

Excitation energies from density-functional orbital energies

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It is shown that the exact difference between the ground-state and first-excited-state electronic energies can be obtained, in principle, as the difference of highest occupied orbital energies from two separate Kohn-Sham calculations. Alternatively, this excitation energy may be taken as the difference between the lowest unoccupied and highest occupied orbital energies of a single Kohn-Sham calculation, provided that one corrects for a certain derivative discontinuity in the exchange-correlation potential that is analogous to the one for the band gap in solids.

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The employment of single-particle orbital energies from effective Hamiltonians, for multiparticle systems, has been ubiquitous since the beginning of quantum theory. These orbital energies have typically been used for qualitative descriptions of excitation energies, in part, because of the simplicity of the corresponding models.

From a quantitative numerical point of view, the beauty of taking the difference between two orbital energies, to ascertain a true physical excitation energy, is that the difference between two small numbers is involved, rather than between two large numbers, as is generally the case when the excitation energy is computed by subtracting the N -electron ground-state energy from the N -electron excited-state energy. Consequently, the employment of orbital energy differences has special appeal for obtaining approximate excitation energies, through approximate methods, because of the ultimate potential for the generation of highly accurate results.

With this in mind, it is the purpose here to show, for a finite electronic system (or a nucleus), that the exact difference between the first-excited-state energy and ground-state energy, of the real physical Hamiltonian, may be obtained, in principle, as the difference between two Kohn-Sham orbital energies [1] within the formulations of Theophilou and Hadjisavvas [2,3] and of Gross, Oliveira, and Kohn [4-6]. In particular, this excitation energy is given as the difference between the highest occupied orbital energy of a calculation involving an ensemble of fractionally occupied states and the highest occupied orbital energy of a ground-state calculation. Alternatively, the excitation energy may be viewed as the difference between the $(N+1)$ th and N th orbital energies of either the ground-state calculation or the ensemble calculation for weight $w \rightarrow 0$, provided that a certain derivative discontinuity is incorporated into the exchange-correlation portion of the appropriate effective potential. This derivative discontinuity, which shall here be shown to be equal to the correction factor in Ref. [4], as $w \rightarrow 0$, is analogous to the familiar derivative discontinuity involving fractional particle number [7] and the band gap in solids [8,9].

Let us consider the ground state and first-excited state of the following N -electron Hamiltonian:

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

where, in atomic units,

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2, \hat{V}_{ee} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N |\vec{r}_i - \vec{r}_j|^{-1},$$

and where $v(\vec{r})$ is a local-multiplicative attractive potential. For this problem, Gross, Oliveira, and Kohn [4,5] generalized the equiensemble formulation of Theophilou [2,3] to different weights, in order to establish their key relation involving orbital energies, and defined a universal density functional to generate E_w , where

$$E_w = (1-w)E_A + wE_B. \quad (2)$$

Here E_A is the ground-state energy of the N -electron Hamiltonian \hat{H} , E_B is its first-excited-state energy, and w is a scalar with $0 \leq w \leq \frac{1}{2}$. The formulation of Theophilou applies for the special case of $w = \frac{1}{2}$.

In the density-functional generation of E_w , upon minimization one obtains [4,5]

$$n_w = (1-w)n_A + wn_B, \quad (3)$$

where n_A is the ground-state electron density of \hat{H} and n_B is the corresponding first-excited-state density. When n_w is a noninteracting ensemble v -representable in a certain sense, there exists a local potential v_s such that

$$\left\{ -\frac{1}{2} \nabla^2 + v_s^w([n_w]; \vec{r}) \right\} \varphi_i^w(\vec{r}) = \varepsilon_i^w \varphi_i^w(\vec{r}), \quad i = 1, 2, \dots, \quad (4)$$

where $\varepsilon_1^w \leq \varepsilon_2^w \leq \varepsilon_3^w \cdots \varepsilon_N^w \leq \varepsilon_{N+1}^w \cdots$, in a manner consistent with the Pauli principle, and where

$$n_w(\vec{r}) = \sum_{i=1}^{N-1} |\varphi_i^w|^2 + (1-w)|\varphi_N^w|^2 + w|\varphi_{N+1}^w|^2. \quad (5)$$

For simplicity of presentation, explicit spin polarization is not shown. However, the results within carry over for a spin-polarized v_s^w as well as for noninteracting systems consisting of more involved ensembles.

In expression (4), adjust $v_s^w([n_w]; \vec{r})$, if necessary, by a constant, so that it vanishes as $|\vec{r}| \rightarrow \infty$. Then, in this limit,

$$\varphi_i^w(|\vec{r}|) \sim \exp(-\sqrt{-2\varepsilon_i^w}|\vec{r}|), \quad i=1,2,\dots,N+1, \quad (6)$$

so that it follows from $\varepsilon_{N+1}^w \geq \varepsilon_i^w$ for all $i < N+1$ and from expression (5) that

$$n_w(|\vec{r}|) \sim \exp(-2\sqrt{-2\varepsilon_{N+1}^w}|\vec{r}|), \quad 0 < w \leq \frac{1}{2}. \quad (7)$$

Next, note that studies [10–20] concerning the asymptotic decay of n_A do not rely on the fact that n_A is an N -electron *ground-state* density. In other words, the asymptotic ground-state proof carries over when the N -electron wave function is an excited state [15], in the sense that for $|\vec{r}| \rightarrow \infty$, n_B decays as

$$n_B(|\vec{r}|) \sim \exp(-2\sqrt{-2\mu_B}|\vec{r}|), \quad (8)$$

just as n_A decays as [10–20]

$$n_A(|\vec{r}|) \sim \exp(-2\sqrt{-2\mu_A}|\vec{r}|), \quad (9)$$

where

$$\mu_B = E_B - E_{N-1}^{\text{g.s.}}, \quad (10)$$

$$\mu_A = E_A - E_{N-1}^{\text{g.s.}}, \quad (11)$$

and where $E_{N-1}^{\text{g.s.}}$ is the $(N-1)$ -electron ground-state energy of \hat{H} . [Only if the corresponding $(N-1)$ -electron ground-state wave function is “inaccessible,” as $|\vec{r}| \rightarrow \infty$, would either expression (8) or expression(9) not hold.]

Now, since $\mu_A < \mu_B$, it follows from Eqs. (3), (8), and (9), that n_w decays as

$$n_w(\vec{r}) \sim \exp(-2\sqrt{-2\mu_B}|\vec{r}|), \quad (12)$$

so that comparison of expressions (7) and (12) implies

$$\varepsilon_{N+1}^w = \mu_B = E_B - E_{N-1}^{\text{g.s.}}, \quad 0 < w \leq \frac{1}{2}. \quad (13)$$

Finally, we already know that [7,17,18,20]

$$\varepsilon_N^{w=0} = \mu_A = E_A - E_{N-1}^{\text{g.s.}}. \quad (14)$$

As a result, for $0 < w \leq \frac{1}{2}$,

$$E_B - E_A = \varepsilon_{N+1}^w - \varepsilon_N^0, \quad (15)$$

which means that the excitation energy, $|E_B - E_A|$, is obtained as the difference of Kohn-Sham orbital energies from two different calculations, one at $w=0$ and one at $0 < w \leq \frac{1}{2}$. This is our first desired result. [Note, however, that the form of Eq. (15) changes whenever the $(N-1)$ -electron ground-state wave function is “inaccessible” as $|\vec{r}_N| \rightarrow \infty$ in the N -electron excited-state wave function, for then $E_{N-1}^{\text{g.s.}}$ in Eq. (10) is replaced by the energy of that “accessible” $(N-1)$ -electron state with the lowest energy as $|\vec{r}_N| \rightarrow \infty$.]

It is important to compare the result at $w=0$ with the result for the limit $w \rightarrow 0$. At $w=0$, n_w in Eq. (3) is $n_0 = n_A$, so that $v_s^0([n_0]; \vec{r})$ is the Kohn-Sham potential for the N -electron ground state of \hat{H} . On the other hand, one should not assume that $v_s^w([n_w]; \vec{r})|_{w \rightarrow 0}$ is the same as

$v_s^0([n_0]; \vec{r})$, because T_s^w is highly nonlocal and because at all $w > 0$, no matter how close w is to zero, n_w has a different asymptotic decay than n_0 ; n_w decays as n_B , and not as n_A .

The result is that, while $\varepsilon_{N+1}^{w=0} = \mu_B$, without further information one should not expect that $\varepsilon_N^{w \rightarrow 0} = \mu_A$. It would be nice if the latter equality were true, for if $\varepsilon_N^{w \rightarrow 0} = \mu_A$, it would mean that $\varepsilon_{N+1}^{w=0} - \varepsilon_N^{w \rightarrow 0}$ would give exactly $E_B - E_A$. In any case, since $\varphi_i^{w \rightarrow 0} = \varphi_i^0$, except as $|\vec{r}| \rightarrow \infty$, the exact expression for $\varepsilon_N^{w \rightarrow 0}$ is

$$\varepsilon_N^{w \rightarrow 0} = \mu_A - \Delta v_{\text{xc}} \quad (16)$$

where

$$\Delta v_{\text{xc}}(\vec{r}) = v_s^0([n_0]; \vec{r}) - v_s^w([n_w]; \vec{r})|_{w \rightarrow 0} \quad (17)$$

and where $\Delta v_{\text{xc}}(\vec{r})$ is *constant* throughout space, except at very large $|\vec{r}|$, where $\Delta v_{\text{xc}}(|\vec{r}|) \rightarrow 0$. Hence, we have

$$E_B - E_A = \varepsilon_{N+1}^{w=0} - \varepsilon_N^{w \rightarrow 0} + \Delta v_{\text{xc}}. \quad (18a)$$

Alternatively, we may express the excitation energy in terms of Δv_{xc} and the orbital energies from the ground-state calculation. That is,

$$E_B - E_A = \varepsilon_{N+1}^0 - \varepsilon_N^0 + \Delta v_{\text{xc}}, \quad (18b)$$

so that

$$\Delta v_{\text{xc}} = \varepsilon_N^{w \rightarrow 0} - \varepsilon_N^0 = \varepsilon_{N+1}^{w \rightarrow 0} - \varepsilon_{N+1}^0. \quad (19)$$

The right-hand side of expression (17) shall now be identified as a discontinuous-change in the exchange-correlation potential. Start with [4,5]

$$E_w = \min_n \left\{ \int v(\vec{r})n(\vec{r}) + T_s^w[n] + \frac{1}{2} \int \int \frac{n(\vec{r}_1)n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3r_1 d^3r_2 + E_{\text{xc}}^w[n] \right\}, \quad (20)$$

where

$$T_s^w[n] = \sum_{i=1}^{N-1} \langle \varphi_i | -\frac{1}{2} \nabla^2 | \varphi_i \rangle + (1-w) \langle \varphi_N | -\frac{1}{2} \nabla^2 | \varphi_N \rangle + w \langle \varphi_{N+1} | -\frac{1}{2} \nabla^2 | \varphi_{N+1} \rangle, \quad (21)$$

where $n(\vec{r})$ is given by the right-hand side of expression (5), except for deletion of the superscript w , and where the φ 's are the first $N+1$ eigenfunctions, consistent with the Pauli principle, of some single-particle multiplicative potential. Hence, $v_s^w([n_w]; \vec{r})$ is given by

$$v_s^w([n_w]; \vec{r}) = v(\vec{r}) + \int \frac{n_w(\vec{r}_2)}{|\vec{r}_2 - \vec{r}|} d^3r_2 + v_{\text{xc}}^w([n_w]; \vec{r}), \quad (22)$$

where

$$v_{xc}^w([n_w]; \vec{r}) = \delta E_{xc}^w[n] / \delta n(\vec{r})|_{n=n_w}. \quad (23)$$

By substituting Eq. (22) into Eq. (17), we identify $\Delta v_{xc}(\vec{r})$ as

$$\Delta v_{xc}(\vec{r}) = v_{xc}^0([n_0]; \vec{r}) - v_{xc}^w([n_w]; \vec{r})|_{w \rightarrow 0}, \quad (24)$$

because

$$\int \frac{n_w(\vec{r}_2)}{|\vec{r}_2 - \vec{r}|} d^3 r_2 \rightarrow \int \frac{n_0(\vec{r}_2)}{|\vec{r}_2 - \vec{r}|} d^3 r_2 \quad \text{as } w \rightarrow 0.$$

The E_{xc}^w in expression (20) is defined through [4,5]

$$E_{xc}^w[n] = F^w[n] - T_s^w[n] - \frac{1}{2} \int \int \frac{n_w(\vec{r}_1) n_w(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3 r_1 d^3 r_2, \quad (25)$$

where

$$F^w[n] = \min\{(1-w)\langle \Psi_I | \hat{T} + \hat{V}_{ee} | \Psi_I \rangle + w\langle \Psi_{II} | \hat{T} + \hat{V}_{ee} | \Psi_{II} \rangle\}, \quad (26)$$

where Ψ_I and Ψ_{II} form an orthonormal set, and consistent with the constrained-search orientation, the Ψ 's in expression (26) are constrained by

$$n = (1-w)\langle \Psi_I | \hat{\rho} | \Psi_I \rangle + w\langle \Psi_{II} | \hat{\rho} | \Psi_{II} \rangle, \quad (27)$$

where $\hat{\rho}$ is a density operator. [Note that each expectation value in Eqs. (26) and (27) may be replaced by an expression involving an ensemble, if necessary.]

For the purpose of establishing new key requirements for Δv_{xc} and E_{xc}^w , in order to approximate them, first combine expression (18) with the following basic expression of Gross, Oliveira, and Kohn [4]:

$$E_B - E_A = \varepsilon_{N+1}^w - \varepsilon_N^w + \left. \frac{\partial E_{xc}^w[n]}{\partial w} \right|_{n=n_w}, \quad w \rightarrow 0, \quad (28)$$

to obtain

$$\Delta v_{xc} = \left. \frac{\partial E_{xc}^w[n]}{\partial w} \right|_{n=n_w}, \quad w \rightarrow 0. \quad (29)$$

Also, from expressions (3), (4), (13), (22), and the Hellmann-Feynman theorem, one arrives at

$$\begin{aligned} & - \int d^3 r |\varphi_{N+1}^w(\vec{r})|^2 \frac{\partial v_{xc}^w([n_w]; \vec{r})}{\partial w} \\ & = \int d^3 r |\varphi_{N+1}^w(\vec{r})|^2 \int \frac{[n_B(\vec{r}_2) - n_A(\vec{r}_2)]}{|\vec{r} - \vec{r}_2|} d^3 r_2 \end{aligned} \quad (30)$$

for all w in the range $0 < w \leq \frac{1}{2}$. Relation (30) is a consequence of the fact that ε_{N+1}^w is independent of w in the latter range. Expressions (29) and (30) should provide useful stringent constraints for helping to model Δv_{xc} and $E_{xc}^w[n]$. Recent scaling constraints [21] should also be considered.

It is appropriate to emphasize in closing that the discontinuity in v_{xc}^w , as manifested on the right-hand side of expression (24), is analogous to what happens in the well-known band-gap problem in solids. The difference is that, unlike with the band-gap problem, the discontinuity in Eq. (24) does not involve a change in the number of electrons, in that n_w refers to the same number of electrons as n_0 and that $E_{xc}^w[n_w]$ is the exchange-correlation energy for the same number of electrons as is given by $E_{xc}^0[n_0]$. Moreover, the band-gap problem involves a *ground-state* ionization energy of N electrons and a *ground-state* electron affinity of N electrons (or the corresponding ground-state ionization energy of $N+1$ electrons).

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