

COMMUNICATIONS

Relationship between long-range charge-transfer excitation energy error and integer discontinuity in Kohn–Sham theory

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Charge-transfer (CT) electronic excitation energies are known to be very poorly predicted by time-dependent density functional theory (TDDFT) using local exchange-correlation functionals. Insight into this observation is provided by a simple analysis of intermolecular CT excitations at infinite separation. It is argued that the first TDDFT CT excitation energy approximately underestimates the experimental excitation by the average of the integer discontinuities of the donor and acceptor molecules; errors are of the order of several electron volts. © 2003 American Institute of Physics. [DOI: 10.1063/1.1633756]

Time-dependent density functional theory (TDDFT) in the adiabatic approximation^{1,2} is now widely used for calculating electronic excitation energies. In general, valence excitations that do not involve substantial charge-transfer (CT) are described reasonably well using conventional exchange-correlation functionals. Rydberg excitations can also be accurately reproduced, providing an asymptotic correction (AC)^{3,4} is applied to the exchange-correlation potential. By contrast, it has been demonstrated^{5–8} that much larger errors are observed for excitations involving substantial CT—calculated values underestimate experiment by up to several electron volts. Errors are particularly large for local functionals such as the local density approximation (LDA) or generalized gradient approximation (GGA). Hybrid functionals, which include a fraction of orbital exchange, offer some improvement. The aim of this Communication is to provide some insight into the error from local functionals.

Consider a donor molecule D and an acceptor molecule A. When infinitely separated, the vertical intermolecular CT excitation energy from the highest occupied molecular orbital (HOMO) of D to the lowest unoccupied molecular orbital (LUMO) of A is given exactly by

$$\omega^{\text{Exact}} = IP^{\text{D}} - EA^{\text{A}}, \quad (1)$$

where IP^{D} and EA^{A} are the exact vertical ionization potential and electron affinity of isolated D and A molecules, respectively. By considering the form of the coupled-perturbed Kohn–Sham equations in this long-range limit, Dreuw *et al.*⁸ have shown that for a local functional such as LDA or GGA, the corresponding TDDFT excitation energy reduces to

$$\omega^{\text{TDDFT}} = \epsilon_{\text{LUMO}}^{\text{A}} - \epsilon_{\text{HOMO}}^{\text{D}}, \quad (2)$$

where $\epsilon_{\text{LUMO}}^{\text{A}}$ and $\epsilon_{\text{HOMO}}^{\text{D}}$ are the Kohn–Sham eigenvalues corresponding to the LUMO and HOMO orbitals on A and D, respectively, which are identical to those obtained from calculations on the two isolated systems. We have confirmed this relationship for the systems considered in this study. It

follows from Eqs. (1) and (2) that the TDDFT excitation energy error for infinitely separated systems is⁹

$$\omega^{\text{TDDFT}} - \omega^{\text{Exact}} = \epsilon_{\text{LUMO}}^{\text{A}} - \epsilon_{\text{HOMO}}^{\text{D}} - (IP^{\text{D}} - EA^{\text{A}}). \quad (3)$$

We first consider the system A = C₂H₄; D = C₂F₄, which was investigated by Dreuw *et al.*⁸ All Kohn–Sham eigenvalues quoted in the present study are determined at optimized geometries using the BLYP¹⁰ GGA exchange-correlation functional with the aug-cc-pVTZ basis set; analogous results are obtained using the LDA and other GGAs. Experimental¹¹ IP and EA values are used. For the isolated donor and acceptor systems we have

$$IP^{\text{D}} = 10.7 \text{ eV}, \quad EA^{\text{A}} = -1.8 \text{ eV}, \\ \epsilon_{\text{LUMO}}^{\text{A}} = -1.0 \text{ eV}, \quad \epsilon_{\text{HOMO}}^{\text{D}} = -6.3 \text{ eV}. \quad (4)$$

Substituting these values into Eq. (3) gives a TDDFT CT excitation energy error of -7.2 eV. This error is almost 60% of the exact excitation energy.

We now demonstrate that this underestimation can be understood from a consideration of how local functionals treat the integer discontinuity. The exact exchange-correlation potential is discontinuous at integer numbers of electrons.¹² For any N -electron system, the exact potential on the electron deficient side of the integer, $v_{\text{XC}}^{-}(\mathbf{r})$, and on the electron abundant side, $v_{\text{XC}}^{+}(\mathbf{r})$, differ by a system dependent constant amount Δ_{XC} at all points in space

$$v_{\text{XC}}^{+}(\mathbf{r}) - v_{\text{XC}}^{-}(\mathbf{r}) = \Delta_{\text{XC}}. \quad (5)$$

The exact HOMO and LUMO eigenvalues associated with $v_{\text{XC}}^{-}(\mathbf{r})$ and $v_{\text{XC}}^{+}(\mathbf{r})$ are, respectively,¹²

$$\epsilon_{\text{HOMO}}^{-} = -IP \quad \epsilon_{\text{LUMO}}^{+} = -EA, \quad (6)$$

where IP and EA are the exact ionization potential and electron affinity, respectively, of the N -electron system. Local functionals such as LDA and GGA do not exhibit an integer discontinuity; they are continuum approximations. In regions

where the HOMO and LUMO orbitals are significant, they approximately average over the discontinuity¹³

$$v_{XC}(\mathbf{r}) \approx \frac{v_{XC}^+(\mathbf{r}) + v_{XC}^-(\mathbf{r})}{2}. \quad (7)$$

It follows from Eqs. (5)–(7) that when a local functional is used, the HOMO eigenvalue of the isolated donor molecule is approximately

$$\epsilon_{\text{HOMO}}^D \approx -IP^D + \frac{\Delta_{XC}^D}{2} \quad (8)$$

(see Ref. 14 for numerical examples) whilst the LUMO eigenvalue of the isolated acceptor is approximately

$$\epsilon_{\text{LUMO}}^A \approx -EA^A - \frac{\Delta_{XC}^A}{2}, \quad (9)$$

where Δ_{XC}^D and Δ_{XC}^A are the integer discontinuities in D and A, respectively. From Eqs. (3), (8), and (9), it follows that

$$\omega^{\text{TDDFT}} - \omega^{\text{Exact}} \approx -\frac{1}{2}(\Delta_{XC}^D + \Delta_{XC}^A), \quad (10)$$

i.e., for a local functional, the TDDFT HOMO–LUMO intermolecular CT excitation energy for infinitely separated systems approximately underestimates experiment by the average of the integer discontinuities of the donor and acceptor molecules.

To illustrate this, we approximate the integer discontinuities of the donor and acceptor in the $A=C_2H_4$; $D=C_2F_4$ system by twice the asymptotic exchange–correlation potential, as defined from the generalized Koopmans theorem in the AC scheme of Ref. 3,

$$\Delta_{XC}^A = 2(\epsilon_{\text{HOMO}}^A + IP^A), \quad \Delta_{XC}^D = 2(\epsilon_{\text{HOMO}}^D + IP^D). \quad (11)$$

Using the values in Eq. (4) and $\epsilon_{\text{HOMO}}^A = -6.6$ eV, $IP^A = 10.7$ eV, gives

$$\Delta_{XC}^A = 8.2 \text{ eV}, \quad \Delta_{XC}^D = 8.7 \text{ eV}. \quad (12)$$

Substituting these values into Eq. (10) gives an error of -8.5 eV, which is close to the true error of -7.2 eV calculated using Eq. (3). As a second illustration, we replace the C_2F_4 donor with a Ne atom. The error from Eq. (3) is now even larger at -11.0 eV, which can be traced to the much larger integer discontinuity in the Ne atom,

$$\begin{aligned} \Delta_{XC}^D &= 2(\epsilon_{\text{HOMO}}^D + IP^D) = 2(-13.4 \text{ eV} + 21.6 \text{ eV}) \\ &= 16.4 \text{ eV}. \end{aligned} \quad (13)$$

The average of the discontinuities in Ne and C_2H_4 gives an error of -12.3 eV, which is again close to the true error. Conversely, systems with smaller integer discontinuities (e.g., alkali metal atoms) will have smaller CT excitation energy errors.

An alternative estimate of the integer discontinuity is twice the system-dependent shift that must be introduced when semi-empirical functionals are determined using fits to high-quality potentials. In the development of the HCTH GGA functional,¹⁵ system-dependent shifts of 3.5 and 7.5 eV were obtained for C_2H_4 and Ne, respectively, giving discontinuities of 7.0 and 15.0 eV, respectively. The average of

these values gives an error of -11.0 eV for the $A=C_2H_4$; $D=Ne$ system. Discontinuities can also be calculated directly from *ab initio* electron densities. In Ref. 14 the C_2H_4 discontinuity was estimated to be 6.5 eV.

Local functionals such as LDA and GGA are, therefore, fundamentally unable to describe these long-range intermolecular CT excitations. The error is not a consequence of the shape of the exchange–correlation potential: The hypothetical local functional whose potential is exactly the average of v_{XC}^- and v_{XC}^+ —which gives the exact density—still gives CT excitations that are in error by the average of the discontinuities. Rather, it reflects the local nature of the approximation, which uses a common average potential for the HOMO on D and LUMO on A.

A simple way to improve the TDDFT HOMO–LUMO intermolecular CT excitation energy, whilst leaving intramolecular excitations unchanged, is to lower all the eigenvalues of the donor species by $\Delta_{XC}^D/2$ and raise all the eigenvalues of the acceptor by $\Delta_{XC}^A/2$. This is equivalent to treating the donor on the electron deficient side of the integer and the acceptor on the electron abundant side, in line with Eq. (6). (We note that Casida *et al.*¹⁶ have also proposed a charge-transfer correction in a different context, based on a Δ SCF approach.) This correction is, of course, of limited use, since it is only appropriate for the case where the donor and acceptor are infinitely separated. At finite distances, a reasonable first-approximation would be to introduce an additional term to account for the electrostatic interaction between the donor and acceptor following the excitation; atomic charges could be used, as in the AC scheme of Ref. 3. Dreuw *et al.*⁸ introduced this electrostatic term by combining DFT with configuration interaction singles (CIS). An alternative way to improve the CT excitations would be to introduce a fraction of orbital exchange into the functional, which is intrinsically discontinuous due to its orbital nature. Equation (2) would then no longer be appropriate. See Refs. 5–7 for examples.

The importance of the integer discontinuity in Rydberg excitation energy calculations is well-known. This study highlights its importance in the context of CT excitations.

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