

Hohenberg-Kohn theorem for nonlocal external potentials*

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The Hohenberg-Kohn theorem is extended to the case that the external potential is nonlocal. It is shown that, in this more general case, a nondegenerate ground-state wave function is a universal functional of the one-particle density kernel $\mu(x, x')$, but probably not of the particle density $n(\vec{r}) = \sum_s \mu(\vec{r}s, \vec{r}s)$. The variational equations for the local and nonlocal cases are compared. The former must be replaced by a variational equation for an equivalent system of noninteracting particles, following a prescription of Kohn and Sham, in order to obtain a Schrödinger-like form, and contains only local potentials. The latter may be obtained directly in Schrödinger-like form, but the exchange-correlation potential is nonlocal. If the nonlocal pseudo-Hamiltonian exists [i.e., if the functional derivative $\delta E/\delta\mu(x, x')$ exists for a nondegenerate ground-state density kernel], then the eigenfunctions of the pseudo-Hamiltonian are natural spin orbitals, and all partially occupied orbitals ($0 < \langle \phi_i | \mu | \phi_i \rangle < 1$) belong to the same degenerate eigenvalue of the pseudo-Hamiltonian. Finally, it is shown, as a corollary of Coleman's theorem for N -representable density kernels, that any finite non-negative differentiable function is an N -representable particle density.

I. INTRODUCTION

Hohenberg and Kohn (HK) proved a remarkable theorem which states that the ground-state wave function of a many-particle system, if nondegenerate, is a unique functional of the particle density.¹ This theorem implies the existence of a universal energy functional of the external potential and particle density which is minimum for the true particle density, so that the true ground-state energy and particle density may be determined by application of a variational principle involving the particle density alone. The original proof was for a local external potential: $v(x, x') = \delta(x - x')v(x)$.

In order to apply the HK theorem, one must be able to construct the universal functional. It is accurately known for the limiting case of a uniform high-density electron gas.² An approximate functional form for a slowly varying inhomogeneous electron gas has been derived,^{1,3,4} but serious questions have been raised regarding the validity of the inhomogeneous terms in view of the fact that the density-gradient expansion near a nucleus, where the density gradient is very high, can be shown to be a divergent series which must be summed to infinite order.⁵ Local-density theories based on the HK theorem have been applied to atoms⁶ and to molecules⁷ in spite of these troublesome questions. The results have been surprisingly good for many applications in view of the fact that the electron densities in atoms and molecules are neither high (except near the nucleus) nor nearly homogeneous, although significant discrepancies have been noted.⁸ However, one would, where possible, prefer to apply the theory to nearly homogeneous systems so that the functional expression obtained by using a density-gradient expansion could more reasonably be expected to have

some still-to-be-discovered justification as an asymptotic expansion.

In all real molecules and solids the external potential consists of one or more nuclei which produce a very inhomogeneous electron-density distribution. In many problems one is interested only in the valence electrons, which have a more nearly uniform density, especially if one uses a pseudo-potential to smooth out the density in the core region. However, if the problem is formulated in terms of the valence electrons alone, treating the nuclei and core electrons as fixed external potential sources, one obtains a nonlocal external potential. It is, therefore, of some interest to investigate the generalization of the HK theorem to nonlocal potentials.

In order to follow the logic of the HK theorem and its extension, one must distinguish between various domains in the functional spaces of one-particle reduced density kernels $\mu(x, x')$ and particle-density distributions $n(\vec{r})$. Let

$$D(x_1 \cdots x_N, x'_1 \cdots x'_N) = \sum_i w_i \Psi_i(x_1 \cdots x_N) \Psi_i^*(x'_1 \cdots x'_N) \quad (1.1)$$

be the von Neumann N -particle statistical density kernel, where Ψ_i are a complete set of orthonormal N -particle wave functions and w_i are non-negative real numbers, normalized so that

$$\sum_i w_i = 1. \quad (1.2)$$

The largest reduced-kernel domain of interest herein is the ensemble N -representable domain consisting of all one-particle kernels which can be obtained from some N -particle kernel by the contraction

$$\mu(x, x') = N \int \cdots \int D(x, x_2 \cdots x_N; x', x_2 \cdots x_N)$$

$$\times dx_2 \cdots dx_N, \quad (1.3)$$

where $x = (\vec{r}, s)$ and $\int dx = \sum_s \int d\vec{r}$. Density kernels

$$\rho(x, x') = N \int \cdots \int \Psi(x, x_2 \cdots x_N) \Psi^*(x', x_2 \cdots x_N) \times dx_2 \cdots dx_N \quad (1.4)$$

which can be obtained from pure N -particle states comprise a subdomain of this ensemble kernel domain. Unless otherwise noted, when we speak of the density kernel we will mean the one-particle reduced ensemble density kernel μ .

The largest particle-density domain of interest consists of all N -representable particle-density distributions, i. e., densities which can be obtained by the construction

$$\begin{aligned} n(\vec{r}) &= \sum_s \mu(\vec{r}s, \vec{r}s) \\ &= \sum_s \int \cdots \int D(\vec{r}s, x_2 \cdots x_N; \vec{r}s, x_2 \cdots x_N) \\ &\quad \times dx_2 \cdots dx_N. \end{aligned} \quad (1.5)$$

One can show that the domain of densities which are N -representable by pure states is the same as the domain of densities which are N -representable by ensembles, and, further, that any non-negative differentiable function such that $\int n(\vec{r}) d\vec{r} = N$ is an N -representable particle density. (See Sec. IV.) The mapping between N -representable density kernels and N -representable particle densities is many-one. The functions $\mu(x, x')$ or $n(\vec{r})$ must be N -representable in order to apply the variational principle.

The smallest domains of interest are the kernels and densities which can be constructed from nondegenerate ground states $\Psi_0(x_1, \dots, x_N)$ of N -body systems with local external potentials. The essential statement of the HK theorem in its original form is that there is a one-one mapping between this restricted class of N -body wave functions and particle densities: $\Psi_0 \leftrightarrow n_0$. (The theorem also extends this mapping to the external potential. The extended mapping is one-one, aside from an unimportant constant, but the one-one character of the potential-wave-function mapping breaks down as soon as spin-dependent potentials are allowed.⁹ The mapping between external potentials and N -body wave functions is unimportant for applications of the theorem.) The existence of a one-one mapping between density kernels and particle densities in these restricted domains is an obvious corollary of the HK theorem.

The intermediate domains of interest consist of those kernels and densities which can be constructed from nondegenerate ground states $\Psi_0(x_1, \dots, x_N)$

of N -body systems with local or nonlocal external potentials. The extension of the HK theorem, reported in Sec. II, consists in showing that there is a one-one mapping between this less restricted class of N -body wave functions and density kernels: $\Psi_0 \leftrightarrow \mu_0$. This result, which uses the method of proof devised by Hohenberg and Kohn for local potentials, does not disprove the existence of a one-one mapping between density kernels and particle densities in the extended ground-state domains, and I do not have an explicit example of a many-one mapping between the kernels and densities of these domains. But plausibility arguments may be given which make it appear unlikely that the kernel-density mapping remains one-one for the extended domains. We can, therefore, assert that, for a nonlocal external potential, there is a universal ground-state functional of the density kernel, but the existence of a universal ground-state functional of the particle density alone is unlikely.

A few of the consequences of the extended HK theorem are explored in Sec. III. Some of the results are as expected; e. g., the variational equations for the nonlocal case can be expressed as eigenvalue equations for the natural spin orbitals, and the exchange-correlation potential in the pseudo-Hamiltonian is nonlocal. An unexpected result is that all partially occupied eigenfunctions (i. e., all natural spin orbitals for which $0 < \langle \phi_i | \mu | \phi_i \rangle < 1$) belong to the same degenerate eigenvalue of the pseudo-Hamiltonian. This paradoxical result appears to be an inescapable consequence of the extended HK theorem unless the universal functional of the density kernel is so ill behaved that the functional derivative with respect to the density kernel does not exist. If so, then the usual prescriptions for constructing approximate functional forms for electronic structure calculations probably cannot be used.

In applying the variational principle, one must restrict the variations of the density kernel and particle density so that both remain N -representable. The necessary constraints for the density kernel may be obtained from a theorem due to Coleman.¹⁰ Von Barth and Hedin have suggested, as a working hypothesis, "that reasonably smooth particle densities do not give an energy less than the ground-state energy when used in the ground-state functional".⁹ One can show that this hypothesis is true, and that any non-negative differentiable function such that $\int n(\vec{r}) d\vec{r} = N$ is an N -representable particle density. This result is established in Sec. IV as a corollary of Coleman's theorem.

The discussion and derivations are presented herein only for the case of fermions; however, many of the results are equally applicable to bosons. The significant difference is that, for bosons, the

upper bound on the eigenvalues of the density kernel $\mu(x, x')$ becomes N rather than 1.

II. GENERALIZATION OF THE HK THEOREM TO NONLOCAL EXTERNAL POTENTIALS

Consider a many-particle system characterized by the Hamiltonian

$$H = T + V + U$$

$$= \sum_i t(i) + \sum_i v(i) + \sum_{i < j} u(i, j) \quad (2.1)$$

with a total energy given by¹¹

$$E\{D, v\} = \langle DH \rangle_N = \langle \mu t \rangle + \langle \mu v \rangle + \langle \langle \sigma u \rangle \rangle, \quad (2.2)$$

where D is the N -particle ensemble density kernel defined by Eqs. (1.1) and (1.2), μ is the one-particle reduced ensemble density kernel defined by Eq. (1.3), and

$$\sigma(x_1 x_2, x'_1 x'_2) = \left(\frac{N}{2} \right) \langle D \rangle_{N-2} \quad (2.3)$$

is the two-particle reduced ensemble density kernel. The curly brackets are used to denote a single-valued functional dependence on the enclosed quantity. The kinetic energy t and the two-body interaction u will always be the same, so that a functional dependence on them need not be indicated.

We must restrict the external potential $v(x, x')$ to that class of potentials for which E is real and has a lower bound, but we do not require that it be local. We will, further, restrict v to that class of potentials for which the ground state Ψ_0 is nondegenerate, so that $D_0 = \Psi_0 \Psi_0^\dagger$. (The subscript 0 will be used for all quantities related to or derived from the ground state.) With these restrictions, Eqs. (1.3) and (1.5) establish functional relations which may be written symbolically as

$$v \rightarrow D_0 \rightarrow \mu_0 \rightarrow n_0, \quad (2.4)$$

where the arrow indicates that the function at the head is uniquely determined by the function at the tail. The implication is that the relation may be many-one or one-one, but not one-many, so that we can, for example, write $D_0\{v\}$ or $\mu_0\{D_0\}$, but not necessarily $v\{D_0\}$ or $D_0\{\mu_0\}$. It is perhaps worth reminding ourselves that the restriction to nondegenerate ground states is rather severe. It excludes all paramagnetic, ferromagnetic, and antiferromagnetic materials and most atoms.

The ensemble energy functional $E = \langle DH \rangle_N$ has been used in Eq. (2.2) rather than the pure-state energy functional $E = \langle \Psi | H | \Psi \rangle$ because the constraints that we shall need for applying the variational principle to reduced energy functionals are known only for ensembles. One obtains the same stationary values for unreduced ensemble or pure-state energy functionals, but there are subtle dif-

ferences in the application of the variational principle, which will be relevant to the discussion in Sec. III, so that it is worthwhile to digress briefly in order to review the derivation of the stationary conditions for an ensemble.

If we impose the constraints $\langle \Psi_i | \Psi_j \rangle = \delta_{ij}$ and $\sum w_i = 1$ by the method of Lagrangian multipliers, and set $w_i = \cos^2 \theta_i$ in order to satisfy the constraint $0 \leq w_i \leq 1$, then the stationary conditions are that the quantity

$$\mathcal{E} = E - \sum_{i,j} \lambda_{ij} \langle j | i \rangle + \lambda \left(1 - \sum w_i \right) \quad (2.5)$$

must be stationary with respect to arbitrary independent variations of Ψ_i , Ψ_i^\dagger , and θ_i , where λ_{ij} and λ are Lagrangian multipliers.¹² This leads to the variational equations

$$\frac{\delta \mathcal{E}}{\delta \Psi_i^\dagger} = w_i H \Psi_i - \sum_j \Psi_j \lambda_{ji} = 0, \quad (2.6)$$

$$\frac{\delta \mathcal{E}}{\delta \Psi_i} = w_i \Psi_i^\dagger H - \sum_j \lambda_{ij} \Psi_j^\dagger = 0, \quad (2.7)$$

and

$$\frac{\partial \mathcal{E}}{\partial \theta_i} = \sin 2\theta_i (E_i - \lambda) = 0, \quad (2.8)$$

where $E_i = \langle i | H | i \rangle$. Using the orthonormality constraint, we obtain

$$\lambda_{ji} = w_i \langle j | H | i \rangle \quad (2.9)$$

from Eq. (2.6). If this equality is used to eliminate λ_{ij} from Eq. (2.6), then we obtain an identity. (Recall that the Ψ_i form a complete set, so that $\sum_i \Psi_i \Psi_i^\dagger = I$, where I is the unit operator.) Equation (2.7) is also an identity, provided that the equality

$$\lambda_{ij} = w_i \langle i | H | j \rangle \quad (2.10)$$

is satisfied. Hence, Eqs. (2.6) and (2.7) reduce to the single condition

$$(w_i - w_j) \langle i | H | j \rangle = 0. \quad (2.11)$$

We now infer from Eq. (2.8) that, for each and every state, one of the following three conditions must be satisfied: (i) $w_i = 1$ ($\theta_i = 0$); (ii) $E_i = \lambda$; or (iii) $w_i = 0$ ($\theta_i = \pi/2$). If (i) is true for any state, then the constraint $\sum w_i = 1$ implies that $w_j = 0$ for all other states and, since $\langle i | H | j \rangle = 0$ for $j \neq i$ from Eq. (2.11), we must have

$$H \Psi_i = E_i \Psi_i. \quad (2.12)$$

If (ii) is satisfied, then all states for which $w_i \neq 0$ must belong to the same degenerate level, so that Eq. (2.12) is still satisfied. Condition (iii) must be satisfied for all other states.

It is of interest to note that we obtain the same solution by eliminating all constraints except $w_i \geq 0$

and requesting the stationary values of the normalized energy expression

$$E = \langle DH \rangle_N / \langle D \rangle_N. \quad (2.13)$$

The conditions for the unrestricted stationary values are (setting $w_i = q_i^2$)

$$\frac{\delta E}{\delta \Psi_i^\dagger} = \frac{w_i}{\langle D \rangle_N} (H \Psi_i - E \Psi_i) = 0, \quad (2.14)$$

$$\frac{\delta E}{\delta \Psi_i} = \frac{w_i}{\langle D \rangle_N} (\Psi_i^\dagger H - E \Psi_i^\dagger) = 0, \quad (2.15)$$

$$\frac{\partial E}{\partial q_i} = \frac{2q_i}{\langle D \rangle_N} (E_i - E \langle i | i \rangle) = 0, \quad (2.16)$$

from which we infer that Eq. (2.12) must be satisfied and the coefficients w_i must vanish for all but one energy level.

Returning to the matter of the existence of functional relations between density kernels and the particle density, the HK theorem for a local external potential states that, under the conditions noted above, "... $v(\vec{r})$ is (to within a constant) a unique functional of $n(\vec{r})$..." [where $v(\vec{r})$ and $n(\vec{r})$ correspond to $v'(\vec{r})$ and $n'_0(\vec{r})$ in our notation].¹ This is equivalent to stating that the many-one relations of Eq. (2.4) are, in fact, one-one relations (provided that we consider two potentials which differ only by a constant as the same potential), i. e.,

$$v' \longleftrightarrow D'_0 \longleftrightarrow \mu'_0 \longleftrightarrow n'_0, \quad (2.17)$$

where a prime is used to indicate a local potential and all quantities derived therefrom. Note that as long as we restrict ourselves to external potentials with nondegenerate ground states (and ignore unimportant phase factors), this mapping is equivalent to $v' \longleftrightarrow \Psi'_0 \longleftrightarrow \rho'_0 \longleftrightarrow n'_0$.

Von Barth and Hedin have shown that when the external potential is allowed to be spin dependent there are many external potentials, differing by more than a constant, which can give the same ground-state wave function.⁹ An even wider class of such potentials can be constructed when the potential is nonlocal; hence, we cannot go beyond the many-one relation $v \rightarrow D_0$ when spin-dependent or nonlocal external potentials are allowed. This is, however, of no consequence. The essential results of the HK theorem hinge only on the existence of the one-one relation $D'_0 \longleftrightarrow n'_0$, which permits us to write the functional relation $D'_0\{n'_0\}$ and define a universal functional $E'\{n'_0, v'\} \equiv E\{D'_0\{n'_0\}, v'\}$. (This is the functional $E_v[n]$ in the notation of Hohenberg and Kohn.)

Let us now consider how the generalization to a nonlocal external potential affects the functional relation between D_0 and n_0 . We may examine this point by going through a slightly modified version of the proof given by Hohenberg and Kohn.

Let v^1 and v^2 be two external potentials which give two distinct nondegenerate ground states Ψ_0^1 and Ψ_0^2 : $H^1 \Psi_0^1 = E_0^1 \Psi_0^1$ and $H^2 \Psi_0^2 = E_0^2 \Psi_0^2$. The corresponding reduced density kernels are $\mu_0^1 = N \langle D_0^1 \rangle_{N-1}$ and $\mu_0^2 = N \langle D_0^2 \rangle_{N-1}$, where $D_0^1 = \Psi_0^1 \Psi_0^{1\dagger}$ and $D_0^2 = \Psi_0^2 \Psi_0^{2\dagger}$. We then have

$$E_0^1 = \langle D_0^1 H^1 \rangle_N < E^1 = \langle D_0^2 H^1 \rangle_N, \quad (2.18)$$

$$E_0^2 = \langle D_0^2 H^2 \rangle_N < E^2 = \langle D_0^1 H^2 \rangle_N, \quad (2.19)$$

and

$$\Delta E \equiv (E^2 - E_0^2) + (E^1 - E_0^1) > 0, \quad (2.20)$$

so that

$$\begin{aligned} \Delta E &= (E^2 - E_0^2) + (E^1 - E_0^1) \\ &= \langle D_0^1 (H^2 - H^1) \rangle_N + \langle D_0^2 (H^1 - H^2) \rangle_N \\ &= - \langle \delta \mu_0 \delta v \rangle > 0, \end{aligned} \quad (2.21)$$

where $\delta \mu_0 = \mu_0^2 - \mu_0^1$ and $\delta v = v^2 - v^1$. Written out explicitly, the inequality is

$$\langle \delta \mu_0 \delta v \rangle = \iint \delta \mu_0(x, x') \delta v(x', x) dx' dx < 0. \quad (2.22)$$

We cannot have $\delta \mu_0 = 0$ without violating the inequality; hence, if Ψ_0^1 and Ψ_0^2 are distinct, μ_0^1 and μ_0^2 must also be distinct, and we can always write

$$D_0 \longleftrightarrow \mu_0. \quad (2.23)$$

Equation (2.23) establishes the existence of a universal functional

$$E\{\mu_0, v\} \equiv E\{D_0\{\mu_0\}, v\} = \langle \mu_0 v \rangle + F\{\mu_0\}, \quad (2.24)$$

where $F\{\mu_0\}$ is a universal function of μ_0 alone. The domain of $F\{\mu\}$, as defined by Eq. (2.24), consists of those density kernels μ_0 which may be constructed from nondegenerate ground-state wave functions Ψ_0 of N -particle systems in local or nonlocal external potentials. We may extend this domain as follows. Let $[\mu]$ be the set of all N -representable density kernels, and let $[D_\mu]$ be a set of N -particle density kernels which includes the nondegenerate ground-state kernels $D_0 = \Psi_0 \Psi_0^\dagger$ as a subset together with any additional N -particle kernels which may be needed to permit a one-one mapping between all members of the set $[\mu]$ and all members of the set $[D_\mu]$. The set $[D_\mu]$ is not uniquely determined because one may construct larger sets of N -particle kernels for which the mapping between the N -particle and reduced one-particle kernels is many-one, and it will be possible to find more than one subset of this larger set which fits the above definition of $[D_\mu]$, but for our purpose any one of these sets will do. This extended definition permits us to write

$$E\{\mu, v\} = E\{D_\mu\{\mu\}, v\} = \langle \mu v \rangle + F\{\mu\}, \quad (2.25)$$

where μ is now any N -representable density kernel.

The external potential v is still restricted to potentials for which the ground state is nondegenerate.

We may easily verify the inequality

$$E\{\mu_0, v\} < E\{\mu_0 + \delta\mu, v\} \quad (2.26)$$

as a direct consequence of the quantum-mechanical variational principle. The density kernel μ_0 in Eq. (2.26) is the unique density kernel which corresponds to the ground state Ψ_0 associated with the external potential v , while $\mu_0 + \delta\mu$ is any other N -representable density kernel.

If the external potential is local, so that Eq. (2.22) reduces to

$$\langle \delta\mu_0 \delta v' \rangle = \langle \delta n'_0 \delta v' \rangle = \int \delta n'_0(\vec{r}) \delta v'(\vec{r}) d\vec{r} < 0, \quad (2.27)$$

then n'_0 and n_0 must be distinct if D_0^1 and D_0^2 are distinct, and we may write

$$D_0' \leftrightarrow n'_0. \quad (2.28)$$

The set $[D_0']$ of nondegenerate ground-state N -particle kernels for local potentials (which is a subset of the set $[D_0]$ of nondegenerate ground-state N -particle kernels for local or nonlocal potentials) can be extended, by the same argument used above, to a set $[D_n]$ of wave functions which may be placed in one-one correspondence with the set $[n]$ of all N -representable particle densities. We may then define the universal functional

$$E'\{n, v'\} \equiv E\{D_n\{n\}, v'\} = \langle v'n \rangle + F'\{n\} \quad (2.29)$$

on the domain of all N -representable particle densities, and establish the inequality

$$E'\{n'_0, v'\} < E'\{n'_0 + \delta n, v'\} \quad (2.30)$$

for the ground-state particle density n'_0 corresponding to v' and any N -representable particle density $n = n'_0 + \delta n$. The domain of the external potential v' is now restricted to local potentials which give nondegenerate ground states. $E'\{n, v\}$ and $F'\{n\}$ are the universal functions $E_v[n]$ and $F[n]$ introduced by Hohenberg and Kohn.

We may gain a better understanding of the relation between the functionals $F\{\mu\}$ and $F'\{n\}$ by replacing the density kernel $\mu(x, x')$ with a density matrix $\mu_{pq} = \mu(x_p, x_q)$ defined on a uniformly dense mesh of points: $x_p = (\vec{r}_i, s) = (i_1\delta, i_2\delta, i_3\delta, s)$, where i_ν are integers, $-\infty < i_\nu < \infty$, and δ is an arbitrarily small, positive real number. The index i stands for a triplet of integers, $i = (i_1, i_2, i_3)$, and $p = (i, s)$. Integrals become sums: $\int f(\vec{r}) d\vec{r} \rightarrow \Delta \sum f_i$, where $\Delta = \delta^3$; and derivatives become differences: $\partial f / \partial z \rightarrow (f_{i_1 i_2 i_3+1} - f_{i_1 i_2 i_3}) / \delta$. We may recover the exact expressions by going to the limit $\delta \rightarrow 0$, provided that the limit exists (which it must for any properly defined quantity of physical significance). The particle density corresponds to the diagonal elements averaged over spin, $n_i = \sum_s \mu_{i_s, i_s} = n(\vec{r}_i)$,

in this discrete representation.

The discrete representation of the functional $F\{\mu\}$ may be written as $F[\mu_{pq}]$, where the brackets indicate a functional dependence on all members of the density-matrix array. The HK theorem for local potentials implies that, for nondegenerate ground states (and the extended domain of particle densities obtained from the N -particle density kernels D_n defined above), there exists a unique function

$$\mu_{pq} = \mu'_{pq}[n_i] \quad (2.31)$$

such that all density-matrix elements are determined by the diagonal elements alone. The functional $F'\{n\}$ is defined as the limiting form of the function

$$F'[n_i] = F[\mu'_{pq}[n_i]] \quad (2.32)$$

for $\delta \rightarrow 0$.

Hohenberg and Kohn established the one-one mapping $D_0' \leftrightarrow n'_0$ for nondegenerate ground states of local potentials. We have seen that an extension of their proof also establishes a one-one mapping $D_0 \leftrightarrow \mu_0$ for nondegenerate ground states of nonlocal potentials. The proof does not lead to the existence of a one-one mapping $D_0 \leftrightarrow n_0$ for nonlocal potentials, but this does not, of course, allow us to infer that such a mapping does not exist. I do not have an example of a many-one mapping which would establish this point, but the following plausibility argument provides some support for the conjecture that the mapping $D_0 \leftrightarrow n_0$ is, in fact, many-one for nonlocal potentials.

Let us introduce a discrete representation of the kind used above and, further, restrict the representations of all operators and wave functions to a finite number of elements, viz., values of the various kernels and functions on a mesh of points in a finite region of space. Let q be the number of mesh points. Then a nonlocal potential and a density kernel will both be represented by matrices with $q(q+1)/2$ independent elements. A local potential and a particle density (ignoring spin) will be diagonal matrices in this representation, each characterized by q elements. It is not surprising that the q elements of the local potential should be uniquely determined by the q elements of the particle density, or that the $\binom{q}{2}$ elements of the nonlocal potential should be uniquely determined by the $\binom{q}{2}$ elements of the density kernel, so that a one-one mapping should exist in each case. But it would be surprising if the $\binom{q}{2}$ elements for all possible nonlocal potentials were uniquely determined by the q elements of the particle density. One should be able to find several different nonlocal potentials which could give the same particle density, simply because the former require more parameters for a unique characterization. This suggests

that the mapping $D_0 \rightarrow n_0$ is many-one for the non-local case. It may be possible to develop this heuristic argument into a rigorous proof, but we shall not attempt to do so here, so that the statement must be left as a conjecture.

III. VARIATIONAL EQUATIONS

The HK theorem and its generalization establish the existence of the universal functionals $E'\{n, v'\}$ and $E\{\mu, v\}$ (which we shall henceforth write as $E'\{n\}$ and $E\{\mu\}$, respectively). One can derive from them, by means of the variational principles expressed by Eqs. (2.30) and (2.26), equations which determine the ground-state particle density and density kernels, respectively. There are some interesting aspects of these equations which merit further discussion.

A. Particle-density equations

Any normalizable and differentiable non-negative function is an N -representable particle density (this is shown in Sec. IV); hence, the only constraints needed for applying the variational principle to $E'\{n\}$ are $n(\vec{r}) \geq 0$ and $\int n(\vec{r}) d\vec{r} = N$. The non-negativity condition may be introduced by writing $n(\vec{r}) = |\psi(\vec{r})|^2$. The normalization constraint may be introduced in the usual manner, replacing the energy functional by the functional $\mathcal{G}'\{n\} = E'\{n\} + \lambda(N - \int |\psi|^2 d\vec{r})$, where λ is a Lagrangian parameter. The variational equations may then be written as

$$\frac{\delta \mathcal{G}'}{\delta \psi^*(\vec{r})} = \frac{\delta E'}{\delta \psi^*(\vec{r})} - \lambda \psi(\vec{r}) = 0, \quad (3.1)$$

with a corresponding adjoint equation. If the functional derivatives exist (a point to which we shall return later when we consider the density-kernel equations), then we may write

$$\frac{\delta E'}{\delta \psi^*(\vec{r})} = \int \frac{\delta E'}{\delta n(\vec{r}')} \frac{\delta n(\vec{r}')}{\delta \psi^*(\vec{r})} d\vec{r}' = h(\{n\}, \vec{r}) \psi(\vec{r}), \quad (3.2)$$

where

$$h(\{n\}, \vec{r}) = \delta E'\{n\} / \delta n(\vec{r}). \quad (3.3)$$

Equation (3.1) can then be rewritten as

$$[h(\{n\}, \vec{r}) - \lambda] \psi(\vec{r}) = 0. \quad (3.4)$$

The operator $h(\{n\}, \vec{r})$ is a pure local potential, not a differential operator; hence, at any point at which $n(\vec{r}) \neq 0$ the particle-density equation reduces to

$$h(\{n\}, \vec{r}) = \lambda, \quad (3.5)$$

where λ must be chosen to give a normalized solution: $\int n(\vec{r}) d\vec{r} = N$. If more than one such value exists, one must choose that value which leads to the smallest value for $E\{n\}$.

Equation (3.5) is a continuous set of nonlinear functional equations for the function $n(\vec{r})$. It is not in a convenient form for finding solutions or for interpreting the properties of many-particle systems. One would like to transform it into an equation that reveals some connection with the Hartree-Fock equations, which are the cornerstone for almost all interpretations of the electronic properties of atoms, molecules, and condensed matter.

In order to convert Eq. (3.5) into a Schrödinger-like equation for a single particle, we need to express $n(\vec{r})$ in terms of orbitals, e.g., by writing it in the form

$$n(\vec{r}) = \sum_{i=1}^N |\psi_i(\vec{r})|^2, \quad (3.6)$$

where ψ_i are normalized one-electron functions, the significance of which remains to be determined.

If we proceed in the obvious manner, replacing \mathcal{G}' in Eq. (3.1) by $\mathcal{G}'' = E' + \sum_{i=1}^N \lambda_i (1 - \int |\psi_i|^2 d\vec{r})$, where $\lambda_1, \dots, \lambda_N$ are Lagrangian multipliers, the variational equations become

$$[h(\{n\}, \vec{r}) - \lambda_i] \psi_i(\vec{r}) = 0, \quad (3.7)$$

which are equivalent to Eqs. (3.4) or (3.5).

In order to obtain a Schrödinger-like form directly from the variational principle, we need to introduce a differential operator $-\frac{1}{2}\nabla^2$ into Eq. (3.7). An obvious prescription for doing so is to define

$$T = -\frac{1}{2} \sum_{i=1}^N \int \psi_i^* \nabla_i^2 \psi_i d\vec{r} \quad (3.8)$$

and write

$$E'\{n\} = T + W, \quad (3.9)$$

where ψ_i are normalized one-electron functions from which $n(\vec{r})$ is constructed by Eq. (3.6). If we proceeded as if T and W were functionals of n alone and the only constraints required were those imposed by normalization, then we would obtain the orbital variational equations

$$(-\frac{1}{2}\nabla^2 + w - \lambda_i) \psi_i = 0, \quad (3.10)$$

where $w(\vec{r}) = \delta W / \delta n(\vec{r})$. Unfortunately, this prescription is not valid, and Eq. (3.10) is false, because T (and, hence, W) is not a functional of n alone and $\delta T / \delta n(\vec{r})$ does not exist.

If T were a functional of n alone, then δT would vanish identically for any variation in the functions $\psi_1^*, \dots, \psi_N^*$ such that $\delta n(\vec{r}) = \sum_{i=1}^N \psi_i(\vec{r}) \delta \psi_i^*(\vec{r}) = 0$. If, for example, we chose $\delta \psi_N^* = -\sum_{i=1}^{N-1} (\psi_i / \psi_N) \delta \psi_i^*$, then, for almost any choice of the infinitesimal increments $\delta \psi_1^*, \dots, \delta \psi_{N-1}^*$ [the only restriction is that $\delta \psi_i^*(\vec{r})$ must vanish at the nodes of $\psi_N^*(\vec{r})$], we should have

$$\delta T = \sum_{i=1}^N \int \left(\frac{\delta T}{\delta \psi_i^*(\vec{r})} \right) \delta \psi_i^*(\vec{r}) d\vec{r}$$

$$= -\frac{1}{2} \sum_{i=1}^{N-1} \int (\psi_N \nabla^2 \psi_i - \psi_i \nabla^2 \psi_N) \left(\frac{\delta \psi_i^*}{\psi_N} \right) d\vec{r} = 0. \quad (3.11)$$

This equality will not, in general, be true. We can obtain almost any value of δT that we please for any value of the increment $\delta n(\vec{r})$.

The situation may be interpreted geometrically by noting that T is a functional in the function space spanned by the variables $\psi_1(\vec{r}), \dots, \psi_N(\vec{r})$. Equation (3.6) defines a "line" in this function space. The only relevant quantity for determining the ground-state density by minimizing $E'\{n\}$ is the gradient of T along the line. The derivatives $\delta T/\delta \psi_i(\vec{r})$ give the gradient in an arbitrary direction in the function space and, hence, introduce spurious functions and false extrema into the variational equations.

One might assume that this difficulty could be circumvented by introducing appropriate constraints to suppress the spurious variations in T . But this would be equivalent to using the equality

$$\frac{\delta T}{\delta \psi_i^*(\vec{r})} = \int \frac{\delta T}{\delta n(\vec{r}')} \frac{\delta n(\vec{r}')}{\delta \psi_i^*(\vec{r})} d\vec{r}' = \frac{\delta T}{\delta n(\vec{r})} \psi_i(\vec{r}), \quad (3.12)$$

and encounters the problems that the derivative operator is eliminated from the variational equations and the functional derivative $\delta T/\delta n(\vec{r})$ does not even exist.

In order to demonstrate the assertion that $\delta T/\delta n(\vec{r})$ does not exist when T is defined by Eqs. (3.6) and (3.9), we note that the functional dependence of T on $n(\vec{r})$ is not explicit, so that the derivative must be obtained by implicit means. This may be done by introducing the function $\mu(\vec{r}, \vec{r}') = \sum_i \psi_i(\vec{r}) \psi_i^*(\vec{r}')$. The explicit functional dependence of T on $\mu(\vec{r}, \vec{r}')$ is given by $T = -\frac{1}{2} \int \nabla^2 \mu(\vec{r}, \vec{r}') |_{\vec{r}=\vec{r}'} d\vec{r}$, and the functional derivative is $\delta T/\delta \mu(\vec{r}, \vec{r}') = -\frac{1}{2} \delta''(\vec{r} - \vec{r}')$, where δ'' is a distribution (the Dirac δ'' function) which is defined so that $\int \delta''(\vec{r} - \vec{r}') \psi_i(\vec{r}') d\vec{r}' = \nabla^2 \psi_i(\vec{r})$. If $\delta T/\delta \mu$ were a well-behaved function we could obtain $\delta T/\delta n$ from the equality $\delta T/\delta n(\vec{r}) = \delta T/\delta \mu(\vec{r}, \vec{r})$.¹³ Unfortunately, the limit

$$\lim_{\vec{r} \rightarrow \vec{r}'} \frac{\delta T}{\delta \mu(\vec{r}, \vec{r}')} = -\frac{1}{2} \lim_{\vec{r} \rightarrow \vec{r}'} \delta''(\vec{r} - \vec{r}')$$

does not exist in any meaningful sense.

Kohn and Sham have circumvented the difficulties described above by means of the following prescription.³ Consider a system of noninteracting electrons in an external potential $u(\vec{r})$ which is chosen so that the ground-state density is the same as that of a system of interacting electrons in an external potential $v(\vec{r})$. The total ground-state energy of the noninteracting system, $E_s'\{n\} = T_s\{n\} + \int u(\vec{r}) n(\vec{r}) d\vec{r}$, will be a functional of the density alone by the HK theorem, and the variational equation for the ground state will be

$$\frac{\delta T_s\{n\}}{\delta n(\vec{r})} + u(\vec{r}) - \lambda_s = 0, \quad (3.13)$$

where λ_s is the Lagrangian parameter for the noninteracting system. The particle density for the noninteracting system cannot be calculated directly from this equation because we do not know the functional form of the single-particle kinetic energy $T_s\{n\}$. However, we can calculate the particle density in the independent-particle case by solving the single-particle equation for the orbitals,

$$\left[-\frac{1}{2} \nabla^2 + u(\vec{r}) - \epsilon_i \right] \psi_i(\vec{r}) = 0, \quad (3.14)$$

and then using Eq. (3.6) to construct the particle-density function.

Returning to the interacting-particle case, we may define an energy functional

$$U\{n\} = E'\{n\} - T_s\{n\} \quad (3.15)$$

and rewrite Eq. (3.5) as

$$\frac{\delta T_s\{n\}}{\delta n(\vec{r})} + \frac{\delta U\{n\}}{\delta n(\vec{r})} - \lambda = 0. \quad (3.16)$$

Comparing Eqs. (3.13) and (3.16), we see that they will be identical if we choose

$$u(\vec{r}) = \delta U\{n\}/\delta n(\vec{r}) \quad (3.17)$$

and $\lambda = \lambda_s$, and then solve Eq. (3.13) self-consistently. But we could then use Eq. (3.17) and solve Eq. (3.14) self-consistently to obtain the same result. Equation (3.14) [together with Eqs. (3.15) and (3.17)], the Kohn-Sham equation, is, therefore, an exact Schrödinger-like equation which will give the ground-state particle density for a nondegenerate system of interacting electrons.

The central problem in applications of the theory is that of constructing a useful approximation to the potential $u(\{n\}, \vec{r})$ [which is normally expressed in terms of an unknown exchange-correlation potential $\mu_{xc}(\{n\}, \vec{r})$ by writing $u(\vec{r}) = v(\vec{r}) + \int n(\vec{r}') \times |\vec{r} - \vec{r}'|^{-1} d\vec{r}' + \mu_{xc}(\vec{r})$]. We note that, even if the exchange-correlation potential were exactly known, solutions of Eq. (3.14) obtained by variational methods would not give an upper bound to the energy of interacting particles because Eq. (3.14) is the variational equation for a different system of noninteracting particles in a fixed potential. This is, of course, a moot point because, in practice, the major uncertainty comes from approximations in the construction of the exchange-correlation potential.¹⁴

B. Density-kernel equations

The constraints needed to limit the density-kernel variations to the N -representable domain may be obtained from a theorem due to Coleman, which states that a Hermitian one-electron operator $\mu(x, x')$ will be ensemble N -representable if and

only if $\int \mu(x, x) dx = N$ and all eigenvalues,

$$\int \mu(x, x') \phi_i(x') dx' = \mu_i \phi_i(x), \quad (3.18)$$

satisfy the inequality $0 \leq \mu_i \leq 1$.¹⁰ We may introduce these constraints by setting $\mu(x, x') = \sum_{i=1}^{\infty} \phi_i(x) \cos^2 \theta_i \phi_i^*(x')$ and varying $\phi_i(x)$, $\phi_i^*(x)$, and θ_i subject to the constraints $\langle i | j \rangle = \int \phi_i^* \phi_j dx = \delta_{ij}$ and $\sum_{i=1}^{\infty} \cos^2 \theta_i = N$. We may assume that the natural spin orbitals ϕ_1, ϕ_2, \dots , form a complete set. The angles may be limited to $0 \leq \theta_i \leq \pi$ without introducing any further restrictions on the eigenvalues $\mu_i = \cos^2 \theta_i$. The constraints may be introduced by replacing the functional E with

$$\mathcal{E}\{\mu\} = E\{\mu\} - \sum_{i,j} \lambda_{ij} \langle j | i \rangle + \lambda \left(N - \sum_{i=1}^N \mu_i \right), \quad (3.19)$$

where λ_{ij} and λ are Lagrangian parameters. We may write the variational equations in a convenient form by making use of the formal identity

$$\begin{aligned} \frac{\delta E}{\delta \phi_i^*(x)} &= \int \frac{\delta E}{\delta \mu(x', x'')} \frac{\delta \mu(x', x'')}{\delta \phi_i^*(x)} dx' dx'' \\ &= \mu_i \int h(\{\mu\}, x, x') \phi_i(x') dx', \end{aligned} \quad (3.20)$$

where

$$h(\{\mu\}, x, x') = \delta E\{\mu\} / \delta \mu(x', x). \quad (3.21)$$

The functional derivative defined by Eq. (3.21) exists and can explicitly be evaluated for the one-electron terms in the total energy. The kinetic-energy term exists only in the sense of a distribution, but this introduces no real difficulty. The only contribution which is not known is that which comes from the exchange-correlation energy E_{xc} , which is known only as a functional of the second-order density kernel $\sigma(x_1 x_2, x'_1 x'_2)$. (We define $E_{xc} = E - E_{ec} - T$, where E_{ec} consists of the energy of interaction with the external field and the Coulomb energy, and $T\{\mu\}$ is the exact kinetic energy.)

We cannot be certain that $\delta E_{xc}\{\mu\} / \delta \mu(x, x')$ exists in any meaningful sense. Such questions of mathematical rigor are usually ignored in physical theories, but the unexpected results we shall obtain shortly compel us to look closely for possible flaws in the logic by which they were obtained. The assumption that $\delta E_{xc} / \delta \mu$ exists appears to be the only weak link in the chain of logic, so that we must remember that it is an unproven assumption. However, if the universal functional $E_{xc}\{\mu\}$ is so ill behaved that $\delta E_{xc} / \delta \mu$ does not exist, even as a limit or a distribution, then it is unlikely that one will be able to find a useful approximate expression for the universal functional. I am inclined to believe that $\delta E_{xc} / \delta \mu$ does exist in some usable sense, even though it may have some unusual properties that we do not yet understand. Let us,

therefore, proceed on the heuristic assumption that $h(\{\mu\}, x, x')$, defined by Eq. (3.18), can be constructed.

The variational equations may now be written as

$$\frac{\delta \mathcal{E}}{\delta \phi_i^*} = \mu_i h \phi_i - \sum_j \phi_j \lambda_{ji} = 0, \quad (3.22)$$

$$\frac{\delta \mathcal{E}}{\delta \phi_i} = \mu_i \phi_i^* h - \sum_j \lambda_{ij} \phi_j^* = 0, \quad (3.23)$$

$$\frac{\partial \mathcal{E}}{\partial \theta_i} = \sin 2\theta_i (\epsilon_i - \lambda) = 0, \quad (3.24)$$

where $\epsilon_i = \langle i | h | i \rangle$.

We note that Eqs. (3.22)–(3.24) are exactly what one would obtain by substituting h for H and μ_i for w_i in Eqs. (2.6)–(2.8). Aside from the fact that H is a known operator while h is not, the only difference in the application of the variational principle is in the substitution of the constraint $\sum \mu_i = N$ for the constraint $\sum w_i = 1$. We can, by the same arguments used earlier, replace Eqs. (3.22) and (3.23) by the condition

$$(\mu_i - \mu_j) \langle i | h | j \rangle = 0, \quad (3.25)$$

so that the natural spin orbitals must be, or may be chosen to be, solutions of the eigenvalue equation

$$h \phi_i = \epsilon_i \phi_i. \quad (3.26)$$

We also infer, from Eq. (3.24), that each term in the natural expansion of the density kernel for the ground state must satisfy one of the following three conditions: (i) $\mu_i = 1$; (ii) $\epsilon_i = \lambda$; or (iii) $\mu_i = 0$. This implies that all partially occupied natural spin orbitals ($0 < \mu_i < 1$) must belong to the same degenerate eigenvalue of Eq. (3.26). This was an expected result for the N -particle ensemble density kernel when the constraint was $\sum w_i = 1$. It is an unexpected and paradoxical result for the one-particle reduced ensemble density kernel, for which $\sum \mu_i = N$.

The result may be interpreted in a consistent manner. The derivative $\partial E / \partial \mu_i = \langle \phi_i | h | \phi_i \rangle = \epsilon_i$ is a measure of the incremental change in the total energy when the occupation of the i th level is changed by an infinitesimal amount. If the i th and j th levels are partly filled, then if ϵ_i is less than ϵ_j one can decrease the total energy by an infinitesimal amount by increasing the occupation of the i th level at the expense of the j th level. Hence, in order to obtain a stationary value of the energy, the levels which are not completely filled or completely empty must all belong to the same eigenvalue of Eq. (3.26). This partly occupied level will correspond to the Fermi level.

The paradoxical aspect is encountered when we examine the implications for small systems. It is

known, from rather accurate calculations, that small systems such as He and H_2 have no fully occupied levels and that the number of partially occupied levels is large, probably infinite.¹⁵ Since the eigenfunctions of h and μ are identical, by construction, we are forced to the conclusion that there is a many-one mapping between the eigenvalues of μ and the eigenvalues of h . All eigenvalues of μ which lie in the interval $0 < \mu_i < 1$ must be mapped into a single eigenvalue of h . This result indicates that if the operator h can be constructed, it must be quite different from the one-electron orbital operators that occur in self-consistent-field theories.¹⁶

The density-kernel equations remain valid for both local and nonlocal external potentials, so that the consequences of the degeneracy problem are important for both cases. The problem disappears in the Hartree-Fock approximation for a closed-shell system because all orbitals are then either fully occupied ($\mu_i = 1$) or empty ($\mu_i = 0$). The difficulty first occurs in the symmetry-restricted Hartree-Fock approximation with more than one open shell.

IV. COROLLARY OF COLEMAN'S THEOREM

We shall now demonstrate that any non-negative differentiable function $n(\vec{r})$ is an N -representable particle density if $\int n(\vec{r}) d\vec{r} = N$. This will be done by giving an explicit algorithm for constructing an N -representable density kernel $\mu(x, x')$ from an integrable particle density $n(\vec{r}) = \sum_s \mu(\vec{r}_s, \vec{r}_s)$. We will, at the same time, show that many such density kernels can be constructed, thereby establishing the assertion that the mapping between N -representable density kernels and N -representable particle densities is many-one. (This last result is obvious in the discrete representation introduced in Sec. II.) The demonstration will be given only for a system with vanishing spin density, so that $\mu(x, x') = \delta_{ss'} \mu(\vec{r}, \vec{r}')$ and $n(\vec{r}) = 2\mu(\vec{r}, \vec{r})$, where $\mu(\vec{r}, \vec{r}')$ is the spinless density kernel, but the proof can easily be extended, *mutatis mutandis*, to the general case of systems with arbitrary spin densities.

We may use a geometrical construction to decompose $n(\vec{r})$ into a sum,

$$n(\vec{r}) = 2 \sum_i \mu_i f_i(\vec{r}) = \sum_i g_i(\vec{r}), \quad (4.1)$$

where $0 \leq \mu_i \leq 1$, $f_i^*(\vec{r}) = f_i(\vec{r}) \geq 0$, $\int f_i(\vec{r}) d\vec{r} = 1$, and $g_i(\vec{r}) = 2\mu_i f_i(\vec{r})$. The construction will be described only for a density function $n(r)$ defined in the one-dimensional interval $-1 \leq r \leq 1$, but an analogous construction could easily be devised for a density function $n(\vec{r})$ defined over an infinite three-dimensional space.

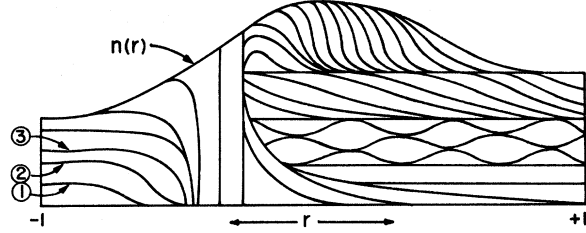


FIG. 1. Sample construction of the particle-density expansion $n(r) = \sum_i g_i(r) = 2 \sum_i \mu_i f_i(r)$. ①, $g_1(r)$; ②, $g_1(r) + g_2(r)$; ③, $g_1(r) + g_2(r) + g_3(r)$, ..., etc.

The construction may be followed by referring to Fig. 1. Starting at a boundary point ($r = -1$ in the one-dimensional example we are using), we may draw an arbitrary curve which lies entirely above the abscissa and below $n(r)$, and encloses an area below the curve which is less than or equal to 2. This curve defines a function which we identify with $g_1(r)$. Then, starting at the far left of the region above $g_1(r)$ and the abscissa, and below $n(r)$, we repeat the process, making sure that the area between $g_1(r)$ (or the abscissa) and the second curve does not exceed 2. This second curve defines a function $g_1(r) + g_2(r)$ from which a function $g_2(r)$ may be obtained by subtraction. We repeat this process until all of the area below $n(r)$ has been used up, and we have drawn M curves which define M functions, $g_1(r) \dots g_M(r)$. At least $N/2$ curves must be drawn, but the number can be arbitrarily large. The only restriction, aside from the restriction on the areas, is that the boundary curves [including $n(r)$ itself] must be smooth enough so that $(dg/dr)^2/g$ and d^2g/dr^2 are integrable functions. [This is to ensure that $\frac{1}{2} \int (dg^{1/2}/dr)^2 dr = -\frac{1}{2} \int g^{1/2} (d^2g^{1/2}/dr^2) dr$ remains finite, so that the kinetic energy will remain finite.] A representative construction, demonstrating the variety of functions that may be used, is shown schematically in Fig. 1. Some constructions are shown with vertical lines. These are actually forbidden because they lead to infinite contributions to the kinetic energy, but one may come arbitrarily close.

Setting $\mu_i = \frac{1}{2} \int g_i(r) dr$ and introducing the normalized functions $f_i(r) = g_i(r)/2\mu_i$, we obtain Eq. (4.1). We now introduce a set of functions $\phi_k(r) = e^{i\omega_k(\vec{r})} f_k^{1/2}(\vec{r})$, where $\omega_k(\vec{r})$ are a set of phase functions chosen so that

$$\int \phi_i^*(\vec{r}) \phi_j(\vec{r}) d\vec{r} = \delta_{ij}. \quad (4.2)$$

We may convince ourselves that phase functions with this property can always be constructed without going through the tedious details of a rigorous mathematical proof. If the curves used to define $g_1(\vec{r})$ were vertical lines, then the functions $\phi_i(\vec{r})$

would be orthogonal with the choice $\omega_i(\vec{r})=0$. If the rectangular like functions obtained by using vertical lines were smoothed out into Gaussian-like peaks, it is intuitively clear that one should still be able to choose phase functions which oscillated in the region of overlapping tails in such a manner that the overlap integrals would vanish. Beyond that, we merely note that M arbitrary functions surely provide enough freedom to make $M(M-1)/2$ overlap integrals vanish. We conjecture that there may be several sets of phase functions for each set of expansion functions $f_i(\vec{r})$ (this is obviously true when the vertical construction is used), but none of the essential conclusions depend on this conjecture.

We may now define density kernels

$$\mu(\vec{r}, \vec{r}') = \sum \phi_i(\vec{r}) \mu_i \phi_i^*(\vec{r}') \quad (4.3)$$

which are different for each different construction of the functions $g_i(\vec{r})$ but which all give the same particle density $n(\vec{r})$. The constructions have been made in such a manner that the density kernels

satisfy the necessary and sufficient conditions for ensemble N -representability; hence, the original particle density, which was restricted only by the conditions $n(r) \geq 0$ and $\int n(\vec{r}) d\vec{r} = N$ (and that d^2n/dr^2 be integrable), must also be N -representable.

We can always choose the partitioning in Fig. 1 so that there are exactly $N/2$ regions, each with an area equal to 2. Hence, an obvious corollary is that any N -representable particle density $n(\vec{r})$ can be obtained from a single Slater determinant.

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¹¹The notation $\langle D \rangle_{N-r} \equiv \int \cdots \int D(x_1 \cdots x_r x_{r+1} \cdots x_N; x'_1 \cdots x'_r x'_{r+1} \cdots x'_N) dx_{r+1} \cdots dx_N, \langle \mu \nu \rangle = \iint \mu(x, x')$

$\times v(x', x) dx' dx$, and $\langle \sigma u \rangle = \iint \iint \sigma(x_1 x_2, x'_1 x'_2) \times u(x'_1 x'_2, x_1 x_2) dx'_1 dx'_2 dx_1 dx_2$ is used.

¹²Equation (2.5) implies that the spectrum of H is discrete. The sums must be replaced by integrals and the argument modified in order to make the derivation mathematically rigorous for a continuous spectrum. We will assume that Born-von Kármán, or similar, boundary conditions are used in order to avoid such complications.

¹³The functional derivatives $\delta F/\delta \mu(x, y)$ and $\delta F/\delta n(x)$ are defined by the equalities $\delta F \equiv F\{\mu + \delta \mu\} - F\{\mu\} = \int [\delta F/\delta \mu(x, y)] \delta \mu(x, y) dx dy$ and $\delta F \equiv F\{n + \delta n\} - F\{n\} = \int [\delta F/\delta n(x)] n(x) dx$, respectively, where $\delta \mu$ and δn are arbitrary infinitesimal functions. In the discrete case $[\mu(x, y) \rightarrow \mu(x_i, x_j) \equiv \mu_{ij}]$ and $n(x) = \mu(x, x) \rightarrow n(x_i) \equiv n_i]$ these equations become $\delta F = \Delta x \Delta y \sum_{i,j} (\partial F/\partial \mu_{ij}) \times \delta \mu_{ij}$ and $\delta F = \Delta x \sum_i (\partial F/\partial n_i) \delta n_i$, where $\Delta x = x_i - x_{i-1}$ and $\Delta y = y_j - y_{j-1}$ are the distances between the mesh points (assumed to be uniformly distributed). We can obtain the second expression from the first in the discrete case by setting $\delta \mu_{ij} = \delta_{ij} \delta n_i / \Delta y$. By analogy, one can obtain $\delta F/\delta n$ from $\delta F/\delta \mu$ directly by setting $\delta \mu(x, y) = \delta n(x) \delta(x-y)$ in the defining relation.

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