle Hamiltonian[6] are denoted by an index λ. A particular row or column of a matrix in the standard irreducible representation λ is denoted by a second index μ. In the case of spherical symmetry, these indices would be identified with the quantum numbers l, m that specify a spherical harmonic $Y_{lm}(\theta,\phi)$. Under a coordinate rotation the spherical harmonics with index l transform into one another by a unitary transformation. The transformation matrices form a $(2l+1)$-dimensional irreducible representation of the rotation group. The rows and columns of these matrices, and the different members of the set of basis functions Y_{lm}, are labeled by the axial quantum number m.

When spin is taken into account the spherical harmonics must be generalized to functions $\chi_{\lambda\mu}(\theta,\phi,\cdots)$, which may depend on other internal variables such as isotopic spin. These functions are to be basis functions for irreducible representations of the combined group of rotations together with any symmetry transformations

of the internal variables. For example, for electrons in an atom, in Russell-Saunders coupling, $\chi_{\lambda\mu}$ would be the product of a spherical harmonic with a Pauli spinor, and the second index μ would denote the pair of quantum numbers m_l, m_s. For a nuclear Hartree-Fock calculation which neglected the Coulomb force, $\chi_{\lambda\mu}$ would be the product of a j-j coupled orbital (spin coupled to the orbital angular momentum) and an isotopic spinor, and μ would denote the pair of quantum numbers m, τ_3.

For a system with spherical symmetry, the traditional Hartree-Fock orbitals would be constrained to be of the form

$$\phi_i=\phi_{n\lambda\mu}=R_{n\lambda}(r)\chi_{\lambda\mu}(\theta,\phi,\cdots).$$

The important constraint is that $R_{n\lambda}$ is taken to be the same for a set of orbitals with different values of μ, and each orbital contains only one angular function. The traditional Hartree-Fock procedure is to substitute orbitals of this form into the expression for the mean value of energy, then to integrate over the angular variables (and the internal variables) before using the variational calculus.[4] In contrast to the unrestricted Hartree-Fock method, where the entire orbital is varied, only the radial functions are varied, since the energy is expressed as a functional of the radial functions. A derivation of the traditional method is given here which defers the angular integration until after the variational calculation, to compare with the unrestricted method.

The radial function $R_{n\lambda}$ may occur several times in a single Slater determinant, multiplied by angular functions $\chi_{\lambda\mu}$ with different values of the second index $\mu(n\lambda)$. For given λ the index n which denotes an independent radial function assumes values $n\leqslant N_\lambda$ for occupied orbitals, and $n>N_\lambda$ for functions orthogonal to occupied orbitals. Each radial function is assumed to be normalized, and orthogonal to all other radial functions with the same value of λ.

The most general variation to be considered is such that the energy $(0|H|0)$ must be stationary under all variations of the form

$$\delta\phi_{n\lambda\mu}=\delta R_{n\lambda}\chi_{\lambda\mu}=R_{t\lambda}d\alpha\chi_{\lambda\mu}, \tag{10}$$

where $d\alpha$ is an infinitesimal constant and $R_{t\lambda}$ is any normalized radial function orthogonal to all $\{R_{p\lambda}\}$, $p\leqslant N_\lambda$. The variation of the Slater determinant Φ_0 is

$$\delta\Phi_0=\sum_{\mu(n\lambda)}\Phi_{n\lambda\mu}{}^{t\lambda\mu}d\alpha. \tag{11}$$

Hence if $\delta(0|H|0)$ is to vanish it follows as in Eqs. (7) that

$$\sum_{\mu(n\lambda)}(R_{t\lambda}{}^*\chi_{\lambda\mu}{}^*,\mathcal{H}_0 R_{n\lambda}\chi_{\lambda\mu})=0 \tag{12}$$

for all $n\leqslant N_\lambda<t$.

To compare with Eqs. (8), and to derive an effective radial operator, it is desirable to divide Eq. (12) by $d(n\lambda)$, the number of values of μ in the set $\mu(n\lambda)$, which specifies the angular factors of occupied orbitals with radial function $R_{n\lambda}$. Then Eq. (12) is equivalent to the

[6] H. Eyring, J. Walter, G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944); L. D. Landau and E. M. Lifshitz, *Quantum Mechanics, Non-Relativistic Theory* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1958), Chap. XII.

radial equations

$$[\mathcal{3C}_0]_{n\lambda}R_{n\lambda} = \sum_{p=1}^{N_\lambda} \epsilon_{pn}{}^\lambda R_{p\lambda}, \quad n \leqslant N_\lambda, \qquad (13)$$

where

$$[\mathcal{3C}_0]_{n\lambda} = \frac{1}{d(n\lambda)} \sum_{\mu(n\lambda)} \int d\Omega \chi_{\lambda\mu}{}^* \mathcal{3C}_0 \chi_{\lambda\mu}. \qquad (14)$$

The integration is over the angular variables, and internal variables. Equations (13) are the traditional Hartree-Fock equations for the radial functions, for occupied orbitals in the Slater determinant Φ_0.

If for given λ, the set of values of $\mu(n\lambda)$ which specify occupied orbitals should be the same for all $n \leqslant N_\lambda$, then the average in Eq. (14) would be independent of n, and the operator $[\mathcal{3C}_0]_{n\lambda}$ would in fact be independent of n. In this special case, since the operator is Hermitian as before, the Hermitian matrix $[\epsilon_{pn}{}^\lambda]$ can be diagonalized by a unitary transformation of the radial functions $\{R_{n\lambda}\}$, $n \leqslant N_\lambda$, under which $[\mathcal{3C}_0]_{n\lambda}$ is invariant. This makes possible a canonical form of the radial equations, free of off-diagonal Lagrange multipliers,

$$[\mathcal{3C}_0]_\lambda R_{n\lambda} = \epsilon_n{}^\lambda R_{n\lambda}, \quad n \leqslant N_\lambda. \qquad (15)$$

The index n is dropped from $[\mathcal{3C}_0]_{n\lambda}$ since the operator is independent of n in the special case under consideration.

In the general case $[\mathcal{3C}_0]_{n\lambda}$ is obtained from the unrestricted Hartree-Fock operator (evaluated for orbitals of the restricted form) by removing, through the integration over angles and internal variables in Eq. (14), all components of $\mathcal{3C}_0$ that connect functions with different transformation properties under group operations, i.e., with different values of λ or of μ. The remaining operator is then averaged over the set of μ values which represent occupied orbitals for each value of n.

The method of symmetry and equivalence restrictions[2] follows an almost identical procedure. First, components of $\mathcal{3C}_0$ that would connect different values of λ or of μ are dropped (this is called the symmetry restriction). Then, in order to secure equations of the canonical form, an effective operator independent of n is obtained either by choosing a particular value of μ and solving the equations

$$[\mathcal{3C}_0]_{\lambda\mu}R_{n\lambda} = \epsilon_n{}^\lambda R_{n\lambda}, \quad n \leqslant N_\lambda, \qquad (16)$$

where

$$[\mathcal{3C}_0]_{\lambda\mu} = \int d\Omega \chi_{\lambda\mu}{}^* \mathcal{3C}_0 \chi_{\lambda\mu}, \qquad (17)$$

or by averaging over a set of values of μ which is independent of n. This is called the equivalence restriction.

In the special case in which the traditional Hartree-Fock equations can be expressed in the canonical form of Eqs. (15) for all values of λ the method of symmetry and equivalence restrictions is identical with the traditional method, if the average over values of μ is taken as in Eq. (14). The total energy in this special case is

given by the formula

$$(0|H|0) = \tfrac{1}{2} \sum_\lambda \sum_{n=1}^{N_\lambda} d(n\lambda)[(n\lambda|K|n\lambda) + \epsilon_n{}^\lambda]. \qquad (18)$$

This follows from the identity[2]

$$(0|H|0) = \tfrac{1}{2} \sum_{i=1}^{N} [(i|K|i) + (i|\mathcal{3C}_0|i)]. \qquad (19)$$

The effect of applying symmetry and equivalence restrictions is to cause certain integrals, matrix elements needed in a calculation of correlation effects, to be nonzero, when these integrals would vanish in the unrestricted method. These matrix elements involve exchange integrals arising only from orbitals outside of closed shells, and they can be expressed by very simple formulas when the equations satisfied by the orbitals [Eqs. (16)] are taken into account.[2] Similar nonvanishing matrix elements occur in the traditional Hartree-Fock method except for closed-shell systems.

III. UNRESTRICTED HARTREE-FOCK METHOD

In the unrestricted Hartree-Fock method the mean value of the many-particle Hamiltonian, calculated for a single normalized Slater determinant, is made stationary subject to no constraint other than normalization. In a certain sense, this particular Slater determinant is as close an approximation as is possible to a wave function which can be thought of intuitively to describe a collection of independent particles interacting through a common average potential. Any improvement to the unrestricted Hartree-Fock function must necessarily be described in terms of the wave interference characteristic to quantum mechanics, since the improved wave function can be represented at best by a linear combination of Slater determinants.

In the open-shell case the unrestricted Hartree-Fock determinant in general belongs to a degenerate set of functions. By applying some of the results of elementary group representation theory, this situation can be discussed in some detail.[2,7] The principal theoretical result is that the orbitals of an open shell unrestricted Hartree-Fock determinant must show some distortion from the degree of symmetry used to describe a closed shell function. This implies that operations in the group of symmetry transformations under which the many-particle Hamiltonian is invariant generate a set of degenerate functions from any open-shell unrestricted Hartree-Fock determinant.

Since this degeneracy cannot be resolved except by constructing linear combinations of determinantal functions, the resultant splitting of the unrestricted Hartree-Fock energy into a set of related levels is properly a correlation or collective phenomenon, and cannot be described in the language of an independent particle

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[7] R. K. Nesbet, Phys. Rev. 109, 1017 (1958).

model. This distinction should be kept in mind in attempting to develop an intuitive understanding of the properties of many-particle systems. The traditional Hartree-Fock approach to open-shell systems resolves this degeneracy from the outset. Only in special cases (when the trial function is actually a single Slater determinant) is there a one-to-one correspondence between particles and orbitals. Without this correspondence intuitive notions of independent particles are not completely adequate to describe the many-particle wave function.

Another property of a single Slater determinant that is not shared by linear combinations of such functions is that the occupied orbitals of a single determinant can be subjected to any unitary transformation, without altering the many-particle wave function except by a phase constant.[8] This freedom of representation can be used to minimize the purely quantum mechanical wave interference effects remaining in the independent particle model.[9] For if a transformation is chosen which localizes these orbitals as much as possible, then the classical concept of nonpenetrating independent particles can be used insofar as it is possible to neglect wave interference for the localized orbitals. Orbitals with different internal quantum numbers, such as spin or isotopic spin, can overlap freely, but there is no interference (as a wave phenomenon) and the particles are simply superimposed.

Thus in the unrestricted Hartree-Fock approximation one can recover, even for strongly interacting quantum mechanical particles, as much as is possible of the intuitive picture of nonpenetrating interacting independent classical particles. This has led to the successful parametrization of energy levels in molecules in terms primarily of geometrical concepts of paired electron bonds and directed lone pairs,[10] and appears to give a valid intuitive description of nuclear matter in terms of localized orbitals occupied by four particles (alpha particles) or by two (neutron pairs).[11]

The usefulness of this intuitive picture depends on the relative importance of correlation and collective motion, not describable in the Hartree-Fock approximation. But the unrestricted Hartree-Fock wave function, particularly when expressed in terms of localized orbitals, provides a simple basis for consideration of these effects.

This follows from the structure of Schrödinger's equation, and from the consequences of a theorem first stated by Brillouin,[1,2] which applies to an unrestricted Hartree-Fock wave function. Brillouin's theorem, Eq. (4), states that an unrestricted Hartree-Fock determinant Φ_0 has no matrix elements over the many-particle

Hamiltonian with any other determinant $\Phi_i{}^a$ which differs from Φ_0 by the occupied Hartree-Fock orbital ϕ_i being replaced by any orbital ϕ_a orthogonal to all occupied Hartree-Fock orbitals. Since a Hamiltonian made up only of one- and two-particle operators has no matrix elements between determinants that differ by three or more orbitals (assumed to be an orthonormal set),[12] the only matrix elements $(0|H|\nu)$ for a complete set of Slater determinants $\{\Phi_\nu\}$ which includes the Hartree-Fock determinant Φ_0 is, except for $(0|H|0)$, of the form $(0|H|_{ij}{}^{ab})$. Here $\Phi_{ij}{}^{ab}$ is a Slater determinant obtained from Φ_0 by replacing any two occupied orbitals ϕ_i and ϕ_j by orbitals ϕ_a and ϕ_b, which are assumed to be orthogonal to all orbitals occupied in Φ_0.

An exact many-particle wave function can be expressed as a linear combination of determinants from the complete set $\{\Phi_\nu\}$ in the form $\Psi=\sum_\nu c_\nu\Phi_\nu$. The matrix representation of Schrödinger's equation implies that

$$\{(0|H|0)-E\}c_0+\sum_{\nu\neq0}{}'(0|H|\nu)c_\nu=0, \qquad (20)$$

or with c_0 set equal to unity (it is assumed that c_0 does not vanish),

$$E=(0|H|0)+\sum_\nu{}'(0|H|\nu)c_\nu. \qquad (21)$$

Hence by Brillouin's theorem

$$E=(0|H|0)+\sum_{ij}\sum_{ab}(0|H|_{ij}{}^{ab})c_{ij}{}^{ab}. \qquad (22)$$

Equation (22) is exact, with no reference to perturbation theory. Hence the energy depends formally only on the Hartree-Fock energy $(0|H|0)$, the two-particle matrix elements $(0|H|_{ij}{}^{ab})$, and the coefficients $c_{ij}{}^{ab}$ of the corresponding Slater determinants in the true steady-state wave function Ψ. If the individual matrix elements $(0|H|_{ij}{}^{ab})$ are small, and if the series converges reasonably rapidly, then a fairly large relative error in estimating the coefficients $c_{ij}{}^{ab}$ can have only a small effect on the total energy E. But the matrix elements are given by[12]

$$(0|H|_{ij}{}^{ab})=(ij|Q|ab)-(ij|Q|ba), \qquad (23)$$

where $Q(1,2)$ is the two-particle operator in the many-particle Hamiltonian, Eq. (1), and all four orbitals ϕ_i, ϕ_j, ϕ_a, ϕ_b are mutually orthogonal. Such integrals diminish rapidly with distance for localized orbitals, for any reasonable operator $Q(1,2)$, and are generally much smaller than the individual integrals in $(0|H|0)$, which are diagonal matrix elements of the one-particle operator K, or are integrals over Q with orbitals identical in pairs.

So long as the perturbation theory gives a useful estimate of the coefficients $c_{ij}{}^{ab}$ [which is all that is needed when the matrix elements $(0|H|_{ij}{}^{ab})$ are small], the coefficients are approximated by ratios of these matrix

[8] J. E. Lennard-Jones, Proc. Roy. Soc. (London) **A198**, 1, 14 (1949).
[9] J. E. Lennard-Jones and J. A. Pople, Proc. Roy. Soc. (London) **A202**, 166 (1950).
[10] J. A. Pople, Proc. Roy. Soc. (London) **A202**, 323 (1950); G. G. Hall and J. E. Lennard-Jones, *ibid.* **A205**, 357 (1951); J. E. Lennard-Jones, J. Chem. Phys. **20**, 1024 (1952).
[11] R. K. Nesbet, Phys. Rev. **100**, 228 (1955).

[12] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1951), pp. 169–174.

elements to the excitation energies of the determinants $\Phi_{ij}{}^{ab}$. For localized orbitals, these denominators are particularly large when the numerators are largest, i.e., when orbitals ϕ_a and ϕ_b are localized in the same region as ϕ_i and ϕ_j. In such a case the spatial functions in orbitals ϕ_a and ϕ_b must have extra nodes in the region of localization, causing a large difference in kinetic energies to appear in the denominator of the perturbation formula. If the spatial functions of ϕ_a, ϕ_b were identical with those of ϕ_i, ϕ_j then $\Phi_{ij}{}^{ab}$ would be degenerate with Φ_0, and would be taken into account in removing the degeneracy of the unrestricted Hartree-Fock wave function.

Thus one can argue qualitatively from the structure of the formulas that it should be possible to describe the correlation energy even for strongly interacting particles in terms of relatively small corrections to the Hartree-Fock energy. When expressed in a basis of localized orbitals the correlation energy would be expected to show pronounced geometrical properties, i.e., it should be most important for pairs of localized Hartree-Fock orbitals which have nearly identical spatial functions but differ in internal coordinates (spin or isotopic spin), and should diminish very rapidly (even for the Coulomb potential) with distance between localized orbitals. Thus energy effects due to correlation should be expressible primarily as corrections to the parameters in the unrestricted Hartree-Fock theory which describe the energy of localized clusters of particles, made up of orbitals that are spatially nearly identical but have different spin or isotopic spin. This argument can account for the usefulness of the α-particle model in parametrizing total nuclear energies[11,13] and of the model of paired electron bonds in describing many properties of molecules.[14]

Resolution of the degeneracy in the unrestricted Hartree-Fock approximation must lead to a set of closely related energy levels. In recent work on collective motion in nuclei[15] it has been shown that the resolution of a degeneracy of this kind, in the case of large distortion from a spherically symmetrical wave function, gives the energy level spectrum characteristic of collective rotation. The axial symmetry assumed in this work has been shown to be consistent with the unrestricted Hartree-Fock approximation.[7]

Since total energies of the ground states of light even-even nuclei follow a pattern that allows parametrization in terms of localized orbitals, expressed by the very crude model of a cluster of α-particles and neutron pairs,[11] one might expect the unrestricted Hartree-Fock functions for these nuclei to exhibit a similar geometrical structure. If this were true, resolution of the degeneracy in the unrestricted Hartree-Fock approximation could

be carried out by projecting these functions of definite geometrical shape onto eigenfunctions of total angular momentum. This amounts to expressing the Hartree-Fock determinant Φ_0 as a linear combination of functions of definite angular momentum, then evaluating the mean value of energy for each component. This procedure would lead to a set of states related to the rigid rotator states postulated in the α-particle model.[16] Since this would be a case of small distortion from spherical shape, rather than large distortion, as postulated in the work of Peierls and Yoccoz,[15] the appearance of the level spacing characteristic of a rotational spectrum has not been accounted for.

If a projection operator is used to resolve the degeneracy of the unrestricted Hartree-Fock function Φ_0 the resulting energy levels are given by an expression of the same form as Eq. (22), even though the resulting wave functions, projections of Φ_0, are not exact eigenfunctions of the Hamiltonian.[17,18] Because of this, only those matrix elements of the projection operator that connect Φ_0 with determinants $\Phi_{ij}{}^{ab}$, in a basis of orthonormal Slater determinants, will appear in the expressions for energies of states projected from Φ_0. Löwdin[17] has shown that these matrix elements, proportional to the coefficients $c_{ij}{}^{ab}$ in Eq. (22), in the case of electron spin depend on total angular momentum S through a term proportional to $S(S+1)$, characteristic of rotational spectra. This fact has been used to discuss the collective phenomena of ferromagnetism and antiferromagnetism.[19] Peierls and Yoccoz[15] showed that a coefficient of the form $L(L+1)$ arises as the first term in matrix elements of the orbital angular momentum projection operator, if a small-angle expansion can be justified.

There is nothing in the Hartree-Fock theory to prevent the unrestricted Hartree-Fock function from exhibiting *lower* symmetry than that of the many-particle Hamiltonian. In fact this must certainly occur for the electronic wave function of two hydrogen atoms at large internuclear distances, as has been shown in calculations by Coulson and Fischer.[20] The usual shell-model ground-state wave function for the O^{16} nucleus could be continuously perturbed into a tetrahedral structure by mixing d orbitals with the occupied p orbitals, and f orbitals with the s orbitals, since linear combinations of these orbitals belong, respectively, to the same irreducible representations of the tetrahedral group.[6]

An important special case arises when there are internal variables (spin or isotopic spin), which do not appear explicitly in the Hamiltonian. In a nonrelativistic electronic calculation, orbitals with positive and negative spin (i.e., $m_s = \pm\frac{1}{2}$, respectively) satisfy different

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This is true because relatively rapid techniques are available for the solution of homogeneous linear eigenvalue equations, and these techniques cannot be used if off-diagonal Lagrange multipliers occur or if the equations are not homogeneous. This has made it possible to construct digital computer programs which carry out approximate Hartree-Fock calculations by matrix methods, using the method of symmetry and equivalence restrictions.[24] These programs are applicable to any open-shell or closed-shell system.

Various calculations on open-shell systems (atomic and molecular electronic wave functions) have been carried out with these programs,[25] although the most extensive of these, calculations on the transition metal atoms by Watson,[26] have not yet been published.

It has been shown in Sec. II that in many cases of physical interest, in addition to the closed-shell case, the method of symmetry and equivalence restrictions can be made identical with the traditional Hartree-Fock method. These cases include, for example, atomic configurations $(2p)^n$ and $(3d)^n$. There are very few Hartree-Fock calculations by the traditional method, with numerical solution of the integro-differential equations, for cases in which the methods are not identical.[26] In general, for atomic wave functions, the difference between the two methods appears to result in an error in the total energy which is comparable to the inherent truncation error in the traditional calculations due to the use of numerical integration.

The method of symmetry and equivalence restrictions is applied always to a single Slater determinant, so degeneracies must be resolved after the Hartree-Fock calculation (as in the unrestricted method), not before (as in the traditional method). If degeneracies are resolved by the use of projection operators,[17] an expression of the same form as Eq. (21) is obtained for the energy. In this expression the Hartree-Fock energy is the leading term, with corrections which for atoms are exchange integrals over higher multipole charge distributions, i.e., quantities of the magnitude of term intervals within a given electronic configuration. If these corrections are small in comparison with the total energy, the effects of altering the sequence of the Hartree-Fock variational calculation and the resolution of degeneracies should be relatively small.

In open-shell cases, the restricted Hartree-Fock equations, Eqs. (16), depend on the second index μ which specifies transformation properties of the orbitals. Choice of a particular value of μ, or averaging over a set of values of μ introduces an element of choice into the

method. Unless the number of particles is very small, most of the terms in the one-particle Hamiltonian, either in the atomic or nuclear shell model case, arise from closed shells, and are independent of the second index μ.[2] The terms which depend on μ are exchange integrals from the unfilled shells only.

The total energy in an unrestricted Hartree-Fock calculation is always given by the identity, Eq. (19),

$$(0|H|0)=\tfrac{1}{2}\sum_i [(i|K|i)+(i|\mathcal{3C}_0|i)].$$

Here K is the one-particle operator that occurs in the many-particle Hamiltonian, Eq. (1), and $\mathcal{3C}_0$ is the effective one-particle Hamiltonian, Eq. (5). Since in the open shell case matrix elements of $\mathcal{3C}_0$ depend on the index μ, ordinarily certain two-particle exchange integrals must be calculated to obtain the total energy in the method of symmetry and equivalence restrictions. These exchange integrals are differences in diagonal matrix elements of $\mathcal{3C}_0$ for orbitals that are the same except for the index μ.

When there is only one shell of orbitals belonging to a particular irreducible representation λ and all other shells are closed, or when all shells of orbitals belonging to λ are occupied in the same way, then the total energy is given simply by Eq. (18) if the effective operator $[\mathcal{3C}_0]_{\lambda\mu}$ of Eqs. (16) is averaged over the occupied values of μ for each λ. This fact was used by Watson[26] and by Allen[25] to calculate total energies in atomic open-shell configurations. By Eq. (14) this choice of average over μ in the restricted Hartree-Fock equations leads to a calculation equivalent to the traditional method.

VI. GENERALIZATIONS

This paper has been concerned with Hartree-Fock variational calculations which determine a basis of orbitals before the calculation of correlation effects in solving the many-particle Schrödinger equation. In the unrestricted case, this variational calculation is carried out before the resolution of degeneracies (described physically in terms of collective phenomena). Various generalizations of the Hartree-Fock method have been proposed which are distinguished by the sequence in which these stages of calculation are carried out.

Löwdin[17] has proposed that a variational calculation to determine orbitals of unrestricted form be performed after the resolution of degeneracies. Here the difficulty in carrying out this resolution with unrestricted orbitals, even with the aid of projection operators, would have to be faced before the variational calculation, which is expressed in equations much more complicated than the unrestricted Hartree-Fock equations. This approach has been applied only to two-electron systems,[27] for which it is equivalent to including the first term of the correlation energy in the variational calculation.[20,28]

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Part of the correlation energy in Eq. (22) can be in-
cluded in the total energy before the variational calcula-
tion by several methods. If expressed in terms of
localized orbitals, the correlation energy for each local-
ized pair (in the electronic case) can be included by the
method of Hurley, Lennard-Jones, and Pople.[29] Actual
calculations by this method would be very difficult and
have not been carried out.

It would be possible formally to include all of the
correlation energy in the Hartree-Fock total energy by
modifying the two-particle operator so that its matrix
elements which occur in the Hartree-Fock energy
$(0|H|0)$ would also include all of the correlation terms
of Eq. (22). The method proposed by Brueckner[30] would
select certain terms from the perturbation expansion of
the coefficients $c_{ij}{}^{ab}$ of Eq. (22) and include the corre-
sponding correlation terms in a modified two-particle
operator, by iterated Hartree-Fock calculations. De-
spite the great practical difficulty of this procedure for a
finite system, it leads to a tractable integral equation in
the case of an infinite uniform system, since the Hartree-
Fock orbitals are determined by symmetry to be plane
waves. In terms of this equation one can deal directly
with a highly singular two-particle potential (such as the
extended hard-core potential in the nuclear Hamil-
tonian), which would cause the Hartree-Fock energy for
a finite system to be infinite.

In Brueckner's method it is difficult to evaluate the
importance of the terms neglected in the perturbation
series. Moreover, for a finite system, there are terms
involving the one-particle operator that are not taken
into account in the formalism.[31] It is also difficult to
assess the approximations involved in using the modified
two-particle operator obtained in calculations on infinite
uniform nuclear matter for calculations on finite nuclei,
as has recently been proposed.[32]

For these reasons it would be desirable to carry out
Hartree-Fock calculations on finite nuclei with an
unmodified two-particle operator, to compare with the
Brueckner method, and to examine the convergence of
the series of correlation terms in Eq. (22). If this series
converged reasonably rapidly, such calculations might
be more reliable than the more elaborate Brueckner
calculations. Such a calculation would require that the
two-particle operator obtained from nuclear scattering
data be parametrized in terms of a functional form
which is not infinite over a finite volume, so that

integrals occurring in the Hartree-Fock energy could all
be finite. This requires a representation of the short-
range repulsion different from that given by the one-
parameter infinite hard core.

Given a Hamiltonian which leads to finite matrix
elements for a finite system, it would probably be de-
sirable in most many-particle problems to carry out
calculations by the methods discussed in the body of
this paper before attempting the considerably more
difficult methods discussed previously, which have been
proposed as generalizations. Even the unrestricted
Hartree-Fock method is unnecessarily difficult in cases
where the effects of distortion of orbitals can be treated
adequately by perturbation theory.

The simplest procedure which is generally applicable
to *ab initio* calculations is to obtain approximate
Hartree-Fock orbitals by the method of symmetry and
equivalence restrictions, resolve degeneracies by the
formal use of projection operators,[17,18] and use perturba-
tion theory to evaluate the effects of correlation. A more
complicated procedure would be indicated if the per-
turbation theory failed to converge sufficiently rapidly.
Few *ab initio* calculations exist that include an adequate
treatment of correlation by methods applicable to
general systems, but the results of Boys and his col-
laborators[33] and other recent calculations[34] suggest that
the procedure recommended here may be adequate for
atomic and molecular electronic wave functions, unless
total energies must be calculated to relativistic ac-
curacy.

A modified Hartree-Fock method which has many of
the advantages of the method of symmetry and equiva-
lence restrictions has recently been proposed by
Roothaan.[35] The calculations in Roothaan's method are
somewhat more complicated but the method is identical
with the traditional Hartree-Fock method in a larger
class of cases than is the method of symmetry and
equivalence restrictions. Preliminary calculations on the
electronic ground state of Li give an energy difference
between the two methods that is very small in compari-
son with the correlation energy, which is of course
neglected in all Hartree-Fock calculations. Details of
these calculations will be published in a separate
paper.[36]

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