Valence Density Functionals

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We derive an extension of the Hohenberg-Kohn (HK) theorem which applies to the valence electrons only, excluding core states. The energy functional of the valence electron density is minimized giving a variational bound on the total ground-state energy. A Kohn-Sham-type approximation suggests treating valence states by the local density approximation (LDA) and the core states by Hartree-Fock. The functional can be used to generate pseudopotentials or to perform all-electron calculations beyond conventional LDA. Our formalism also yields a simple derivation of the HK theorem for Dirac electrons.

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Density functional theory is the cornerstone of much of computational condensed matter physics and quantum chemistry [1–5]. Its success comes from a combination of both being based upon a rigorous many-body theorem, and because it provides good approximations for calculating total energies without requiring a full solution to the many-body problem. The most widely used of these approximations are the local density approximation (LDA) [1], and improvements to LDA based upon various gradient corrections [6–8]. These approximations are accurate when the electron density is slowly varying. Unfortunately in most real atoms, molecules, and solids the deep atomic core states are not well represented by LDA or gradient approximations. The core state energies are dominated by kinetic, Coulomb, and exchange contributions, with correlation playing a relatively minor role. An exact nonlocal exchange treatment of the core electrons should therefore be superior to LDA. On the other hand, for the valence electrons, where exchange and correlation are both important, LDA, perhaps including gradient corrections, is more appropriate than Hartree-Fock exchange alone. The aim of the present paper is to show that there exists a new extension of the Hohenberg-Kohn theorem which applies to the valence electrons alone, excluding core states. This functional provides a simple, but rigorous, framework in which valence states may be approximated by LDA while core states are treated more appropriately, for example, with exact exchange.

There is also an urgent need for approximations beyond LDA because of the recent development of variational and quantum Monte Carlo calculations (QMC) in solids [9, 10]. Especially there is a need for new types of pseudopotentials which are more accurate than standard ones, and which do not assume LDA in treatment of the core states. This led Shirley and co-workers [11] to investigate several different combinations of nonlocal exchange together with local correlation. They found that Hartree-Fock exchange together with local correlation provides better atomic energies and more transferable pseudopotentials than pure LDA. Subsequently Bylander and Kleinman [12] developed pseudopotentials based upon a Hartree-Fock approximation for the core states together with LDA for the valence states. These pseudopotentials were substantially better than simply using LDA for the valence states alone, and were comparable in accuracy and transferability to conventional LDA pseudopotentials with core corrections [13] while being more straightforward to implement. We show below that these semiempirical improvements over LDA can be rigorously justified as the first-order approximations to an entirely new Hohenberg-Kohn energy functional.

In this Letter we show that there exists a new family of Hohenberg-Kohn (HK) density functionals which are functionals of the *valence electron density.* We therefore explicitly eliminate the core states from the functional. Second, we show that a natural set of approximations similar to the original derivation of LDA leads to a simple physically motivated approximation: valence only LDA and Hartree-Fock core-core and valence-core exchange. This new functional should be useful in several types of calculations. First, it should allow one to generate pseudopotentials which are more accurate than present ones based upon all-electron LDA [14, 15]. Indeed the first-order approximation suggested by the new method is essentially the same as in Bylander and Kleinman's recent work [12]. Second, since the core states are not treated by LDA but by an explicitly many-body wave function, pseudopotentials generated in this scheme can be directly used in both density functional theory and full many-body calculations of solids or atoms and molecules. Finally, the new functional is not limited to pseudopotential calculations, but could also be used in full all-electron calculations for solids [16]. Here the method again provides approximations beyond LDA, and would be useful even when the core states are overlapping on neighboring atoms and pseudopotentials cannot be used.

The derivation of a Hohenberg-Kohn theorem for valence electrons closely parallels the derivation of the ordinary HK theorem given by Levy [17]. First we must define "core" and "valence" wave functions and the assumption which lets us separate these two sets of degrees of freedom. We suppose that the core states are described by a given, fixed, wave function of the n core electrons: $\psi_c(x_1, x_2, \ldots, x_n)$, where, for brevity, $x \equiv (\mathbf{r}, \sigma)$. ψ_c may be a Hartree-Fock state, but could also include any arbitrary core-core correlations. Now suppose that there are m valence electrons, described by a many-body wave function: $\psi_v(x_1, x_2, \ldots, x_m)$. All of the discussion below will be based on the approximate wave function for the whole system:

$$\Psi(x_1, \ldots, x_N) = \mathcal{A}\psi_c(x_1, x_2, \ldots, x_n) \times \psi_v(x_{n+1}, x_{n+2}, \ldots, x_N) , \qquad (1)$$

where $N = n + m$ is the total number of electrons and $\mathcal{A}$ is the antisymmetrization operator. This approximation amounts to the neglect of core-valence correlation, but full inclusion of core-valence exchange, and core-core and valence-valence exchange and correlation. It is this approximate factorized wave function which allows us to develop the density functional theory we seek. Since we restrict ourselves to this variational class of wave functions the rigorous density functional we derive is itself a variational approximation to the true ground-state energy.

As well as Eq. (1) we shall also find it useful to impose another condition. We shall restrict the set of valence many-body wave functions to those which satisfy

$$0 = \int dx\, \psi_c^*(x, x_2, \ldots, x_n)\psi_v(x, x_{n+2}, \ldots, x_N) , \qquad (2)$$

where $\int dx \equiv \sum_\sigma \int d^3r$. This condition is a generalized form of orthogonality. For brevity we shall refer to this as 1-orthogonality, since integration is over any one of the many particle coordinates. If ψ_c and ψ_v are simple Slater determinant wave functions, then they are 1-orthogonal if all the valence single-particle states are orthogonal to all the core states. Product wave functions obeying generalized orthogonality conditions such as Eq. (2) are a well-known approximation [18]. The 1-orthogonality condition is especially useful in deriving a density functional theory, since if it is satisfied it is easy to see that the all electron density $\rho(\mathbf{r})$ obeys

$$\rho(\mathbf{r}) = \rho_c(\mathbf{r}) + \rho_v(\mathbf{r}) \qquad (3)$$

for wave functions in the form of Eq. (1), where ρ_c and ρ_v are the core and valence electron densities, respectively.

We are now in a position to state and derive the Hohenberg-Kohn theorem. Let the many-body Hamiltonian be of the form

$$\hat{H} = \hat{T} + \hat{V} + \int d^3r\, V_{\text{ext}}(\mathbf{r})\hat{\rho}(\mathbf{r}) , \qquad (4)$$

where $\hat{T} = \sum_i \hbar^2\nabla^2/2m$ is the kinetic energy operator, $\hat{V} = \frac{1}{2}\sum_{i,j} |\mathbf{r} - \mathbf{r}'|^{-1}$ is the particle-particle interaction, $V_{\text{ext}}(\mathbf{r})$ is the external potential, and $\hat{\rho}(\mathbf{r})$ is the electron density operator. Then the expectation of the total energy in the full wave function 1 is

$$E = \frac{\langle\Psi|\hat{T} + \hat{V}|\Psi\rangle}{\langle\Psi|\Psi\rangle} + \int d^3r\, V_{\text{ext}}(\mathbf{r})[\rho_c(\mathbf{r}) + \rho_v(\mathbf{r})] . \qquad (5)$$

Following Levy's derivation of density functional theory (DFT) we define the functional $Q[\rho_v]$ as

$$Q[\rho_v] = \min \frac{\langle\Psi|\hat{T} + \hat{V}|\Psi\rangle}{\langle\Psi|\Psi\rangle} , \qquad (6)$$

where Ψ is given by Eq. (1) and the minimum is taken varying all valence wave functions with the given valence density ρ_v:

$$\rho_v(\mathbf{r}) = \langle\psi_v|\hat{\rho}(\mathbf{r})|\psi_v\rangle / \langle\psi_v|\psi_v\rangle , \qquad (7)$$

which are 1-orthogonal to ψ_c. In the search for the minimum over valence states the core wave function ψ_c is regarded as a *fixed* external constraint. We can now define the valence density functional:

$$E_v[\rho_v] = Q[\rho_v] + \int d^3r\, V_{\text{ext}}(\mathbf{r})[\rho_c(\mathbf{r}) + \rho_v(\mathbf{r})] . \qquad (8)$$

Clearly $E_v[\rho_v]$ is minimized at the valence density ρ_v corresponding to the lowest variational energy of wave functions defined by Eq. (1) and the constraint 2. This is sufficient to prove the theorem.

An equivalent way to derive the theorem is to first note that the set of m-body valence wave functions $\psi_v(x_1, x_2, \ldots, x_m)$ which satisfy the 1-orthogonality constraint, Eq. (2), forms a Hilbert space, since the constraint is linear. We can thus define a valence only many-body Hamiltonian by the restriction of the full Hamiltonian to the states in this Hilbert space. For example, if ψ_{vi} and ψ_{vj} are any two m-body states in this space, we can define the matrix elements of the effective m-body Hamiltonian

$$\langle\psi_{vi}|\hat{H}_{\text{eff}}|\psi_{vj}\rangle = \langle\mathcal{A}\psi_{vi}\psi_c|\hat{H}|\mathcal{A}\psi_{vj}\psi_c\rangle \qquad (9)$$

and overlap matrix elements

$$\langle\psi_{vi}|\psi_{vj}\rangle = \langle\mathcal{A}\psi_{vi}\psi_c|\mathcal{A}\psi_{vj}\psi_c\rangle . \qquad (10)$$

The ground-state eigenvector of this effective m-particle Hamiltonian gives the valence density $\rho_v(\mathbf{r})$ which minimizes the functional $E_v[\rho_v]$, and the lowest eigenvalue corresponds to the value of $E_v[\rho_v]$ at that density.

Before proceeding, two comments are necessary. First, the functional is only defined for valence electron densities which are N representable, i.e., which correspond to an m-particle many-body wave function. Furthermore, the density must be N representable in terms of wave functions satisfying the 1-orthogonality constraint of Eq. (2). By construction the valence density which minimizes the functional satisfies these conditions, since it corresponds to the actual wave function with the variational minimum energy. A more detailed analysis of the domain of N-representable densities is beyond the scope of this Letter; see the works of Gilbert [19], Harriman [20], and Levy for more discussion of this problem [21]. The second comment is to note that the 1-orthogonality condition, Eq. (2), is possibly more strict than absolutely required. It was chosen because it is a sufficient condition to prove the theorem (rather than being a necessary condition) and it will probably be most useful in practical calculations. If the class of 1-orthogonal valence wave functions prove too limited in accurate calculations, then this could be extended relatively easily.

We now show how the above theorem might be applied straightforwardly in realistic calculations, and we also find the simplest generalization of the Kohn-Sham single-particle wave functions [1]. We first suppose that the core wave function is adequately represented by a single Slater determinant:

$$\psi_c(x_1,\ldots,x_n)=\mathcal{A}\phi_1(x_1)\phi_2(x_2)\cdots\phi_n(x_n)\,. \qquad (11)$$

For a single atom the HF orbitals $\phi_i(x)$ will be the atomic core states, while in a solid they may be the Bloch wave functions of deep bands which are well away from the Fermi surface. Without loss of generality the ϕ_i form an orthonormal set. For now we assume that the ϕ_i are a fixed known set of functions. They are essentially free variational parameters since they can be chosen to give the best overall many-body energy at the end of the calculation. Given these fixed core states we can now define the Hilbert space of possible valence orbitals. Choosing an infinite set of functions $\phi_{n+1},\phi_{n+2},\ldots$ which are orthonormal to each other and to the core orbitals we can construct possible valence wave functions as sums of Slater determinants:

$$\psi_v(x_{n+1},\ldots,x_N) = \sum_{j,k,..,l} c_{j,k,..,l}\mathcal{A}\phi_j(x_{n+1})\phi_k(x_{n+2})\cdots\phi_l(x_N) \qquad (12)$$

with $j,k,\ldots,l>n$. Any wave function of this form automatically satisfies the 1-orthogonality condition of Eq. (2). At least in principle, one can minimize the energy over these possible valence wave functions for any given set of core states. Such a calculation would yield the exact functional minimum of $E_v[\rho_v]$ and the density ρ_v at that minimum. Such a calculation is certainly possible for finite systems such as atoms and molecules, using configuration interaction (CI) or Monte Carlo techniques. Indeed the damped-core QMC calculations of Hammond, Reynolds, and Lester [22] make it possible to evaluate the energy, $E_v[\rho_v]$, exactly, since they correspond to a product many-body wave function with a fixed trial core wave function and an exact QMC evaluation of the valence wave function.

Density functional theory is mostly useful because it provides accurate approximate answers, using say LDA, even in cases where exact many-body results are not available. To construct an approximate scheme analogous to LDA we follow the original development of Kohn and Sham [1]. First introduce a new set of orthonormal single-particle functions, $\psi_{n+1},\psi_{n+2},\ldots,\psi_N$, which we shall call the valence Kohn-Sham orbitals. It is natural to enforce the orthogonality of these *valence Kohn-Sham* orbitals to the *core Hartree-Fock* orbitals. The reason for this is that then the valence density

$$\rho_v(\mathbf{r}) = \sum_{i=n+1,N,\sigma} |\psi_i(\mathbf{r},\sigma)|^2 \qquad (13)$$

is explicitly N representable with a many-body wave function 1-orthogonal to the core wave function (construct a Slater determinant out of the valence Kohn-Sham orbitals). Just as in conventional DFT the valence Kohn-Sham orbitals generally have no direct physical significance. In contrast the HF core orbitals are a real part of the approximate all electron many-body wave function. Following Percus [23] we can define a functional, $T[\rho_v]$, corresponding to the kinetic energy of a set of noninteracting valence electrons with density ρ_v:

$$T[\rho_v] = \min \sum_{i=n+1,N} \langle\psi_i| -\frac{\hbar^2\nabla^2}{2m}|\psi_i\rangle\,, \qquad (14)$$

where the minimum is taken over all possible valence Kohn-Sham orbitals which give the density ρ_v and are orthogonal to the core HF orbitals. Collecting terms we can write the total energy in its final form:

$$E_v[\rho_v] = T[\rho_v] + \int d^3r\, V_{\text{ext}}(\mathbf{r})\rho_v(\mathbf{r}) + \frac{1}{2}\int d^3r\, d^3r'\frac{\rho_v(\mathbf{r})\rho_v(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \int d^3r\, d^3r'\frac{\rho_c(\mathbf{r})\rho_v(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_c + E_{\text{vxc}}[\rho_v]\,. \qquad (15)$$

Here E_c is the core only Hartree-Fock energy:

$$\begin{aligned} E_c = &\sum_{i=1,n}\langle\phi_i| -\frac{\hbar^2\nabla^2}{2m}|\phi_i\rangle + \int d^3r\, V_{\text{ext}}(\mathbf{r})\rho_c(\mathbf{r}) + \frac{1}{2}\int d^3r\, d^3r'\frac{\rho_c(\mathbf{r})\rho_c(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &-\frac{1}{2}\sum_{i,j,\sigma}\int d^3r\, d^3r'\frac{\phi_i^*(\mathbf{r},\sigma)\phi_j(\mathbf{r},\sigma)\phi_j^*(\mathbf{r}',\sigma)\phi_i(\mathbf{r}',\sigma)}{|\mathbf{r}-\mathbf{r}'|}\,. \end{aligned} \qquad (16)$$

The remaining term in Eq. (15), $E_{\text{vxc}}[\rho_v]$, we shall call the valence exchange-correlation energy functional. The Kohn-Sham orbitals satisfy self-consistent equations found by minimizing Eq. (15):

$$\hat{Q}_c\left(-\frac{\hbar^2\nabla^2}{2m} + V_{\text{ext}}(\mathbf{r}) + \int d^3r'\frac{\rho(\mathbf{r}')+\rho_c(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + V_{\text{vxc}}[\rho_v]\right)\psi_i = \epsilon_i\psi_i\,, \qquad (17)$$

where $\hat{Q}_c$ is a projection operator enforcing orthogonality to the core states, and $V_{\text{vxc}}[\rho_v] = \partial E_{\text{vxc}}[\rho_v]/\partial\rho_v(\mathbf{r})$.

Whether or not the valence density functional proves useful depends upon obtaining accurate approximations to $E_{\text{vxc}}[\rho_v]$ in Eq. (15). The simplest reasonable approximation for this term,

$$E_{\text{vxc}}[\rho_v] \approx -\sum_{i=1,n,j=n+1,N,\sigma}\int d^3r\, d^3r'\frac{\phi_i^*(\mathbf{r},\sigma)\psi_j(\mathbf{r},\sigma)\psi_j^*(\mathbf{r}',\sigma)\phi_i(\mathbf{r}',\sigma)}{|\mathbf{r}-\mathbf{r}'|} + E_{\text{xc}}[\rho_v], \qquad (18)$$

consists of core-valence exchange energy and valence only exchange-correlation energy $E_{\text{xc}}[\rho_v]$. The latter may, for example, be approximated by the conventional LDA or gradient corrected LDA. This combination of Hartree-

Fock core and valence LDA exactly corresponds to the approximation used by Bylander and Kleinman [12], providing a rigorous justification for their approach. Furthermore, by evaluating the full valence energy functional $E_v[\rho_v]$ exactly by QMC, as discussed above, one could use Eq. (18) to compare the exact valence only exchange-correlation functional $E_{\mathrm{xc}}[\rho_v]$ with the LDA, and thus, perhaps, develop more accurate functionals. Certainly more work is necessary to test the accuracy of using LDA in Eq. (18) for a wider range of systems than explored by Bylander and Kleinman [12].

Finally, the formalism developed here also provides a very straightforward derivation of the Hohenberg-Kohn theorem for Dirac electrons [24–26]. This density functional is a nontrivial extension of the conventional Schrödinger electron density functional theory because the Dirac Hamiltonian

$$\hat{H}_D = \hat{T}_D + \hat{V} + \int d^3r V_{\mathrm{ext}}(\mathbf{r})\hat{\rho}(\mathbf{r}) \;, \tag{19}$$

with $\hat{T}_D = \sum_i c\boldsymbol{\alpha}\cdot\mathbf{p}$, has both positive and negative energy solutions. The spectrum is only bounded below when the negative-energy Dirac sea of states is assumed occupied and thus explicitly excluded from the electron Hilbert space. The similarity to the valence-core problem discussed above comes from identifying the single-particle core orbitals $\phi_1, \phi_2, \ldots, \phi_n$ with the infinite set of negative-energy single-particle Dirac spinors. Since all the states in the negative-energy Dirac sea are unavailable to positive-energy electrons the many-body wave function of a set of Dirac electrons $\psi_D(x_1, x_2, \ldots, \psi_m)$ must be 1-orthogonal to all of the states in the sea. In exact parallel to our derivation above one can simply define the Hohenberg-Kohn density functional for Dirac electrons by minimizing the energy in the Hilbert space of m-body electron wave functions 1-orthogonal to all the Dirac sea states. This derivation is more straightforward than the usual derivation of relativistic density functional theories [24, 25], and places more emphasis on the importance of the restricted Hilbert space due to the 1-orthogonality constraints.

In summary, we have shown that it is possible to explicitly construct density functionals of the valence electron density, within a class of variational many-body wave functions. The functional does not include core-valence correlation, but in principle exactly accounts for core-core and valence-valence exchange-correlation energies as well as core-valence exchange. The valence density functional can provide a starting point for calculations with higher numerical accuracy than possible with standard all-electron DFT-LDA. It can be useful for generating pseudopotentials for DFT calculations with only the valence electrons, and those same pseudopotentials could also be used in full variational Monte Carlo calculations since they do not assume LDA for the core states. The valence density functional can also be used in all-electron calculations in which the core states are treated by Hartree-Fock and the valence electrons by DFT. Finally, the method is not restricted to situations where the core states on neighboring atoms are nonoverlapping, but can even be applied when they form extended Bloch states.

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