Variational Principle and Slater's Generalized Hartree-Fock Theory for Nuclei

Donald H. Kobe

Department of Physics, North Texas State University, Denton, Texas 76203

The Hartree-Fock (HF) equations are generalized to take correlation into account, without replacing the exchange potential by a local approximation as Slater originally did. The nonlocal generalized HF equations are then obtained from a variational principle, that an energy functional be stationary at the true ground-state energy with respect to variations of the orbitals from orthogonality. The single-particle Hamiltonian is Hermitian, and there are no off-diagonal Lagrangian multipliers, in contrast to the multiconfiguration variational approaches. The best local approximation to the nonlocal equation gives essentially Slater's original equation, in which the average potential due to the other particles is given in terms of an integral over the product of the two-body potential and the true pair correlation function divided by the local density.

I. INTRODUCTION

SHORTLY after Hartree[1] on intuitive grounds proposed his famous self-consistent equations, they were derived from the Rayleigh-Ritz energy variational principle by Fock[2] and Slater.[3] An exchange term in the self-consistent potential was shown to be necessary because the particles were fermions. The Hartree-Fock (HF) equations remain the paradigm of the independent-particle model and the foundation of atomic structure.

In nuclear physics the time-independent HF equations have had only limited success, in spite of the existence of shell structure in nuclei. The primary reason why the HF equations have not provided a theoretical justification for the phenomenological nuclear-shell model is that most realistic velocity-independent nucleon-nucleon potentials[4] contain a repulsive hard core which gives an infinite self-consistent potential in the HF equations. Recently, some progress has been made in fitting soft-core potentials[5] and velocity-dependent potentials[6] to the two-nucleon scattering data. With these potentials the HF equations can then be used to obtain a theoretical basis for shell structure in nuclei.[7]

There have been numerous attempts to generalize the HF equations to take correlations into account.[8]

The usual justification for the nuclear shell model is based on the Brueckner reaction-operator theory.[9] The argument is made that the HF equations should be solved with the two-body reaction operator instead of the two-body potential.[10] The reaction operator is finite and describes an "effective interaction" between nucleons. In spite of the hard-core two-body potential, the average effective interaction that a nucleon experiences is thus a "smooth" function. The reaction operator is calculated from the Lippmann-Schwinger equation, which must be solved self-consistently with the modified HF equations. The complication introduced by the additional self-consistency requirement is considerable, and this program has not yet been completely carried through.[11] There is little doubt of the general correctness of this procedure, but the underlying variational principle on which it is based has been clouded with confusion.[12]

An alternative suggestion for determining the shell-model potential is given by Migdal[13] on the basis of a Green's-function theory for determining the natural orbitals. He proposes that the frequency-dependent self-energy be used as the effective potential. Then

[1] D. R. Hartree, Proc. Cambridge Phil. Soc. 24, 89 (1928).

[2] V. Fock, Z. Physik 61, 126 (1930).

[3] J. C. Slater, Phys. Rev. 35, 210 (1930).

[4] T. Hamada and I. D. Johnston, Nucl. Phys. 34, 382 (1962); K. E. Lassila, M. H. Hull, Jr., H. M. Rappel, F. A. McDonald, and G. Breit, Phys. Rev. 126, 881 (1962).

[5] E. Rochleder and K. Erkelenz, Phys. Rev. 172, 1013 (1968); G. Saunier and J. M. Pearson, ibid. 160, 740 (1967).

[6] F. Tabakin, Ann. Phys. (N.Y.) 30, 51 (1964).

[7] R. Muthukrishnan and M. Baranger, Phys. Letters 18, 160 (1965); K. T. R. Davies, S. J. Krieger, and M. Baranger, Nucl. Phys. 84, 545 (1966); A. K. Kerman, J. P. Svenne, and F. M. H. Villars, Phys. Rev. 147, 710 (1966); W. H. Bassichis, A. K. Kerman, and J. P. Svenne, ibid. 160, 746 (1967).

[8] For electronic systems see, e.g., W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965); L. J. Sham and W. Kohn, ibid. 145, 561 (1966); B. Y. Tong and L. J. Sham, ibid. 144, 1 (1966); J. E. Robinson, F. Bassani, R. S. Knox, and J. R. Schrieffer, Phys. Rev. Letters 9, 215 (1962); S. Olszewski, Phys. Rev. 121, 42 (1961); S. Lundqvist and C. W. Ufford, ibid. 139, A1 (1965).

[9] K. A. Brueckner and J. L. Gammel, Phys. Rev. 109, 1023 (1958); H. A. Bethe, ibid. 103, 1353 (1956).

[10] K. A. Brueckner, J. L. Gammel, and H. Weitzner, Phys. Rev. 110, 431 (1958); K. A. Brueckner, A. M. Lockett, and M. Rotenberg, ibid. 121, 255 (1961); B. H. Brandow, ibid. 152, 863 (1966); M. W. Kirson, Nucl. Phys. A115, 49 (1968); B. H. Brandow, in *Lectures in Theoretical Physics*, edited by K. T. Mahanthappa (Gordon and Breach, Science Publishers, Inc., New York, to be published), Vol. XI.

[11] M. K. Pal and A. P. Stamp, Phys. Rev. 158, 924 (1967); T. T. S. Kuo and G. E. Brown, Nucl. Phys. 85, 40 (1966).

[12] Some previous energy variational attempts are H. S. Köhler, Nucl. Phys. 38, 661 (1962); K. A. Brueckner and D. T. Goldman, Phys. Rev. 116, 424 (1959); B. H. Brandow, Phys. Letters 4, 8 (1963); 4, 152 (1963). For a critique of these methods and a discussion of the shell-model potentials see B. H. Brandow, Rev. Mod. Phys. 39, 771 (1967), Sec. X. For a discussion of a mass-operator variational principle, see B. H. Brandow, Ref. 10. An alternative to energy variational methods has been given by W. Brenig, Nucl. Phys. 4, 363 (1957). See also, P.-O. Löwdin, J. Math. Phys. 3, 1171 (1962).

[13] A. B. Migdal, Nucl. Phys. 57, 29 (1964); A. B. Migdal and A. I. Larkin, ibid. 51, 561 (1964); A. B. Migdal, *Theory of Finite Fermi Systems and Applications to Atomic Nuclei* (Wiley-Interscience, Inc., New York, 1967).

the eigenvalue problem is to be solved for frequency-dependent orbitals, which are not the natural orbitals, and energies. The frequency dependence is removed by making a "pole" approximation. However, the resulting orbitals are no longer orthogonal, as they were originally assumed to be, and their connection with the natural orbitals is obscure.

A unitary-operator method[14] has also been proposed as a justification for the shell model. This model does give a procedure for obtaining an effective two-body potential from the true one, but in the process, three-body and higher effective interactions are also created. These latter terms must be shown to be small. The effective interaction is used in a HF calculation,[15] but it is not clear what the underlying variation principle is. A similar approach has been used by Coester and Kümmel.[16] Clark and Westhaus[17] have been investigating the method of correlated basis functions.

An earlier attempt to take correlations into account in HF theory was made by Slater in 1953.[18] He had previously noticed that the nonlocal exchange potential could be simplified by replacing it with an average local one.[19] In the local HF equation, the self-consistent potential is calculated from the pair correlation function obtained from a Slater determinant. If strong correlations are present, he argued that this pair correlation function should be replaced by the true one. Slater's generalized HF theory is thus applicable to hard-core potentials, since the true pair correlation function vanishes inside the hard core. The average potential felt by a nucleon is consequently finite and smooth. The local approximation to the exchange potential is not necessary to Slater's argument, and the full HF equations can also be generalized in the same way.

Slater's generalized HF equations were thus proposed on intuitive grounds, and Slater himself said that they could probably not be obtained from an energy variational principle. However, two years later Löwdin,[20] following an early suggestion by Frenkel,[21] used a finite superposition of configurations for the trial wave function in the Rayleigh-Ritz principle to obtain a set of nonlocal orbital equations with a non-Hermitian single-particle Hamiltonian. The best local approximation was only Slater's generalized HF theory[18] with an approximate pair correlation function. In the limit as the number of configurations increased to infinity, his pair correlation function approached the true one. However, the variational principle broke down in this limit because the true ground-state energy cannot be varied. In the orbital equations the number of Lagrangian multipliers approached infinity in this limit, and thus no constraint was placed on the orbitals. The same approach was used by McWeeny,[22] and more recently by Adams.[23] Similar methods have been used by other authors.[24]

In this paper another type of variational principle is used to obtain a set of nonlocal orbital equations, to which the best local approximation is Slater's generalized HF theory.[18] An energy functional of a complete set of orbitals, which gives the true ground-state energy when the orbitals become orthonormal, is used. The orbitals for which this functional is stationary with respect to variations from orthogonality are shown to satisfy the nonlocal generalized HF equations. A calculation of the ground-state energy is thus insensitive to rounding-off errors which cause the orbitals to deviate from orthogonality. The single-particle Hamiltonian in this theory is automatically Hermitian, so that the orbital energies are real. There is no arbitrariness in the orbitals due to nondiagonal Lagrangian multipliers, in contrast to previous theories.[20,22,23]

In Sec. II, the HF equations are generalized without first making a local approximation. In Sec. III the variational principle is developed. The variation is performed in Sec. IV to give the eigenvalue problem for the nonlocal generalized HF orbitals and energies. The best local approximation to the nonlocal operators is made in Sec. V to obtain Slater's original generalized HF theory. Finally, the conclusion discusses various aspects of the variational principle, applicability of the theory, and a justification of the nuclear shell model.

II. NONLOCAL GENERALIZED HF EQUATIONS

The generalization of the HF equations was originally made by Slater[18] after making a local approximation for the exchange potential.[19] The local approximation is not at all necessary, and the original HF equations can be generalized in the same intuitive way as Slater used. The best local approximation to

[14] F. Villars, in *Proceedings of the International School of Physics*, *"Enrico Fermi," Course 23, 1961* (Academic Press Inc., New York, 1963); J. S. Bell, in *The Many-Body Problem*, edited by C. Fronsdal (W. A. Benjamin, Inc., New York, 1962), p. 214 ff; J. Da Providencia and C. M. Shakin, Ann. Phys. (N. Y.) **30**, 95 (1964); C. M. Shakin, Y. R. Waghmere, and M. H. Hull, Jr., Phys. Rev. **161**, 1006 (1967).
[15] C. M. Shakin, Y. R. Waghmere, M. Tomaselli, and M. H. Hull, Jr., Phys. Rev. **161**, 1015 (1967).
[16] F. Coester, Nucl. Phys. **7**, 421 (1958); F. Coester and H. Kümmel, *ibid.* **17**, 477 (1960); H. Kümmel, in *Lectures on the Many-Body Problem*, edited by E. R. Caianiello (Academic Press Inc., New York, 1962), p. 265 ff; F. Coester, in *Lectures in Theoretical Physics*, edited by K. T. Mahanthappa (Gordon and Breach, Science Publishers, Inc., New York, to be published), Vol. XI.
[17] J. W. Clark and P. Westhaus, Phys. Rev. **141**, 833 (1966).
[18] J. C. Slater, Phys. Rev. **91**, 528 (1953).
[19] J. C. Slater, Phys. Rev. **81**, 385 (1951).
[20] P.-O. Löwdin, Phys. Rev. **97**, 1474 (1955).
[21] J. Frenkel, *Wave Mechanics, Advanced General Theory* (Clarendon Press, Oxford, England, 1934), pp. 460–462.

[22] R. McWeeny, Proc. Roy. Soc. (London) **A232**, 114 (1955).
[23] W. H. Adams, Phys. Rev. **156**, 109 (1967).
[24] T. L. Gilbert, J. Chem. Phys. **43**, S248 (1965); A. P. Yutsis, Zh. Eksperim. i Teor. Fiz. **23**, 129 (1952); A. P. Yutsis, Ya. I. Vizbaraite, T. D. Strotskite, and A. A. Bandzaites, Opt. i Spectroskopiya **12**, 157 (1962) [English transl.: Opt. Spectry. (USSR) **12**, 83 (1962)].

the nonlocal generalized equations is then essentially Slater's generalized theory. The method used by Slater to take correlation into account is to replace the pair correlation function calculated from a Slater determinant by the true one. In the nonlocal equations, the determinantal one- and two-particle density matrices are replaced by the true ones.

Because of the presence of exchange forces in the nucleon-nucleon potential, the HF equations are given here in terms of a general nonlocal two-body interaction $v(x, y; y', x')$, where each coordinate is position, spin, and isospin. If the operator T is the sum of the kinetic-energy operator K and an external potential U, the HF equation for the spin orbital $\phi_\nu(x)$ with orbital energy ϵ_ν is[25]

$$T(x)\phi_\nu(x) + \iiint dy dz dw [v(x, z; w, y) - v(x, z; y, w)]$$
$$\times \rho_0(z, w)\phi_\nu(y) = \epsilon_\nu \phi_\nu(x), \quad (2.1)$$

when the Lagrangian multipliers are put in diagonal form. The Fock-Dirac density matrix is defined as

$$\rho_0(x_0 \, y) = \langle \Phi_0 | \psi^\dagger(x)\psi(y) | \Phi_0 \rangle = \sum_i \phi_i{}^*(x)\phi_i(y), \quad (2.2)$$

where the sum is only over $i \in$ FS, the HF Fermi sea (FS) of occupied states, which are those present in the ground-state Slater determinant Φ_0.

The density matrix in Eq. (2.2) is expressed in second-quantized notation in terms of the field creation operator $\psi^\dagger(x)$ and annihilation operator $\psi(y)$ which satisfy the usual fermion anticommutation relations.[26] The integral in Eq. (2.1) includes a sum over spin and isospin as well as the spatial integral.

Equation (2.1) may be rewritten in a more compact form for $\nu \in$ FS as

$$\int dy \, g_0(x, y)\phi_\nu(y) = \epsilon_\nu \phi_\nu(x). \quad (2.3)$$

The HF single-particle Hamiltonian is

$$g_0(x, y) = T(x)\rho_0(y, x) + \iiint dudwdz \, v(x, z; w, u)$$
$$\times \langle \Phi_0 | \psi^\dagger(y)\psi^\dagger(z)\psi(w)\psi(u) | \Phi_0 \rangle, \quad (2.4)$$

where Φ_0 is the ground-state Slater determinant. Equations (2.3) and (2.4) reduce exactly to Eq. (2.1) if use is made of the well-known factorization of the determinantal two-particle density matrix in terms of products of two Fock-Dirac density matrices.[27]

Slater's method for generalizing the HF equations to take correlation into account can be used directly on Eqs. (2.3) and (2.4) without first making a local approximation for g_0. The determinantal one- and two-particle density matrices in Eq. (2.4) are replaced by

the true ones, so that Eq. (2.3) becomes

$$\int dy \, g(x, y)\phi_\nu(y) = \epsilon_\nu \phi_\nu(x) \quad (2.5)$$

for all ν. The nonlocal single-particle Hamiltonian g is of the same form as g_0,

$$g(x, y) = T(x)\rho(y, x) + \iiint dudwdz \, v(x, z; w, u)$$
$$\times \langle \Psi | \psi^\dagger(y)\psi^\dagger(z)\psi(w)\psi(u) | \Psi \rangle, \quad (2.6)$$

but Φ_0 has been replaced everywhere by Ψ, the normalized true ground-state wave function. The true one-particle density matrix is $\rho(x, y)$. Since the equations now involve the true wave function Ψ, it is clear why Slater[18] was skeptical that this procedure could ever be justified by a variational principle. Using a multiconfiguration trial wave function instead of Ψ, Löwdin[20] and McWeeny[22] obtained equations similar to Eqs. (2.5) and (2.6) from the Rayleigh-Ritz variational principle. However, in their theory Ψ is replaced by the trial function, and nondiagonal Lagrangian multipliers appear. In the limit as the number of configurations approaches infinity, their trial wave function approaches the true one. There is thus nothing left to vary, and the variational principle collapses. In their orbital equations, the number of Lagrangian multipliers approaches infinity, and the equations provide no restriction on the orbitals. Of course, the Lagrangian multipliers can be arbitrarily put in diagonal form, and Eqs. (2.5) and (2.6) are formally obtained. This procedure is followed by Adams.[23]

There is a serious criticism to the single-particle Hamiltonian in Eq. (2.6)—it is not Hermitian. The eigenvalues in Eq. (2.5) can therefore be complex. One point of view is that this is the price which must be paid for building correlation into the theory. The resulting complications are accepted and a physical interpretation is attempted.[28] On the other hand, it can be argued that the anti-Hermitian part of the single-particle Hamiltonian in Eq. (2.6) should be discarded because excitation energies should be real. Then Eq. (2.5) is replaced by

$$\int dy \, h(x, y)\phi_\nu(y) = \epsilon_\nu \phi_\nu(x). \quad (2.7)$$

The Hermitian single-particle Hamiltonian,

$$h(x, y) = \tfrac{1}{2}[g(x, y) + g^*(y, x)], \quad (2.8)$$

is just the Hermitian part of Eq. (2.6).

In the absence of any variational principle, either approach is valid. The multiconfiguration variational principle would suggest the former, but it breaks down for an infinite number of configurations. Ease of physical interpretation would favor the latter, Hermitian, approach. It is shown in Sec. IV that the variational principle developed in Sec. III gives only Eqs. (2.7) and (2.8).

[25] See, e.g., J. G. Valatin, in *Lectures in Theoretical Physics*, edited by W. E. Brittin, B. W. Downs, and J. Downs (Wiley-Interscience, Inc., New York, 1962), Vol. IV, p. 15. Some slight changes in notation for v and ρ_0 have been made here.

[26] For a discussion of second quantization, see, e.g., D. H. Kobe, Am. J. Phys. **34**, 1150 (1966).

[27] Reference 25, p. 10.

[28] For nuclear matter this point of view is adopted by D. J. Thouless, Phys. Rev. **114**, 1383 (1959).

III. VARIATIONAL PRINCIPLE

In this section, a variational principle different from the traditional Rayleigh-Ritz energy variational principle is developed. Instead of using a trial wave function which is varied, this variational principle focuses attention on the matrix expression for the true ground-state energy. This expression is made stationary with respect to variations of the complete set of orbitals from orthogonality. For the orbitals satisfying this variational principle, first-order variations from orthogonality cause, at most, a second-order variation from the true ground-state energy.

The true ground-state energy E_0 of the system of fermions considered in Sec. II is

$$E_0 = \int dx \, \langle \Psi \,|\, \psi^\dagger(x) T(x) \psi(x) \,|\, \Psi \rangle$$
$$+ \tfrac{1}{2} \int\int dx\,dy\,dx'\,dy' \, v(x, y; \, y', \, x')$$
$$\times \langle \Psi \,|\, \psi^\dagger(x)\psi^\dagger(y)\psi(y')\psi(x') \,|\, \Psi \rangle. \quad (3.1)$$

This energy can be expressed in matrix form if any complete set of orthonormal functions is used. If the set is complete, but not orthonormal, the same matrix expression may be used to define a functional of the orbitals. Thus, the energy functional

$$E[\phi] = \sum_{\alpha,\beta} \langle \phi_\alpha \,|\, T \,|\, \phi_\beta \rangle \langle \Psi \,|\, a^\dagger(\phi_\alpha) a^\dagger(\phi_\beta) \,|\, \Psi \rangle$$
$$+ \tfrac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} \langle \phi_\alpha \phi_\beta \,|\, v \,|\, \phi_\gamma \phi_\delta \rangle$$
$$\times \langle \Psi \,|\, a^\dagger(\phi_\alpha) a^\dagger(\phi_\beta) a(\phi_\gamma) a(\phi_\delta) \,|\, \Psi \rangle \quad (3.2)$$

can be defined for all $\phi \in \mathcal{C}$, where the set $\mathcal{C}$ is composed of all complete sets of functions $\phi = \{\phi_\mu\}$ which are normalized, but not necessarily orthogonal. The matrix elements of the single-particle operator T and of the two-particle operator v in Eq. (3.2) are defined in the usual way. The annihilation operator for a particle in the orbital ϕ_α is defined as

$$a(\phi_\alpha) = \int dx \, \phi_\alpha^*(x) \psi(x) \quad (3.3)$$

and the creation operator is its Hermitian conjugate.

When the orbitals in Eq. (3.2) are orthogonal as well as normalized, the functional reduces to the true ground-state energy E_0. Let $\mathcal{O}$ be the set of all complete orthonormal sets of functions $\phi = \{\phi_\mu\}$, so that $\mathcal{O}$ is a subset of $\mathcal{C}$. The completeness relation for complete orthonormal functions can be used, so that Eq. (3.2) becomes

$$E[\phi] = E_0 \quad \text{for all } \phi \in \mathcal{O}. \quad (3.4)$$

The functional $E[\phi]$ cannot be varied if the constraint of orthonormality is imposed.

What is the purpose of defining the functional in Eq. (3.2)? After all, if the matrix elements of the operator T, v and of the one- and two-particle density matrices are known in some complete orthonormal

representation $\phi^0 \in \mathcal{O}$, the true ground-state energy can be calculated by virtue of Eq. (3.4). Suppose, however, that the set of functions is not exactly orthonormal due, e.g., to rounding-off errors. Then the ground-state energy is actually being calculated in the representation $\phi' = \phi^0 + \delta\phi \in \mathcal{C}$ because of the rounding-off errors $\delta\phi$. The deviation of the calculated ground-state energy $E[\phi']$ from the true ground-state energy $E[\phi^0] = E_0$ is

$$\delta E[\phi^0] = E[\phi^0 + \delta\phi] - E[\phi^0]. \quad (3.5)$$

The optimum orbitals for the calculation of the ground-state energy are those for which the deviation in Eq. (3.5) is as small as possible. In particular, the deviation can be made zero. Thus, the optimum orbitals would be given by the variational principle

$$\delta E[\phi] = 0, \quad \text{for } \phi \in \mathcal{C} \quad (3.6)$$

with the stipulation that the set ϕ^0 which satisfies Eq. (3.6) be orthonormal, i.e., $\phi^0 \in \mathcal{O}$, so that the stationary point occurs at E_0.

Equation (3.6) states that first-order variations from orthogonality in calculating the true ground-state energy cause at most a second-order variation from the true value. In Sec. IV this variational principle is applied to determine an eigenvalue problem for the orbitals.

IV. EIGENVALUE PROBLEM

The variational principle for the functional $E[\phi]$ in Eq. (3.6) determines an eigenvalue problem for the orbitals. The eigenvalue problem is complicated by the fact that the single-particle Hamiltonian is nonlocal as in HF theory, and depends on the true wave function. However, it is Hermitian, so that the orbital energies are real.

Since the function ϕ_μ is complex, it and its complex conjugate ϕ_μ^* can be varied independently, subject only to the constraint of normalization. The set $\phi = \{\phi_\mu\} \in \mathcal{C}$ is *complete*, so that an arbitrary variation of ϕ_μ can be expanded in terms of it:

$$\delta\phi_\mu = \sum_\nu \xi_{\mu\nu} \phi_\nu, \quad (4.1)$$

where $\xi_{\mu\nu}$ is an arbitrary coefficient. An arbitrary variation of ϕ_μ^* can likewise be expanded to

$$\delta\phi_\mu^* = \sum_\nu \eta_{\mu\nu} \phi_\nu^*. \quad (4.2)$$

The set of coefficients $\eta_{\mu\nu}$ is not completely arbitrary, but must satisfy the constraint that the orbitals be normalized, $(\phi_\mu, \phi_\mu) = 1$. Variation of the normalization condition gives the restriction on the coefficient

$$\eta_{\mu\mu} = -\xi_{\mu\mu} - \sum_{\nu\neq\mu} (\eta_{\mu\nu} S_{\nu\mu} + \xi_{\mu\nu} S_{\mu\nu}), \quad (4.3)$$

where the sum is over $\nu \neq \mu$ for fixed μ. The overlap

between the orbitals ϕ_μ and ϕ_ν is defined as

$$S_{\mu\nu} = (\phi_\mu, \phi_\nu). \tag{4.4}$$

The normalization condition gives $S_{\mu\mu} = 1$.

The variational principle in Eq. (3.6) for the functional $E[\phi]$ gives

$$\delta E[\phi] = 2 \sum_{\mu,\nu} (\xi_{\mu\nu} + \eta_{\nu\mu}) h_{\mu\nu} = 0. \tag{4.5}$$

The matrix $\mathbf{h}$ is a single-particle Hamiltonian with matrix elements defined as

$$h_{\mu\nu} = \tfrac{1}{2}(g_{\mu\nu} + g_{\nu\mu}{}^*), \tag{4.6}$$

which is explicitly Hermitian. The matrix element $g_{\mu\nu}$ is defined as

$$g_{\mu\nu} = \sum_\alpha \langle \phi_\mu \mid T \mid \phi_\alpha \rangle \langle \Psi \mid a^\dagger(\phi_\nu) a(\phi_\alpha) \mid \Psi \rangle$$

$$+ \sum_{\alpha,\beta,\gamma} \langle \phi_\mu \phi_\alpha \mid v \mid \phi_\beta \phi_\gamma \rangle$$

$$\times \langle \Psi \mid a^\dagger(\phi_\nu) a^\dagger(\phi_\alpha) a(\phi_\beta) a(\phi_\gamma) \mid \Psi \rangle. \tag{4.7}$$

The sum over states in Eq. (4.7) cannot in general be performed because the orbitals are not necessarily orthogonal. Thus, this matrix $\mathbf{g}$ is in general different from the matrix form of Eq. (2.6), but reduces to it when the orbitals are orthogonal. The matrix $\mathbf{h}$ in Eq. (4.6) becomes the matrix form of the operator in Eq. (2.8).

The coefficients in Eq. (4.5) are not all independent, due to the normalization constraint. If the condition in Eq. (4.3) is substituted into Eq. (4.5), the equation

$$\delta E[\phi] = 2 \sum_{\mu \neq \nu} \xi_{\mu\nu} (h_{\mu\nu} - S_{\mu\nu} h_{\mu\mu})$$

$$+ 2 \sum_{\mu \neq \nu} \eta_{\nu\mu} (h_{\mu\nu} - S_{\mu\nu} h_{\nu\nu}) = 0 \tag{4.8}$$

is obtained. The coefficients $\xi_{\mu\nu}$ and $\eta_{\mu\nu}$ for $\mu \neq \nu$ are now all arbitrary and independent. The only way that Eq. (4.8) can be satisfied is for the coefficients of both $\xi_{\mu\nu}$ and $\eta_{\mu\nu}$ to vanish. The vanishing of the coefficient of $\xi_{\mu\nu}$ gives

$$h_{\mu\nu} = S_{\mu\nu} h_{\mu\mu}, \qquad \mu \neq \nu \tag{4.9}$$

and the vanishing of the coefficient of $\eta_{\nu\mu}$ gives

$$h_{\mu\nu} = S_{\mu\nu} h_{\nu\nu}, \qquad \mu \neq \nu. \tag{4.10}$$

However, the diagonal elements of $\mathbf{h}$ are not in general equal:

$$h_{\mu\mu} \neq h_{\nu\nu}, \qquad \mu \neq \nu. \tag{4.11}$$

The only way Eqs. (4.9) and (4.10) can both be satisfied in general is to have

$$S_{\mu\nu} = \delta_{\mu\nu}. \tag{4.12}$$

Equations (4.12) and (4.4) show that at the stationary point of $E[\phi]$ the orbitals are orthonormal, and thus from Eq. (3.4) the value of $E[\phi]$ at the

stationary point is E_0. Therefore, the additional requirement of the variational principle in Eq. (3.6) is satisfied. Because of Eq. (4.12), Eq. (4.7) for $g_{\mu\nu}$ reduces to the matrix form of g in Eq. (2.6), when the sum over states is performed.

If Eq. (4.12) is used in Eqs. (4.9) and (4.10), both equations state that the off-diagonal elements of the matrix $\mathbf{h}$ must vanish. The matrix is then in diagonal form,

$$h_{\mu\nu} = \epsilon_\mu \delta_{\mu\nu}, \tag{4.13}$$

where the eigenvalue ϵ_μ is real. Thus, the variational principle gives an eigenvalue problem for the determination of the orbitals. There is no arbitrariness in choosing the representation, since there are no off-diagonal Lagrangian multipliers in this theory. If Eq. (4.13) is multiplied by $\phi_\mu(x)$ and summed over all μ, the result is Eq. (2.7) with the Hermitian single-particle Hamiltonian given in Eq. (2.8). Therefore, the variational principle used here gives the same equation as obtained intuitively.

Equation (2.7) can be rewritten as

$$h\phi_\nu = (\hat{K} + \hat{U} + \hat{V}))\phi_\nu = \epsilon_\nu \phi_\nu, \tag{4.14}$$

which shows the nonlocal kinetic energy $\hat{K}$, external potential $\hat{U}$, and average potential due to all the other particles V. The eigenvalue problem in Eq. (4.14) is complicated by the fact that the single-particle Hamiltonian in Eq. (2.8) is not a local operator. If the true ground-state wave function is known, the equation is linear, however. If a perturbation expansion is used for Ψ, a highly nonlinear set of equations is obtained. Because only the Hermitian part of $g(x, y)$ is used in Eq. (2.7), it does not reduce to the HF equation if Ψ is replaced by Φ_0, in contrast to Eq. (2.5).

V. BEST LOCAL APPROXIMATION

The generalized HF equation obtained in Sec. IV from the variational principle is nonlocal, and is thus different from Slater's generalized theory.[18] However, the best local approximation to the nonlocal equations can be sought, and gives essentially Slater's theory. It is expected that the orbitals satisfying the best local equations will be approximately the same as the orbitals satisfying the nonlocal equations.

The local form of Eqs. (2.7) and (4.14) is

$$[-(\hbar^2/2m^*)\nabla^2 + \tilde{U}(x) + \tilde{V}(x)]\phi_\nu(x) = \omega_\nu \phi_\nu(x), \tag{5.1}$$

where m^* is an effective mass, $\tilde{U}(x)$ is an "effective" external potential, and $\tilde{V}(x)$ is the average local potential due to all the particles. Because of the presence of the true single-particle density matrix ρ in $\hat{K}$ and $\hat{U}$, the orbital $\phi_\nu(x)$ in Eq. (4.14) is multiplied by its occupation number

$$\rho_{\nu\nu} = n_\nu = \langle \Psi \mid a^\dagger(\phi_\nu) a(\phi_\nu) \mid \Psi \rangle. \tag{5.2}$$

In order to give the same weight to each equation in Eq. (4.14) as in Eq. (5.1), Eq. (4.14) can be divided

by $n_\nu \neq 0$. The orbital energy in Eq. (5.1) is then $\omega_\nu = \epsilon_\nu / n_\nu$.

The effective mass in Eq. (5.1) is chosen such that the local-kinetic-energy operator is the best approximation to the nonlocal one in the sense that the function of m/m^*,

$$\sum_\nu n_\nu \, || \, n_\nu^{-1} \hat{K} \phi_\nu - (m/m^*) K \phi_\nu \, ||^2 = \min. \quad (5.3)$$

The kinetic-energy operator is K, and the nonlocal operator K is defined as in Eq. (4.14). The weighted sum over the states weights each orbital according to its occupation number $n_\nu \neq 0$. Without the sum, the effective mass would be state-dependent. It is assumed that the number of orbitals with occupation number identically zero is small, so that the set $\{\phi_\nu\}$ with $n_\nu \neq 0$ is still complete to a very good approximation.

The effective-mass ratio obtained from Eq. (5.3) is

$$m/m^* = \int dx \, \nabla_x^2 \nabla_{x'}^2 \rho(x', x) / \int dy \, \nabla_y^2 \nabla_{y'}^2 \tau(y', y), \quad (5.4)$$

where the prime is dropped after differentiation and before integration. The function τ is defined as

$$\tau(x, y) = \sum_\nu n_\nu \phi_\nu^*(x) \phi_\nu(y). \quad (5.5)$$

If the orbitals ϕ_ν are natural orbitals,[20] then τ and ρ are the same function and the effective-mass ratio is unity. The effective-mass ratio measures the deviation of the orbitals from the natural ones.

In his multiconfigurational variational principle, Löwdin[20] restricts the orbitals to be natural ones. He then obtains Eq. (5.1) as an approximate equation for the natural orbitals by putting the Lagrangian multipliers in diagonal form. However, the natural orbitals are not invariant under a unitary transformation, and the role played by the diagonalization of the Lagrangian multipliers is unclear.

The local effective single-particle potential $\tilde{U}(x)$ can be defined in a manner similar to Eq. (5.3). The norm squared of the difference between the effective local and nonlocal single-particle potential can be minimized with respect to $\tilde{U}$. In other words, the functional of $\tilde{U}$

$$\sum_\nu n_\nu \, || \, n_\nu^{-1} \hat{U} \phi_\nu - \tilde{U} \phi_\nu \, ||^2 = \min. \quad (5.6)$$

If this expression is functionally varied with respect to $\tilde{U}$, the result is

$$\tilde{U}(x) = U(x) \rho(x, x) / \tau(x, x). \quad (5.7)$$

Thus, the best approximation to the nonlocal external potential term is the external potential multiplied by the "renormalization" factor ρ/τ, which measures the deviation of the orbitals from natural orbitals.

The average potential due to all the other particles is of most interest. The average local interaction $\tilde{V}(x)$ can be defined such that the difference between it and the nonlocal interaction $\hat{V}$ is a minimum in the

sense that the functional[29] of $\tilde{V}$

$$\sum_\nu n_\nu \, || \, n_\nu^{-1} \hat{V} \phi_\nu - \tilde{V} \phi_\nu \, ||^2 = \min. \quad (5.8)$$

If Eq. (5.8) is functionally varied, the result is

$$\tilde{V}(x) = [2\tau(x, x)]^{-1} \iiint du \, dw \, dy \, v(x, y; w, u)$$
$$\times \langle \Psi \, | \, \psi^\dagger(x) \psi^\dagger(y) \psi(w) \psi(u) \, | \, \Psi \rangle + \text{c.c.}, \quad (5.9)$$

where c.c. denotes the complex conjugate and τ is defined in Eq. (5.5). Thus, the best local approximation of the average potential due to all the other particles involves the full two-particle density matrix when the potential is a general velocity-dependent potential.

In order to understand better the significance of the true two-particle density matrix in Eq. (5.9), it is helpful to specialize it to the case of a local two-body potential. Coulomb and Wigner forces, for example, have the form

$$v(x, y; w, u) = v(x, y) \delta(y - w) \delta(x - u). \quad (5.10)$$

If Eq. (5.10) is substituted into Eq. (5.9) the average local potential is

$$\tilde{V}(x) = \int dy [v(x, y) \Gamma(x, y) / \tau(x, x)]. \quad (5.11)$$

The true pair correlation function Γ is defined as

$$\Gamma(x, y) = \langle \Psi \, | \, \psi^\dagger(x) \psi^\dagger(y) \psi(y) \psi(x) \, | \, \Psi \rangle \quad (5.12)$$

and is $N(N-1)$ times the probability density of finding a particle at x and another one at y. If the orbitals which satisfy the generalized HF equations are natural orbitals, then $\tau(x, x)$ is the density, and Eq. (5.11) is Slater's generalized local self-consistent potential.

Even though the particles interact with a potential $v(x, y)$, which has a hard core, the integral in Eq. (5.11) is still finite, since the true pair correlation function Γ vanishes if the particles are within hard-core radius. An average potential due to the other particles exists in Slater's generalized HF theory, but does not, in ordinary HF theory, when the particles interact with hard cores. Equation (5.1) is of the same form as the nuclear-shell-model equation, if the external potential U is zero and the effective mass is unity. The shell-model potential could thus be calculated from the known two-body potential, the observed density, and a calculated pair correlation function.

Slater originally proposed that a local HF self-consistent potential be written in the form[19]

$$\tilde{V}_0(x) = \int dy [v_0(x, y) \Gamma_0(x, y) / \rho_0(x, x)], \quad (5.13)$$

where Γ_0 is defined as in Eq. (5.12) using a Slater determinant, ρ_0 is defined in Eq. (2.2), and $v_0(x, y)$

---

[29] This expression with norm replaced by absolute value was used in Ref. 20, with a result similar to Eq. (5.11) obtained.

is the two-body interaction. Equation (5.11) can approximately be equated to Eq. (5.13) if $v_0(x, y)$ is taken to be a Hermitian effective two-body potential

$$v_0(x, y) = v(x, y)\Gamma(x, y)/\Gamma_0(x, y). \quad (5.14)$$

The density can still be approximated by $\rho_0(x, x)$, and so we have $\rho_0(x, x) \cong \tau(x, x)$. This effective potential vanishes inside the hard-core region since $\Gamma(x, y)$ vanishes there. For large separations $|\mathbf{x} - \mathbf{y}|$ the effective potential v_0 would be essentially the same as the potential v, if long-range correlations are not present. Just outside the hard core, the potential v_0 would not be as attractive as $v(x, y)$, because we have $\Gamma < \Gamma_0$ due to the short-range correlations.

A good approximation to the effective potential would thus be solely the long-range part of the true two-body potential $v(x, y)$ cut off somewhere between the hard-core radius and the distance at which v_0 begins to approach v. The conclusion that the effective nuclear potential is solely the long-range part was reached by Moszkowski and Scott.[30] They obtain a velocity-dependent effective interaction by discarding the hard core and just enough of the attractive part to give a zero free-scattering phase shift. They find, however, that a constant separation distance of 1.062 f is a good approximation. It is difficult to use Eq. (5.14) to define a precise separation distance, but it does define a unique nonsingular effective interaction.

VI. CONCLUSION

The variational principle developed in this paper states that the optimum representation is that for which the matrix expression for the ground-state energy is stationary at the true ground-state energy with respect to variations of the orbitals from orthogonality. If the true one- and two-particle density matrices are known, then the true ground-state energy, as well as the expectation value of other operators, can be calculated directly. However, it is convenient to use a matrix representation for the operators. Since the basis functions cannot be exactly orthogonal in practice, it is desirable that the ground-state energy is not sensitive to these deviations.

The stationary point of the functional $E[\phi]$ in Eq. (3.2) is not a simple maximum or minimum. The functional $E[\phi]$ is constant in the set of all sets of complete orthonormal functions. A first-order variation from orthogonality about any other set of orthonormal orbitals would cause a first-order variation in the energy. The stationary point thus corresponds to a point of inflection. Therefore, the functional $E[\phi]$ does not provide a bound to the true energy, but

this is not as essential as knowing that it is stationary at the true ground-state energy.

The single-particle Hamiltonian obtained in Eq. (2.8) involves the true one- and two-particle density matrices. In order to calculate it exactly, the true wave function must be known, but then the problem is solved. A natural expansion of the true single-particle density matrix could then be made to obtain an orbital picture, but occupation numbers instead of energy eigenvalues would be obtained. In order to obtain energies, the single-particle Hamiltonian obtained here could be diagonalized instead of the density matrix. In general, the two matrices do not commute and the choice as to which matrix to diagonalize must be made.[31]

The local approximation in Eq. (5.1) is a more practical set of equations to solve than Eq. (2.8), and provides a justification for the nuclear shell model. The nuclear pair correlation function may soon be known experimentally[32] and can be used together with the observed nuclear density[33] in Eq. (5.11). Instead of calculating the pair correlation function from the true wave function, the pair correlation function for the corresponding homogeneous system could be used. The short-range correlations would then be built into the function, and the function could be cut off at the surface of the system. Thus, the pair correlation function for nuclear matter could be used for nuclei, or the one for the electron gas could be used for atoms. Unfortunately, nuclear calculations have been concentrated on the pair wave function[34] instead of the pair correlation function.[35] The pair correlation function may also be estimated crudely by using the free Fermi gas value where the function is not zero.[36]

[30] S. A. Moszkowski and B. L. Scott, Ann. Phys. (N. Y.) **11**, 65 (1960).

[31] A single-particle Hamiltonian for natural orbitals has been obtained from another variational principle by W. H. Adams, Phys. Rev. **183**, 31 (1969); **183**, 37 (1969). However, his single-particle Hamiltonian is different from the one in Eqs. (4.14) or (5.1).

[32] See, e.g., Y. N. Srivastava, Phys. Rev. **135**, B612 (1964); D. U. L. Yu, Ann. Phys. (N. Y.) **38**, 392 (1966).

[33] See, e.g., R. Hofstadter, F. Bumiller, and M. R. Yearian, Rev. Mod. Phys. **30**, 482 (1958).

[34] See, e.g., L. C. Gomes, J. D. Walecka, and V. F. Weisskopf, Ann. Phys. (N. Y.) **3**, 241 (1958).

[35] One paper which does deal with the pair correlation function is R. J. Eden, V. J. Emery, and S. Sampanthar, Proc. Roy. Soc. (London) **A253**, 186 (1959).

[36] This method has been used by W. E. Drummond, Phys. Rev. **116**, 183 (1959).