PHYSICAL REVIEW A VOLUME 26, NUMBER 3 SEPTEMBER 1982

Electron densities in search of Hamiltonians

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(Received 20 October 1981)

By utilizing the knowledge that a Hamiltonian is a unique functional of its ground-state density, the following fundamental connections between densities and Hamiltonians are revealed: Given that $\rho_\alpha, \rho_\beta, \ldots, \rho_\omega$ are ground-level densities for interacting or noninteracting Hamiltonians $H_1, H_2, \ldots, H_M$ (M arbitrarily large) with local potentials $v_1, v_2, \ldots, v_M$, but *given that we do not know which* ρ *belongs with which* H, the correct mapping is possible and is obtained by minimizing $\int d\vec{r}\,[v_1(\vec{r})\rho_\alpha(\vec{r})+v_2(\vec{r})\rho_\beta(\vec{r}) + \cdots v_M(\vec{r})\rho_\omega(\vec{r})]$ with respect to optimum permutations of the ρ's among the v's. A tight rigorous bound connects a density to its interacting ground-state energy via the one-body potential of the interacting system and the Kohn-Sham effective one-body potential of the auxiliary noninteracting system. A modified Kohn-Sham effective potential is defined such that its sum of lowest orbital energies equals the true interacting ground-state energy. Moreover, of all those effective potentials which differ by additive constants and which yield the true interacting ground-state density, this modified effective potential is the most invariant with respect to changes in the one-body potential of the true Hamiltonian. With the exception of the occurrence of certain linear dependencies, *a density will not generally be associated with any ground-state wave function* (is *not wave function v representable*) if that density can be generated by a special linear combination of three or more densities that arise from a common set of degenerate ground-state wave functions. Applicability of the "constrained search" approach to density-functional theory is emphasized for non-v-representable as well as for v-representable densities. In fact, a particular constrained ensemble search is revealed which provides a general sufficient condition for non-v representability by a wave function. The possible appearance of *noninteger occupation numbers* is discussed in connection with the existence of non-v representability for some Kohn-Sham noninteracting systems.

I. INTRODUCTION

The crucial role of the density for elucidation of the electronic structure of atoms, molecules, and solids is manifested by the fact that the electronic Hamiltonian is a unique functional of its ground-state density[1] (the ground-state electron density must change when the local one-body potential changes by more than an additive constant). Knowledge of the existence of this unique functional relationship between density and Hamiltonian, as first given by Hohenberg and Kohn, has stimulated intense research in formal density- and spin-density-functional theories.[1–48]

The local one-body potential portion of the Hamiltonian has played an important part in formal existence theorems; the union between density and local potential is indeed a close one. Consequently, it is natural to ask if it is possible to match Hamiltonians to their corresponding ground-state densities by means of just the local potentials and the densities. As proved within, the answer is yes when a multiple choice is presented, and a specific method shall be provided. (Consult also Ref. 36.)

As we shall observe, rigorous interacting energy bounds exist in terms of just a ground-state density and local potentials of both the interacting system and its corresponding Kohn-Sham noninteracting system.[3] Moreover, a modified Kohn-Sham effective potential shall be defined such that its ground-state energy equals the true interacting ground-state energy. The Hellmann-Feynman theorem dictates that this potential must respond in a special way to processes involving the corresponding interacting

Hamiltonian.

Are there instances when a well-behaved and reasonable density belongs to no ground-state wave function? The answer to this question is yes, as we shall see. This is a significant point because it has generally been assumed, in formal applications of the variational portion of the Hohenberg-Kohn theorem, that any "reasonable" density belongs to some ground-state wave function. Several recent formulations of density-functional theory, on the other hand, employ the constrained search approach[21] which does not necessarily require that a trial density belong to some ground-state wave function.

II. DENSITY TO HAMILTONIAN MAPPING

Consider a set of M Hamiltonians $H_1, H_2, \ldots, H_M$ (with *M arbitrarily large*), where H_k corresponds to N interacting electrons in the local multiplicative spin-free potential v_k. Specifically,

$$H_k = T + Vee + \sum_{i=1}^{N} v_k(\vec{r}_i) , \tag{1}$$

where v_k is not necessarily restricted to be a Coulomb operator, but where T signifies the usual kinetic energy operator and Vee signifies the usual electron-electron repulsion operator. Form the following N-electron ensemble density matrix $D_k^{(N)}$ and its corresponding density ρ_k from the $n(k)$ ground-state degenerate wave functions Ψ_l^k of H_k with ground-state energy E_k:

$$D_k^{(N)}(x_1'x_2' \cdots x_N' \,|\, x_1x_2 \cdots x_N) = \sum_{l=1}^{n(k)} c_l^k \Psi_l^k(x_1'x_2' \cdots x_N')^* \Psi_l^k(x_1x_2 \cdots x_N) ; \tag{2}$$

$$\rho_k(\vec{r}) = N \int D_k^{(N)}(xx_2 \cdots x_N \,|\, xx_2 \cdots x_N) \times ds\, dx_2 \cdots dx_N , \tag{3}$$

with

$$H_k(\vec{r}_1\vec{r}_2 \cdots \vec{r}_N) D_k^{(N)}(x_1'x_2' \cdots x_N' \,|\, x_1x_2 \cdots x_N) = E_k D_k^{(N)}(x_1'x_2' \cdots x_N' \,|\, x_1x_2 \cdots x_N) , \tag{4}$$

where $\vec{r}$ denotes space coordinate, s denotes spin coordinate, and x denotes space-spin coordinate. The c_l^k are restricted by $0 \le c_l^k \le 1$ and $\sum_l^{n(k)} c_l^k = 1$. For a nondegenerate E_k, $n(k)$ must equal unity. (Incidentally, integration of ρ_k over all space gives N which is enough to specify the operators T and Vee.)

By the variational theorem

$$\langle H_1 D_\alpha^{(N)} \rangle + \langle H_2 D_\beta^{(N)} \rangle + \cdots + \langle H_M D_\omega^{(N)} \rangle \ge \langle H_1 D_1^{(N)} \rangle + \langle H_2 D_2^{(N)} \rangle + \cdots + \langle H_M D_M^{(N)} \rangle , \tag{5}$$

where the D's on the left-hand side of Eq. (5) are permutations of the D's on the right-hand side. The equality clearly holds if and only if $\alpha = 1$, $\beta = 2, \ldots, \omega = M$. Furthermore, the sum of the $\langle T + Vee \rangle$'s on the left-hand side must equal the sum of the $\langle T + Vee \rangle$'s on the right-hand side, from which it follows that

$$\int d\vec{r} [v_1(\vec{r})\rho_\alpha(\vec{r}) + v_2(\vec{r})\rho_\beta(\vec{r}) + \cdots + v_M(\vec{r})\rho_\omega(\vec{r})] \ge \int d\vec{r} [v_1(\vec{r})\rho_1(\vec{r}) + v_2(\vec{r})\rho_2(\vec{r}) + \cdots + v_M(\vec{r})\rho_M(\vec{r})] , \tag{6}$$

where the equality applies if and only if $\alpha = 1$, $\beta = 2, \ldots, \omega = M$. Thus, if we do not know which ρ belongs with which H, we would be able to match the ρ's to their H's through minimization of

$$G_{1,2,\ldots,M}^{\alpha,\beta,\ldots,\omega} = \int d\vec{r} [v_1(\vec{r})\rho_\alpha(\vec{r}) + v_2(\vec{r})\rho_\beta(\vec{r}) + \cdots + v_M(\vec{r})\rho_\omega(\vec{r})] \tag{7}$$

by the optimum ordering of the superscripts in the functional $G_{1,2,\ldots,M}^{\alpha,\beta,\ldots,\omega}$.

It should be clear from the above development that a functional G, to be minimized, exists also for noninteracting Hamiltonians with multiplicative local potentials of the form

$$H_{\text{eff}} = T + \sum_{i=1}^{N} v_{\text{eff}}(\vec{r}_i) \tag{8}$$

as well as for interacting Hamiltonians. Finally, for nonlocal one-body potentials, the densities in G are simply replaced by first-order reduced density matrices. In fact, one is allowed to replace densities by first-order density matrices even when the one-body potentials are local.[15] (For pertinent discussions of density-Hamiltonian mappings see the study by Katriel, Appellof, and Davidson.[36])

III. INTERACTING ENERGY BOUNDS FROM LOCAL ONE-BODY POTENTIALS

Consider a ground state ρ of an interacting system. Assume further that ρ belongs simultaneously to a ground state of some auxiliary noninteracting system, of the form of Eq. (8), obtained, let us say, by means of the exact Kohn-Sham formulation.[3] For these densities are there known equalities which directly relate the interacting ground state E to $v(\vec{r})$ of the interacting system and to $v_{\text{eff}}(\vec{r})$ of the auxiliary noninteracting system? The answer, at least at present, appears to be no. Towards an affirmative end, however, we shall now put forth rigorous bounds that are reasonably tight.

The virial theorem, when applied to the interacting ground state, gives the energy in terms of the one matrix

$$E=-\langle T\rangle+\int d\vec{r}\,v(\vec{r})\rho(\vec{r})+\int d\vec{r}\rho(\vec{r})\sum_i q_i\frac{\partial v(\vec{r})}{\partial q_i}\ , \tag{9}$$

where q_i refers to a Cartesian coordinate and $\langle T\rangle$ is the kinetic energy of the interacting system. Likewise, application of the virial theorem to the auxiliary noninteracting ground state yields

$$\tfrac{1}{2}\int d\vec{r}\rho(\vec{r})\sum_i q_i\frac{\partial v_{\text{eff}}(\vec{r})}{\partial q_i}=\langle T\rangle_{\text{eff}}\ , \tag{10}$$

where $\langle T\rangle_{\text{eff}}$ is the kinetic energy of the noninteracting ground state. Since $\rho(\vec{r})$ is the same for both the interacting and noninteracting systems, it follows that[17]

$$\langle T\rangle_{\text{eff}}\leq\langle T\rangle\ . \tag{11}$$

Consequently, addition of Eqs. (9)–(11) provides the desired bound, namely,

$$E\leq\int d\vec{r}\,\bar{v}(\vec{r})\rho(\vec{r})\ , \tag{12}$$

where

$$\bar{v}(\vec{r})=v(\vec{r})+\sum_i q_i\frac{\partial}{\partial q_i}[v(\vec{r})-\tfrac{1}{2}v_{\text{eff}}(\vec{r})]\ . \tag{13}$$

For the special case of an atom, Eq. (13) reduces to

$$\bar{v}(\vec{r})=-\tfrac{1}{2}\sum_i q_i\frac{\partial}{\partial_i}v_{\text{eff}}(\vec{r}_i)\ . \tag{14}$$

In any case, a trapezoid rule approximation, when applied to the coupling-constant integration[10,11,13] between the interacting and noninteracting systems, suggests that the right-hand side of Eq. (12) is expected to generally differ from E by roughly the magnitude of the electron-electron correlation energy. This conclusion also follows if it is assumed that the noninteracting wave function or ensemble density matrix is optimum with respect to scaling within the interacting system.

IV. CHANGES IN EFFECTIVE POTENTIALS FOR INTERACTING PROCESSES

Once the Kohn-Sham v_{eff} is known for one situation it would be nice to be able to immediately put down v_{eff} for a new isoelectronic situation corresponding to changes in, let us say, nuclear positions or nuclear charges. This would, of course, be impossible to do exactly, but towards this end a helpful relation is now presented which involves a modification of v_{eff} formed by the addition of a constant to v_{eff}.

First, let us denote a point along an isoelectronic path by λ. Accordingly, the interacting Hamiltonian is now written as

$$H(\lambda)=T+\sum_{i=1}^{N}v(\vec{r}_i,\lambda)+\sum_{i<j}^{N-1}\sum^{N}r_{ij}^{-1}\ , \tag{15}$$

and the auxiliary Kohn-Sham noninteracting Hamiltonian is now expressed by

$$H_{\text{eff}}(\lambda)=T+\sum_{i=1}^{N}v_{\text{eff}}(\vec{r}_i,\lambda)\ , \tag{16}$$

$$v_{\text{eff}}(\vec{r},\lambda)=v(\vec{r},\lambda)+\int\rho(\vec{r}_2,\lambda)\,|\vec{r}-\vec{r}_2|^{-1}d\vec{r}_2+v_{\text{xc}}[\rho(\vec{r},\lambda)]\ , \tag{17}$$

where v_{xc} is the exchange-correlation potential. Denote the ground state of $H(\lambda)$ by $\Psi(\lambda)$ and the ground state of $H_{\text{eff}}(\lambda)$ by $\Psi_{\text{eff}}(\lambda)$. Now add a constant $C(\lambda)$ to $H_{\text{eff}}(\lambda)$ and form $\tilde{H}_{\text{eff}}(\lambda)$ so that the lowest eigenvalue of $\tilde{H}_{\text{eff}}(\lambda)$ is shifted to become identical to the corresponding interacting ground-state energy $E(\lambda)$. Specifically,

$$\tilde{H}_{\text{eff}}(\lambda)=T+\sum_{i=1}^{N}v_{\text{eff}}(\vec{r}_i,\lambda)+C(\lambda) \tag{18}$$

or

$$\tilde{H}_{\text{eff}}(\lambda)=T+\sum_{i=1}^{N}v(\vec{r}_i,\lambda)+\sum_{i=1}^{N}\bar{v}(\vec{r}_i,\lambda) \tag{19}$$

with

$$E(\lambda)=\langle\Psi(\lambda)\,|\,H(\lambda)\,|\,\Psi(\lambda)\rangle$$

$$=\langle\Psi_{\text{eff}}(\lambda)\,|\,\tilde{H}_{\text{eff}}(\lambda)\,|\,\Psi_{\text{eff}}(\lambda)\rangle\ . \qquad (20)$$

Application of the Hellmann-Feynman theorem to Eq. (20) gives

$$\frac{\partial E(\lambda)}{\partial\lambda}=\int d\vec{r}\rho(\vec{r},\lambda)\frac{\partial v(\vec{r},\lambda)}{\partial\lambda}$$

$$=\int d\vec{r}\rho(\vec{r},\lambda)\frac{\partial v(\vec{r},\lambda)}{\partial\lambda}$$

$$+\int d\vec{r}\rho(\vec{r},\lambda)\frac{\partial\tilde{v}(\vec{r},\lambda)}{\partial\lambda} \qquad (21)$$

which means

$$\int d\vec{r}\rho(\vec{r},\lambda)\frac{\partial\tilde{v}(\vec{r},\lambda)}{\partial\lambda}=0\ , \qquad (22)$$

where an infinitesimal change in λ may represent any *arbitrary* isoelectronic process (for instance, a change in any nuclear position or in any nuclear charge, etc.). Moreover, Appendix A reveals that in a certain sense the average value of $(\partial\tilde{v}/\partial\lambda)^2$ is a minimum.

Perhaps intensive studies of $\tilde{v}(r,\lambda)$ should be initiated. Perhaps the latter potential, which simply differs by the additive constant $C(\lambda)$ from that part of the Kohn-Sham potential given by

$$\int\rho(\vec{r}_2)\,|\,\vec{r}_2-\vec{r}\,|^{-1}d\vec{r}_2+v_{\text{xc}}[\rho]\ ,$$

might be sufficiently transferable for small changes in λ and thus might not have to be recalculated for every new λ. In contrast, it is well known that each part of

$$\int\rho(\vec{r}_2)\,|\,\vec{r}_2-\vec{r}\,|^{-1}d\vec{r}_2+v_{\text{xc}}[\rho]$$

is not transferable.

V. DENSITIES FOR WHICH THERE ARE NO GROUND-STATE WAVE FUNCTIONS

The question of whether or not a given ρ corresponds to some ground-state wave function is an important one. Accordingly, let us introduce some terminology: If ρ belongs to a ground-state wave function of some interacting H of the form of Eq. (1), where v is not necessarily restricted to be a Coulomb operator, then ρ shall be said to be "interacting wave function v representable." If ρ belongs to a ground-state wave function of some noninteracting H_{eff} of the form of Eq. (8), where v_{eff} is also not restricted to be a Coulomb operator, then ρ shall be said to be "noninteracting wave function v representable." Similarly, for an interacting or a noninteracting situation, if ρ can be realized by an ensemble composed entirely of a set of degenerate ground-state wave functions, as in Eq. (2), for instance, then ρ shall be said to be, respectively, "interacting ensemble v representable" or "noninteracting ensemble v representable." Clearly, there follow numerous extensions of the above definitions. Finally, note that according to the present literature the simple expression v representable[49] usually signifies "wave function v representable," but as a result of the following discussion, a more elaborate set of definitions is going to be required in the future. (It is important to mention that it has now been definitely established that it is safe to assume wave function N representability for an arbitrary density.[7,38] This is significant because N representability is necessary for v representability.)

It has often been explicitly or tacitly assumed in density-functional theories that reasonable ρ's are simultaneously interacting wave function v representable and noninteracting wave function v representable. It is the purpose of this section to prove the existence of reasonable densities which are not wave function v representable, however uncommon.[36]

Assume that a ground energy level, for a given interacting or noninteracting H, has a degeneracy of order q. Form the following ensemble density matrix,[50] of rank q, from the degenerate ground-state wave functions ψ_i:

$$D^{(N)}(1',2',\ldots,N'\,|\,1,2,\ldots,N)$$

$$=\sum_{i=1}^{q}d_i\psi_i(1',2',\ldots,N')^*$$

$$\times\psi_i(1,2,\ldots,N)\ , \qquad (23)$$

where $0\le d_i\le 1$ and $\sum_{i=1}^{q}d_i=1$. Consider that density given by

$$\rho(\vec{r})=N\int D^{(N)}(xx_2\cdots x_N\,|\,xx_2\cdots x_N)$$

$$\times ds\,dx_2\cdots dx_N \qquad (24)$$

or

$$\rho(\vec{r})=\sum_{i=1}^{q}d_i\rho_{ii}(\vec{r})\ , \qquad (25)$$

where

$$\rho_{ij}(\vec{r})=N\int\psi_i(xx_2\cdots x_N)^*\psi_j(xx_2\cdots x_N)$$

$$\times ds\,dx_2\cdots dx_N\ . \qquad (26)$$

It shall now be proved that ρ is not wave function v representable unless certain linear dependencies happen to appear.

First of all, since the $D^{(N)}$ of Eq. (23) is expanded entirely in terms of ground states of the same given Hamiltonian, Appendix B may be invoked and its theorem immediately dictates that ρ *cannot* belong to a *ground-state wave function* of any Hamiltonian H' which differs from the given Hamiltonian H by more than an additive constant in the one-body local potential. To rule out wave function v representability, it remains for us to prove that no ground-state wave function of the given Hamiltonian yields ρ. Accordingly, form the ground-state wave function Q:

$$Q=\sum_{i=1}^{q} a_i\psi_i \,, \tag{27}$$

where, with orthonormal ψ_i, $0\leq |a_i| \leq 1$ and $\sum_i |a_i|^2=1$, and let us show that, in general, there exists no set of a_i such that the $\rho(\vec{r})$ in Eq. (25) may be simultaneously generated by

$$\rho(\vec{r})=N\int Q(xx_2\cdots x_N)^*Q(xx_2\cdots x_N)\times ds\,dx_2\cdots dx_N \,. \tag{28}$$

Set Eq. (25) equal to Eq. (28) and obtain

$$\sum_{i=1}^{q}\sum_{j=1}^{q}(\delta_{ij}d_j-a_i^*a_j)\rho_{ij}(\vec{r})=0 \,. \tag{29}$$

Except when certain linear dependencies [excluding those due to $\rho_{ij}(\vec{r})=\rho_{ji}(\vec{r})$] might happen to exist among the $\rho_{ij}(\vec{r})$, no solution of Eq. (29) for the a_i is generally possible for $q>2$, because the number of independent equations for the a_i would exceed the number of unknowns. Hence, for $q>2$, wave function v representability is not expected for those densities which can be constructed by the linear combinations given in Eq. (25). [For $q=2$, and real ψ_1 and ψ_2, $Q=d_1^{1/2}\psi_1+id_2^{1/2}\psi_2$ would satisfy Eq. (29).] The densities in Eq. (25) are, however, clearly ensemble v representable.

The noninteracting case is particularly important in Kohn-Sham theory where it has generally been assumed that well-behaved densities are noninteracting wave function v representable. On the contrary, we shall now present readily available counterexamples.

Consider the following noninteracting Coulomb Hamiltonian:

$$H_{\text{eff}}=T-\sum_{i=1}^{N} Zr_i^{-1} \,, \tag{30}$$

where Z signifies nuclear charge. Assume, for example, that the number of electrons N is equal to 11. For this case, let $\{\psi(n,l,m)\}$ denote the set of q degenerate antisymmetric ground-state Na-like wave functions which are schematically represented, in obvious notation, by

$$\psi(n,l,m)=A\psi(\text{Ne})\phi(n,l,m) \,, \quad n=3;\ l=0,1,2;\ m=-l,\ldots,+l \tag{31}$$

where A is a normalizer-antisymmetrizer, $\psi(\text{Ne})$ symbolizes the electronic configuration for the noninteracting ground-state neonlike atom or ion, and the familiar $\phi(n,l,m)$ denotes that one-electron orbital which is occupied by the last electron, where (n,l,m) denotes the orbital's set of quantum numbers. Specifically,

$$\phi(n,l,m)=R_{nl}(r)Y_{lm}(\theta,\phi) \,, \tag{32}$$

where the R_{nl} are Laguerre polynomials and the Y_{lm} are spherical harmonics. For a good spherical density, let $D^{(N)}$ contain equal occupancies, namely,

$$D^{(N)}(1',2',\ldots,N'\,|\,1,2,\ldots,N)=\tfrac{1}{9}\sum_{l=0}^{2}\sum_{m=-l}^{+l}\psi(3',l',m')^*\psi(3,l,m) \,. \tag{33}$$

Multiplication by N and integration of Eq. (33) yields

$$\rho(\vec{r})=2\sum_{n=1}^{2}\sum_{l=0}^{n-1}\sum_{m=-l}^{+l}\phi(n,l,m)^*\phi(n,l,m)+\tfrac{1}{9}\sum_{l=0}^{2}\sum_{m=-l}^{+l}\phi(3,l,m)^*\phi(3,l,m) \,. \tag{34}$$

(An infinite number of nonspherical densities are also possible.) The density given by Eq. (34) is indeed reasonable; it is far from pathological. It is even always monotonically decreasing from the nucleus,[51] but it is *not* noninteracting wave function v representable. Moreover, this means that for the $\rho(r)$ given in Eq. (34), *there is no one-body Hamiltonian of the form*

$$h_{\text{eff}}(\vec{r})=-\tfrac{1}{2}\nabla^2+v_{\text{eff}}(\vec{r}) \tag{35}$$

such that the densities of the first 11 eigenstates of $h_{\text{eff}}(\vec{r})$ *add to* $\rho(\vec{r})$. Or, here one can say that *no ground-state single determinant gives* $\rho(\vec{r})$.

VI. CLOSING REMARKS

For the variational portion of the original Hohenberg-Kohn formulation, a trial density had to be wave function v representable; that is, the trial density had to belong to some antisymmetric ground-state wave function. When a wave function v representable ρ_l is employed, for example, as a trial density for the interacting H_k in Eq. (1), then according to Hohenberg and Kohn, there exists a universal functional F such that

$$E_k \leq \int d\vec{r}\, v_k(\vec{r})\rho_l(\vec{r}) + F[\rho_l] \, , \tag{36}$$

$$F[\rho_l] = \langle \Psi_l \mid T + Vee \mid \Psi_l \rangle \, , \tag{37}$$

where Ψ_l is a ground-state antisymmetric wave function of some H_l which may differ from H_k only in the local one-body potential. But, what if the trial ρ_l is not wave function v representable, so that F is undefined. Well, if the trial ρ_l happens to be ensemble v representable, then Secs. II and V dictate that there is a modification of $F[\rho_l]$ which may be employed; just replace the Ψ_l in Eq. (37) by that ensemble density matrix $D_l^{(N)}$, of the form of Eq. (2), which yields ρ_l and is composed entirely of degenerate ground-state wave functions, so that Eq. (4) is satisfied with respect to some H_l. However, what if the trial ρ is not even ensemble v representable? Is everything lost? No; on the contrary, just replace $F[\rho]$ by $Q[\rho]$, where[19,21]

$$Q[\rho] = \min \langle \Psi_\rho \mid T + Vee \mid \Psi_\rho \rangle \; . \tag{38}$$

(Related functionals[21,28] are appropriate for one-matrix formulations.[7,8,15,16,21,28]) The universal variational functional $Q[\rho]$ searches each and every antisymmetric wave function Ψ_ρ that generates the given trial ρ. The functional $Q[\rho]$ then delivers that value of $\langle T + Vee \rangle$ which is a minimum.[21] It is obvious that $Q[\rho]$ requires neither wave function nor ensemble v representability, only N representability.[52] Moreover,

$$F[\rho] = Q[\rho] \tag{39}$$

when ρ is wave function v representable, *so that* $Q[\rho]$ *may be viewed as an explicit formal identification of* $F[\rho]$.[21] Use of $Q[\rho]$ and related functionals constitute the constrained search approach to density-functional theory. In calculations $Q[\rho]$ is approximated.

For extensive constrained searches over ensembles see Ref. 28, for a momentum-space theory consult Ref. 33, for the recently developed time-dependent density-functional theory see Ref. 39, and for a very recent non-Born-Oppenheimer density-functional theory consult Ref. 40.

For a *general sufficient condition* of non v representability by an interacting wave function, simply extend[28] the constrained search[21] in Eq. (38) to include all those unreduced, N-electron, ensemble density matrices[28] that give ρ. If the constrained minimum in $\langle T + Vee \rangle$ cannot be attained by any idempotent unreduced density matrix, then ρ is not interacting wave function v representable. For the noninteracting case, replace $\langle T + Vee \rangle$ by $\langle T \rangle$.

The development in Sec. V pertaining to noninteracting systems supports the growing feeling that freedom and necessary adjustments should be given to Kohn-Sham-like formulations to allow for the possibilities of noninteger occupation numbers because not every density can be realized by a single-determinant ground-state wave function for some noninteracting system.[53–55] There is even speculation that there are reasonable densities which cannot be realized by orbitals which are all eigenfunctions of the same one-body Hamiltonian, with a local potential, even if holes are allowed to appear below the Fermi level.[56] In any case, it has been shown[34,54] that constrained ensemble searches[28] are especially applicable for kinetic energy evaluation.[34,54]

The constrained search approach has recently been invoked to prove rigorously that each optimum single orbital density has to be self-interaction-free in the exact energy-density functional for the interacting ground state, regardless of the v representability status of the orbital density.[34] By "self-interaction-free," it is meant that the exchange-correlation self-interaction for the orbital density exactly cancels its direct electrostatic self-interaction.[34] Moreover, this implies that the self-correlation energy of an optimum orbital density must be zero. [See Eqs. (30) and (31) in Ref. 34].

As stated at the end of Sec. II, Eq. (6) is also valid if each density is replaced by its corresponding ground-state one matrix (see the related pertinent assertion in Ref. 15). Hence, the *combination* of Eqs. (6) and (9) allows one to obtain *energies from 1-matrices*, given *far less information than might have been suspected would be necessary.* Specifically, given a set of M Hamiltonians and a set of M ground-state 1-matrices, where M is arbitrarily large, but given that we do not know which 1-matrix belongs with which Hamiltonian, the minimization of the appropriate G in Eq. (7) correctly maps each 1-matrix to its Hamiltonian, and Eq. (9) then computes each corresponding ground-state energy.

Note added in proof. I have recently read a manuscript by E. H. Lieb entitled "Denisty Functionals for Coulomb Systems," to be published in a volume edited by H. Feshbach and A. Shimony (MIT, Cambridge). Although derived independently, part of Lieb's analysis of non-v representability and part of the analysis of non-v representability in the present article are similar in that both papers use degeneracies. Note also that Lieb's $\widetilde{F}$ corresponds to Q [Ref. 21 and Eq. (38) here] and, if desired, Q is made convex by replacing wave functions with ensembles (Ref. 28) in the constrained search. Convexity, however, is not necessarily desirable when one seeks only pure-state solutions.

ACKNOWLEDGMENTS

It is a pleasure to thank Professor Robert G. Parr, Professor John P. Perdew, Professor Ernest R. Davidson, Professor William E. Palke, Professor John E. Harriman, Professor Jerome A. Goldstein, Professor Alan L. Goodman, and Professor T. Tung Nguyen-Dang for enlightening discussions and helpful criticisms.

APPENDIX A

From the definition of $\tilde{v}$, it follows that

$$\frac{\partial \tilde{v}(\vec{r},\lambda)}{\partial \lambda}=\frac{\partial w(\vec{r},\lambda)}{\partial \lambda}+N^{-1}\frac{\partial C(\lambda)}{\partial \lambda}\ , \tag{A1}$$

where

$$w(\vec{r},\lambda)=\int \rho(\vec{r}_2,\lambda)\,|\vec{r}-\vec{r}_2|^{-1}d\vec{r}_2 +v_{\mathrm{xc}}[\rho(\vec{r},\lambda)]\ . \tag{A2}$$

Insertion of Eq. (A1) into Eq. (22) gives

$$\frac{\partial C(\lambda)}{\partial \lambda}=-\int \rho(\vec{r},\lambda)\frac{\partial w(\vec{r},\lambda)}{\partial \lambda}\ . \tag{A3}$$

Substitution of Eq. (A3) into Eq. (A1) yields[57]

$$\frac{\partial \tilde{v}(\vec{r},\lambda)}{\partial \lambda} =\frac{\partial w(\vec{r},\lambda)}{\partial \lambda}-N^{-1}\int \rho(\vec{r},\lambda)\frac{\partial w(\vec{r},\lambda)}{\partial \lambda}d\vec{r}\ . \tag{A4}$$

Now, let us square Eq. (A4) and take expectation values. We obtain

$$\langle(\partial\tilde{v}/\partial\lambda)^2\rangle =\left\langle\left[\frac{\partial w}{\partial \lambda}\right]^2\right\rangle-N^{-1}\left\langle\left[\frac{\partial w}{\partial \lambda}\right]\right\rangle^2 , \tag{A5}$$

or

$$\left\langle\left[\frac{\partial \tilde{v}}{\partial \lambda}\right]^2\right\rangle\le\left\langle\left[\frac{\partial w}{\partial \lambda}\right]^2\right\rangle , \tag{A6}$$

where

$$\left\langle\left[\frac{\partial \tilde{v}}{\partial \lambda}\right]^2\right\rangle\equiv\int \rho(\vec{r},\lambda)\left[\frac{\partial \tilde{v}}{\partial \lambda}\right]^2 d\vec{r}\ ,$$

etc. Equation (A6) reveals the minimum property of $\partial\tilde{v}/\partial\lambda$ as mentioned in Sec. IV.

APPENDIX B

We have the following.

Theorem:

If ρ is an *ensemble* density associated with a degenerate ground energy level of a Hamiltonian H with local potential v, then ρ is not the ground-pure-state density of any Hamiltonian H' with local potential v', where v' differs from v by more than an additive constant.

Proof:

Assume

$$HD^{(N)}=ED^{(N)}\ , \tag{B1}$$

$$H'\Psi'=E'\Psi'\ , \tag{B2}$$

where both E and E' are ground energy levels. Further, assume that both the ensemble $D^{(N)}$ and the pure state Ψ' yield ρ. To prove the above theorem, it suffices to show that this common density assumption leads to the familiar Hohenberg-Kohn-like contradiction. Accordingly, Eq. (B1) implies

$$\langle\Psi'\,|\,H\,|\,\Psi'\rangle>E \tag{B3}$$

and Eq. (B2) implies

$$\langle H'D^{(N)}\rangle>E'\ . \tag{B4}$$

[Observe, by the way, that Eq. (B4), as well as (B3), contains a strict inequality because there is a strict inequality associated with each ground-state wave function within $D^{(N)}$.] Employ $H=H'+(H-H')$ in Eq. (B3) and $H'=H+(H'-H)$ in Eq. (B4), then add the two resultant equations to obtain the desired contradiction $E'+E>E+E'$ which completes the proof.

Note that Eq. (6) can be used for an alternative direct proof. The left-hand side of Eq. (6) *has* to be greater than the right-hand side when the left-hand side involves *any* permutation of two densities on the right-hand side. It follows, then, that a density can only appear once on each side.

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