

Discontinuities of the exchange-correlation kernel and charge-transfer excitations in time-dependent density-functional theory

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We identify the key property that the exchange-correlation (XC) kernel of time-dependent density-functional theory must have in order to describe long-range charge-transfer excitations. We show that the discontinuity of the XC potential as a function of particle number induces a space- and frequency-dependent discontinuity of the XC kernel that diverges as $r \rightarrow \infty$. In a combined donor-acceptor system, the same discontinuity compensates for the vanishing overlap between the acceptor and donor orbitals, thereby yielding a finite correction to the Kohn-Sham eigenvalue differences. This mechanism is illustrated to first order in the Coulomb interaction.

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I. INTRODUCTION

The theoretical prediction of the excitation spectra of interacting electronic systems is a major challenge in quantum chemistry and condensed-matter physics. A method that has been gaining popularity is time-dependent density-functional theory (TDDFT), offering a rigorous and computationally efficient approach for treating excited states of large molecules and nanoscale systems. In TDDFT the interacting electronic density is calculated from a system of noninteracting electrons moving in an effective local Kohn-Sham (KS) potential [1]. The KS potential is the sum of the external, the Hartree, and the so-called exchange-correlation (XC) potential $v_{xc}(\mathbf{r}t)$, which, due to the Runge-Gross theorem [2], is a functional of the density. In the linear response regime, the excitation energies can be extracted from the poles of the linear density response function. As a consequence, given the variational derivative $f_{xc}(\mathbf{r}t, \mathbf{r}'t') = \delta v_{xc}(\mathbf{r}t) / \delta n(\mathbf{r}'t')$, also known as the XC kernel [3], it is possible to formulate a random-phase-approximation-like equation for the exact excitation spectrum [4,5]. In practical calculations, this equation is solved using some approximate XC potential and kernel where the most popular ones are based on the adiabatic local-density approximation (ALDA), leading to kernels local in both space and time. Despite this simple structure, optical excitations of small molecules are successfully predicted. However, several shortcomings have also been reported: Excitons in solids are not captured [6,7], double excitations are missing [8], and charge-transfer (CT) excitations are qualitatively incorrect [9–12]. In this work we will be concerned with the last problem and to see why ALDA fails in this case, we consider a charge transfer between two neutral Coulombic fragments. The asymptotic limit of the excitation energy is then given by

$$\omega_{CT} = I_d - A_a - 1/R, \quad (1)$$

where I_d is the ionization energy of the donor, A_a is the affinity of the acceptor, and R is their separation. In TDDFT the starting point is the KS system, which yields the exact I_d but only an approximate A_a . Thus the XC kernel must both account for the $1/R$ correction and shift the KS affinity. The linear response equations, however, involve only matrix elements of f_{xc} between so-called excitation functions $\Phi_{ia}(\mathbf{r}) = \varphi_i(\mathbf{r})\varphi_a(\mathbf{r})$, i.e., products of occupied and

unoccupied KS orbitals. As the distance between the fragments increases these products vanish exponentially and thus there is no correction to the KS eigenvalue differences unless the kernel diverges [13,14]. Kernels from the ALDA, or adiabatic generalized gradient approximations for that matter, do not contain such divergency and it is as yet not understood how this extreme behavior should be incorporated in approximate functionals.

Whenever two subsystems are spatially well separated it is possible to treat one of the subsystems in terms of an ensemble containing states with different number of particles. Density-functional theory (DFT) has been generalized to noninteger charges and as an important consequence it was found that the XC potential jumps discontinuously by a constant at integer particle numbers in order to align the highest occupied KS eigenvalue with the chemical potential [15]. In this way, the true affinity A is equal to the sum of the KS affinity A_s and the discontinuity. Not surprisingly, it has therefore been argued that the discontinuity must play an important role in describing CT excitations within TDDFT [16].

So far, only the XC potential has been the target of investigating discontinuities in DFT and TDDFT [17–19]. In this work we instead examine possible discontinuities of the XC kernel. We demonstrate the existence of a discontinuity and we study its properties. Furthermore, we give an explicit example through a numerical study of the exact-exchange (EXX) functional. Finally, as a first application, we demonstrate the crucial role of the discontinuity for capturing CT excitations in linear response TDDFT.

II. DERIVATIVE DISCONTINUITY IN DFT

We start by considering a static system of electrons described by a statistical operator $\hat{\rho} = \sum_k \alpha_k |\Psi_k\rangle \langle \Psi_k|$, where $|\Psi_k\rangle$ denotes the ground state of k particles corresponding to the Hamiltonian $\hat{H} = \hat{T} + \hat{V} + \int d\mathbf{r} w(\mathbf{r})\hat{n}(\mathbf{r})$, in which \hat{T} is the kinetic energy, \hat{V} is the interparticle interaction, and w is the external potential. The ground-state energy E_0 of the system with average number of particles N is obtained by minimizing the functional $E_w[n] = F[n] + \int d\mathbf{r} w(\mathbf{r})n(\mathbf{r})$, where $F[n] = \min_{\hat{\rho} \rightarrow n} \text{Tr}[\hat{\rho}(\hat{T} + \hat{V})]$, under the constraint that $N = \int d\mathbf{r} n(\mathbf{r})$. At the minimum $n = n[w, N]$ coincides with the ground-state density. The XC energy

is defined as $E_{xc}[n] = F[n] - T_s[n] - U[n]$, where $T_s[n] = \min_{\hat{\rho} \rightarrow n} \text{Tr}[\hat{\rho}\hat{T}]$ is the noninteracting kinetic energy and $U[n]$ is the Hartree energy. Assuming that the density can be reproduced by an ensemble of noninteracting electrons, the XC part of the KS potential is given by $v_{xc}(\mathbf{r}) = \delta E_{xc}/\delta n(\mathbf{r})$. In general E_0 (and in particular $E_{xc}[n[w, N]]$) has derivative discontinuities at integer particle numbers N_0 [20,21]. The partial derivative of E_{xc} with respect to N ,

$$\frac{\partial E_{xc}}{\partial N} = \int d\mathbf{r} v_{xc}(\mathbf{r}) \frac{\partial n(\mathbf{r})}{\partial N}, \quad (2)$$

has two sources of discontinuous behavior: (i) the quantity

$$f(\mathbf{r}) \equiv \frac{\partial n(\mathbf{r})}{\partial N}, \quad (3)$$

known as the Fukui function [22], may have different right and left limits f^+ and f^- (the superscript \pm refers to the value of the quantity at $N = N_0 + 0^\pm$) and (ii) the XC potential may be discontinuous $v_{xc}^+(\mathbf{r}) = v_{xc}^-(\mathbf{r}) + \Delta_{xc}$, where Δ_{xc} is a constant. Below we will show that also the second variation of E_{xc} with respect to the density, the static XC kernel $f_{xc}(\mathbf{r}, \mathbf{r}') = \delta v_{xc}(\mathbf{r})/\delta n(\mathbf{r}')$, has discontinuities that are related to derivative discontinuities in the density itself. As pointed out in previous work [5,23,24], the particle number conserving density response is unaffected by adding to f_{xc} a function depending only on one of the coordinates. In line with the results of Ref. [25], we therefore argue that the discontinuities of f_{xc} must be of the form

$$f_{xc}^+(\mathbf{r}, \mathbf{r}') = f_{xc}^-(\mathbf{r}, \mathbf{r}') + g_{xc}(\mathbf{r}) + g_{xc}(\mathbf{r}'). \quad (4)$$

In the following we will show a simple procedure for determining Δ_{xc} and $g_{xc}(\mathbf{r})$ that is useful whenever E_{xc} is an implicit functional of the density via, e.g., the KS Green's function.

A. XC potential

For $N > N_0$, we write $v_{xc}(\mathbf{r}) = v_{xc}^-(\mathbf{r}) + \Delta_{xc}(\mathbf{r})$ and cast Eq. (2) into

$$\int d\mathbf{r} \Delta_{xc}(\mathbf{r}) f(\mathbf{r}) = \frac{\partial E_{xc}}{\partial N} - \int d\mathbf{r} v_{xc}^-(\mathbf{r}) f(\mathbf{r}). \quad (5)$$

In the limit $N \rightarrow N_0^+$, $\Delta_{xc}(\mathbf{r}) \rightarrow \Delta_{xc}$ and we find a formal expression for the discontinuity of v_{xc} ,

$$\Delta_{xc} = \left. \frac{\partial E_{xc}}{\partial N} \right|_+ - \int d\mathbf{r} v_{xc}^-(\mathbf{r}) f^+(\mathbf{r}). \quad (6)$$

This expression can be used as the starting point for deriving the well-known many-body perturbation theory (MBPT) formula for the correction to the gap [26], as we will now demonstrate. From the Klein functional within MBPT [27] it is possible to construct an XC energy functional in terms of the KS Green's function $G_s(\mathbf{r}, \mathbf{r}', \omega)$ [28]. In this case $\Sigma_{xc} = i\delta E_{xc}/\delta G_s$, where Σ_{xc} is the self-energy evaluated at G_s . The derivative of E_{xc} with respect to N is then given by

$$\frac{\partial E_{xc}}{\partial N} = -i \int \frac{d\omega}{2\pi} \int d\mathbf{r} d\mathbf{r}' \Sigma_{xc}(\mathbf{r}, \mathbf{r}', \omega) \frac{\partial G_s(\mathbf{r}, \mathbf{r}', \omega)}{\partial N}. \quad (7)$$

In order to evaluate the derivative of G_s with respect to N we consider an ensemble described by a spin-compensated mixture of states with electron number N_0 and $N_0 + 1$. A spin-component of the KS ensemble Green's function for

$N \in [N_0, N_0 + 1]$ is given by

$$G_s(\mathbf{r}, \mathbf{r}', \omega) = \sum_{k=1}^{\tilde{N}} \frac{\varphi_k(\mathbf{r})\varphi_k(\mathbf{r}')}{\omega - \varepsilon_k - i\eta} + \sum_{k=\tilde{N}+2}^{\infty} \frac{\varphi_k(\mathbf{r})\varphi_k(\mathbf{r}')}{\omega - \varepsilon_k + i\eta} + \frac{p}{2} \frac{\varphi_L(\mathbf{r})\varphi_L(\mathbf{r}')}{\omega - \varepsilon_L - i\eta} + \left(1 - \frac{p}{2}\right) \frac{\varphi_L(\mathbf{r})\varphi_L(\mathbf{r}')}{\omega - \varepsilon_L + i\eta}, \quad (8)$$

where $\tilde{N} = N_0/2$, $p = N - N_0$ and the subscript L signifies the lowest unoccupied molecular orbital (LUMO) of the KS system, which is considered partially occupied and partially unoccupied. Note that the KS orbitals φ_k and eigenvalues ε_k also depend on N via the KS potential V_s . The derivative of G_s with respect to N is now easily carried out,

$$\frac{\partial G_s(\mathbf{r}, \mathbf{r}', \omega)}{\partial N} = \frac{1}{2} \frac{\varphi_L(\mathbf{r})\varphi_L(\mathbf{r}')}{\omega - \varepsilon_L - i\eta} - \frac{1}{2} \frac{\varphi_L(\mathbf{r})\varphi_L(\mathbf{r}')}{\omega - \varepsilon_L + i\eta} + \int d\mathbf{r}_1 \frac{\delta G_s(\mathbf{r}, \mathbf{r}', \omega)}{\delta V_s(\mathbf{r}_1)} \frac{\partial V_s(\mathbf{r}_1)}{\partial N}. \quad (9)$$

From Eqs. (9) and (7) we find

$$\left. \frac{\partial E_{xc}}{\partial N} \right|_+ = \int d\mathbf{r} d\mathbf{r}' \varphi_L^+(\mathbf{r}) \Sigma_{xc}^+(\mathbf{r}, \mathbf{r}', \varepsilon_L^+) \varphi_L^+(\mathbf{r}') - i \int \frac{d\omega}{2\pi} \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}_1 \Sigma_{xc}^+(\mathbf{r}, \mathbf{r}', \omega) \times \left. \frac{\delta G_s(\mathbf{r}, \mathbf{r}', \omega)}{\delta V_s(\mathbf{r}_1)} \frac{\partial V_s(\mathbf{r}_1)}{\partial N} \right|_+. \quad (10)$$

The second term on the right-hand side of Eq. (6) can be written as

$$\int d\mathbf{r} v_{xc}^-(\mathbf{r}) f^+(\mathbf{r}) = \int d\mathbf{r} v_{xc}^-(\mathbf{r}) |\varphi_L^+(\mathbf{r})|^2 + \int d\mathbf{r}' d\mathbf{r}_1 v_{xc}^-(\mathbf{r}') \frac{\delta n(\mathbf{r}')}{\delta V_s(\mathbf{r}_1)} \frac{\partial V_s(\mathbf{r}_1)}{\partial N} \Big|_+. \quad (11)$$

The discontinuity Δ_{xc} is now easily determined. The second terms on the right-hand sides of Eqs. (10) and (11) will cancel by virtue of the linearized Sham-Schlüter equation [29] and we find

$$\Delta_{xc} = \int d\mathbf{r} d\mathbf{r}' \varphi_L(\mathbf{r}) \Sigma_{xc}^+(\mathbf{r}, \mathbf{r}', \varepsilon_L^+) \varphi_L(\mathbf{r}') - \int d\mathbf{r} v_{xc}^-(\mathbf{r}) |\varphi_L(\mathbf{r})|^2, \quad (12)$$

where we have omitted the superscript on the orbitals since they are continuous with respect to N . Equation (12) agrees with the one in Ref. [26].

B. XC kernel

Next we turn to the XC kernel for which we exhibit the discontinuities by taking the functional derivative of $\partial E_{xc}/\partial N$ [Eq. (2)] with respect to w . This yields

$$\frac{\delta}{\delta w(\mathbf{r}_1)} \frac{\partial E_{xc}}{\partial N} = \int d\mathbf{r} d\mathbf{r}' \chi(\mathbf{r}_1, \mathbf{r}') f_{xc}(\mathbf{r}', \mathbf{r}) f(\mathbf{r}) + \int d\mathbf{r} v_{xc}(\mathbf{r}) \frac{\delta f(\mathbf{r})}{\delta w(\mathbf{r}_1)}, \quad (13)$$

where we have used the chain rule

$$\frac{\delta v_{xc}(\mathbf{r})}{\delta w(\mathbf{r}_1)} = \int d\mathbf{r}' \frac{\delta v_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')} \frac{\delta n(\mathbf{r}')}{\delta w(\mathbf{r}_1)} \quad (14)$$

and identified the linear density response function $\chi(\mathbf{r}_1, \mathbf{r}') = \delta n(\mathbf{r}')/\delta w(\mathbf{r}_1)$. Then we write $f_{xc}(\mathbf{r}, \mathbf{r}') = f_{xc}^-(\mathbf{r}, \mathbf{r}') + g_{xc}(\mathbf{r}, \mathbf{r}')$, insert in Eq. (13), and take the limit $N \rightarrow N_0^+$. According to the discussion above, in this limit $g_{xc}(\mathbf{r}, \mathbf{r}') \rightarrow g_{xc}(\mathbf{r}) + g_{xc}(\mathbf{r}')$. Using, furthermore, that $\int d\mathbf{r} \chi(\mathbf{r}, \mathbf{r}') = 0$ and $\int d\mathbf{r} f(\mathbf{r}) = 1$, we find the following equation for the discontinuity g_{xc} of f_{xc} :

$$\begin{aligned} & \int d\mathbf{r} \chi(\mathbf{r}_1, \mathbf{r}) g_{xc}(\mathbf{r}) \\ &= \frac{\delta}{\delta w(\mathbf{r}_1)} \frac{\partial E_{xc}}{\partial N} \Big|_+ - \int d\mathbf{r} d\mathbf{r}' \chi(\mathbf{r}_1, \mathbf{r}) f_{xc}^-(\mathbf{r}, \mathbf{r}') f^+(\mathbf{r}') \\ & \quad - \int d\mathbf{r} v_{xc}^+(\mathbf{r}) \frac{\delta f(\mathbf{r})}{\delta w(\mathbf{r}_1)} \Big|_+. \end{aligned} \quad (15)$$

We note that Eq. (15) only determines g_{xc} up to a constant. This constant can, however, be easily fixed by considering $\partial^2 E_{xc}/\partial N^2$ in the limit $N \rightarrow N_0^+$,

$$\begin{aligned} 2 \int d\mathbf{r} f^+(\mathbf{r}) g_{xc}(\mathbf{r}) &= \frac{\partial^2 E_{xc}}{\partial N^2} \Big|_+ - \int d\mathbf{r}' v_{xc}^+(\mathbf{r}') \frac{\partial f(\mathbf{r}')}{\partial N} \Big|_+ \\ & \quad - \int d\mathbf{r} d\mathbf{r}' f^+(\mathbf{r}) f_{xc}^-(\mathbf{r}, \mathbf{r}') f^+(\mathbf{r}'). \end{aligned} \quad (16)$$

This equation does not allow an arbitrary constant in g_{xc} . Consequently, Eqs. (15) and (16) together uniquely determine the discontinuity of f_{xc} .

To gain insight into the \mathbf{r} dependence of $g_{xc}(\mathbf{r})$ we employ a common energy denominator approximation (CEDA) [30] to Eq. (15). To do so, we first note that the derivative with respect to w can be replaced by the derivative with respect to V_s using the chain rule since the density is a functional of w only via V_s . The CEDA then allows us to partially invert the KS response function χ_s analytically. We will focus on the left-hand side of Eq. (15) and on the last term on the right-hand side. These terms are less sensitive to the approximation used for E_{xc} and therefore should give rise to a general behavior. If all energy denominators are set to the constant $\Delta\epsilon$ we find on the left-hand side of Eq. (15)

$$\begin{aligned} \int d\mathbf{r} \chi_s(\mathbf{r}_1, \mathbf{r}) g_{xc}(\mathbf{r}) &\approx -\frac{2}{\Delta\epsilon} n(\mathbf{r}_1) g_{xc}(\mathbf{r}_1) \\ & \quad + \frac{2}{\Delta\epsilon} \int d\mathbf{r} \gamma(\mathbf{r}_1, \mathbf{r}) g_{xc}(\mathbf{r}) \gamma(\mathbf{r}, \mathbf{r}_1), \end{aligned} \quad (17)$$

where γ is the KS density matrix. If we focus on the last term in Eq. (15) and use $f^+(\mathbf{r}) \approx |\varphi_L(\mathbf{r})|^2$ we find in the CEDA

$$\begin{aligned} & \int d\mathbf{r} v_{xc}^+(\mathbf{r}) \frac{\delta f(\mathbf{r})}{\delta V_s(\mathbf{r}_1)} \Big|_+ \\ &\approx -\frac{2}{\Delta\epsilon} |\varphi_L(\mathbf{r}_1)|^2 v_{xc}^-(\mathbf{r}_1) + \frac{2}{\Delta\epsilon} |\varphi_L(\mathbf{r}_1)|^2 \int d\mathbf{r} |\varphi_L(\mathbf{r})|^2 \\ & \quad \times v_{xc}^-(\mathbf{r}) + \frac{4}{\Delta\epsilon} \varphi_L(\mathbf{r}_1) \int d\mathbf{r} \gamma(\mathbf{r}_1, \mathbf{r}) \varphi_L(\mathbf{r}) v_{xc}^-(\mathbf{r}). \end{aligned} \quad (18)$$

From Eqs. (17) and (18) we can extract an approximate asymptotic behavior

$$g_{xc}(\mathbf{r}) \sim \frac{|\varphi_L(\mathbf{r})|^2}{n(\mathbf{r})} \sim e^{2(\sqrt{2I} - \sqrt{2A_s})r}, \quad (19)$$

where I is the ionization energy [31] and A_s is the KS affinity. Thus we can conclude that if $I > A_s$, g_{xc} contains a term that diverges exponentially as $r \rightarrow \infty$. That the first term of Eq. (15) would exactly cancel the term of Eq. (19) is highly unlikely and we will explicitly see that within an approximation that accounts for the derivative discontinuity as the EXX approximation this is not the case. To obtain Eq. (19) we have used the CEDA, but we will show below that the discontinuity obtained from the full solution of Eq. (15) exhibits the same behavior. In addition, we will demonstrate that this feature is responsible for sharp peak structures as well as divergences in the kernel of a combined donor-acceptor system.

III. DISCONTINUITY OF THE DYNAMICAL XC KERNEL

So far the analysis has been limited to the static case. To investigate if the kernel has discontinuities at finite frequency the discussion above must be generalized to an ensemble that allows the number of particles to change in time. To this end, we consider the statistical operator $\hat{\rho}(t) = \sum_k \alpha_k(t) |\Psi_k(t)\rangle \langle \Psi_k(t)|$, where $\alpha_k(t)$ are given time-dependent coefficients whose sum is equal to 1 and $|\Psi_k(t)\rangle$ is the many-body state of k particles at time t . It is possible to prove a Runge-Gross-like theorem for this ensemble that allows us to define the XC potential as a functional of the ensemble density. In this way, the functional derivative $\delta v_{xc}(\mathbf{r}t)/\delta n(\mathbf{r}'t')$ contains no arbitrariness, but leaves the possibility for a discontinuity of the form

$$\begin{aligned} f_{xc}^+(\mathbf{r}, \mathbf{r}'; t - t') &= f_{xc}^-(\mathbf{r}, \mathbf{r}'; t - t') \\ & \quad + g_{xc}(\mathbf{r}; t - t') + g_{xc}(\mathbf{r}'; t - t'). \end{aligned}$$

If we vary $v_{xc}(\mathbf{r}t)$ with respect to the time-dependent number of particles $N(t')$ and evaluate the derivative at the ground state with $N = N_0^+$ an expression for the frequency-dependent discontinuity $g_{xc}(\mathbf{r}, \omega)$ can be derived

$$\begin{aligned} \frac{\delta v_{xc}(\mathbf{r}t)}{\delta N(t')} \Big|_{n_0^+} &= \int d\mathbf{r}' f_{xc}^-(\mathbf{r}, \mathbf{r}', t - t') f^+(\mathbf{r}') \\ & \quad + \int d\mathbf{r}' g_{xc}(\mathbf{r}', t - t') f^+(\mathbf{r}') + g_{xc}(\mathbf{r}, t - t'), \end{aligned} \quad (20)$$

where we again have used the chain rule. Below we will see with a numerical example how the frequency dependence modifies the discontinuity, making the divergency stronger than in the static case, and allows for a correct description of CT excitations in a combined donor-acceptor system. This will be illustrated in the time-dependent exact-exchange (TDEXX) approximation. For a derivation and analysis of the EXX kernel we refer the reader to Refs. [32,33]. From now on the subscript "xc" will be replaced by "x" to denote quantities in the TDEXX approximation.

IV. RESULTS

In the single-pole approximation (SPA) [4] of TDDFT the XC correction to the KS excitation energy ω_q is given by twice the matrix element

$$\langle q | f_{xc}(\omega) | q \rangle = \int d\mathbf{r} d\mathbf{r}' \Phi_q(\mathbf{r}) f_{xc}(\mathbf{r}, \mathbf{r}', \omega) \Phi_q(\mathbf{r}')$$

at $\omega = \omega_q$, where the index $q = ia$ corresponds to an arbitrary excitation. In Ref. [34] it was shown that in TDEXX $2\langle q | f_x(\omega_q) | q \rangle = \langle a | \Sigma_x - v_x | a \rangle - \langle i | \Sigma_x - v_x | i \rangle - \langle aa | v | ii \rangle$, where v is the Coulomb interaction. Considering a CT excitation between the highest occupied molecular orbital (HOMO) ($i = H$) and the LUMO ($a = L$), we see that the last term goes as $1/R$. Setting, as usual [35], $\langle H | \Sigma_x - v_x | H \rangle = 0$ and using the previously mentioned result $\langle L | \Sigma_x - v_x | L \rangle = \Delta_x$, we can deduce that [36]

$$\begin{aligned} \omega_{CT} &= \omega_{HL} + 2\langle HL | v + f_x(\omega_{HL}) | HL \rangle \\ &\rightarrow \omega_{HL} + \Delta_x - 1/R. \end{aligned} \quad (21)$$

The kernel f_x thus produces a finite correction if evaluated at ω_{HL} and yields exactly the results corresponding to first-order Görling-Levy perturbation theory [34,37–39]. In the following we will see that it is the discontinuity of the kernel that yields this correct result. We have deliberately used the SPA and not the full solution of Casida equations in conjunction with the EXX kernel, a procedure that would imply the inclusion of higher orders in the explicit dependence on the Coulomb interaction. Our motives are to study an exact property of the kernel well captured in the SPA of TDEXX, but may be subject to errors inherent to the approximation when including higher orders [32].

We model [40] a stretched diatomic molecule in terms of one-dimensional atoms described by $Q/\sqrt{(x-x_0)^2+1}$, where x_0 is the location of the atom and Q is the nuclear charge, and replace everywhere the Coulomb interaction v with a soft Coulomb interaction $1/\sqrt{(x-x')^2+1}$. We study two different systems, one ionic and one neutral system. In the ionic system the discontinuity is important already at the level of the XC potential, whereas in the neutral system the discontinuity appears only in the XC kernel.

A. Ionic system

In the first example we study an ionic system and set $Q = 2$ on the left atom (donor) and $Q = 4$ on the right atom (acceptor) and solve the ground-state KS problem with four electrons. In the ground state at internuclear separation $R = 10$ a.u. we find two electrons on each atom and in Fig. 1 (left panel) the EXX potential is displayed (solid gray line) in arbitrary units. Two steps are clearly visible, one between the atoms and another one on the right side of the acceptor. As a consequence, v_x is shifted upward in the acceptor region placing the KS LUMO of the isolated acceptor above the HOMO of the isolated donor. This implies that the KS affinity of the acceptor becomes closer to the true affinity. In the same figure and panel we also display the quantity $F_{HL}(x, \omega) = \int dx' f_x(x, x', \omega) \Phi_{HL}(x')$ at $\omega = 0$. The function F_{HL} is seen to have peaks in correspondence with the steps of v_x and is shifted downward over the acceptor with respect to the donor. Despite the fact that Φ_{HL}

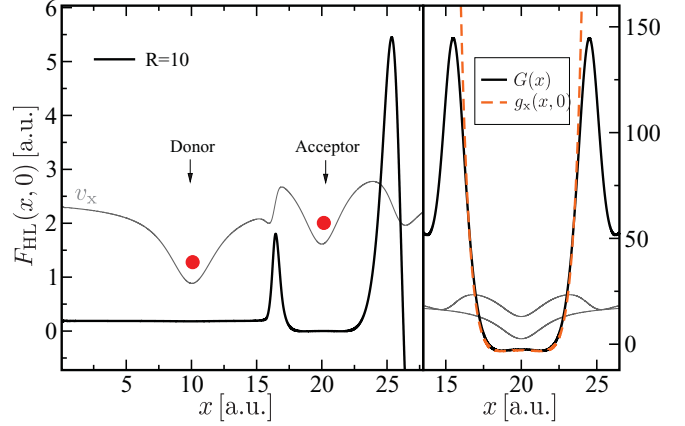


FIG. 1. (Color online) Left: EXX potential and kernel for a heteronuclear system of four electrons. Right: the discontinuity $g_x(x, 0)$ calculated from Eq. (15) for the isolated two-electron subsystem as well as $G(x)$ for $N = 2.0001$. Note that the potentials have been rescaled and shifted for better visibility.

tends to zero as R increases, the peaks of F_{HL} become sharper and higher and the shift increases in size. The right panel in the same figure shows the function $G(x) = \int dx' f_x(x, x', 0) f(x')$, accessible from Eq. (15), for the isolated acceptor when $N = 2.0001$ (solid black line), as well as the discontinuity $g_x(x, 0)$ in the limit $N = 2^+$ (dashed line). The potentials v_x are also shown (solid gray lines) calculated from the same ensembles, i.e., $N = 2.0001$ and 2 . The function $G(x)$ has peaks whose positions follow the steps of v_x and whose height increases as N approaches 2^+ . In the same limit, also the difference between the $G(\infty)$ value and the value of G in the central plateaulike region increases consistently with the fact that $\int dx G(x) f(x)$ has to remain finite [see Eq. (16)]. Eventually $G(x)$ turns into the discontinuity $g_x(x, 0)$, which diverges as $x \rightarrow \infty$, in agreement with our previous analysis. Notice that the CEDA has not been made here. If we compare F_{HL} and G from the different panels we see a very similar structure. We therefore conclude that the peaked structure of the kernel in the donor-acceptor system is just the discontinuity of the ensemble EXX kernel. As discussed above, most part of the CT excitation energy is contained already in the KS eigenvalue differences due to the step in v_x . A more critical example is therefore the neutral system, studied below.

B. Neutral system

An example where the kernel needs to account for Δ_x is the same system but with six electrons, i.e., a neutral system. The ground-state has two electrons on the left atom (acceptor) and four electrons on the right atom (donor). In Fig. 2 we plot the EXX potential (solid gray line) for $R = 12$ a.u. and a steplike structure between the atoms can be observed. However, as R is increased the step reduces in size and eventually goes to zero. In the left panel we plot F_{HL} at $\omega = 0$, i.e., in the adiabatic exact-exchange (AEXX) approximation, and for different separations R . Again, we find a peak structure in the kernel between the donor and the acceptor as well as a shift that increases exponentially with R . In this case, compared to the previous, the peaks are less pronounced, but the step due

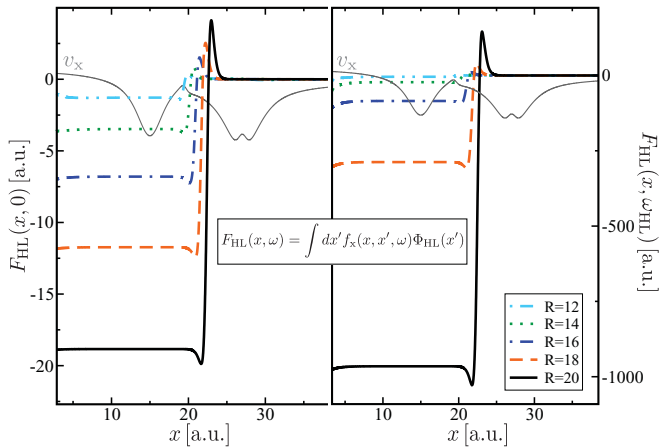


FIG. 2. (Color online) Same system as in Fig. 1 but with six electrons. Left: AEXX kernel. Right: TDEXX kernel at ω_{HL} . Note that the potentials have been rescaled for better visibility.

to the plateau is much larger. Evaluating the kernel at the first KS CT excitation frequency increases the exponential growth of the step by a factor of approximately 2 (right panel). Thus, whereas the overall shape remains unaltered, the magnitude of the shift is strongly influenced by the frequency dependence. This fact plays a crucial role in the description of the CT excitation for this system. We notice here that even if the step in v_{xc} disappears, in the dissociation limit the step in f_{xc} remains. This is not a contradiction as the discontinuity might show up only in the second derivative. Figure 3 illustrates the behavior of the single-pole CT excitation energy as a function of R for the system of Fig. 2 in four different approximations. In TDEXX with the correction $\langle HL|f_x(\omega_{HL})|HL\rangle$ we find that the divergency of the kernel over the acceptor exactly compensates for the decreasing overlap Φ_{HL} , thus yielding a finite value as $R \rightarrow \infty$ as well as the right $1/R$ asymptotic behavior, as it should according to Eq. (21). In the adiabatic case we find instead that $\langle HL|f_x(0)|HL\rangle$ tends to 0 as

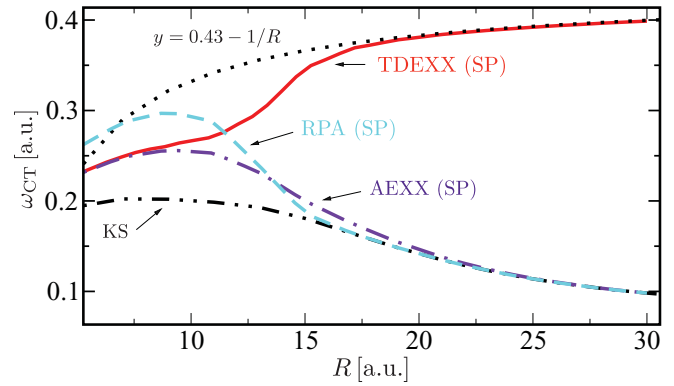


FIG. 3. (Color online) CT excitation energies as a function of separation R in different approximations.

$R \rightarrow \infty$, although reproducing the fully frequency-dependent result up to around $R = 8$. We note that even if the kernel is very large over the acceptor it will not affect the excitations that are localized there since any constant will vanish by the fact that Φ_q integrates to zero. Thus only excitations involving a transfer of charge from one atom to the other will be influenced by the discontinuity.

V. CONCLUSION

In conclusion, we have analyzed the discontinuity of the XC kernel of an ensemble with time-dependent particle numbers. In a combined system of two atoms we have seen that the divergency of the discontinuity as $r \rightarrow \infty$ can generate a kernel that diverges in the dissociation limit and thus compensate for the vanishing overlap of acceptor and donor orbitals. This feature is crucial for the description of CT excitations, but may also be important whenever there are excitations for which the KS orbital overlap is too small to give a correction.

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