Progress at the interface of wave-function and density-functional theories

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The Kohn-Sham (KS) potential of density-functional theory (DFT) emerges as the minimizing effective potential in a variational scheme that does not involve fixing the unknown single-electron density. Using Rayleigh Schrödinger (RS) perturbation theory (PT), we construct *ab initio* approximations for the energy difference, the minimization of which determines the KS potential directly—thereby bypassing DFT's traditional algorithm to search for the density that minimizes the total energy. From second-order RS PT, we obtain variationally stable energy differences to be minimized, solving the severe problem of variational collapse of orbital-dependent exchange-correlation functionals based on second-order RS PT.

Originally, the concept of the virtual Kohn-Sham (KS) [1] noninteracting system was conceived in order to improve the representation of the kinetic energy in the Hohenberg-Kohn (HK) [2] universal energy functional of the density. Kohn and Sham did not employ a variational approach but instead imposed the constraint of exact density: The KS system of noninteracting electrons has the same ground-state (g.s.) single-particle density as the system of interacting electrons of interest. From the work of Hohenberg and Kohn [2], we know that this constraint determines the noninteracting system fully. A direct consequence of the exact-density property is that the energy ε_N of the highest occupied orbital is the negative of the ionization energy [3].

Our work revisits the *ab initio* approach to density-functional theory (DFT), whose foundations were laid by Levy's seminal work on the constrained search formulation of DFT [4]. The term *ab initio DFT* was coined by Bartlett *et al.* [5]; it involves the employment of quantum chemical techniques to derive expressions for the exchange and correlation functional that can be further improved systematically. The first such approach, termed *DFT perturbation theory*, was proposed in the early 1990s by Görling and Levy [6,7] and appeared to be a promising route bridging efforts in quantum chemistry and DFT. By employing Rayleigh-Schrödinger (RS) perturbation theory (PT) and using the KS Hamiltonian as the zeroth-order approximation, accurate correlation energy functionals were derived. The initial suggestion was followed by rapid development [5,8–13].

Unfortunately, the straightforward application of second-order RS PT gives rise to correlation energy expressions that are unbound from below; when these expressions are used in a KS minimization of the total energy, as a matter of principle, the search for the minimum is expected to yield energies that are too low and even to lead ultimately to the variational collapse of the total energy. This effect has been observed in a number of studies [14,15]. Note that when the correlation potential is omitted from the zeroth-order Hamiltonian, as in the original formulation of DFT PT [6,7], the tendency to variational collapse is probably hindered. Also, Bartlett's *ab initio* DFT yields improved second-order energies [16,17] due to the weaker perturbation, the diagonal part of which has been absorbed in the zeroth-order, semicanonical Hamiltonian.

Our work here overlaps traditional wave-function theory and DFT from a fresh perspective: Armed with the Rayleigh-Ritz variational principle, we develop an *ab initio* approach whereby the *effective noninteracting Hamiltonian is optimized* rather than the noninteracting state, as is customary. The approach does not focus on the electronic density and initially appears unrelated to DFT and the KS theory. Nevertheless, the resulting optimal local potential of the effective Hamiltonian turns out to be exactly the KS potential. This result is important for the question of physical content of the KS system, as until now the exact density property had to be imposed on the KS system in an intuitive but *ad hoc* manner and it was never expected that the exact density could result simply from an unconstrained Rayleigh-Ritz energy optimization.

To demonstrate the applicability of our approach, we derive approximate forms of the energy difference to be minimized using second-order RS PT. These non-negative expressions are functionals of the local potential of the effective noninteracting Hamiltonian and can be used to obtain directly the KS potential and yield variationally stable, as far as possible, correlation energies from second-order RS PT.

To proceed, we let E denote the energy of the g.s. Ψ of the system of N interacting electrons that we are interested in (nondegenerate g.s.):

$$H \Psi = E \Psi, \tag{1}$$

where H is the Hamiltonian of the system,

$$H = T + V_{ee} + V_{en}, \tag{2}$$

T is the electronic kinetic energy operator, V_{ee} is the electron-electron Coulomb repulsion operator, and $V_{en} = \sum_i v_{en}(\mathbf{r}_i)$ is the nuclear Coulomb attraction that binds the electrons. Single-particle quantities are denoted by lowercase characters, and N-electron quantities are represented by uppercase characters.

We denote by E_v and ρ_v the energy and single-particle density of Φ_v, the g.s. of a system of N noninteracting electrons ($V_{ee} = 0$) confined by a local potential $V = \sum_i v(\mathbf{r}_i)$:

$$H_v \Phi_v = E_v \Phi_v, \tag{3}$$

where $H_v = T + V$. The subscript denotes dependence on $v(\mathbf{r})$. It is traditional in DFT to restrict the space of v to $L^{3/2} + L^\infty$. This choice ensures that the lowest eigenvalue of $h_v = -\nabla^2/2 + v(\mathbf{r})$ is finite [18]. Less restricted spaces also make sense [19].

We have assumed that the potential $v(\mathbf{r})$ has N or more bound single-particle levels (counting each level twice for spin degeneracy). In that case, the energy E_v is the sum of single-particle energies $E_v = \sum_i \epsilon_{v,i}$. For potentials $v(\mathbf{r})$ with fewer than N bound levels, E_v can be generalized to be the infimum of the expectation value of H_v over all normalized N-electron states. When $v(\mathbf{r})$ has at least N bound levels, the infimum will coincide with the minimum. In the subsequent formulation of the variational problem, it is desirable not to exclude potentials with fewer than N bound levels in the domain of single-particle potentials, because otherwise arbitrary variations in the domain of potentials would not be permitted. The problem is analogous to the v-representability problem in DFT, which was solved by the constrained search formulation of Levy [4] and later by Lieb [19].

Then, rather than asking what Slater determinant minimizes the interacting Hamiltonian H, we ask the physically equivalent question: What effective Hamiltonian H_v (3) adopts the interacting g.s. Ψ optimally (but approximately) as its ground state? Using the Rayleigh-Ritz variational principle, the following inequality holds:

$$T_\Psi[v] \doteq \langle \Psi | H_v | \Psi \rangle - E_v > 0. \quad (4)$$

The variational principle was considered by Davidson in a different context [20]. We may think of H_v in inequality (4) as an approximation of the interacting Hamiltonian H in Eqs. (1) and (2). It makes sense to ask about the quality of the approximation and to optimize it: Keeping Ψ fixed, what is the effective (i.e., noninteracting) Hamiltonian (3) that approximates best the interacting one?

For fixed Ψ, the energy difference on the left-hand side of inequality (4) is a functional of the potential $v(\mathbf{r})$; we chose to denote this energy difference by $T_\Psi[v]$ because the minimum of $T_\Psi[v]$ over v will turn out to contain kinetic energy contributions only.

Theorem 1. The potential v_{s} that minimizes $T_\Psi[v]$ is the Kohn-Sham potential.

Strictly, $T_\Psi[v]$ has an infimum only. We assume that the minimum exists. We further assume differentiability of $T_\Psi[v]$ at least at the minimum and that the minimizing potential v_{s} together with any potential that lies sufficiently close to it are deep enough to bind N or more electrons. These assumptions are sufficient to establish the noninteracting v-representability of the density $\rho_\Psi(\mathbf{r})$ of Ψ.

Proof. It is straightforward to obtain the functional derivative of $T_\Psi[v]$ with respect to v:

$$\frac{\delta T_\Psi[v]}{\delta v(\mathbf{r})} = \rho_\Psi(\mathbf{r}) - \rho_v(\mathbf{r}). \quad (5)$$

At the minimizing potential v_{s} we have for all $\mathbf{r}$

$$\rho_\Psi(\mathbf{r}) - \rho_{v_{\mathrm{s}}}(\mathbf{r}) = 0, \quad (6)$$

where $\rho_{v_{\mathrm{s}}}(\mathbf{r})$ is the density of the KS determinant Φ_{s}. We have shown that the noninteracting potential $V_{\mathrm{s}} = \sum_i v_{\mathrm{s}}(\mathbf{r}_i)$ has the same g.s. density as the interacting external potential $V_{en} = \sum_i v_{en}(\mathbf{r}_i)$. By definition, the KS potential is the noninteracting potential with the same g.s. density as the interacting one [1]. The basic theorem of DFT by Hohenberg and Kohn [2] says that we cannot have two potentials (here both noninteracting)

with the same g.s. density that differ by more than a constant. Therefore, v_{s} is the single-particle KS potential and Φ_{s} is the N-electron KS state. ∎

The second derivative $\delta T_\Psi[v]/\delta v(\mathbf{r})\delta v(\mathbf{r}')$ is equal to $-\frac{1}{2}\chi_v(\mathbf{r},\mathbf{r}')$, where $\chi_v(\mathbf{r},\mathbf{r}')$ is the density-density response function of the noninteracting system,

$$\chi_v(\mathbf{r},\mathbf{r}') = \sum_{a,i} \frac{\phi_{v,i}(\mathbf{r})\,\phi_{v,i}^*(\mathbf{r}')\,\phi_{v,a}(\mathbf{r}')\,\phi_{v,a}^*(\mathbf{r})}{\epsilon_{v,i} - \epsilon_{v,a}} + \mathrm{c.c.} \quad (7)$$

$\phi_{v,i}, \phi_{v,a}$ are occupied and unoccupied orbitals, respectively, in Φ_v and $\epsilon_{v,i}, \epsilon_{v,a}$ are their orbital energies. Since $-\chi_v(\mathbf{r},\mathbf{r}')$ is a positive definite operator, $T_\Psi[v]$ is a convex functional and the stationary point (6) is the minimum, as expected.

The value of $T_\Psi[v]$ at the minimum,

$$T_\Psi[v_{\mathrm{s}}] = \langle \Psi | T | \Psi \rangle - \langle \Phi_{\mathrm{s}} | T | \Phi_{\mathrm{s}} \rangle > 0, \quad (8)$$

is the kinetic part, $T_{\mathrm{c}}[\rho_\Psi]$, of the correlation energy functional,

$$E_{\mathrm{c}}[\rho_\Psi] \doteq \langle \Psi | T + V_{ee} | \Psi \rangle - \langle \Phi_{\mathrm{s}} | T + V_{ee} | \Phi_{\mathrm{s}} \rangle. \quad (9)$$

Already, the negative of $T_{\mathrm{c}}[\rho_\Psi]$ is a meaningful approximation for the correlation energy functional $E_c[\rho_\Psi]$,

$$E_{\mathrm{c}}[\rho_\Psi] \approx -T_{\mathrm{c}}[\rho_\Psi]. \quad (10)$$

In fact, Levy and Perdew showed that to second order in an expansion in e^2, $T_{\mathrm{c}}[\rho_\Psi] + E_{\mathrm{c}}[\rho_\Psi] = 0$ [21].

In consideration of the community working with DFT, we write the total energy functional of the density:

$$E_{v_{en}}[\rho] = \langle \Phi_{\mathrm{s}}[\rho] | T + V_{ee} + V_{en} | \Phi_{\mathrm{s}}[\rho] \rangle + E_c[\rho] \geqslant E. \quad (11)$$

$\Phi_{\mathrm{s}}[\rho]$ is the KS state with g.s. density ρ. The time-honored DFT strategy is to vary the density ρ in order to minimize $E_{v_{en}}[\rho]$ and obtain the KS state, the density, and the total energy from the minimum value of $E_{v_{en}}[\rho]$. Alternatively, if we had, from a different source, an accurate approximation for the KS state $\Phi_{\mathrm{s}}[\rho]$ and for the g.s. density, we could substitute them in (11) to obtain the total energy in one step, *without further optimization*.

Theorem 1 offers a direct way to determine the KS potential, provided an approximation for $T_\Psi[v]$ were available. Consequently, we propose here the novel approach in electronic structure to obtain the KS potential v_{s} directly by minimizing appropriate approximations for the energy difference $T_\Psi[v]$ (4) rather than by minimizing the total energy $E_{v_{en}}[\rho]$ (11). The challenge of course is to approximate the energy difference $T_\Psi[v]$ without a priori knowledge (approximate or exact) of the interacting ground state Ψ, since otherwise our method would be of limited interest.

Mathematically, the traditional KS approach, to minimize the KS total energy in order to determine the exact density, and the one we propose here, to minimize the energy difference $T_\Psi[v]$ in order to optimize the effective Hamiltonian, are equivalent. They lead to the same exact result but only when the exact potential functional $T_\Psi[v]$ and the exact

density functional $E_c[\rho]$ are employed. This is not the case with approximate functionals. For example, total energy minimizations which employ approximations for $E_c[\rho]$ that are unbound from below can be expected to yield unphysically low total energies [14,15].

Since the g.s. density and the potential are in 1:1 correspondence, the total energy (11) and its components can be regarded as potential functionals. Then v_s can be determined directly by minimizing the total energy potential functional [22]. These approaches, often referred to as optimized effective potential methods, should not be confused with our approach here, where *the energy difference $T_\Psi[v]$—not the total energy—is the potential functional to be minimized in order to obtain v_s*.

In the rest of this Rapid Communication and to demonstrate the applicability of the method, we derive *ab initio* approximations for $T_\Psi[v]$ and $E_c[\rho]$ using RS PT. The approximate second-order expressions for $E_c[\rho]$ are unbound from below, making unpractical a minimization of the total energy: During such a minimization, exact or near degeneracies would develop between the occupied and virtual orbital energies in the denominators of $E_c[\rho]$, leading to a (full or near) divergence of $E_c[\rho]$ to negative infinity and consequently to a total energy that is too low. On the other hand, the approximate second-order expressions for $T_\Psi[v]$ are bound from below as they are strictly non-negative. Hence, the minimization of $T_\Psi[v]$ is meaningful, allowing the *ab initio* determination of the KS potential and the total energy. In the present approach, the tendency of $T_\Psi[v]$ to diverge is suppressed as far as possible. Such a tendency would develop here too, if $T_\Psi[v]$ were maximized rather than minimized, but this is not the case.

To proceed, we employ RS PT to approximate the interacting state Ψ in (4). We consider a perturbation expansion, where the zeroth-order approximation is based on a noninteracting Hamiltonian with a local potential $v_{en}(\mathbf{r}) + u(\mathbf{r})$, where $u(\mathbf{r})$ (initially undetermined) mimics the electron interaction potential. The zeroth-order Hamiltonian is

$$H_{v_{en}+u} = T + V_{en} + U, \quad U = \sum_i u(\mathbf{r}_i). \quad (12)$$

The eigenstates and eigenvalues of $H_{v_{en}+u}$ are $\Phi_{u,n}$, $E_{u,n}$. For small α, the weakly interacting Hamiltonian is

$$H_u(\alpha) = H_{v_{en}+u} + \alpha(V_{ee} - U), \quad 0 < \alpha \ll 1. \quad (13)$$

The g.s. (to first order) of $H_u(\alpha)$ will be denoted by $\Psi_u(\alpha)$.

Using $\Psi_u(\alpha)$, we may construct the energy difference $T_{\Psi_u(\alpha)}[v]$, whose minimization will yield the optimal potential v_s. The resulting effective Hamiltonian H_{v_s} will have $\Psi_u(\alpha)$ as an accurate approximate ground state. For small α, v_s must be close to $v_{en} + u$, since for $\alpha = 0$, obviously, $v_s = v_{en} + u$. Consequently, we write $v = v_{en} + u + \alpha v'$. So, to describe the KS system, we consider the noninteracting Hamiltonian, $H_{v_{en}+u} + \alpha V'$, $V' = \sum_i v'(\mathbf{r}_i)$, with g.s. $\Phi_{u+\alpha v'}$.

We shall optimize v' and also choose u appropriately; v'_s (the optimal v') will be the first-order KS potential: $v_s(\mathbf{r}) = v_{en} + u(\mathbf{r}) + \alpha v'_s(\mathbf{r})$. The expansion of v_s may continue to higher orders in α.

By putting everything together and expanding $T_{\Psi_u(\alpha)}[v_{en} + u + \alpha v']$ around $\alpha = 0$, the lowest nonvanishing term is

second order:

$$T_{\Psi_u(\alpha)}(v_{en} + u + \alpha v') = \alpha^2 T_u(u + v') + O(\alpha^3), \quad (14)$$

$$T_u[v] = \sum_{n \neq \text{g.s.}} \frac{|\langle \Phi_u | V_{ee} - V | \Phi_{u,n} \rangle|^2}{E_{u,n} - E_u} > 0. \quad (15)$$

There are several local potentials u, such that the RS perturbation series expansion, with zeroth-order Hamiltonian $H_{v_{en}+u}$ and perturbation operator $\alpha(V_{ee} - U)$, converges. Consequently, the expansion of the exact functional T_Ψ and of the KS potential in powers of α is not unique but depends on the choice of u. We write $v_s = v_s[u]$.

For fixed u, a small variation in v leads to the change $\Delta T_u \doteq T_u[v + \delta v] - T_u[v]$ in the energy difference $T_u[v]$:

$$\Delta T_u = \int \delta v(\mathbf{r}) \frac{\delta T_u[v]}{\delta v(\mathbf{r})} - \frac{1}{2} \int \delta v(\mathbf{r}) \delta v(\mathbf{r}') \chi_u(\mathbf{r}, \mathbf{r}'), \quad (16)$$

where

$$\frac{\delta T_u[v]}{\delta v(\mathbf{r})} = \sum_{a,i} \frac{\langle \phi_{u,i} | \mathcal{J}_u - \mathcal{K}_u - v | \phi_{u,a} \rangle}{\epsilon_{u,a} - \epsilon_{u,i}}$$
$$\times \phi_{u,a}^*(\mathbf{r}) \phi_{u,i}(\mathbf{r}) + \text{c.c.} \quad (17)$$

$\mathcal{J}_u, \mathcal{K}_u$ are the Coulomb direct and exchange operators. The second derivative of T_u with respect to v is equal to minus half the density-density response function $\chi_u(\mathbf{r}, \mathbf{r}')$ (7). Thus, for fixed u, the energy difference $T_u[v]$ is a convex functional of v and the stationary condition,

$$\left. \frac{\delta T_u[v]}{\delta v(\mathbf{r})} \right|_{v=v_{\text{Hxc}}} = 0, \quad (18)$$

and determines the minimizing potential $v_{\text{Hxc}}[u]$ of $T_u[v]$. From (14) and (15) follows $v_{\text{Hxc}}[u] = u + v'_s[u]$. Equation (18) is the condition that $\Psi_u(\alpha)$ and $\Phi_{u+\alpha v'_s}$ have the same density to first order in α, for any u. Hence, the potential $v_s[u] = v_{en} + u + \alpha(v_{\text{Hxc}}[u] - u)$ is indeed the KS potential to first order. Note that in a minimization of the total energy, with zeroth-order the KS Hamiltonian and correlation energy functional $E_c[\rho] = -T_u[v]$, even when the resulting energy is not too low, the density at the stationary point will correspond to a potential that is not a stationary point of $T_u[v]$. Hence, for any u, the resulting density will differ in first order from the density of the underlying weakly interacting state $\Psi_u(\alpha)$.

It remains to find a good choice for u.

It is argued elsewhere [23] that the KS state $\Phi_{v_s[u]}$ is close to the first-order interacting state $\Psi_u(\alpha)$. However, it would be desirable if $\Psi_u(\alpha)$ were close to its own zeroth-order state Φ_u, because then the perturbative correction would be small. Therefore, a natural choice for u seems to be the potential for which the first-order correction $v'_s[u]$ vanishes and u coincides with $v_{\text{Hxc}}[u]$. Interestingly, for $v_{\text{Hxc}}[u] = u$, Eqs. (17) and (18) become the well-known exact exchange optimized effective potential (xOEP) equations [24–26].

Corollary. The zeroth-order potential $v_{en} + u$ for which the first-order Kohn-Sham correction vanishes is the exchange-only optimized effective potential.

This result is not surprising, as xOEP is the first-order KS potential according to DFT PT [6,7].

For the converged potential v_{Hxc} ($= u$), the minimum energy difference $T_{v_{\text{Hx}}}[v_{\text{Hx}}]$ ($= \min_v T_{v_{\text{Hx}}}[v]$) equals the negative of the second-order energy in a perturbative expansion with $H_{v_{en}+v_{\text{Hx}}}$ as the zeroth-order Hamiltonian and $V_{ee} - \sum_i v_{\text{Hx}}(\mathbf{r}_i)$ as the perturbation. Hence, *the correlation energy to second order is $E_c = -T_{v_{\text{Hx}}}[v_{\text{Hx}}]$.*

The minimization of $T_u[v]$ over v at $u = v_{\text{Hxc}}[u]$ offers a new definition of xOEP. Compared with the traditional minimization of the total energy, the new definition is advantageous with finite basis sets, since the use of a complete orbital basis set in the objective function (15) is here explicit; see [27].

In summary, the Rayleigh-Ritz minimum principle (4) allowed the variational optimization of the noninteracting Hamiltonian H_v (3), so that it adopts optimally the interacting g.s. Ψ as its approximate g.s. Contrary to current wisdom that the KS system must be constrained in order to yield the exact density, the best local potential turned out be the KS potential.

Primarily, the variational principle (4) sheds new light on the KS system. In addition, it offers an elegant way for the direct determination of the KS potential and also gives rise to *ab initio* expressions for the correlation energy: Based on second-order RS PT, we derived the correlation energy for the zeroth-order potential, $v_{en} + v_{\text{Hx}}$, whose first-order KS correction vanishes, yielding xOEP. Other choices are possible and generate a nonvanishing first-order KS correction and a correlation potential. Of interest is choosing u to minimize the contribution of double excitations in $T_u[v]$ (15) before optimizing v.

The *ab initio* methodology presented here is akin to quantum chemistry and it is hoped it will lead to further insight at the interface of DFT and wave-function theory.

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