# Variational Density-Functional Theory for an Individual Excited State

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It is shown that there exists a variational Kohn-Sham density-functional theory, with a minimum principle, for the self-consistent determination of an individual excited-state energy and density. Exact properties of the required functional are ascertained, including a Koopmans theorem. This knowledge allows the employment of an effective potential that gives encouraging numerical results, and also helps to explain the success of a recent perturbation theory and its time-dependent counterpart.

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Density-functional theory (DFT) is now in widespread use as an effective approach for ground-state electronic structure calculations. The development of accurate functionals within the popular Kohn-Sham formulation of DFT has enabled us to perform efficient ground-state variational calculations with remarkable accuracy. In Kohn-Sham theory, the simplicity of the three-dimensional electron density is coupled with the use of a relatively small number of orbitals to ensure Fermi statistics, through the use of an auxiliary noninteracting system (see, for instance, Refs. [1–5]).

There has also been noteworthy progress in excited-state DFT (see, for example, Refs. [3–28]). These studies have stimulated us into asking if there exists a variational Kohn-Sham theory for an individual excited state, which is analogous to the ground-state theory, because an affirmative answer implies the possibility that accurate excited-state calculations might be performed routinely, in a manner comparable to today's ground-state calculations. Accordingly, it is our purpose to show that there does indeed exist such a variational Kohn-Sham theory, with a minimum principle, for an individual excited state. In our proof, the necessary universal functional is identified and several of its properties are ascertained for the purpose of approximation. This enables us to actually carry out illustrative self-consistent calculations, and encouraging results are obtained for the systems studied.

Consider the Hamiltonian of interest $\hat{H}_v$:

$$\hat{H}_v = \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v(\vec{r}_i), \tag{1}$$

where $\hat{T}$ is the kinetic energy operator, $\hat{V}_{ee}$ is the electron-electron repulsion operator, and $v(\vec{r})$ is the local-multiplicative attractive potential of interest. Assume we want the energy and density of the $k$th state of $\hat{H}_v$. (In this Letter, all interacting and noninteracting states shall be assumed nondegenerate to facilitate the presentation.) For this purpose we start by generalizing earlier excited-state functionals [12,13] and define the universal by

$$F[\rho, \rho'] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle, \tag{2}$$

where both $\rho$ and $\rho'$ are arbitrary electron densities. In Eq. (2), it is understood that each $\Psi$ is orthogonal to the first $k-1$ states of that Hamiltonian, $\hat{H}_{v'} = \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v'(\vec{r}_i)$, for which $\rho'$ is the ground-state density. It follows from the definition of $F[\rho, \rho']$ that $E_k$, the energy of the $k$th state of $\hat{H}_v$, is given by

$$E_k = \min_{\rho} \left\{ \int v(\vec{r}) \rho(\vec{r})\, d^3r + F[\rho, \rho_0] \right\}$$
$$= \int v(\vec{r}) \rho_k(r)\, d^3r + F[\rho_k, \rho_0], \tag{3}$$

where $\rho_0$ is the ground-state density of $\hat{H}_v$ and $\rho_k$ is the density of its $k$th state. Analogous with the constrained-search proof of the ground-state Hohenberg-Kohn variational theorem, Eq. (3) is true because

$$E_k = \min_{\rho} \min_{\Psi \to \rho} \langle \Psi | \hat{H}_v | \Psi \rangle, \tag{4}$$

where the $\Psi$'s are understood to be restricted to be orthogonal to the first $k-1$ states of $\hat{H}_v$. Note that $\int v(\vec{r}) \rho(\vec{r}) d^3r$ in Eq. (3) follows from the $\Psi \to \rho$ restriction in Eq. (4); the orthogonality requirement only has to be embodied in the $F$ in Eq. (3). (A special case of the $F$ in Eq. (2) is simply the familiar one associated with the determination of the energy of the lowest excited state of a given symmetry, when this symmetry differs from the ground state's [6–8]. The orthogonality restriction in Eq. (2) implies that the excited state $F$ is bounded below by the ground state $F$ when both $F$'s contain the *same* trial $\rho$, because the ground state $F$ is Eq. (2) without any orthogonality restriction.)

Our object now is to derive the Kohn-Sham equations for the generation of $\rho_k$ and $E_k$. For this purpose, first observe that the minimization in Eq. (3) gives, within an additive constant,

$$v(\vec{r}) = -\left. \frac{\delta F[\rho, \rho_0]}{\delta \rho(\vec{r})} \right|_{\rho = \rho_K}. \tag{5}$$

  

Next, define the noninteracting Hamiltonian,

$$\hat{H}_w = \hat{T} + \sum_{i=1}^{N} w([\rho_k, \rho_0]; \vec{r}_i), \tag{6}$$

where $\hat{H}_w$ is a noninteracting Hamiltonian with an excited density equal to $\rho_k$. Further, consistent with the adiabatic connection described later, of all such Hamiltonians, $\hat{H}_w$ is identified as the one whose ground-state density resembles $\rho_0$ most closely in a least-squares sense. Now define the noninteracting kinetic energy $T[\rho, \rho_0]$ by

$$T[\rho, \rho_0] = \min_{\Phi \to \rho} \langle \Phi | \hat{T} | \Phi \rangle = \langle \Phi[\rho, \rho_0] | \hat{T} | \Phi[\rho, \rho_0] \rangle, \tag{7}$$

where each $\Phi$ is orthogonal to the first $m - 1$ states of $\hat{H}_w$ if $\rho_k$ is the density of the $m$th state of $\hat{H}_w$. It then follows that $\Phi[\rho_k, \rho_0]$ is the noninteracting Kohn-Sham excited-state wave function of $\hat{H}_w$ whose density is $\rho_k$. (Because of the assumed nondegeneracy, $\Phi[\rho_k, \rho_0]$ turns out to be a single determinant even though $\Phi[\rho, \rho_0]$ is not so restricted.) Moreover, we have the minimum principle

$$T[\rho_k, \rho_0] + \int w([\rho_k, \rho_0]; \vec{r}) \rho_k(\vec{r})\, d^3 r = \min_\rho \left\{ T[\rho, \rho_0] + \int w[\rho_k, \rho_0]; \vec{r}) \rho(\vec{r})\, d^3 r \right\}, \tag{8}$$

and thus

$$w([\rho_k, \rho_0]; \vec{r}) = - \frac{\delta T[\rho, \rho_0]}{\delta \rho(\vec{r})} \bigg|_{\rho = \rho_k}. \tag{9}$$

Partition $F[\rho, \rho_0]$ as

$$F[\rho, \rho_0] = T[\rho, \rho_0] + G[\rho, \rho_0], \tag{10}$$

from which

$$w([\rho_k, \rho_0]; \vec{r}) = v(\vec{r}) + \frac{\delta G[\rho, \rho_0]}{\delta \rho(\vec{r})} \bigg|_{\rho = \rho_k}. \tag{11}$$

Consequently $\varphi_i$, the orbitals of $\Phi[\rho_k, \rho_0]$, satisfy the following Kohn-Sham equations:

$$\left\{ -\frac{1}{2} \nabla^2 + w([\rho_k, \rho_0]; \vec{r}) \right\} \varphi_i = \epsilon_i \varphi_i, \tag{12}$$

where the orbitals are occupied, as necessary, so that

$$\sum_i n_i |\varphi_i|^2 = \rho_k. \tag{13}$$

The occupation numbers $n_i$ will be 0, 1, or 2 for the nondegenerate case. As in the usual Kohn-Sham scheme, the equations are solved in a self-consistent manner. Finally, with $T[\rho_k, \rho_0] = -\frac{1}{2} \sum_i n_i \langle \varphi_i | \nabla^2 | \varphi_i \rangle$, it follows that the resultant total excited-state energy for $\hat{H}_v$ is

$$E_k = \int v(\vec{r}) \rho_k(\vec{r})\, d^3 r - \frac{1}{2} \sum_i n_i \langle \varphi_i | \nabla^2 | \varphi_i \rangle + G[\rho_k, \rho_0]. \tag{14}$$

The excitation energy, $E_k - E_0$, may be usefully expressed as

$$E_k - E_0 = I_0 - I_k, \tag{15}$$

where $I_j$, equal to $E_0^{N-1} - E_j$ with $j = 0$ or $j = k$, is the ionization energy from the $j$th state of $\hat{H}_v$. Also, $E_0$ is the $N$-electron ground-state energy of our $\hat{H}_v$ in Eq. (1) while $E_0^{N-1}$ is the ground-state energy of $\hat{H}_v$ with one electron removed. $I_0$ may be obtained from either two separate ground-state calculations, one for $E_0$ and the other for $E_0^{N-1}$, or by taking the highest-occupied orbital energy from a single $N$-electron ground-state calculation [25–27]. Likewise, $I_k$ may be obtained either by subtracting the excited-state energy $E_k$ from the $(N-1)$-electron ground-state energy $E_0^{N-1}$ or by taking the highest-occupied orbital energy in Eq. (12). That is, analogous to the ground-state ionization energy theorem [25–27], it has recently been observed that [16], unless prevented by symmetry, the known asymptotic decay of excited-state densities [25–28] dictates

$$I_k \equiv E_0^{N-1} - E_k = -\epsilon, \tag{16}$$

where $\epsilon$ is the highest-occupied orbital energy in Eq. (12). In fact, the satisfaction of Eq. (16) may be used as a severe constraint on approximations for an excited-state calculation. The extent of satisfaction of Eq. (16) is a gauge on the accuracy of approximations to $G$ and $\frac{\delta G}{\delta \rho}$.

For practical calculations, where $G$ must be approximated, it is convenient to partition it into

$$G[\rho, \rho_0] = Q[\rho, \rho_0] + E_c[\rho, \rho_0], \tag{17}$$

where $Q$ is the Hartree plus exchange component and $E_c$ is the correlation component of $G$. That is,

$$Q[\rho, \rho_0] = \langle \Phi[\rho, \rho_0] | \hat{V}_{ee} | \Phi[\rho, \rho_0] \rangle, \tag{18}$$

$$E_c[\rho, \rho_0] = F[\rho, \rho_0] - T[\rho, \rho_0] - Q[\rho, \rho_0]. \tag{19}$$

A crucial constraint for approximating $Q$ and $\frac{\delta Q}{\delta \rho}$ is

$$Q[\rho_k, \rho_0] - \langle \Phi^{N-1}[\rho_k, \rho_0] | \hat{V}_{ee} | \Phi^{N-1}[\rho_k, \rho_0] \rangle = \int d^3 r\, |\varphi|^2 \frac{\delta Q[\rho, \rho_0]}{\delta \rho(\vec{r})} \bigg|_{\rho = \rho_k}, \tag{20a}$$

where $\Phi^{N-1}$ is the ground state of $H_w$ in Eq. (6), but with $N - 1$ electrons, and $\varphi$ is the highest-occupied orbital in Eq. (12). It is understood that both $w$ and $\frac{\delta Q}{\delta \rho}$ vanish as $|\vec{r}| \to \infty$. Equation (20a) is analogous to the ground-state exchange-only Koopmans relation that has been previously obtained for finite systems [29,30] and for infinite systems [31].

To prove relation (20a), we follow Ref. [30] and employ the adiabatic connection Hamiltonian $\hat{H}_\alpha = \hat{T} + \alpha \hat{V}_{ee} + \sum_{i=1}^{N} v_\alpha(\vec{r}_i)$, where $\alpha$ is a coupling constant. The potential $v_\alpha$ is such that $v_1$ is $v$ in Eq. (1) and $v_0$ is $w$ in Eq. (6). Further, at each $\alpha$, $v_\alpha$ is such that an excited-state density of $\hat{H}_\alpha$ is $\rho_k$. Moreover, in order to provide a smooth adiabatic connection, of all the Hamiltonians with $\alpha \hat{V}_{ee}$, $\hat{H}_\alpha$ is identified as the one whose ground-state density resembles $\rho_0$ most closely in a least-squares sense. Finally, we employ the fact that the ionization energy associated with $\rho_k$ is independent of $\alpha$, and employ the Hellman-Feynman theorem in the $\alpha \to 0$ limit for both the $N$-electron excited state of $\hat{H}_\alpha$, whose density is $\rho_k$, and for the $(N-1)$-electron ground state of $\hat{H}_\alpha$. We obtain Eq. (20a) after utilization of the fact that the arguments in Refs. [30,32] dictate that $-\alpha \frac{\delta Q}{\delta \rho}$ is the linear term in $v_\alpha$.

The incorporation of $v_c$ and relation (16) into Eq. (20a) gives

$$I_k = \langle \Phi^{N-1} | \hat{H}_{v+v_c} | \Phi^{N-1} \rangle - \langle \Phi | \hat{H}_{v+v_c} | \Phi \rangle, \quad (20b)$$

In the above expression, which interestingly gives the *exact* $I_k$, the $N$-electron $\hat{H}_{v+v_c}$ is $\hat{H}_v$ in Eq. (1) with $v_c = \frac{\delta E_c[\rho,\rho_0]}{\delta \rho}|_{\rho=\rho_k}$ added to $v$, while the other $\hat{H}_{v+v_c}$ contains $N-1$ electrons. Recently, the numerical success of the first-order adiabatic connection perturbation theory (ACPT) [18,32], or coupling-constant perturbation theory, was reported [21]. One reason for this success is that Eq. (20b) applies for $k = 0$, so that ACPT gives $I_0$ exactly, and $I_0$ is larger than $I_k$. The other reason is that ACPT approximates $I_k$ by an expression with the very same form as Eq. (20b), but with slightly different Kohn-Sham orbitals (occupied and unoccupied ones from a ground-state calculation) and, correspondingly, with a somewhat different correlation potential than the $v_c$ in Eq. (20b). In ordinary first-order perturbation theory, $I_0$ is not obtained exactly and $v_c$ is completely missing. Hence, the numerical results are not nearly as good as those from ACPT [21]. Although also not as accurate as the ACPT ones, the zero-order results are actually surprisingly accurate, as explained by quasiparticle comparisons [20,21]. For two electrons, it has been ascertained [21] that ACPT is the same as the single pole approximation [19] in the appealing time-dependent DFT for excited states [19,23,24].

The addition of $E_c$ to both sides of Eq. (20b) results in the following separate constraint for approximating $E_c$ and its functional derivative:

$$E_0^{N-1} = \langle \Phi^{N-1} | \hat{H}_v | \Phi^{N-1} \rangle + E_c[\rho_k, \rho_0] - \int d^3r \, |\varphi(\vec{r})|^2 \frac{\delta E_c[\rho,\rho_0]}{\delta \rho(\vec{r})} \Big|_{\rho=\rho_k}. \quad (20c)$$

While $E_0^{N-1}$ may be obtained from a ground-state calculation, all of the quantities on the right-hand side are obtained from the individual excited-state calculation.

Other useful constraints follow directly from the definition of $F$. For instance, the exact excited state $F$ is such that $\min_{\rho'} F[\rho,\rho']$ is the familiar universal ground state $F[\rho]$. Also, through Ref. [13] we here obtain

$$\max_{\rho'} \min_{\rho} \left\{ \int v(\vec{r})\rho(\vec{r}) \, d^3r + F[\rho,\rho'] \right\} = \int v(\vec{r})\rho_k(\vec{r}) \, d^3r + F[\rho_k,\rho_0] = E_k. \quad (21)$$

In other words, the object is to find an approximate $F$ such that

$$\min_{\rho} \left\{ \int v(\vec{r})\rho(\vec{r}) \, d^3r + F[\rho,\rho'] \right\} \le \int v(\vec{r})\rho_k(\vec{r}) \, d^3r + F[\rho_k,\rho_0] \quad (22)$$

for *all* $\rho'$. Equation (21) follows from Eq. (22), which in turn follows from the fact that there exists some linear combination of the first $k$ states of $\hat{H}_v$ that is orthogonal to the set of $k-1$ functions associated with $\rho'$. Finally, observe that $F[\rho,\rho_0]$ for state $k$ is bounded below by $F[\rho,\rho_0]$ for state $k-1$, etc.

We have performed simple illustrative self-consistent calculations by approximating $E_c$ by zero, for now, and by approximating $\frac{\delta Q}{\delta \rho}$ by the sum of the Hartree potential and the multiplicative KLI [29] exchange potential, as modified for individual excited states [22]. It is noteworthy that, as in the ground-state case [29], this sum here satisfies Eq. (20a). That is, Eq. (20a) is satisfied when this approximation is used for $\frac{\delta Q}{\delta \rho}$ in the right-hand side and the exact $\Phi$ and $\Phi^{N-1}$ are used in the left-hand side. In the nondegenerate calculations, system (12) is solved to self-consistency, with the constraint that the lowest $\frac{N-1}{2}$ space orbitals are doubly occupied but the higher orbitals are unoccupied, as necessary, in order to give the necessary desired excited-state configuration. The ionization energy from each excited state is approximated in Table I by means of the highest-occupied orbital energy $\epsilon$ through Eq. (16). The nondegenerate presentation in this Letter can be extended to degeneracies by a more lengthy argument through linear combinations of determinants and subspace theory (see Ref. [33] for a relevant ground-state discussion). The $\epsilon$'s from the degeneracy theory are used for He and Ne in Table I. For each atom, observe that the exact singlet-triplet splitting energy is obtained by subtracting the exact singlet $\epsilon$ from the exact triplet $\epsilon$.

The essence of this paper has been the generation of Euler equation (11) from minimum principle (8) for an individual excited state, the establishment of a corresponding Kohn-Sham formulation [the single particle system in (12)], and the derivation of constraints for approximation purposes. Further research shall include approximations to the correlation component of the effective potential in (12). An orbital-dependent correlation potential would help incorporate its dependence on $k$, and constraints [(16),(20b)–(22)] should help to incorporate the orthogonality requirements that are embodied in $E_c$. Also helpful for correlation is the $\alpha > 0$ counterpart of Eq. (20a), as developed in ground-state theory [34].

TABLE I. Ionization Energy (in Ry) from excited state, through highest-occupied orbital energy ($\epsilon$). (Ground-state energy of ion minus excited-state energy of atom.)

| Atom | Configuration | $-\epsilon$ | Experimental [41] |
|---|---|---|---|
| Li | [He]$2p$ | 0.262 | 0.260 |
| | [He]$3s$ | 0.150 | 0.148 |
| | [He]$3p$ | 0.116 | 0.114 |
| | [He]$4s$ | 0.078 | 0.077 |
| | [He]$4p$ | 0.065 | 0.064 |
| Na | [Ne]$3p$ | 0.223 | 0.208 |
| | [Ne]$4s$ | 0.144 | 0.143 |
| | [Ne]$4p$ | 0.103 | 0.102 |
| | [Ne]$5s$ | 0.076 | 0.075 |
| | [Ne]$4d$ | 0.063 | 0.063 |
| He | $1s2p$ $^3$P | 0.270 | 0.266 |
| | $1s2p$ $^1$P | 0.255 | 0.248 |
| Ne | [He]$2p^5 3s$ $^3$P | 0.357 | 0.361 |
| | [He]$2p^5 3s$ $^1$P | 0.346 | 0.349 |

Relevant developments have occurred since the original submission of this Letter. We have ascertained that the existence of $\Psi \rightarrow \rho$ in Eq. (2) is guaranteed by Ref. [35] and that, if so desired, many entities from the ground-state calculation, such as any Kohn-Sham orbital or $v$ itself, may replace $\rho_0$ in the $F$ in Eq. (3) and in the components of $F$. Very recently, a different excited-state theory with a stationary principle has been developed [36], and by use of Ref. [23], it has been proven [37] that excitation energies from first-order ACPT [18,32] are identical to those from time-dependent DFT when just the frequency-dependent exchange kernel is employed in the Laurent approximation [19], thus generalizing the two-electron equivalence [21] to any number of electrons [37]. Consequently, our analysis concerning the ACPT success applies equally well to its time-dependent counterpart, where recent advances have utilized asymptotically improved potentials [38,39] and the Tamm-Dancoff approximation [40].

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