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Variational principle for the ground-state energy as a functional of the one-particle density matrix: Beyond Hartree-Fock theory

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In parallel with standard density-functional theory, we study the energy of the ground state of a finite many-body system as a functional of the one-particle density matrix. We show that the formulation of a variational principle that is valid beyond the Hartree-Fock limit requires that two-body correlations be included not only in the ground-state energy but also in the constraints. As an illustration, we apply a linear-response argument to derive formulas for first-order corrections to the Hartree-Fock density matrix. Further analysis suggests an approach in terms of the density matrix of an independent-particle system, which can be introduced by the application of an alternative variational principle. This approach is reminiscent of Kohn-Sham theory, but the effective external potential is not required to be local. This variational method can be implemented in a systematic fashion by means of the linked-cluster expansion. In an appendix we study a variant of the Hohenberg-Kohn theorem for nonlocal potentials. [S1050-2947(98)06104-6]

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I. INTRODUCTION

Since the publication more than three decades ago of the Hohenberg-Kohn theorem [1] asserting that the ground-state energy of a many-particle system is a unique functional of the one-particle density, followed shortly by the Kohn-Sham (KS) formulation [2], there has been a vast enterprise of theoretical development and useful applications to condensed matter, atoms, molecules, and nuclei [3–11]. As a side issue, it was natural to ask whether and in what form similar theorems could be formulated and applications carried out for the ground-state energy as a functional of the one-particle density matrix (one-matrix). Compared to the quantity of literature associated with the density-functional development, the number of papers that consider the problem of the one-matrix set forth above has been miniscule [12–21].

We shall make no effort to summarize this work, which is largely associated with questions of existence rather than of implementation. An exception to this general characterization is the paper of Levy [20], which, first of all contains a brief characterization of almost all the references cited above that predated it. More significantly, it investigates a number of properties of the correlation energy, including scaling, bounds, convexity, and asymptotic behavior. Finally, it contains a suggested structure for this correlation function that satisfies all the requirements established earlier. To our knowledge, the ideas contained in this work have not been carried further. In this paper we take another route on which we shall be concerned exclusively with the problem of how to formulate appropriately and to possibly apply a variational method based on a functional of the one-matrix that goes beyond the Hartree-Fock (HF) approximation.

Let us first consider the question of ‘‘appropriate formulation.’’ To see what is involved, we consider a many-body Hamiltonian of the form (summation over repeated indices throughout this paper)

$$\hat{H}=h_{\alpha\beta}\hat{\rho}_{\beta\alpha}+\frac{1}{2}W_{\alpha\beta\gamma\delta}\hat{\sigma}_{\delta\gamma\beta\alpha}, \tag{1}$$

$$\hat{\rho}_{\alpha\beta}=\hat{\psi}^{\dagger}_{\beta}\hat{\psi}_{\alpha}, \tag{2}$$

$$\hat{\sigma}_{\delta\gamma\beta\alpha}=\hat{\psi}^{\dagger}_{\alpha}\hat{\psi}^{\dagger}_{\beta}\hat{\psi}_{\delta}\hat{\psi}_{\gamma}. \tag{3}$$

Here the greek indices refer to an arbitrary single-particle basis, $h_{\alpha\beta}$ is the sum of the kinetic energy plus any single-particle potential that may be present, $W_{\alpha\beta\gamma\delta}$ is a matrix element of the two-particle interaction, $\hat{\rho}$ is the one-body density operator (whose expectation value in the ground state is the one-matrix), $\hat{\sigma}$ is the two-body density operator, and $\hat{\psi}$ is the single-particle annihilation operator. If Ψ_0 is the ground-state vector, with nondegeneracy assumed, the ground-state energy $E_0=\langle\Psi_0|\hat{H}|\Psi_0\rangle$ is given by the expression

$$E_0=h_{\alpha\beta}\rho_{\alpha\beta}+\frac{1}{2}W_{\alpha\beta\gamma\delta}\sigma_{\delta\gamma\beta\alpha}, \tag{4}$$

where clearly the removal of carets from symbols indicates that an expectation value has been taken. The restriction to degeneracy is for simplicity of presentation (and application). Further brief discussion of this point is given in Sec. VI.

If we want to formulate the variational property of Eq. (4) with respect to the density matrix, we have a double prob-

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lem. The first, which has been universally recognized, is that we need the two-matrix as a functional of the one-matrix in such a form as to guarantee their common origin in a trial state vector. This problem has never been solved in full generality [22]. In fact, the difficulty of expressing the two-matrix in terms of the exact one-matrix in any useful form (beyond the HF approximation) leads us, as a practical measure, to replace the first form of the variational principle with an alternative that is more easily carried into practice.

The second problem appears to have been completely overlooked in the existing literature. It can be formulated and solved, assuming that the first problem has been dealt with in some reasonable way. This second problem is how to include constraints on variation of the one-matrix arising from the Pauli principle. That there should be such constraints is well known from HF theory, which must be contained as a special case of the formulation under construction, just as the Hartree approximation is a limiting case of density-functional theory. Whereas the only constraint on the density is that it integrate to the fixed total number of particles, for the full HF theory we have the additional constraint

$$\rho_{\alpha\beta}\rho_{\beta\gamma}-\rho_{\alpha\gamma}=0, \tag{5}$$

i.e.,

$$\rho^2-\rho=0, \tag{6}$$

which guarantees that ρ is associated with a Slater determinant. Condition (6) is a consequence of the HF factorization (cf. the extended discussion in Sec. II)

$$\sigma_{\delta\gamma\beta\alpha}=\rho_{\delta\beta}\rho_{\gamma\alpha}-\rho_{\delta\alpha}\rho_{\gamma\beta}. \tag{7}$$

It is instructive to review how Eq. (6) makes its presence felt in the formulation of HF theory in terms of the one-matrix. The point is simply that we must constrain the variations of the HF energy both by number conservation and by Eq. (6), i.e., we may carry out unconstrained variations for the functional

$$\mathcal{G}_{HF}=h_{\alpha\beta}\rho_{\beta\alpha}+\frac{1}{2}\widetilde{W}_{\alpha\beta\gamma\delta}\rho_{\delta\beta}\rho_{\gamma\alpha}-\Omega_{\alpha\beta}[\rho^2-\rho]_{\beta\alpha}-\mu\rho_{\alpha\alpha}, \tag{8}$$

where $\widetilde{W}_{\alpha\beta\gamma\delta}=W_{\alpha\beta\gamma\delta}-W_{\beta\alpha\gamma\delta}$ is the antisymmetrized matrix element of the potential, $\Omega_{\alpha\beta}$ is a Lagrange multiplier matrix, and μ is the chemical potential. The unconstrained variation of Eq. (8) yields the conditions

$$[\mathcal{H}-(\Omega\rho)-(\rho\Omega)+\Omega]_{\alpha\beta}-\mu\delta_{\alpha\beta}=0, \tag{9}$$

$$\mathcal{H}=h+\mathcal{V}, \tag{10}$$

$$\mathcal{V}_{\alpha\beta}=\widetilde{W}_{\alpha\gamma\beta\delta}\rho_{\delta\gamma}. \tag{11}$$

By forming the commutator of ρ with Eq. (9) and enforcing the constraints, we regain the more familiar form of HF theory,

$$[\rho,\mathcal{H}]=0, \tag{12}$$

which allows us to introduce a complete set of orbitals that yields ρ and $\mathcal{H}$ simultaneously in diagonal form.

It now stands to reason that if we are to have a variational principle that generalizes the one just reviewed, we must enforce a constraint that generalizes Eq. (6). The formal structure of this constraint is easily obtained and will be derived in Sec. II as part of our discussion of the generalized variational principle. Conceptually, it should be clear that just as the advance beyond HF requires the introduction of dynamical correlations, these same correlations must also be present in and generalize the constraint conditions associated with the Pauli principle. As a result, we shall find that the commutator (12), which vanishes for HF theory (where $\mathcal{H}$ continues to mean the derivative of the energy with respect to the one-matrix), no longer vanishes and thus the two matrices cannot be diagonalized simultaneously.

The body of this paper is given over initially to the task of how the more complicated equations of the full theory may be formulated and solved. In Sec. II we derive the variational method that is meant to provide the advertised extension of HF theory. The practical difficulty inherent in this approach is to obtain useful expressions for the correlation energy in terms of the exact one-matrix. The only direct method that suggests itself is to study the equations of motion, within the single-time formalism, that couple lower-order density matrices to higher-order ones and to solve these equations as series in the one-matrix. This option is not studied in the present paper. We restrict ourselves, in Sec. III, to the presentation of a calculation that utilizes the formalism to obtain first-order corrections to the one-matrix beyond the HF approximation.

In Sec. IV we discuss a solution to the practical difficulty mentioned by the introduction of a modified variational treatment. The idea is to introduce a mapping from the exact one-matrix to the one-matrix ρ^s of an independent-particle system. This can be done in a general way, for example, by a Green's-function diagram expansion, equivalent to a linked-cluster expansion, and the results can be used to express the energy as a functional of ρ^s. By application of the variational argument to the new variable, where now we need only the simpler constraint conditions associated with a Slater determinant, we can determine the optimum choice of the single-particle system. How this can be done most conveniently in practice is studied in Sec. V. We first review certain aspects of a fully diagrammatic definition of the reference single-particle system; this is the definition of such a system that one encounters in the usual discussion of linked-cluster expansions. The variational description is then developed and contrasted with the former.

The theory studied in Secs. IV and V can be likened to the implementation of the Hohenberg-Kohn theorem by the KS method. The connection of the present work to linked-cluster expansions bears a resemblance to recent work on density-functional theory [23,24]. In Sec. VI we first summarize our results, then consider the feasibility of application of the theory developed in this paper, and finally comment briefly on the possibility of extensions of the theory.

The paper also contains two appendixes. In Appendix A we give formulas for the computation of derivatives of a functional of the one-matrix of a Slater determinant with respect to matrix elements of this one-matrix. In Appendix B we discuss a matter tangential to the main thrust of this paper, developing the point of view that, in contrast to the density-functional formulation, there is, in principle, nothing so special about a local potential. If one considers a nonlocal potential in the representation of its eigenstates, assumed complete, it appears that considerations thought to depend on locality can be carried over.

II. VARIATIONAL PRINCIPLE FOR GROUND-STATE ENERGY

Starting with the Hamiltonian (1), our aim in this section is to obtain a system of equations for the calculation of the one-matrix $\rho_{\alpha\beta}$ from a version of the ground-state variational principle in which we consider $E_0=\langle\Psi_0|\hat{H}|\Psi_0\rangle$ as a functional of this matrix. We shall vary E_0 subject to constraints that incorporate both the Pauli principle and number conservation. We write

$$\sigma_{\delta\gamma\beta\alpha}=\rho_{\delta\beta}\rho_{\gamma\alpha}-\rho_{\gamma\beta}\rho_{\delta\alpha}+s_{\delta\gamma\beta\alpha}, \tag{13}$$

which serves as a formal definition of the correlation function s, which must satisfy the antisymmetry requirements

$$s_{\delta\gamma\beta\alpha}=-s_{\gamma\delta\beta\alpha}=-s_{\delta\gamma\alpha\beta}. \tag{14}$$

The practical success of any procedure built upon the equations derived below will depend on our ability to provide useful approximate forms of s. The choice $s=0$ will return us to a well-known result, the HF approximation.

Of course, for the variational principle to provide an upper bound to the ground-state energy $\sigma_{\delta\gamma\beta\alpha}$ must be derivable from an approximate state vector. For approximations for which this is not the case, the sign of the error will be unknown. Based on extensive experience with algebraic methods applied to relatively simple problems in quantum mechanics and to the nuclear many-body problem, which avoid completely the use of wave functions [25,26], we believe that this is more a matter of theoretical rather than practical concern. For the methods to be applied in this paper, our approximations will correspond closely to state vectors derived from perturbation theory. Nevertheless, we have to admit that the sign of the error is not guaranteed.

To derive useful constraints to incorporate into the variational principle for E_0, we set $\beta=\delta$ in Eq. (13) and sum over indices. Assuming that we are dealing with a system with N particles, we deduce

$$(N-1)\rho_{\gamma\alpha}=N\rho_{\gamma\alpha}-(\rho^2)_{\gamma\alpha}+S_{\gamma\alpha}, \tag{15}$$

$$S_{\gamma\alpha}=s_{\gamma\beta\beta\alpha}. \tag{16}$$

In matrix notation we therefore have the constraint

$$\rho^2-\rho-S=0. \tag{17}$$

To determine the ground-state energy, we vary the functional

$$\mathcal{G}=\langle\Psi_0|\hat{H}|\Psi_0\rangle-\mathrm{tr}\Omega(\rho^2-\rho-S)-\mu\ \mathrm{tr}\rho=h_{\alpha\beta}\rho_{\beta\alpha}+\frac{1}{2}\tilde{W}_{\alpha\beta\gamma\delta}\rho_{\delta\beta}\rho_{\gamma\alpha}+\frac{1}{4}\tilde{W}_{\alpha\beta\gamma\delta}s_{\delta\gamma\beta\alpha}-\Omega_{\alpha\beta}[\rho^2-\rho-S]_{\beta\alpha}-\mu\rho_{\alpha\alpha}, \tag{18}$$

where, as before, $\tilde{W}_{\alpha\beta\gamma\delta}=W_{\alpha\beta\gamma\delta}-W_{\beta\alpha\gamma\delta}$, $\Omega_{\alpha\beta}$ is a Lagrange multiplier matrix, and μ is the chemical potential. The unconstrained variation of $\mathcal{G}$ at fixed Ω and μ now yields the conditions

$$[\mathcal{H}-(\Omega\rho)-(\rho\Omega)+\Omega]_{\alpha\beta}+\frac{\delta}{\delta\rho_{\beta\alpha}}(\mathrm{tr}\Omega S)-\mu\delta_{\alpha\beta}=0, \tag{19}$$

where

$$\mathcal{H}=h+\mathcal{V}+\mathcal{U}, \tag{20}$$

$$\mathcal{V}_{\alpha\beta}=\tilde{W}_{\alpha\gamma\beta\delta}\rho_{\delta\gamma}, \tag{21}$$

$$\mathcal{U}_{\alpha\beta}=\frac{1}{4}\frac{\delta}{\delta\rho_{\beta\alpha}}(\tilde{W}_{\gamma\epsilon\delta\sigma}s_{\sigma\delta\gamma\epsilon}). \tag{22}$$

As we shall see below, to have a full set of equations to determine all the variables, we need one more set of equations, which we obtain by computing the commutator of ρ with $\mathcal{H}$, using both Eqs. (19) and (17). We thereby find the equations

$$[\rho,\mathcal{H}]=-P, \tag{23}$$

$$P=[\Omega,S]+\left[\rho,\frac{\delta}{\delta\rho}\mathrm{tr}(\Omega S)\right]. \tag{24}$$

In contrast to the HF case, we see that the density matrix cannot be diagonalized simultaneously with the operator $\mathcal{H}$, which would appear to be a natural candidate for single-particle Hamiltonian. In the following section, we show how the set (17), (19), and (23), which constitutes the basic equations of the variational method, can be used to calculate first-order corrections to the one-matrix of HF theory.

III. CALCULATION OF THE FIRST-ORDER CHANGE IN THE DENSITY MATRIX

To carry out this calculation, we write

$$\rho=\rho^0+\rho^1, \tag{25}$$

$$\mathcal{H}=\mathcal{H}^0+\mathcal{H}^1, \tag{26}$$

$$\Omega=\Omega^0+\Omega^1, \tag{27}$$

$$s=s^1[\rho^0], \tag{28}$$

$$S=S^1[\rho^0]. \tag{29}$$

Here ρ^0 is the density matrix for a Slater determinant satisfying Eq. (17) with $S=0$ and determined by the equation of motion

$$[\rho^0,\mathcal{H}^0]=0, \tag{30}$$

$$\mathcal{H}^0=h+\mathcal{V}[\rho^0]. \tag{31}$$

We suppose $\mathcal{H}^0$ to generate a complete set $|a)$ of single-particle functions. In the following $a=h$ will identify occupied orbitals in the Slater determinant and $a=p$ unoccupied ones. From Eq. (19) we learn that

$$(\Omega^0)_{hh'}=(\Omega^0)_{hh}\delta_{hh'}, \tag{32}$$

$$(\Omega^0)_{pp'}=(\Omega^0)_{pp}\delta_{pp'}, \tag{33}$$

$$(\Omega^0)_{hh}=(\mathcal{H}^0)_{hh}-\mu\equiv\epsilon_h-\mu, \tag{34}$$

$$-(\Omega^0)_{pp}=(\mathcal{H}^0)_{pp}-\mu\equiv\epsilon_p-\mu. \tag{35}$$

Furthermore, $(\Omega^0)_{ph}$ is undetermined and may be set to zero.

To proceed to first order, one should understand that for what follows the right-hand sides of Eqs. (28) and (29) are considered to be known quantities. It is not necessary, however, to restrict these quantities to their lowest-order approximations, though that is what would likely be done initially.

We require also a note about the form of $\mathcal{H}^1$ [Eq. (26)]. To start with, this form is

$$\mathcal{H}^1=\widetilde{W}\rho^1+\frac{1}{4}\,\frac{\delta}{\delta\rho^0}(\mathrm{tr}\widetilde{W}s^1)\frac{\delta\rho^0}{\delta\rho}. \tag{36}$$

In the lowest approximation, the last factor of the second term may be replaced by unity. The formulas necessary for the calculation of the remaining derivative are given in Appendix A and applied in detail to the theory discussed in Sec. V. We shall write the two terms of Eq. (36) as

$$\mathcal{H}^1=\mathcal{H}^{11}+\mathcal{U}^0. \tag{37}$$

Turning to the constraint condition (17), the first-order equations read

$$\rho^0\rho^1+\rho^1\rho^0-\rho^1=S^1. \tag{38}$$

The apparently straightforward conclusions from these equations are

$$(\rho^1)_{hh'}=(S^1)_{hh'}, \tag{39}$$

$$(\rho^1)_{pp'}=-(S^1)_{pp'}, \tag{40}$$

$$0=(S^1)_{ph}. \tag{41}$$

Of these statements, only the last one defies credence. [It is straightforward to check that the right-hand side of Eq. (41) does not vanish.] We can, however, extricate ourselves from its unacceptable consequences by noting that because $(\Omega^0)_{ph}=0$, we can argue that the particle-hole (ph) matrix elements of Eq. (38) are not part of the constraint condition when the latter is expressed in the appropriate basis.

This leaves the matrix elements $(\rho^1)_{ph}$ to be determined. For this purpose, we turn to the equations of motion (23). To first order, we must solve the equations

$$[\rho^0,\mathcal{H}^1]+[\rho^1,\mathcal{H}^0]=-P^1, \tag{42}$$

$$P^1=[\Omega^0,S^1]+\left[\rho^0,\frac{\delta}{\delta\rho^0}\mathrm{tr}(\Omega^0S^1)\right] \tag{43}$$

and $\mathcal{H}^1$ has been defined in Eqs. (36) and (37). From Eq. (43) we see that we do not require Ω^1 for this calculation. In fact, this equation yields, for the matrix elements of P^1, the values

$$(P^1)_{hh'}=(\epsilon_h-\epsilon_{h'})(S^1)_{hh'}, \tag{44}$$

$$(P^1)_{pp'}=(\epsilon_{p'}-\epsilon_p)(S^1)_{pp'}, \tag{45}$$

$$(P^1)_{ph}=-(\epsilon_p+\epsilon_h-2\mu)(S^1)_{ph}+\frac{\delta\ \mathrm{tr}(\Omega^0S^1)}{\delta(\rho^0)_{hp}}, \tag{46}$$

$$(P^1)_{hp}=(\epsilon_p+\epsilon_h-2\mu)(S^1)_{hp}+\frac{\delta\ \mathrm{tr}(\Omega^0S^1)}{\delta(\rho^0)_{ph}}. \tag{47}$$

We proceed finally to the study of the equation of motion (42). We verify immediately the reassuring fact that the hh' and pp' matrix elements of Eq. (42) contain no new information in comparison to Eqs. (39) and (40). The remaining matrix elements yield coupled linear inhomogeneous equations for the ph and hp matrix elements of the form

$$\begin{aligned}&[(\epsilon_p-\epsilon_h)\delta_{hh'}\delta_{pp'}+\widetilde{W}_{ph'hp'}](\rho^1)_{p'h'}+\widetilde{W}_{pp'hh'}(\rho^1)_{h'p'}\\&\quad=(\mathcal{P}^1)_{ph},\end{aligned} \tag{48}$$

$$\begin{aligned}&[(\epsilon_p-\epsilon_h)\delta_{hh'}\delta_{pp'}+\widetilde{W}_{hp'ph'}](\rho^1)_{h'p'}+\widetilde{W}_{hh'pp'}(\rho^1)_{p'h'}\\&\quad=-(\mathcal{P}^1)_{hp},\end{aligned} \tag{49}$$

where

$$\begin{aligned}(\mathcal{P}^1)_{ph}={}&(P^1)_{ph}+(\mathcal{U}^0)_{ph}+\widetilde{W}_{pp'hp''}(\rho^1)_{p''p'}\\&+\widetilde{W}_{ph'hh''}(\rho^1)_{h''h'},\end{aligned} \tag{50}$$

$$\begin{aligned}(\mathcal{P}^1)_{ph}={}&(P^1)_{ph}+(\mathcal{U}^0)_{ph}+\widetilde{W}_{pp'hp''}(\rho^1)_{p''p'}\\&+\widetilde{W}_{ph'hh''}(\rho^1)_{h''h'}.\end{aligned} \tag{51}$$

The structure of Eqs. (48) and (49) is not unfamiliar. If we write these equations in the matrix form

$$M\rho^1=\tau_3\mathcal{P}^1, \tag{52}$$

where τ_3 is the diagonal Pauli matrix, we recognize that M is the linear operator associated with the eigenvalue problem of the random-phase approximation (RPA). The solution of the inhomogeneous equation (52) by expansion of ρ^1 in the RPA eigenvectors is then standard.

IV. GENERALIZED KOHN-SHAM THEORY: ALTERNATIVE VARIATIONAL APPROACH

In this section we make a transition to a form of the theory that is analogous to the transition from the original form for the realization of the Hohenberg-Kohn theorem to the more useful KS form. We have noted above the difficulty of creating a general formalism with the full one-matrix as the fundamental entity. Though not out of the question formally, there is no immediate incentive to pursue this direction, especially in view of the simpler alternative that we shall now expound.

The basic idea behind the simplified approach is to make use of a mapping from the full one-matrix ρ to a one-matrix ρ^s for a Slater determinant,

$$(\rho^s)_{\alpha\beta}=\sum_a \psi_a^*(\beta)\psi_a(\alpha), \tag{53}$$

$$(\rho^s)^2=\rho^s, \tag{54}$$

where the label a specifies the basis of natural orbitals for ρ^s. This mapping can be taken to be defined explicitly as a limiting form of Eq. (66) of Sec. V, which expresses the relationship between the exact one-particle Green's function G and the independent-particle Green's function G^s for propagation by the single-particle Hamiltonian $h+v^s$. Since ρ is directly an equal time limit of G, it remains only to convince ourselves that the right-hand side of this equation can be considered as a functional of ρ^s. This relationship need not be explicit; all that is necessary in practice is that we be able to calculate the change of the right-hand side when we alter the value of ρ^s. The explicit calculations that establish this as fact are given in Appendix A.

If we accept the existence of this mapping, which is certainly true to any finite order of perturbation theory, then we can consider the variation

$$\frac{\delta E_0}{\delta\rho^s}=\frac{\delta E_0}{\delta\rho}\frac{\delta\rho}{\delta\rho^s}=0 \tag{55}$$

because $\delta E_0/\delta\rho=0$. Thus, given the variational principle of Sec. II, Eq. (55) provides us with a means of optimizing the choice of ρ^s, namely, it is that independent-particle one-matrix that ''minimizes'' the ground-state energy. To derive equations that exploit this new condition, we must add to E_0 constraint conditions, which may here be chosen of the same form as in HF theory. Thus we study the functional

$$\mathcal{G}^s=\langle\Psi_0|\hat{H}|\Psi_0\rangle-\mathrm{tr}\Omega^s[(\rho^s)^2-\rho^s]-\mu^s\mathrm{tr}\rho^s, \tag{56}$$

where the constraints specify the nature of the trial density matrix as well as number conservation. This variational principle, which should be compared with Eq. (18), is nevertheless formally exact.

Varying this equation with respect to ρ^s, we obtain

$$\frac{\delta\mathcal{G}^s}{\delta\rho^s}=0=\mathcal{H}^s-\Omega^s\rho^s-\rho^s\Omega^s+\Omega^s-\mu^s, \tag{57}$$

$$\mathcal{H}^s=\frac{\delta E_0}{\delta\rho^s} \tag{58}$$

and E_0 is found in Eq. (8). From Eq. (57) it follows that

$$[\rho^s,\mathcal{H}^s]=0, \tag{59}$$

so that ρ^s and $\mathcal{H}^s$ can be diagonalized simultaneously.

The application of these equations depends on the use of suitable approximating functionals for the total energy. Toward this end we shall apply several versions of linked-cluster perturbation theory (Green's-function and time-independent forms) in order to exhibit all terms of the energy as functionals of ρ^s. Essential details of this approach, which seems the only feasible one, are supplied in Sec. V, where, for the sake of comparison, we start with a brief review of a standard, alternative, diagrammatic approach to the choice of a single-particle Hamiltonian.

As a final observation of the present discussion, we note the following: If we were dealing with the density in configuration space rather than with a general density matrix, then it is a property of KS theory that a Slater determinant can be chosen that yields the exact density. The variation can then be restricted to the class of such Slater determinants. Though the solution procedure suggested below bears a striking resemblance to the standard KS formulation, in the present theory the density matrix $\rho\neq\rho^s$. As we shall see, the further calculations necessary to build the exact density matrix from the trial matrix ρ^s are part of the procedure used to construct the total-energy functional.

V. DIAGRAMMATIC EXPANSIONS

A. Linked-cluster expansions

In the previous text several single-particle operators played an essential role in the formulation and application of the variational principles. In Sec. II we encountered the operator $\mathcal{H}$ and in Sec. IV the operator $\mathcal{H}^s$. The construction of useful approximate forms of these operators depends first on the choice of approximations for either the total ground-state energy or the potential energy, depending on the specifics of the formulation used. This section and Appendix A are devoted to a brief account of the information needed.

In this section we shall first describe a version of the historical approach to the choice of a single-particle basis for the application of the linked-cluster theorem. The main reason for the injection of this material, which interrupts the main flow of the argument, is that it leads to what appears to be a natural definition of the single-particle potential. Nevertheless, as we show in Sec. V B, this definition contains only a subclass of the terms yielded by the variational definition. It therefore serves both as an introduction and an interesting contrast to the ''new'' treatment that follows it.

For the purposes of this discussion, we use the Feynman form of the theory, which is by far the simplest version for our initial theoretical aims. Treatments of the relationship of this approach to linked-cluster expansions can be found in [27,28]. As a preliminary study we consider the Feynman one-particle Green's function

$$G(1|2)=i\langle\Psi_0|T(\hat{\psi}(1)\hat{\psi}^\dagger(2)|\Psi_0\rangle, \tag{60}$$

where an integer stands for a position coordinate, a spin coordinate, and a time coordinate. G is a reciprocal of the differential operator that we consider together with two simpler differential operators, namely,

$$G^{-1}=-i\partial_t+h+\Sigma, \tag{61}$$

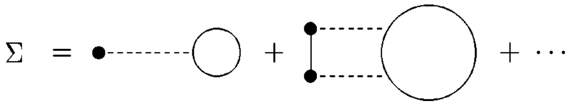

FIG. 1. Decomposition of the irreducible self-energy operator Σ according to the number of interaction emerging from the open line. Each term of this sum contains terms of all orders in the interaction.

$$(G^s)^{-1}=-i\partial_t+h+v^s, \tag{62}$$

$$(G^0)^{-1}=-i\partial_t+h. \tag{63}$$

Here Σ is the irreducible self-energy operator, whose structure is reviewed below, and v^s is one of the potentials to be discussed, either the one defined in this subsection or that derived in the next subsection.

The matrices G and G^s satisfy the integral equations

$$G=G^0+G^0\Sigma G, \tag{64}$$

$$G^s=G^0+G^0v^sG^s. \tag{65}$$

By eliminating G^0 between these two equations, we obtain the formal solution

$$G=G^s[1-(\Sigma-v^s)G^s]^{-1}=G^s\sum_{n=0}^{\infty}[(\Sigma-v^s)G^s]^n. \tag{66}$$

This formula suggests that we choose v^s, which is at our disposal, so as to cancel ''as much as possible'' of Σ. This requires a discussion of the structure of the latter matrix.

Let $(\mathbf{x}|a)$ be the coordinate space representation of the single-particle eigenfunction

$$\mathcal{H}^s|a)=(h+v^s)|a)=\epsilon_a|a). \tag{67}$$

We look more closely at G^s, which, in analogy with Eq. (60), is defined by the expression

$$G^s(1|2)=i\langle\Phi_0|T(\hat\psi^s(1)\hat\psi^{s\dagger}(2)|\Phi_0\rangle, \tag{68}$$

where the operators $\hat\psi^s$ propagate in time according to the Hamiltonian $\mathcal{H}^s$ and Φ_0 is the ground-state Slater determinant of this Hamiltonian. We may thus expand

$$\hat\psi^s(1)=\hat\psi^s(\mathbf{x}_1,t_1)=\sum_a\hat\psi^s_a(t_1)(\mathbf{x}_1|a),$$

$$\hat\psi^s_a(t)=\exp(-i\epsilon_at)\hat\psi^s_a \tag{69}$$

and thus identify $\hat\psi_a$ as the destruction operator for the mode a. Because of the relationship of these operators to the state Φ_0, it follows that

$$G^s(at_1|bt_2)=\int d\mathbf{x}_1d\mathbf{x}_2(a|\mathbf{x}_1)G^s(1|2)(\mathbf{x}_2|b)$$
$$=\delta_{ab}G^s(a,t_1-t_2). \tag{70}$$

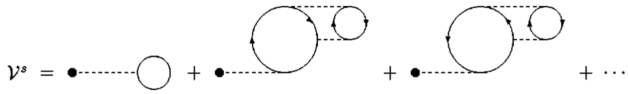

FIG. 2. Sum of terms to third order defining the effective external potential v^s suggested by the time-dependent linked-cluster expansion.

We study Σ as a matrix in the same representation, $\Sigma(bt_2|at_1)$ describing a transition from a single-particle state a at time t_1 to a single-particle state b at time t_2. We write [27,28]

$$\Sigma=\sum_{n=1}^{\infty}\Sigma_n, \tag{71}$$

$$\Sigma_1(bt_2|at_1)=-i\delta(t_1-t_2)\widetilde{W}_{bdac}(P_1)_{dc}, \tag{72}$$

$$\Sigma_2(bt_2|at_1)=(-i)^2G_s(a',t_1-t_2)$$
$$\times\widetilde{W}_{bd'a'c'}\widetilde{W}_{a'dac}(P_2)_{c'cd'd}, \tag{73}$$

$$\vdots \quad . \tag{74}$$

Here P_n is the most general closed-loop structure that can be attached by n instantaneous interactions to the remainder of a diagram for *any* quantity. The decomposition of Σ is illustrated in Fig. 1. The first term is a special case to which we return below. Σ_2 already exhibits the general structure, in that from the two times associated with the Green's function representing propagation along the open line, the two emerging interactions ''connect'' with the closed-loop structure P_2. By extension, Σ_n contains an open line with $n-1$ G^s functions from which emanate n interactions connected to an irreducible closed-loop structure P_n. Reducible structures, connected only by a single G^s line, arise from higher terms in the expansion (66). We emphasize that each term Σ_n is itself an infinite series in the strength of the potential, arising from the complex structure of P_n. It is also evident that in general, terms beyond the first in Eq. (71) cannot be associated, within this theoretical framework, with an instantaneous interaction (see the end of this subsection, however).

Thus, within this diagrammatic description, the ''natural'' choice for v^s is

$$v^s_{ba}=\widetilde{W}_{bdca}(P_1)_{db}. \tag{75}$$

With this definition, the contributions to v^s through third order are illustrated in Fig. 2. As shown in Fig. 3, the absence of contributions of second order is a consequence of the definition (75). In lowest approximation, v^s is equal to the HF potential. In higher order the solution of Eq. (67) is considerably more difficult because we cannot separate the problem of determining the h orbitals from that of determin-

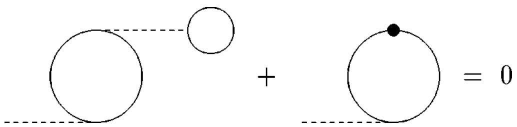

FIG. 3. Illustration of the cancellation of single-interaction insertions and potential insertions.

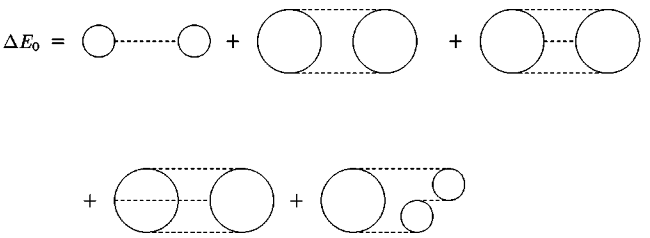

FIG. 4. Representation of the correlation energy to third order when the effective external potential is chosen according to the suggestion from time-dependent linked-cluster theory.

ing the p orbitals, as is true for the HF problem. As we shall see for a related case, studied in more detail below, they both occur in higher-order terms of the self-consistent potential.

We turn next to the energy, where we use the linked-cluster expansion in the form that follows from the Hellman-Feynman theorem

$$E_0=\sum_h \epsilon_h+\Delta E_0$$

$$=\sum_h \epsilon_h+\int_0^1 d\lambda'\langle\Psi_0(\lambda')|(\hat{W}-\hat{v}^s)|\Psi_0(\lambda')\rangle. \quad (76)$$

When we expand the integrand in powers of λ', using the Feynman form of the contributions, and then do the λ' integration, we are led to a conventional form of the linked-cluster expansion. This approach also informs us that the linked-cluster expansion for potential energy and the linked-cluster expansion for ΔE_0 are term for term the same except that in the former each contribution of order n occurs with an additional factor of n compared to the latter. With the definition of v^s currently in force the linked-cluster expansion takes a form from which potential insertions are absent. This is represented diagrammatically to third order in Fig. 4, which still refers to Feynman diagrams.

In these diagrams, an nth-order contribution has $n-1$ time integrals. Carrying out these integrals leads to the more widely applied time-independent form of the linked-cluster expansion [29,30]. To the order shown, the time-independent form can be represented by the same set of diagrams as in Fig. 4, but the interpretation of each diagram is quite different.

Before returning to our main subject, we address a point of possible concern to those readers who are familiar with the Brueckner theory of nuclear matter [31]. At first sight the latter appears to embody a contradiction to our definition of the single-particle potential: In that theory the definition of v^s involves not only terms from Σ_1, but also contributions from Σ_n for any n. The resolution of the apparent contradiction is that the extended potential is also energy dependent. If we consider, for instance, the matrix element $v^s_{hh'}$ in the ‘‘hole’’ space, in the Brueckner theory it also depends on the eigenvalues ϵ_h and $\epsilon_{h'}$, $v_{hh'}=v_{hh'}(\epsilon_h,\epsilon_h')$. This expresses the property that the potential in question will, in general, be not only nonlocal in space but also not instantaneous when viewed from the time-dependent form of the theory.

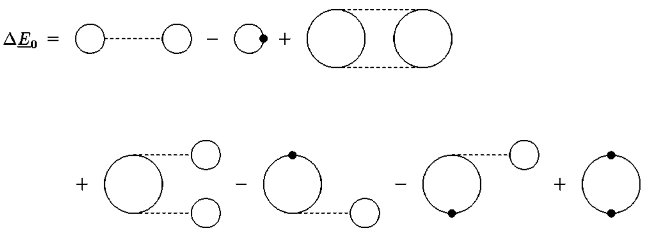

FIG. 5. Correlation energy functional as a linked-cluster expansion to second order before variation with respect to the single-particle density matrix, corresponding to Eq. (80).

B. Variational considerations

In view of the aesthetic qualities of the standard linked-cluster expansion, we should justify why it is necessary or desirable to venture beyond its confines. The reason is that it does not answer the following question: Suppose we carry out an evaluation of the total energy up to nth order, expanding about an unperturbed independent-particle system defined by some choice of v^s in Eq. (67). What is the choice of single-particle basis that ‘‘minimizes’’ this approximation to the energy? From a practical point of view, this can be understood to be the question addressed in Sec. IV.

We next show that this question yields a different answer for the choice of v^s than the diagrammatic argument given in Sec. V A. It is convenient to base the further considerations on the formula (76) for the energy. From the requirement

$$\mathcal{H}^s=h+v^s=(\delta E_0/\delta\rho^s), \quad (77)$$

since

$$\frac{\delta\sum_h \epsilon_h}{\delta\rho^s}=\frac{\delta(\mathrm{tr}\mathcal{H}^s\rho^s)}{\delta\rho^s}=\mathcal{H}^s, \quad (78)$$

it follows that

$$\delta\Delta E_0/\delta\rho^s=0, \quad (79)$$

and as we shall see momentarily this last formula gives us a means of calculating v^s.

The main alternative physics that follows from the definition (79) of the effective external potential can be illustrated by limiting our considerations to second order in the strength of the interaction. To this order ΔE_0 is given as a sum of diagrams in Fig. 5. We shall carry out an explicit calculation and for that purpose we record the actual expression for ΔE_0 in the time-independent form, using the standard rules for the linked-cluster expansion [29,30]. Namely,

$$\Delta E_0=\frac{1}{2}\tilde{W}_{hh'hh'}-v^s_{hh}+\frac{1}{2}\frac{|\tilde{W}_{h'ph'h}-v^s_{ph}|^2}{\epsilon_h-\epsilon_p}$$

$$+\frac{1}{4}\frac{|\tilde{W}_{pp'hh'}|^2}{\epsilon_h+\epsilon_{h'}-\epsilon_p-\epsilon_{p'}}. \quad (80)$$

The derivative of this quantity with respect to the elements of ρ^s can be calculated by applying Eqs. (A3)–(A6) to Eq. (79). To first order, e.g., we find, writing

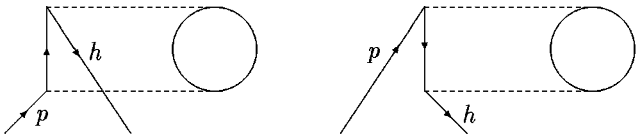

FIG. 6. Diagrammatic representation of the second-order term v_{hp}^2 given by Eq. (83).

$$v^s = v^1 + v^2 + \cdots, \tag{81}$$

the expected result

$$v_{hp}^1 = \widetilde{W}_{hh'ph'}. \tag{82}$$

This guarantees not only that the third term on the right-hand side of Eq. (80) does not contribute to the second order of the energy, but also, as shown by a straightforward calculation, its derivative does not contribute to the second order of the potential. However, this is not true of the last term of Eq. (80). We obtain contributions from differentiating both the numerator and the denominator of this expression, but the latter is of third order. Neither term was a part of the definition of v^s obtained by the diagram cancellation method of Sec. V A. The second-order terms

$$v_{hp}^2 = \frac{1}{2}\frac{\widetilde{W}_{h'hp'p''}\widetilde{W}_{p'p''h'p}}{\epsilon_{h'}+\epsilon_h-\epsilon_{p'}-\epsilon_{p''}} - \frac{1}{2}\frac{\widetilde{W}_{h'h''p'p}\widetilde{W}_{p'hh'h''}}{\epsilon_{h'}+\epsilon_{h''}-\epsilon_{p'}-\epsilon_p} \tag{83}$$

may also be assigned diagrams as shown in Fig. 6. Note that these extra terms depend on the single-particle energies [32].

By studying the structure of higher-order terms, it is not difficult to show that v^n contains as a subset all the contributions obtained by the diagram cancellation, but the minimization procedure introduces additional contributions to the potential, as has been shown explicitly for the second-order contribution. As noted previously, inclusion of any terms beyond the HF approximation complicates the construction of a complete set of orbitals because we can no longer separate the problems of computing the h orbitals from that of computing the p orbitals since the self-consistent potential contains the latter. What is finally of interest, from a practical standpoint, is whether the variational approach yields improved values for observables compared to the standard linked-cluster expansion.

VI. CONCLUDING REMARKS

We first summarize the basic contents of this paper. For density-functional theory, the original Hohenberg-Kohn formulation led to a generalized Thomas-Fermi (TF) theory to determine the ground-state density. The practical difficulties of this theory were bypassed by the Kohn-Sham formulation, which is based on the fact that the exact density may be calculated as the density of a system of independent particles moving in an effective one-body local potential. The practical formulation of both the generalized TF theory and the KS theory is given in terms of (related) variational principles for the ground-state energy. In this paper we have sought to develop corresponding theoretical structures when the ground-state energy is considered, not as a functional of the physical density, but as a functional of the physical one-particle density matrix (one-matrix). We bypassed any discussion of rigorous existence theorems that have been explored fully in previous work [12–21]. Rather, we went directly to the variational formulation of the dynamics. We derived a variational principle in terms of the physical one-matrix that contains the Hartree-Fock theory as a special case. We discovered that to include correlations in the variational principle, the same correlations that occur in the energy functional must find expression in the kinematical constraints on the one-matrix associated with the Pauli principle. This led to equations that may be viewed as the nonlocal analogs of generalized TF theory. For a systematic treatment by this method we need a representation for the correlation function in terms of the one-matrix. An effort in this direction that appears to be worthy of further study can be found in [20]. It may also be of interest to try to develop a representation of the correlation energy as a series in the one-matrix based on the study of single-time equations of motion for the associated density operators. In any event, much remains to be done along these lines. As one application, we have outlined a calculation of first-order corrections to the HF values of the one-matrix.

The study of the formalism just described does not immediately commend itself by its simplicity and therefore in the second part of the paper our aim was to simplify matters by constructing an analog of KS theory, i.e., by constructing a theory in terms of a model one-matrix of independent particles moving this time in an effective nonlocal one-particle potential. There are several characteristic differences between the resulting theory and KS theory. On the one hand, by using the linked-cluster expansion, we could write down a formally exact expression for the correlation energy that we study as a perturbation expansion, but that can also be studied in various partially summed forms [31]. Such expressions are not so readily available in KS theory. On the other hand, the ‘‘natural’’ formulation of the KS-like theory yielded a one-matrix that is not equal to the physical one-matrix.

If we examine the elements of the formalism as they finally emerged in Sec. V, it becomes clear that we are confronted with a generalized HF problem. The major difference with ordinary HF theory is that evaluation of the potential involves sums of the type encountered in perturbation theory for the correlation energy. The solution by iteration of the associated one-particle Schrödinger equation, where occupied and unoccupied orbits play a more equal role than in HF theory, means that such sums have to be calculated repetitively. A survey of some of the review literature on HF theory and its extensions to include correlations [33–37] indicates that such calculations are within the realm of present capabilities. Indeed, the calculation of perturbation sums has been a standard part of the repertoire since the seminal work of Kelly more than three decades ago [38,39]. Physically we have a sequence of approximations that in its treatment of correlations appears to be distinct from anything in the literature of atomic and molecular physics. Whether this makes the problem of interest to practitioners in the field is for them to answer. In its present form, the theory applies only to closed-shell atoms.

Beyond what we have set forth in this paper, it is clear that all the well-known generalizations of density-functional theory formulated for a nondegenerate ground state (degenerate ground state, superconducting system, etc.; see [5]) are open for further investigation along lines developed in this paper. However, there is small incentive to carry out such extensions of the theory unless and until the nondegenerate theory has been applied.

ACKNOWLEDGMENTS

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APPENDIX A: FORMULAS FOR DERIVATIVES WITH RESPECT TO THE DENSITY MATRIX

We need formulas for derivatives of one-particle matrix elements θ_{ab} and two-particle matrix elements Θ_{abcd} with respect to the density matrix ρ^s. The basic formulas are (suppressing the superscript s after the first line)

$$\delta|b) = \delta(\rho^s|b) + (1-\rho)^s|b))$$

$$= \delta_{bh}\sum_{p'} |p')\,\delta\rho_{p'h} - \delta_{bp}\sum_{h'} |h')\,\delta\rho_{h'p}\,, \qquad \text{(A1)}$$

$$\delta(a| = \delta_{ah}\sum_{p'} (p'|\,\delta\rho_{h'p} - \delta_{ap}\sum_{h'} (h'|\,\delta\rho_{ph'}, \qquad \text{(A2)}$$

where we have used the Hermiticity requirement $\rho^*_{ab} = \rho_{ba}$ and the property of any density matrix for a Slater determinant that its first-order variations have only ph and hp nonvanishing matrix elements.

Since $\theta_{ab} = (a|\theta|b)$, etc., we have as a consequence

$$\frac{\delta\theta_{ab}}{\delta\rho_{ph}} = -\theta_{hb}\delta_{ap} + \theta_{ap}\delta_{bh}\,, \qquad \text{(A3)}$$

$$\frac{\delta\theta_{ab}}{\delta\rho_{hp}} = \theta_{pb}\delta_{ah} - \theta_{ah}\delta_{bp}\,, \qquad \text{(A4)}$$

$$\frac{\delta\Theta_{abcd}}{\delta\rho_{ph}} = -\delta_{ap}\Theta_{hbcd} + \delta_{ch}\Theta_{abpd} - \delta_{bp}\Theta_{ahcd} + \delta_{dh}\Theta_{abcp}\,, \qquad \text{(A5)}$$

$$\frac{\delta\Theta_{abcd}}{\delta\rho_{hp}} = \delta_{ah}\Theta_{pbcd} + \delta_{bh}\Theta_{apcd} - \delta_{cp}\Theta_{abhd} - \delta_{dp}\Theta_{abch}\,. \qquad \text{(A6)}$$

These formulas are needed and applied in Sec. V. Here we note the preliminary aspects of their application to the single-particle Hamiltonian

$$\mathcal{H}^s_{ab} = h_{ab} + \widetilde{W}_{ah'bh'} + \mathcal{U}^s_{ab}\,, \qquad \text{(A7)}$$

which is an approximation to the single-particle Hamiltonian $\mathcal{K}^s$ defined in Sec. IV. We find

$$\frac{\delta\mathcal{H}^s_{ab}}{\delta\rho^s_{ph}} = -\delta_{ap}\mathcal{H}^s_{hb} + \delta_{bh}\mathcal{H}^s_{ap} + \widetilde{W}_{ahbp} + \frac{\delta\mathcal{U}^s_{ab}}{\delta\rho^s_{ph}}, \qquad \text{(A8)}$$

$$\frac{\delta\mathcal{H}^s_{ab}}{\delta\rho^s_{hp}} = \delta_{ah}\mathcal{H}^s_{pb} - \delta_{bp}\mathcal{H}^s_{ah} + \widetilde{W}_{apbh} + \frac{\delta\mathcal{U}^s_{ab}}{\delta\rho^s_{hp}}. \qquad \text{(A9)}$$

Diagonal elements of these formulas are needed in the evaluation of derivatives of the energy denominators that occur in the linked-cluster contribution to the energy; they can be calculated with the help of Eqs. (A3)–(A6).

APPENDIX B: FORMAL EXTENSION OF THE HOHENBERG-KOHN THEOREM

We start from a Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{W} + \sum_{\alpha,\beta} \hat{\rho}_{\alpha\beta} v_{\beta\alpha}\,, \qquad \text{(B1)}$$

where $\hat{H}_0$ is a one-body operator, which may be the kinetic energy or may include a potential, $\hat{W}$ is the two-body interaction,

$$\hat{\rho}_{\alpha\beta} = \hat{\psi}^\dagger_\beta \hat{\psi}_\alpha \qquad \text{(B2)}$$

is the one-particle density operator, and $v_{\beta\alpha}$ is the one-body potential on which we focus. The greek indices indicate that we are writing the Hamiltonian with respect to a general single-particle basis, so that in fact the potential may be local or nonlocal, though we shall emphasize the latter. It is naturally assumed that the set of single-particle functions $\phi_\alpha(\mathbf{r},\sigma,\ldots)$ that define the representation are given. Therefore, knowledge of the matrix $v_{\alpha\beta}$ implies knowledge of the nonlocal potential $v(\mathbf{r},\sigma,\mathbf{r}',\sigma')$ that gives rise to it. Note, however, that when we introduce a basis from the beginning, we can think of H as defined only on a finite-dimensional vector space. The interaction $\hat{W}$ would then play the role of residual interaction.

We shall also write the last term of Eq. (B1) as $\hat{H}_1$ and if we replace v by another potential v' we shall also replace $\hat{H}_1$ by $\hat{H}'_1$, etc. Thus let Ψ_0 and Ψ'_0 be the ground states, assumed nondegenerate, of $\hat{H}$ and $\hat{H}'$, respectively. We define a permissible variation

$$\delta\hat{H}_1 = \hat{H}'_1 - \hat{H}_1 \qquad \text{(B3)}$$

as one that has at least one nonvanishing matrix element connecting different eigenstates Ψ_i of $\hat{H}$. We now review the various parts of the Hohenberg-Kohn procedure, making such changes as are required by the altered framework.

(a) If $v \neq v'$, then $\Psi_0 \neq \Psi'_0$. We reproduce the standard proof. If $\Psi_0 = \Psi'_0$, we deduce

$$\delta\hat{H}_1\Psi_0 = (E_0 - E'_0)\Psi_0\,, \qquad \text{(B4)}$$

which leads to a contradiction if we take an off-diagonal matrix element.

(b) Ψ_0 uniquely determines v, even if nonlocal, within a set of nonlocal potentials, to be defined. To see this, choose the single-particle representation in which v is diagonal (supposing its eigenfunctions to form a complete set),

$$\hat{H}_1 = \sum_a v(a)\hat{\psi}_a^\dagger \hat{\psi}_a = \sum_a v(a)\hat{n}(a). \tag{B5}$$

According to our assumptions, the eigenvalues $v(a)$ completely determine a nonlocal potential. We define the associated set of potentials as those that are diagonal in the same single-particle basis (an infinite set). Let the N-dimensional vector $\mathbf{a}=(a_1,a_2,\ldots,a_N)$ define a Slater determinant with the occupied orbitals as given. Now write the solution of the Schrödinger equation for the ground state as an expansion with respect to these determinants,

$$\Psi_0 = \sum_{\mathbf{a}} c(\mathbf{a})|\mathbf{a}\rangle. \tag{B6}$$

In this basis the Schrödinger equation takes the form

$$\left[\sum_i v(a_i)\right] c(\mathbf{a}) = \sum_{\mathbf{b}} [E_0 \delta_{\mathbf{a},\mathbf{b}} - \langle \mathbf{a}|(\hat{H}_0 + \hat{W})|\mathbf{b}\rangle] c(\mathbf{b}). \tag{B7}$$

In analogy with the case of a local potential, the same argument can be made that because of the multiplicative character of the factor on the left-hand side of this equation, it is uniquely determined within the set of potentials that also appear as such factors, namely, the set of associated potentials as defined above. From this point of view, the local potentials appear as a singular limit of potentials that are diagonal in the basis of improper eigenfunctions $|\mathbf{r},\sigma\rangle$. We turn next to the relationship between the ground-state eigenfunction and the occupation density, which is the standard one.

(i) Ψ_0 uniquely determines the occupation density (dropping the boldface)

$$n(a) = \langle \Psi_0 | \hat{n}(a) | \Psi_0 \rangle. \tag{B8}$$

(ii) Conversely $n(a)$ uniquely determines Ψ_0. We have the two conditions

$$\langle \Psi_0|\hat{H}|\Psi_0\rangle \leq \langle \Psi_0'|\hat{H}'|\Psi_0'\rangle + \sum_a [v(a)n'(a) - v'(a)n'(a)], \tag{B9}$$

$$\langle \Psi_0'|\hat{H}'|\Psi_0'\rangle \leq \langle \Psi_0|\hat{H}|\Psi_0\rangle + \sum_a [v'(a)n(a) - v(a)n(a)]. \tag{B10}$$

If $n(a)=n'(a)$, by adding the two inequalities, we obtain a contradiction unless $\Psi_0=\Psi_0'$.

We also note a more standard version of the theory that does not require us to choose a special basis. (This is the form that we have actually studied in the body of our paper.) In an arbitrary single-particle representation, with $\rho = \langle \Psi_0|\hat{\rho}|\Psi_0\rangle$, we have

$$v \rightarrow \Psi_0 \leftrightarrow \rho, \tag{B11}$$

$$\rho \rightarrow n \leftrightarrow \Psi_0 \leftrightarrow v, \tag{B12}$$

within the class of comparison potentials satisfying

$$[v,v'] = 0. \tag{B13}$$

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