

Qualitatively Correct Charge-Transfer Excitation Energies in HeH^+ by Time-Dependent Density-Functional Theory Due to Exact Exchange Kohn–Sham Eigenvalue Differences

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Abstract: Time-dependent density-functional theory in the response regime is shown to yield qualitatively correct charge-transfer excitation energies in the system HeH^+ if the exact Kohn–Sham exchange potential is employed to determine the Kohn–Sham orbitals and eigenvalues entering the time-dependent density-functional calculation. The employed exact-exchange kernel is frequency-independent and, like conventional kernels in the local density approximation or in generalized gradient approximations, does not contribute to the charge-transfer excitation energy. This shows that it can be that not the exchange-correlation kernel, as generally believed, but the exchange-correlation potential plays the crucial role in the description of charge-transfer excitations.

One of the presently most widely used approaches to calculate electronic excitation energies of molecules or clusters is time-dependent density-functional theory (TDDFT) in the response regime.^{1–8} Besides excitation energies, oscillator strengths and thus UV/vis spectra are also accessible. Furthermore, circular dichroism spectra can be calculated.

While current density-functional response methods,^{9–17} that is, methods based on TDDFT in the response regime, are often very successful, they also exhibit a number of serious shortcomings due to the necessary approximations in the required exchange-correlation functionals. Excitations into states with Rydberg character are poorly described.¹⁸ This problem can be solved by determining the Kohn–Sham (KS) orbitals and eigenvalues that enter a density-functional response calculation with asymptotically corrected exchange-correlation potentials^{19–26} or more fundamentally²⁷ with an exact-exchange (EXX) KS method,^{28–31} that is, a KS method that employs the exact local KS exchange potential. For other failures of current density-functional response methods, no convincing, generally applicable remedies are available at present. Excitation energies of molecules with long conju-

gated systems of π electrons^{32–36} are systematically underestimated, and the description of two-electron excitations is problematic.³⁷

The perhaps most important deficiency of density-functional response methods employing presently available approximations for the exchange-correlation functionals is their incapability to correctly describe charge-transfer (CT) excitations.^{16,40–44} Excitations with significant CT can be underestimated by several electron volts, and the behavior of CT excitations between two separated units with the distance of the units is described qualitatively wrong. CT excitation energies between neutral fragments, in particular, excitations from the highest occupied molecular orbital (HOMO) of one fragment to the lowest unoccupied molecular orbital (LUMO) of the other, should approach $(I - A) - 1/R$, with I denoting the ionization energy of the donor, A denoting the electron affinity of the acceptor, and R standing for the distance of the units. Present density-functional response methods do not yield this $-1/R$ behavior. Instead, the CT excitation energies, at relatively small distances R approach a constant given by the difference between the KS eigenvalues of the LUMO of the acceptor and those of the HOMO of the donor. HOMO–LUMO CT excitations from a neutral to a cationic unit, on the other hand, approach

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$(I - A)$ at small distances R , while current density-functional response methods exhibit an erroneous $1/R$ behavior. In the limit of an infinite distance R , the current density-functional response methods yield CT excitation energies that equal the eigenvalue difference between the LUMO and the HOMO. This eigenvalue difference, however, in general, does not equal the CT excitation energy given by $(I - A)$ in this limit. While the negative of the HOMO eigenvalue equals the ionization energy I ^{45,46} in the exact formalism and represents a well-defined approximation for I in practice, the negative of the LUMO eigenvalue differs from the electron affinity A by the derivative discontinuity of the exchange-correlation energy at integer electron numbers^{47,48,51} and therefore cannot serve as an approximation for A .

The failure of current density-functional response methods to describe CT excitations usually is attributed to shortcomings in the employed approximations for the exchange-correlation kernel, the frequency-dependent functional derivative of the exchange-correlation potential with respect to the electron density. In particular, the neglect of the frequency dependency of the kernel, the adiabatic approximation, is made responsible for the failure to describe CT excitations. Here, we show that in certain cases problems in describing CT excitations are caused by shortcomings of the approximations of the exchange-correlation potential, not the kernel.

For the simple test system HeH^+ ,^{49,50} we here show that a density-functional response method that employs the EXX KS potential and kernel and neglects correlation yields a qualitative correct behavior with the HeH^+ distance R for the energy of the CT excitation from the He 1s orbital to the H^+ 1s orbital. To our knowledge, this is the first time that a density-functional response method has correctly described the distance behavior of a CT excitation without the introduction of special correction terms to enforce the correct behavior.^{41,51} Even more important is the finding that the EXX kernel employed in the density-functional response calculation turns out to be not responsible for the correct distance behavior of the CT excitation. Indeed, in the system HeH^+ , the exchange kernel does not contribute at all to the excitation energy at large distances R . The CT excitation energy like in conventional TDDFT methods using functionals within the local density-approximation (LDA) or generalized gradient approximations (GGA) equals the difference between the KS eigenvalue of the LUMO of the acceptor, the H^+ 1s orbital, and the HOMO of the donor, the He 1s orbital. However, in contrast to LDA or GGA eigenvalue differences, the EXX eigenvalue difference does not exhibit an unphysical $1/R$ behavior but correctly approaches a constant already at small distances, R . This means that, for HeH^+ , the adiabatic approximation or, generally, approximations to the exchange-correlation kernel, in contrast to what is generally believed, are not responsible for the failure of conventional TDDFT methods, that is, density-functional response methods employing the LDA or GGAs, to describe CT excitations.

Most density-functional response methods for excitation energies are based on the nonlinear eigenvalue equation

$$[\varepsilon^2 - 4\varepsilon^{1/2}\mathbf{K}(\omega)\varepsilon^{1/2}]\mathbf{z}(\omega) = \omega^2\mathbf{z}(\omega) \quad (1)$$

introduced by Casida.^{5,13,52} The dimension of eq 1 is given by the product of the number of occupied KS orbitals times the number of unoccupied KS orbitals. In eq 1, the eigenvalue ω^2 equals the square of the excitation frequency or energy ω . The eigenvector $\mathbf{z}(\omega)$ determines the transition density $\rho(\omega, \mathbf{r})$ of the excitation via

$$\rho(\omega, \mathbf{r}) = \sum_i^{\text{occ}} \sum_a^{\text{unocc}} z_{ia}(\omega) \varepsilon_{ia}^{(-1/2)} \phi_i(\mathbf{r}) \phi_a(\mathbf{r}) \quad (2)$$

in terms of products of occupied KS orbitals times unoccupied KS orbitals, ϕ_i and ϕ_a , respectively, with $\varepsilon_{ia} = \varepsilon_a - \varepsilon_i$ denoting the difference of the corresponding KS eigenvalues ε_a and ε_i . The elements $K_{ia,jb}(\omega)$ of the matrix $\mathbf{K}(\omega)$ are given by

$$K_{ia,jb}(\omega) = \int d\mathbf{r} d\mathbf{r}' \phi_i(\mathbf{r}) \phi_a(\mathbf{r}) f_{\text{uxc}}(\omega, \mathbf{r}, \mathbf{r}') \phi_j(\mathbf{r}') \phi_b(\mathbf{r}') \quad (3)$$

and the elements $\varepsilon_{ia,jb}$ of the diagonal matrix ε are given by $\varepsilon_{ia,jb} = \delta_{ia,jb}(\varepsilon_a - \varepsilon_i)$. The indices ia and jb are superindices labeling the products of occupied times unoccupied KS orbitals. The sum of the Coulomb kernel $1/|\mathbf{r} - \mathbf{r}'|$ and the exchange-correlation kernel is denoted by f_{uxc} . In practice, almost always the frequency dependence of the matrix \mathbf{K} is neglected. That is, the adiabatic approximation is made, and the nonlinear eigenvalue, eq 1, turns into a linear one.

We now consider an intermolecular CT excitation that can be described as an excitation from an occupied orbital, ϕ_i , of one molecule into an unoccupied orbital, ϕ_a , of another molecule. At large intermolecular distances R , the spatial overlap of the two orbitals vanishes, and the product $\phi_i\phi_a$ approaches zero everywhere. As a result, one row and one column of \mathbf{K} approach zero, and one eigenvector of eq 1 is a unit vector with an entry of one at the position ia . The corresponding eigenvalue is given by ε_{ia}^2 . This means that the CT excitation energy obtained with a conventional density-functional response method equals the corresponding KS eigenvalue difference $\varepsilon_a - \varepsilon_i$. The only way to obtain a CT excitation energy that differs from the corresponding KS eigenvalue difference seems to be seen when the kernel f_{uxc} approaches infinity in such a way that the matrix elements $K_{ia,jb}(\omega)$, eq 3, containing the vanishing product $\phi_i\phi_a$ approach finite values. This represents a complicated demand on the kernel that is believed to be intimately related to the frequency dependence of the kernel. Adiabatic LDA or GGA kernels are finite and clearly cannot exhibit the required behavior. Therefore, all density-functional response methods employing LDA or GGA kernels yield CT excitation energies that equal the corresponding KS eigenvalue differences.

For the special case of a nonspin-polarized two-electron system, the exact local KS exchange potential is known. It equals simply the negative of half of the Coulomb potential. For a nonspin-polarized two-electron system, the exchange kernel is also known exactly.⁵⁴ It equals the negative of half of the Coulomb kernel; that is, it is given by $-1/(2|\mathbf{r} - \mathbf{r}'|)$. Thus, in this special case, the exchange kernel is frequency-independent, does not approach infinity except at $\mathbf{r} = \mathbf{r}'$,

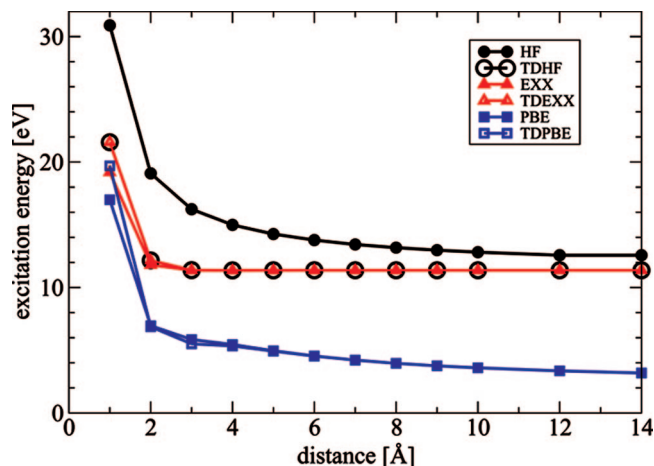


Figure 1. Charge-transfer excitation energies in HeH^+ ($\text{He } 1s \rightarrow \text{H}^+ 1s$) for varying HeH^+ distances as obtained by TDPBE, TDHF, and TDEXX and corresponding eigenvalue differences (PBE, HF, and EXX). The EXX and TDEXX curves as well as the PBE and TDPBE curves in most regions cannot be distinguished from each other.

and thus does lead to vanishing matrix elements $K_{ia,jb}(\omega)$ in eqs 1 and 3 for indices ia or jb referring to a CT excitation. Therefore, time-dependent exact-exchange (TDEXX) calculations have to yield CT excitation energies that equal the corresponding KS eigenvalue difference for nonspin-polarized two-electron systems.

For a nonspin-polarized two-electron system, it is straightforward to turn any Hartree–Fock (HF) and any time-dependent Hartree–Fock (TDHF) method into an EXX KS and a TDEXX density-functional response method, respectively. It is merely necessary to multiply the terms originating from exchange in the HF and TDHF method by zero, that is, to neglect them, and to multiply the terms originating from the Coulomb potential and Coulomb kernel by one-half. We carried out such a modification in the program package TURBOMOLE⁵⁵ and then performed HF/TDHF, EXX/TDEXX, LDA/TDLDA (LDA and time-dependent LDA), and PBE/TDPBE (GGA and time-dependent GGA with the exchange-correlation potential and kernel attributable to Perdew, Burke, and Ernzerhof)⁵³ calculations for HeH^+ and the CT excitation from the He 1s orbital to the H^+ 1s orbital.

Five different basis sets, the aug-cc-pVXZ basis sets of Dunning^{56,57} with $X = \text{D, T, Q, 5, and 6}$, were employed in the calculations. In Figure 1, results for the aug-cc-pV6Z basis set are shown, which are fully converged with respect to the basis set size. The TDHF energy for the considered CT excitation differs strongly from the corresponding HF eigenvalue difference. As expected, the TDHF CT energy exhibits a qualitative correct behavior with the HeH^+ distance R . TDHF considers the response of the first-order density matrix not the response of the density, like TDDFT. A representation of the response of the first-order density matrix in terms of products $\varphi_i(\mathbf{r})\varphi_a(\mathbf{r}')$ of occupied times unoccupied orbitals does not vanish in CT cases due to the occurrence of the two different variables, \mathbf{r} and \mathbf{r}' , in the products. Therefore, TDHF describes charge-transfer excitations qualitatively correctly.

Figure 1 shows that the TDPBE as well as the TDEXX energies for the considered CT excitation equal the corresponding KS eigenvalue differences, as could be expected from the discussion above. However, while the TDPBE CT excitation energies exhibit a qualitatively wrong $1/R$ behavior with the HeH^+ distance R , TDEXX CT excitation energies exhibit the qualitative correct behavior. Indeed, the TDEXX results are identical to the TDHF ones. LDA/TDLDA results, which are not displayed here, show the same behavior as the PBE and TDPBE results.

The differences between LDA and PBE eigenvalue differences, on the one hand, and the TDEXX eigenvalues, on the other, can be explained as follows. For a HeH^+ distance R that is large compared to the spatial extent of the 1s orbitals of He and H^+ , the effective KS potential around the He atom equals that of an isolated He atom plus the constant $-1/R$, the constant being the term originating to leading order in the HeH^+ distance R from the electrostatic potential of the H^+ , that is, of a proton. The He 1s orbital eigenvalue therefore, to leading order in R , equals the eigenvalue of the 1s orbital of an isolated He atom minus $1/R$. This holds true for the LDA and the PBE as well as the EXX eigenvalues of the He 1s orbital. The eigenvalue of the H^+ 1s orbital in the LDA and the PBE cases, to leading order in R , equals that of an isolated proton, that is, that of atomic hydrogen, for large R values. The reason is that the effective KS potential of He is short-range because the LDA and PBE exchange-correlation potentials erroneously are short-range and because the Hartree potential and the electrostatic potential of the He nucleus cancel each other asymptotically. This means that the eigenvalue of the H^+ 1s orbital in the LDA and the PBE cases is constant for large distances R . The difference between the H^+ 1s eigenvalue and the He 1s eigenvalue therefore exhibits the erroneous $1/R$ behavior for large distances R .

In the EXX case, the effective KS potential of He, on the other hand, is long-range and correctly approaches $-1/r$ for large distances r , from the He nucleus because the exact-exchange KS potential exhibits such a $-1/r$ behavior. As a result, the He atom contributes, to leading order in R , a constant $-1/R$ to the effective KS potential around the H^+ . Therefore, the H^+ 1s eigenvalue like the He 1s eigenvalue equals the eigenvalue of an isolated H^+ minus $1/R$. In the difference between the H^+ 1s and the He 1s eigenvalue, the $1/R$ terms cancel, and the eigenvalue difference at large distances R is constant, as it should be. The wrong behavior of the LDA and PBE eigenvalue difference thus has its origin in the qualitatively wrong asymptotic behavior of LDA and PBE exchange potentials that are caused by unphysical Coulomb self-interactions of each electron that are not canceled completely by the approximate LDA and PBE exchange functionals. The fact that the LDA and PBE exchange-correlation potential and not the kernel causes the qualitatively wrong CT excitation energies is confirmed by carrying out density-functional response calculations employing the LDA or GGA kernel but EXX orbitals and eigenvalues. Such calculations yield de facto identical results as the EXX/TDEXX calculations.

Of course, other GGA functionals than the PBE lead to the same qualitatively wrong results for the considered CT excitation in HeH^+ . Moreover, CT excitation energies from neutral to positively charged units in other systems than HeH^+ , including systems with more than two electrons, are also described in the same way wrongly with LDA and GGA functionals in density-functional response methods.

The simple two-electron example of HeH^+ certainly is a special case. Not only are the exchange potential and kernel exactly known in terms of the electron density in this case, but, moreover, in this special case, the negative of the eigenvalue of the LUMO, the 1s orbital of H^+ , exactly equals the electron affinity for large He H^+ distances. This is not the case in general, and therefore EXX eigenvalue differences in general are not sufficient to describe CT excitations qualitatively correctly. Nevertheless, this special case does point to a new aspect of the CT problem of TDDFT, namely, that the KS eigenvalue differences at least in special cases may be essential for the behavior of excitation energies with the distance R . Indeed, in the special case of HeH^+ , the KS eigenvalue differences exclusively determine this behavior, while the exchange-correlation kernel does not contribute to it at all. This means for the CT problem that not only the exchange-correlation kernel is of importance but also the exchange-correlation potential in the KS calculation determining the KS eigenvalues, and their differences may be crucial.

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