



Is charge transfer transitions really too difficult for standard density functionals or are they just a problem for time-dependent density functional theory based on a linear response approach

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ABSTRACT

It is well known that standard time-dependent density functional theory (TD-DFT) affords both a quantitative and qualitative incorrect picture of charge transfer transitions between two spatially separated regions. It is shown here that the well-known failure can be traced back to the use of linear response theory. Further, it is demonstrated that the inclusion of higher order response terms readily affords a qualitatively correct picture even for simple functionals based on the local density approximation. By using the higher order response terms, we finally derive a correction that can be added as a perturbation to charge transfer excitation energies calculated by standard TD-DFT.

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1. Introduction

Over the past decade time-dependent DFT (TD-DFT) [1,2] has emerged as a new and promising approach in the study of excited state properties [3,4]. Experience has shown that excitation energies calculated by TD-DFT often are in reasonably good agreement with experiment. It is thus not surprising that TD-DFT is applied widely as a good compromise between accuracy and computational expediency [3,4]. Nevertheless, the use of the generalized gradient approximation (GGA) and other popular approximate functionals (in conjunction with TD-DFT) have revealed some systematic errors [5,9] in the calculated excitation energies. Errors are especially large for transitions of electrons between two separated regions of space or between orbitals of different spatial extend. We have in a previous study [10] demonstrated that the simple linear response approach taken in standard TD-DFT introduces serious problems not present in the corresponding Hartree–Fock [2] time-dependent formulation. It was further shown that higher order response contributions might be needed to calculate excitation energies accurately with DFT. We shall here use our analysis to demonstrate how higher order response terms can be used to give a qualitatively correct picture of charge transfer transitions.

2. Results and discussion

Many elegant studies [5–9] have shown that charge transfer transitions are treated even qualitatively incorrect in TD-DFT. Some of these studies have in addition proposed schemes that remedy these problems efficiently by introducing modified functionals or correction terms based on sound physical arguments [5–9,11]. Our task here is to demonstrate that there is nothing wrong with TD-DFT if one goes beyond the simple first order approach. In fact with higher order terms included there is nothing wrong with standard functionals such as the one based on the local [12–15] density approximation or GGA's [14,15] either. In order to demonstrate this, we shall make use of a simple model of charge transfer in which some simplifying assumptions are introduced that might be of quantitative importance. However, they should not change the qualitative picture.

2.1. Formulation of a simple model for charge transfer

Let us now consider a simple model in which we have a neutral donor molecule D and a neutral acceptor molecule AC separated completely in space by a distance R. Both D and AC are closed shell molecules and the entire system can be described in KS-theory [13,14] by a single Slater determinant

$$\Psi^0 = |\psi_1 \psi_2 \dots \psi_i \psi_j \dots \psi_n|, \quad (1)$$

for which the associated density matrix

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$$\rho(1, 1') = \sum_i^{\text{occ}} \psi_i^*(1') \psi_i(1), \quad (2)$$

optimizes the energy expression

$$E_{KS} = E_{T+V_{Ne}} + E_C + E_{XC,KS}. \quad (3)$$

Here

$$E_{T+V_{Ne}} = \int [\hat{h}^0(1') \rho(1, 1')]_{(1=1')} d\tau_1, \quad (4)$$

where \hat{h}^0 contains the kinetic energy operator \hat{T}_e for a single electron as well as the electron potential V_{Ne} due to the attraction of all the nuclei. Further,

$$E_C = \frac{1}{2} \int \rho(1, 1) \frac{1}{r_{12}} \rho(2, 2) d\tau_1 d\tau_2, \quad (5)$$

is the interaction of the molecular electron density with itself and

$$E_{XC,KS} = \int E_{XC,KS}[\rho(1, 1)] d\tau_1, \quad (6)$$

is the exchange correlation energy expressed as a functional of $\rho(1, 1)$.

The set of spin-orbitals $\{\psi_i(1); i = 1, \text{occ}\}$ making up the optimized ground state Slater determinant satisfy the one-electron KS-equation

$$\hat{F}^{KS}(1) \psi_i(1) = \varepsilon_i \psi_i(1), \quad (7)$$

where

$$\hat{F}_{KS}(1) = \hat{h}^0 + \int \rho(2, 2) \frac{1}{r_{12}} d\tau_2 + V_{XC}(1), \quad (8)$$

and the exchange correlation potential is given as

$$V_{XC}[\rho] = \frac{\delta E_{XC}}{\delta \rho(1, 1)}. \quad (9)$$

Eq. (8) has as solutions the optimized set of “occupied” spin-orbitals $\{\psi_i(1); i = 1, \text{occ}\}$ as well as a set of “virtual spin-orbitals” $\{\psi_a(1); a = 1, \text{vir}\}$. We can consider the combined set of spin-orbitals $\{\psi_p(1); p = 1, \text{vir} + \text{occ}\}$ as being orthonormal. It further holds that

$$F_{rs}^{KS} = \int \psi_r^*(1) \hat{F}_{KS}(1) \psi_s(1) d\tau_1 = \delta_{rs} \varepsilon_r. \quad (10)$$

We shall now transfer a single electron from an occupied orbital ψ_i situated completely on D to a virtual orbital ψ_a situated completely on AC, thus the KS-Slater determinant representing our excited state can be represented by

$$\Psi_{i \rightarrow a} = |\psi_1 \psi_2 \dots \psi_a \psi_j \dots \psi_n|. \quad (11)$$

For simplicity let ψ_i and ψ_a be of the same spin. In this case the KS-determinant $\Psi_{i \rightarrow a}$ represents a 50–50 mixture of a singlet and a triplet. We shall not be concerned about singlet–triplet splittings since the exchange integral responsible for such a splitting is vanishing for large R . In fact the charge transfer state $i \rightarrow a$ is better described as two separated molecules D^+ and AC^- , each in a doublet state.

2.2. Formulation of a simple model for charge transfer within TD-DFT

The TD-DFT scheme [1,2] is based on response theory in which changes in the ground state is described by a coupling of all occupied orbitals with all virtual orbitals $\{\psi_a(1); a = 1, \text{vir}\}$ thus constructing a new KS-determinant [10]

$$\Psi'[U] = |\psi'_1 \psi'_2 \dots \psi'_i \psi'_j \dots \psi'_n|, \quad (12)$$

where

$$\psi'_i(1) = \psi_i(1) + \sum_a U_{ai} \psi_a(1), \quad (13)$$

one can after normalization of $\Psi'[U]$ evaluate a KS-density matrix $\rho'[U]$ from which it is possible to evaluate the corresponding energy $E'^{KS}[U]$. In TD-DFT this energy is evaluated just to second order in U as [10]

$$E'^{KS}[U] = E^{KS}[0] + \frac{1}{2} (U^* \quad U) \begin{pmatrix} \mathbf{A}^{KS} & \mathbf{B}^{KS} \\ \mathbf{B}^{KS} & \mathbf{A}^{KS} \end{pmatrix} \begin{pmatrix} U \\ U^* \end{pmatrix} + O^{(3)}[U]. \quad (14)$$

In deriving Eq. (14) use has been made of Eq. (6) and the expansion in terms of functional derivatives [10]

$$\begin{aligned} E_{XC}[\rho^{(0)} + \Delta\rho] &= E_{XC}[\rho^{(0)}] + \int \left(\frac{\delta E_{XC}[\rho]}{\delta \rho} \right)_{(0)} \Delta\rho d\tau \\ &+ \frac{1}{2} \int \left(\frac{\delta^2 E_{XC}[\rho]}{\delta^2 \rho} \right)_{(0)} \Delta\rho^2 d\tau = E_{XC}[\rho^{(0)}] \\ &+ \int V_{XC}[\rho^{(0)}] \Delta\rho d\tau + \frac{1}{2} f_{XC}[\rho^{(0)}] \Delta\rho^2 d\tau + O^{(3)}[U] \end{aligned} \quad (15)$$

where $f_{XC}[\rho^{(0)}]$ is referred to as the exchange correlation kernel and $\rho^{(0)}$ in our case is the ground state density corresponding to the KS-determinant of Eq. (1).

Further in Eq. (14)

$$A_{ai,bj}^{KS} = \delta_{ab} \delta_{ij} (\varepsilon_a - \varepsilon_i) + K_{ai,bj}^{KS}; \quad B_{ai,bj}^{KS} = K_{ai,bj}^{KS}, \quad (16)$$

with

$$\begin{aligned} K_{rs,tq}^{KS} &= K_{rs,tq}^H + K_{rs,tq}^{KSXC} \\ &= \int \psi_r^*(1) \psi_s(1) \frac{1}{r_{12}} \psi_t(2) \psi_q^*(2) d\tau_1 d\tau_2 \\ &+ \int \psi_r^*(1) \psi_s(1) f_{XC}(\rho^{(0)}) \psi_t(1) \psi_q^*(1) d\tau_1 d\tau_2 \end{aligned} \quad (17)$$

The combined matrix in Eq. (14) with the elements $A_{ai,bj}^{KS}$ and $B_{ai,bj}^{KS}$ is often referred to as the electronic ground state Hessian [10]. It should hopefully not cause any confusion that the A and B matrices in some TD-DFT formulations [1,2] correspond to the negative of the two electronic Hessian matrices defined in Eq. (16). In the simplest form of TD-DFT, which we shall adopt here, one introduces the Tamm–Dancoff approximation [16] by setting B to zero in Eq. (14). This approximation has proven to be excellent and to have little influence on charge transfer excitation energies calculated by TD-DFT. By requesting that $E'^{KS}[U]$ with $B = 0$ be stationary with respect to any real variation of U one obtain within the constraint $U^+ U = 1$. We obtain in this way the well known TD-DFT eigenfunction equation

$$A^{KS} U^{(I)} = \lambda_I U^{(I)}, \quad (18)$$

based on the TD-approximation. Here λ_I is the excitation energy for transition I .

In the case of our simple charge transfer model where the electron moves from $\psi_i(1)$ to $\psi_a(1)$ we get that $U_{ib} = \delta_{ij} \delta_{ab}$ and $\lambda_{ai} = A_{ai,ai}^{KS} = \varepsilon_a - \varepsilon_i + K_{ai,ai}$.

2.3. Qualitative and quantitative problem with TD-DFT for charge transfer

It has been shown by several groups [5–9] that charge transfer excitation energies calculated by TD-DFT can be too small by several eV's. Also several elegant investigations have shown that the analytic form of λ_{ai} is qualitatively incorrect. This can be demonstrated by bringing D and AC to infinite separation ($R \rightarrow \infty$) and

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