A General Minimum Principle for Correlated Densities in Quantum Many-Particle Systems

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It is shown that interacting many-particle quantum systems can be described in terms of fully correlated n-particle densities, which determine uniquely the potential acting on the system and satisfy a minimum principle with respect to the ground-state energy. This leads to a generalization of ordinary density functional theory in terms of n-particle densities which allows the direct and self-consistent treatment of correlation effects within electronic structure methods for atoms, molecules, and solids. [S0031-9007(96)01364-6]

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The treatment of correlations in interacting quantum many-particle systems presents a significant challenge to mathematical and computational condensed-matter physics. Of all possible forms of correlation and systems affected by it, the electron gas in an atom, a molecule, or a solid has received the greatest attention by solid-state physicists and quantum chemists. As a consequence, a number of well-known approximation methods have been developed for its study. Among the most prominent, the local density approximation (LDA) to density functional theory (DFT) [1,2], the various forms of the Hartree-Fock (HF) [3] approximation, the GW approximation [4–7], methods based on the direct study of two-particle quantities [8–11], such as two-particle Fermion reduced density matrices [12], can be mentioned. These methods, and many of their modifications and improvements [13–16], have been discussed in a number of review articles [1,17,18], and their numerous applications along with theoretical studies have revealed [18] much about their internal structure as well as their advantages and limitations when compared to one another, or against general criteria of a formal nature.

In spite of the great effort that has been expended toward the study of correlated systems, however, no single unifying framework for this study has appeared which would provide direct insight into the electron correlation problem, would apply to systems of arbitrary size, would provide for well-defined and systematic extensions and generalizations as well as approximation schemes for its numerical implementation, and could be shown to become exact in a uniquely defined limit. The purpose of this Letter is to introduce such a formal construct based on the general formalism of density functional theory. The basis of the method is that DFT applies to *any* collection of interacting particles in d-dimensional space, particularly when the many-particle system is taken to consist of n-particle units which are treated as a *single particle* in a space of nd dimensions. For ease of presentation, in what follows we develop the method for the case of electrons,

but the application to other particles interacting by pair potentials is evident.

The formal construct presented here combines two different general approaches that have been used in the study of the electron gas, namely, DFT and methods [19,20] used in the study of "small" systems, such as atoms and molecules. In these methods, the N electrons in a system are viewed as forming a single particle in a space of $3N$ dimensions (which is the direct-space part of a $6N$-dimensional phase space). In this N-particle phase space or hyperspace, the single particle satisfies a Schrödinger equation in which all interparticle interactions appear as an external potential. A partial-wave analysis in terms of hyperspherical harmonics [21] can be used to obtain the solution of this single-particle equation determining the N-particle states of the system. This idea can be used to study systems of large numbers N of particles in terms of n-particle units. The methodology for accomplishing this by using essentially a *single-particle* formalism forms the central contribution of this paper.

Let us consider the Hamiltonian of a fully interacting N-particle system,

$$H = \sum_i -\nabla_i^2 + \sum_i v_i + \frac{1}{2} \sum_{ij} v_{ij}, \qquad (1)$$

where ∇_i^2 is the Laplacian operator for particle i, $v_i = v(\mathbf{r}_i)$ is a single-particle potential for particle i, and $v_{ij} = v(\mathbf{r}_i, \mathbf{r}_j)$ is the interparticle potential, with $v_{ii} = 0$.

The Hamiltonian of Eq. (1) can also be written in a form describing distinct, nonoverlapping pairs of particles [22] (so that a given particle belongs to only one pair), labeled by I,

$$H = \sum_I -\nabla_I^2 + \sum_I V_I + \frac{1}{2} \sum_{IJ} V_{IJ}. \qquad (2)$$

We view each pair of particles with respective coordinates $\mathbf{r}_{i_1}$ and $\mathbf{r}_{i_2}$ as a *single* point particle in a space defined by the orthogonal (Euclidean) combination of the individual

particle spaces. A point in this two-particle space has the form $\mathbf{x}_I = (\mathbf{r}_{i_1}, \mathbf{r}_{i_2})$ so that for each such pair $\nabla_I^2 = \nabla_{\mathbf{x}}^2 = \nabla_{i_1}^2 + \nabla_{i_2}^2$ is the six-dimensional Laplacian,

$$V_I \equiv V(\mathbf{x}_I) = V(\mathbf{r}_{i_1}, \mathbf{r}_{i_2})$$

$$= \upsilon(\mathbf{r}_{i_1}) + \upsilon(\mathbf{r}_{i_2}) + \frac{1}{|\mathbf{r}_{i_2} - \mathbf{r}_{i_1}|} \qquad (3)$$

is the external potential acting on a pair of particles, which includes the interaction between the ordinary particles forming the pair, and

$$V_{IJ} \equiv V(\mathbf{x}_I, \mathbf{x}_J) = V(\mathbf{r}_{i_1}, \mathbf{r}_{i_2}; \mathbf{r}_{j_1}, \mathbf{r}_{j_2})$$

$$= \frac{1}{|\mathbf{r}_{i_1} - \mathbf{r}_{j_1}|} + \frac{1}{|\mathbf{r}_{i_1} - \mathbf{r}_{j_2}|} + \frac{1}{|\mathbf{r}_{i_2} - \mathbf{r}_{j_1}|}$$

$$+ \frac{1}{|\mathbf{r}_{i_2} - \mathbf{r}_{j_2}|}, \qquad (4)$$

which describes the interaction between single particles in hyperspace or, equivalently, between pairs of ordinary particles. In analogy with the Hamiltonian of Eq. (1), $V_{II} = 0$. We have now completely defined the Hamiltonian in Eq. (2). Given the formal similarity between the Hamiltonians defined in Eqs. (1) and (2), it follows that the ground-state energy, E, is given in terms of a universal functional of the (pair) density, $n(\mathbf{x})$, attaining its minimum value for the exact pair density. Furthermore, within a Kohn-Sham scheme, the form of this functional is identical to the functional of ordinary DFT but is given in terms of the pair density. The details of this derivation are identical to those of ordinary DFT, and we confine ourselves to the final result. The energy functional which determines the density in two-particle phase space can be written in the form

$$E[n(\mathbf{x})] = T_s[n(\mathbf{x})] + U[n(\mathbf{x})] + E_{xc}[n(\mathbf{x})], \qquad (5)$$

where $T_s[n(\mathbf{x})]$ represents the kinetic energy of a system of noninteracting particles (in two-particle space) at the density $n(\mathbf{x})$, the quantity $U[n(\mathbf{x})]$ is defined by

$$U[n(\mathbf{x})] = \int d^6x V(\mathbf{x}) n(\mathbf{x})$$

$$+ \int d^6x_1 \int d^6x_2 n(\mathbf{x}_1) V(\mathbf{x}_1, \mathbf{x}_2) n(\mathbf{x}_2), \quad (6)$$

and $E_{xc}[n(\mathbf{x})]$ contains the difference between the exact kinetic energy $T[n(\mathbf{x})]$ and that represented by $T_s[n(\mathbf{x})]$, as well as the difference between the exact interparticle interaction and its "classical" approximation given by Eq. (6),

$$E_{xc}[n(\mathbf{x})] = T[n(\mathbf{x})] - T_s[n(\mathbf{x})] + \int d^6x_1 \int d^6x_2$$

$$\times V(\mathbf{x}_1, \mathbf{x}_2)[n(\mathbf{x}_1, \mathbf{x}_2) - n(\mathbf{x}_1)n(\mathbf{x}_2)]. \quad (7)$$

Here, $n(\mathbf{x}_1, \mathbf{x}_2)$ represents the two-particle correlated density in two-particle space or, equivalently, the correlated density of four ordinary particles. As in ordinary DFT,

the exchange-correlation functional is not known, but can be used in a LDA sense through, for example, the study of 6-dimensional jellium.

Both formal analysis and computational developments associated with DFT can be carried over intact to nDFT. For example, the exact two-particle ground-state density, $n_0(\mathbf{x})$, can be determined through a constrained search [23] for that many-particle, properly symmetrized or antisymmetrized wave function, with symmetry imposed with respect to ordinary particles, which yields n_0 and also minimizes the many-particle energy, $T + V_{pp}$, where V_{pp} denotes the interparticle interaction in two-particle phase space. Essentially any method developed within a single-particle application of DFT for the study of electronic structure can, with appropriate technical modifications, be extended to two- or n-particle states. The use of multiple-scattering theory as a possible way to calculate fully correlated two-particle densities in solids will be given in a future publication.

We now comment on the general scheme which leads to the minimization of the energy functional within 2LDA. We first note that the concept of an effective potential acting on a particle pair is a sensible one since the exact many-body Hamiltonian can be written as a sum over single-particle terms (suppressing internuclear repulsion)

$$H = \sum_I \left[V_I + \frac{1}{2} \sum_J V_{IJ} \right]. \qquad (8)$$

Correspondingly, we search for an effective "single-particle" Hamiltonian and associated "single-particle" states that satisfy the equation

$$[-\nabla_{\mathbf{x}}^2 + \upsilon^{eff}(\mathbf{x})]\psi_\alpha(\mathbf{x}) = E\psi_\alpha(\mathbf{x}). \qquad (9)$$

In analogy with ordinary DFT, υ^{eff} consists of the external potential acting on a particle in two-particle space, which includes (i) the action of the nuclei with the pair, (ii) the interaction between the particles of the pair, (iii) the interaction of the other pairs with a given pair, which is mediated by $V(\mathbf{x}, \mathbf{x}')$, and (iv) the exchange-correlation potential defined by the functional derivative of the exchange-correlation energy with respect to the two-particle density. From $\psi_\alpha(\mathbf{x})$, the fully correlated pair density is obtained in the form

$$n(\mathbf{x}) = \sum_\alpha^{occ} |\psi_\alpha(\mathbf{x})|^2, \qquad (10)$$

consisting of a sum over the lowest in energy, occupied, two-particle states. We note that from $n(\mathbf{x}) = n(\mathbf{r}_1, \mathbf{r}_2)$, the single-particle density, $n(\mathbf{r}_1)$, is obtained through integration over $\mathbf{r}_2$. This density can be used to construct a single-particle potential in hyperspace which would lead directly to the corresponding single-particle electronic structure of the system.

In order to illustrate the role played by the two-particle density in the determination of the electronic structure, we study the single-particle spectrum of four electrons of

total spin zero on a four site single-band ring described by a Hubbard Hamiltonian

$$H = \sum_i \epsilon_i c_i^\dagger c_i + \frac{1}{2} \sum_{i>j} t_{ij} c_i^\dagger c_j + U \sum_i n_{i\sigma} n_{i\bar{\sigma}} , \quad (11)$$

where $c_i^\dagger$ and c_i are creation and annihilation operators for an electron on site i, the site energies ϵ_i are chosen equal to zero, the hopping term t_{ij} is confined to near neighbors and set equal to 1.0, and the on-site Coulomb interaction U felt by electrons of opposite spin is taken to have the values 1.0 and 10.0, with the respective results shown in Figs. 1 and 2. In order to validate the results of an effective two-particle approach, we include the exact single particle spectrum as well as the results obtained within a version of the *GW* approximation.

The single-particle spectra are obtained from the familiar expression

$$\rho_i(E) = -\frac{1}{\pi} \mathrm{Im}\hat{G}_{ii}(E), \quad (12)$$

where the Green function $\hat{G}_{ii}(E)$ is determined in three different ways.

For the exact spectrum, we use the definition of the Green function as the probability amplitude for adding and removing particles to obtain $\hat{G}_{ii}(E)$ by summing over (integrating out) the degrees of freedom (coordinates) of three particles in the four-particle Green function:

$$\hat{G}_{i_1 j_1}(E) = \sum_{\substack{i_2,i_3,i_4 \\ j_2,j_3,j_4}} G_{i_1,i_2,i_3,i_4;j_1,j_2,j_3,j_4}(E) \quad (13)$$

$G_{i_1,i_2,i_3,i_4;j_1,j_2,j_3,j_4}(E)$, in turn, is obtained through the usual procedure as a "single-particle" Green function in a four-particle phase space, which in the present case leads to a 256-dimensional matrix. A similar procedure can be used to obtain exact two-particle Green functions which will be used below.

For the *GW* approximation, $\hat{G}_{ii}(E)$ is a single-particle Green function in which the self-energy,

$$\Sigma_{ij}(E) = \lim_{\eta \to 0} \frac{1}{2\pi} \int e^{-i\omega\eta} W_{ij}(\omega) G_{ij}(E - \omega) \, d\omega ,$$

$$(14)$$

is given in terms of the exact single-particle Green function and the exact screened interaction which is determined in terms of the noninteracting (zero superscript), and exact two-particle Green functions, $W_{ij;kl}(E) = \{G^{(0)-1}_{ij;kl} - G^{-1}_{ij;kl}\}$.

For single-particle spectra which are derived from an effective two-particle approach, $\hat{G}_{ii}(E)$ is derived through down-folding from an effective two-particle Green function in which two-particle states are obtained in the presence of another pair of particles. For example, for *each* configuration of a pair of particles on the ring, one calculates the energy of the system for *every* configuration of an *additional* pair. The corresponding states are consistent with the Pauli exclusion principle, but neglect the interactions among configurations associated with the first existing pair. These configurations are treated independently of one another.

In all three cases the energy was assigned an imaginary part of $0.25t$ for presentation purposes.

As is seen in these figures, the results based on an effective two-particle Green function are in considerably better agreement with the exact spectra than those obtained in the present version of the *GW* approximation, particularly for large values of U. One also sees that these results overestimate the gap in the strong U limit as may be expected in a non-self-consistent procedure of this type. Even for $U/t = 1.0$, a region in which the *GW* approximation has been found to give accurate results for real systems, the averaging of the two-particle Green function in the presence of a finite density resolves the electronic structure much more accurately. We note the resonance at $U = 1.0$ which is missed in the *GW* results, and that both approximate results are displaced somewhat with respect to the exact ones. Much of this effect, along with the wider gap in the strong U limit mentioned above can be traced back to the incomplete treatment of the Pauli principle, i.e., the neglect of
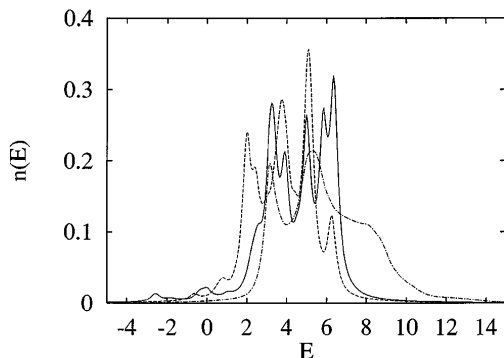

FIG. 1. Exact single-particle spectrum (solid line) for four electrons on a four-site ring compared with the results of a *GW* approximation (dash-dotted line) and those obtained from an effective two-particle Green function (dashed line) for $U = 1.0$.
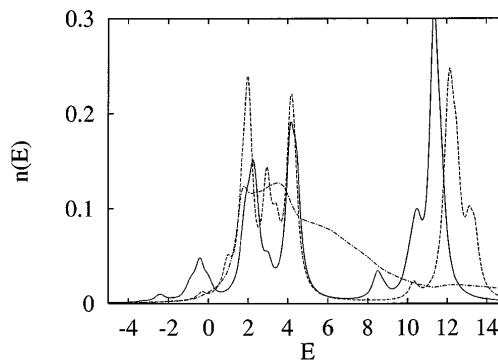

FIG. 2. Results analogous to those of the previous figure, but for $U = 10.0$.

configuration interactions. Both of these approximations can be expected to improve with increased dimensionality and lattice connectivity. More detailed discussions of these and other similar numerical results than can be presented here will be given in a future publication.

The formalism presented here indicates the unifying power of DFT and provides an extension of the theory to the treatment of fully correlated two-particle states (and by a straightforward extension of n-particle states). Thus, it leads to a general minimum principle governing correlated densities in quantum systems which is analogous to the principle governing single-particle densities. Although its computational implementation, say within a partial-wave analysis, increases in difficulty rapidly with increasing dimensionality of the n-particle phase space, its application to two-particle states is well within the domain of present computational technology.

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