

## Comment on calculations of excited states by the density functional theory

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### Abstract

Valone and Capitani [Phys. Rev. A 23 (1981) 2127] proposed a method for calculating a single selected excited state by finding the ground state energy of the square of a shifted Hamiltonian. Here we prove that this approach can not enable one to calculate excited states on the basis of the Hohenberg and Kohn density functional theory. The justification for the use of the density functional theory for a single excited state on the basis of Kato's cusp theorem is briefly discussed. © 2000 Elsevier Science B.V. All rights reserved.

It has been demonstrated [1–5] that the electronic Hamiltonian (can be atomic, molecular, cluster or quantum dot systems) is uniquely determined by the ensemble of one-electron probability amplitudes,  $\sum_i \rho_i$ . As far as we know, the only paper which proposes a method for calculating a single specific excited state on the basis of the time-independent density functional theory (DFT) is that of Valone and Capitani [6] (see also Section 9.2 in Ref. [7]). Valone and Capitani used a modification of the original Hohenberg–Kohn theorem [8] but did not attempt to prove a Hohenberg–Kohn like theorem for the square of the shifted Hamiltonian they have used. Here, however, we address ourselves to the question as to whether Valone and Capitani's method is based on the Hohenberg and Kohn theorem, since

there is no other time-independent method that has been proposed in the literature for calculating a *single* excited state by DFT.

The statement of Valone and Capitani is based on MacDonald's proof [9] that the spectrum of  $(\hat{H} - \epsilon)^2$

$$(\hat{H} - \epsilon)^2 \psi = \lambda \psi \quad (1)$$

has a ground state eigenvalue  $\lambda$  which is equal to

$$\lambda = \text{Min}\{E_j - \epsilon\}_{j=1, \dots, \infty}^2 \equiv (E_n - \epsilon)^2, \quad (2)$$

where

$$\hat{H}\phi_j = E_j\phi_j. \quad (3)$$

$E_j$  is associated with the excited state  $\phi_j \equiv \psi$ , and  $E_n$  is the excited energy level which is the closest to  $\epsilon$ . Even in the case where the ground state of  $(\hat{H} - \epsilon)^2$  is degenerate, one can still find a linear combination of the degenerate eigenfunctions which

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provide the eigenfunctions of  $\hat{H}$ . Therefore, if we define  $\mathcal{H}_1$  and  $\mathcal{H}_2$  as

$$\mathcal{H}_1 \equiv (\hat{H} - \epsilon)^2, \quad \mathcal{H}_2 \equiv (\hat{H} - \epsilon)^2 + v, \quad (4)$$

where  $\hat{v}$  is a one-electron potential, then, it is clear that the Hohenberg–Kohn theorem holds [8]. Namely, it can not be that  $\mathcal{H}_1$  and  $\mathcal{H}_2$  differ by  $\hat{v}$  which is *not* a constant and it can not be that there are two *different* normalized eigenfunctions which both provide the same one-electron density. However,  $(\hat{H} - \epsilon)^2$  is not the physical Hamiltonian, but  $\hat{H}$  is.

The question we address here is whether one can add a one-electron potential to  $\hat{H}$  which is not a constant and obtain two *different* normalized eigenfunctions with the same  $\rho$ . That is,  $\mathcal{H}_2 \equiv (\hat{H} + v - \epsilon)^2$  and *not* as stated above. In other words,

$$(\hat{H} - \epsilon)^2 \phi_n = \lambda_0 \phi_n, \quad (5)$$

where

$$\lambda_0 = (E_n - \epsilon)^2 = \text{Min} \left\{ (E_j - \epsilon)^2 \right\}_{j=1, \dots, \infty} \quad (6)$$

and

$$\hat{H} \phi_j = E_j \phi_j. \quad (7)$$

Similarly,

$$\begin{aligned} (\hat{H} + \hat{v} - \epsilon)^2 \psi_m &= \tilde{\lambda}_0 \psi_m, \\ \tilde{\lambda}_0 &= (W_m - \epsilon)^2 \\ &= \text{Min} \left\{ (W_j - \epsilon)^2 \right\}_{j=1, \dots, \infty}, \end{aligned} \quad (8)$$

$$(\hat{H} + \hat{v}) \psi_j = W_j \psi_j, \quad (8)$$

where  $\hat{v}$  is a one-electron potential.

Let us assume that one can find two functions, such that

$$\psi_m \neq \phi_n, \quad (9)$$

but both functions provide the same one-electron density probability, which is given by

$$\rho^{(\psi_m)} = \rho^{(\phi_n)} \equiv \rho. \quad (10)$$

From the variational principle it is clear that

$$\langle \psi_m | (\hat{H} - \epsilon)^2 | \psi_m \rangle > (E_n - \epsilon)^2 \quad (11)$$

$$\langle \phi_n | (\hat{H} + \hat{v} - \epsilon)^2 | \phi_n \rangle > (W_m - \epsilon)^2. \quad (12)$$

From (8) and (11) we obtain

$$\begin{aligned} \langle \psi_m | [(\hat{H} + \hat{v} - \epsilon) - \hat{v}]^2 | \psi_m \rangle \\ = [(W_m - \epsilon)^2 - 2\langle \hat{v} \rangle (W_m - \epsilon) + \langle \hat{v}^2 \rangle] \\ > (E_n - \epsilon)^2. \end{aligned} \quad (13)$$

Similarly, from (12) and (7) one can deduce

$$\begin{aligned} [(E_n - \epsilon)^2 + 2\langle \hat{v} \rangle (E_n - \epsilon) + \langle \hat{v}^2 \rangle] \\ > (W_m - \epsilon)^2. \end{aligned} \quad (14)$$

The sum of these two inequalities gives:

$$\langle \hat{v}^2 \rangle > (W_m - E_n) \langle \hat{v} \rangle. \quad (15)$$

If inequality (15) is satisfied we *may* have  $v \neq$  constant such that  $\psi_m \neq \phi_n$  and obtain  $\rho^{(\psi_m)} = \rho^{(\phi_n)}$ .

Let us consider now a special case where  $m = n = 1$ . For the ground states where  $m = n = 1$  we know that

$$\langle \psi_1 | \hat{H} | \psi_1 \rangle > E_1, \quad \langle \phi_1 | \hat{H} + \hat{v} | \phi_1 \rangle > W_1. \quad (16)$$

Since

$$\langle \psi_1 | \hat{H} + \hat{v} | \psi_1 \rangle = W_1, \quad (17)$$

then

$$\langle \psi_1 | \hat{H} | \psi_1 \rangle = [W_1 - \langle \hat{v} \rangle] > E_1 \quad (18)$$

and, therefore, we have proven that

$$W_1 - E_1 > \langle \hat{v} \rangle, \quad (19)$$

for any continuous family of one-electron potentials  $v$ .

From (15) and (19) it is clear that Valone and Capitani's approach leads, for the *ground* state, to the following result:

$$\langle \hat{v}^2 \rangle > \langle \hat{v} \rangle^2. \quad (20)$$

Since

$$\langle \hat{v}^2 \rangle - \langle \hat{v} \rangle^2 = \langle (\hat{v} - \langle \hat{v} \rangle)^2 \rangle > 0, \quad (21)$$

it is clear that (20) ((19) for ground states) holds even for the ground state for any one-electron potential  $\hat{v}$ . Therefore, by taking the square of the shifted Hamiltonian, as proposed in Ref. [6], we may have two different wavefunctions associated with different

Hamiltonians, which provide the *same* one-electron density probability. This is a simple proof that the use of the method suggested in Ref. [6] can not be justified on the basis of the Hohenberg and Kohn theorem for the ground state. *It should be stressed, however, that we do not claim here that the Valone and Capitani theorem must fail. We have proven that this method does not stand on rigorous mathematical ground based on the Hohenberg and Kohn theorem. Perhaps there is another unknown reason why the method may work in some cases. In this sense, however, there is no reason to prefer the use of this method for calculating excited states over any other known time-independent DFT procedure which is used for calculating excited states and does not have a formal mathematical justification.*

Yet, the Kohn–Sham method has been successfully applied for calculations of excitation energies [10,11]. Recently, Nagy [12] presented DFT for a single excited state using Kato’s theorem (known as the ‘cusp conditions’). The theorem implies that  $-0.5$  times the logarithmic derivative of the one-electron density function with respect to the electron coordinates, evaluated at a nucleus position, is equal to the corresponding nuclear charge. The integral of the density gives the number of electrons. Thus, from the one-electron density one determines the charges of the nuclei in coordinate space and the number of electrons in a molecule. In other words, the molecular Hamiltonian is uniquely determined by the one-electron density function. However, it is well known that Gaussian basis functions do not satisfy the cusp conditions. When Gaussians are used as a basis set, then  $-\text{dln}\rho(r)/\text{d}r = 0$  at the nuclei and is not equal to the nuclear charge  $Z$ . This result holds for any number of basis functions. Therefore one can *not* get information about the charges of the nuclei in the molecule from the calculations of one-electron density functions when Gaussians are used as a basis set. Yet, the use of a finite number of Gaussians as a basis set does provide the ground and excited state energies to any given accuracy. This is due to the fact that the exact energy (even for an excited state) can be obtained by calculating the expectation value of the Hamiltonian with a wavefunction that deviates from the exact eigenfunction in a *finite* number of points in the coordinate space. Consequently, Kato’s theorem does not cancel the possibility of calculating

two different functions (associated with two different Hamiltonians) which yet provide the same one-electron density function (but not necessarily at a finite number of points, for example, at the nuclei). It implies, for example, that whenever Gaussians are used as a basis set (for which Kato’s theorem does not hold), one cannot cancel the possibility of calculating the numerically exact eigenvalues of two different Hamiltonians from two different variational wavefunctions which provide the *same* one-electron density function, on the basis of Kato’s cusp theory. Gross [13] reached the same conclusion (i.e., there is no DFT on the basis of Nagy’s arguments) but his reasoning goes as follows: Nagy’s argument proves a one-to-one correspondence between the excited-state density and the external potential only for a very restricted class of potentials (namely the bare nuclear Coulomb potentials). In the Kohn–Sham scheme, the one-electron density function is associated with the Hamiltonian of non-interacting particles in which the one-electron potential does *not* belong to the class of bare Coulomb potentials (note that only for that class is Nagy’s argument valid).

Therefore, so far, there is no known proof that single excited states can be calculated from the time-independent DFT. It would be most desirable, of course, to have a rigorous proof that would include the conditions for which the excited bound states are uniquely determined by the calculation of the one-electron density function.

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