Undoing static correlation: Long-range charge transfer in time-dependent density functional theory

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(Dated: February 15, 2005)

Long-range charge transfer excited states are notoriously badly underestimated in time-dependent density functional theory (TDDFT). We resolve how *exact* TDDFT captures charge transfer between open-shell species: in particular the role of the step in the ground-state potential, and the severe frequency-dependence of the exchange-correlation kernel. An expression for the latter is derived, that becomes exact in the limit that the charge-transfer excitations are well-separated from other excitations. The exchange-correlation kernel has the task of undoing the static correlation in the ground state introduced by the step, in order to accurately recover the physical charge-transfer states.

I. INTRODUCTION

How or whether excited states of long-range charge transfer character are captured in time-dependent density functional theory (TDDFT) has recently received much attention [1–9], partly because of its importance in systems of biological and chemical interest. Many of these molecules are big enough that traditional wave-function methods to calculate excited states become prohibitively expensive; TDDFT, on the other hand, scales favorably with the number of electrons, while remaining reliably accurate for many excitations. There is therefore much interest in applying TDDFT to such systems, and understanding why, when, and where it is expected to work well.

TDDFT is an exact theory, based on the mapping of the interacting electronic system to a non-interacting one [10], far faster to solve. In practise the unknown time-dependent exchange-correlation potential must be approximated, introducing errors in excitation energies. These are not always well-understood, although there has been some recent progress [11], for example in the significance of the asymptotic behaviour of the potential [12, 13], and in the severe frequency-dependence needed for double-excitations [14–16]).

It has been found [1–9], that excitations involving charge-transfer (CT) between widely separated species within a molecule are severely underestimated in TDDFT. This is in contrast to most excitations, which are accurate to within a few tenths of an electron-volt. This has serious consequences. For example [3], prediction of CT quenching of fluorescence in light-harvesting bacteria, contrary to observation.

There have been several recent attempts to overcome this charge-transfer problem. In Ref. [8], a ΔSCF correction is made, while in Ref. [1], it is proposed that TDDFT be mixed with configuration interaction singles. In Ref. [9], a long-range correction using Hartree-Fock is implemented. Ref. [2] suggests a simple improvement by shifting the donor HOMO and acceptor LUMO energies based on the derivative discontinuity [17]. Ref. [4], on the other hand, remains purely within TDDFT, and suggests an empirical asymptotically-corrected kernel that diverges with separation.

In the present paper, we also stay strictly within TDDFT, and ask, in contrast to all other approaches, what is the *exact* TDDFT description of charge-transfer in one simple case: charge-transfer between two open shell species, when the charge transfer states are well-separated from the other excitations of the system. By solving a simple model we deduce what the exchange-correlation kernel must be in this case.

An important feature of the present analysis involves the step in the exact ground-state Kohn-Sham (KS) potential that appears between two widely-separated open shell species of different ionization potentials. This step is also present in orbital approximations such as exact exchange (or the KLI approximation to it [18]). It is not present in local or semi-local gradient approximations: so our model for the exact exchange-correlation kernel does not apply to these cases. Our purpose here is to explore how charge-transfer is described exactly in a simple model case.

We begin in Section II with a review of TDDFT linear response theory, and present the problem of long-range charge transfer. A simple model to study this is introduced in section III. We describe the significance of the step that develops in the KS potential when a (closed-shell) molecule composed of two different open-shell species are pulled apart. The KS ground-state is of a fundamentally different nature than the true ground-state, resembling the problems of homonuclear dissociation; the KS charge-transfer energies become zero! We show how inclusion of the electron-electron interaction breaks the degeneracy and yields the correct nature of the ground-state and the CT states. In section IV we describe the implication of static correlation for the TDDFT exchange-correlation kernel, and derive a model

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for it that is valid in the limit that the charge-transfer excitations are well-separated from all other excitations in the system. The features are strong-frequency dependence and exponential dependence on the separation of the two species. Finally, in section V, we discuss other ways that static correlation haunts TDDFT, so far unexplored.

II. TDDFT LINEAR RESPONSE AND CT STATES

We begin by briefly reviewing the TDDFT linear response formalism.

Although the density of the KS system is defined to be that of the interacting system, the excitation energies are not the same: linear response theory tells us how to correct them. Applying a small perturbing potential to a ground-state, and measuring the density response defines the susceptibility, or density-density response function, $\chi[n_0](\mathbf{r},\mathbf{r}',t-t') = \delta v_{\rm ext}(\mathbf{r}t)/\delta n(\mathbf{r}'t')|_{n_0}$. The susceptibility of the true interacting system is related to that of its non-interacting Kohn-Sham counterpart, $\chi_{\rm S}[n_0](\mathbf{r},\mathbf{r}',t-t') = \delta v_{\rm S}(\mathbf{r}t)/\delta n(\mathbf{r}'t')|_{n_0}$, through an integral equation, written in the frequency-domain as [19]:

$$\overleftrightarrow{\chi}^{-1}(\omega) = \overleftrightarrow{\chi}_{\rm S}^{-1}(\omega) - \overleftrightarrow{f}_{\rm HXC}(\omega) \tag{1}$$

Here the Hartree-exchange-correlation kernel is the sum $f_{\rm HXC}[n_0](\mathbf{r},\mathbf{r}',\omega) = f_{\rm H}(\mathbf{r},\mathbf{r}') + f_{\rm XC}[n_0](\mathbf{r},\mathbf{r}',\omega)$. The Hartree kernel is the density-functional-derivative of the Hartree potential, $f_{\rm H}(\mathbf{r},\mathbf{r}') = 1/|\mathbf{r}-\mathbf{r}'|$, and the exchange-correlation kernel is that of the exchange correlation potential, $f_{\rm XC}[n_0](\mathbf{r},\mathbf{r}',t-t') = \delta v_{\rm XC}(\mathbf{r}t)/\delta n(\mathbf{r}',t')$. Transition frequencies of the true system lie at the poles of $\chi(\mathbf{r},\mathbf{r}',\omega)$, and oscillator strengths may be obtained from the residues. The poles of $\chi_{\rm S}(\mathbf{r},\mathbf{r}',\omega)$ are at the KS single excitations; these are shifted to the true excitations through the action of the Hartree-exchange-correlation kernel. So, Eq. (1) enables us to obtain the interacting excitation energies and oscillator strengths from the KS susceptibility and the Hartree-exchange-correlation kernel. In principle, the exact spectrum of the interacting system is obtained; in practise, approximations must be made for (a) the xc contribution to the ground-state KS potential, and (b) the xc kernel $f_{\rm XC}(\omega)$.

In the Lehman representation,

$$\chi(\mathbf{r},\mathbf{r}';\omega) = \sum_I \left\{ \frac{F_I(\mathbf{r})F_I^*(\mathbf{r}')}{\omega-\omega_I+i0^+} - \frac{F_I^*(\mathbf{r})F_I(\mathbf{r}')}{\omega+\omega_I+i0^+} \right\}, \tag{2}$$

where, $F_I(\mathbf{r}) = \langle 0|\hat{n}(\mathbf{r})|I\rangle$ with $\hat{n}(\mathbf{r})$ being the one-body density operator, I labels the excited states of the interacting system, and ω_I is their transition frequency. This expression also holds for the KS susceptibility where the excited-states are excited Slater determinants and the transition frequencies are orbital energy differences. Excitations of atoms and molecules are often calculated in a matrix formulation of these equations [20]: one lets $q = (i,a)$ be an index representing a single excitation: a transition from an occupied KS orbital ϕ_i to an unoccupied one ϕ_a, and let ω_q be the difference in the KS orbital energies, $\omega_q = \epsilon_a - \epsilon_i$. Then, the squares of the true transition frequencies $\Omega_I = \omega_I^2$ are the eigenvalues of the matrix

$$\widetilde{\Omega}(\omega)_{qq'} = \delta_{qq'}\omega_q^2 + 4\sqrt{\omega_q\omega_{q'}}[q|f_{\rm HXC}(\omega)|q'], \tag{3}$$

where

$$[q|f_{\rm HXC}(\omega)|q'] = \int d\mathbf{r}d\mathbf{r}'\phi_i^*(\mathbf{r})\phi_a(\mathbf{r})f_{\rm HXC}(\mathbf{r},\mathbf{r}',\omega)\phi_{i'}(\mathbf{r}')\phi_{a'}^*(\mathbf{r}'). \tag{4}$$

Oscillator strengths of the true system are related to the eigenvectors [20].

When the coupling between excitations is very small, one may neglect the off-diagonal elements of the matrix, producing the "small-matrix approximation" [11, 21, 22]:

$$\omega^2 = \omega_q^2 + 4\omega_q[q|f_{\rm HXC}(\omega_q)|q] \tag{5}$$

This is equivalent to keeping only the backward and forward transitions at frequency ω_q in the Lehman representation of the response function. When the shift from the KS transition is small, one may simplify this further to get the "single-pole approximation" [19]:

$$\omega = \omega_q + 2[q|f_{\rm HXC}(\omega_q)|q]\,. \tag{6}$$

Now, consider applying the theory to long-range charge-transfer excited states. In the limit of large separations R, the *exact* energy cost for transferring an electron from donor to acceptor, is

$$\omega = I_D - A_A - 1/R \tag{7}$$

where I_D is the ionization energy of the donor, and A_A is the electron affinity of the acceptor. As discussed in Refs. [1, 2], the failure of TDDFT to reproduce this is evident from a single-pole analysis (Eq. (6)), where

$$\begin{aligned}\omega &= \epsilon_A^L - \epsilon_D^H + \int d^3r_1 d^3r_2 F(\mathbf{r}_1)f_{\rm HXC}(\mathbf{r},\mathbf{r}',\omega_q)F(\mathbf{r}_2)\\ &\approx \epsilon_A^L - \epsilon_D^H = I_D - A_{\rm S,A}\end{aligned} \tag{8}$$

Here $F(\mathbf{r}) = \phi_D^H(\mathbf{r})\phi_A^L(\mathbf{r})$ is the product of the HOMO of the donor (KS orbital energy ϵ_D^H) and the LUMO of the acceptor (KS orbital energy ϵ_A^L). Because there is exponentially small overlap between the atomic orbitals on the widely separated donor and acceptor, the integral term vanishes, and the TDDFT energy collapses to the bare KS energy, as indicated in the second line. We have used the fact that the KS HOMO energy is exactly the negative of the ionization energy, but the LUMO energy differs from the negative affinity by the discontinuity [17, 23–25]:

$$A = A_{\rm S} + A_{\rm XC} = -\epsilon_L + A_{\rm XC} \tag{9}$$

Now, common approximations underestimate I, but how does *exact* TDDFT get the exact energy? That is, suppose we had the exact ground-state Kohn-Sham potential and also the exact exchange-correlation kernel. Then the exact TDDFT HOMO energy is indeed I_D, but how does the exact TDDFT retrieve the discontinuity $A_{\rm xc}$, and the $-1/R$ Coulomb fall-off? We address this in the next two sections.

III. CT BETWEEN TWO OPEN SHELL SPECIES: THE ROLE OF STATIC CORRELATION

To study this question, we consider first the simplest model: electron transfer between two one-electron neutral "atoms", separated by a large distance R. Let $I_{1(2)}$ be the ionization energy of atom 1(2); then the atomic orbital occupied in the ground-state has energy $\epsilon_H = -I_{1(2)}$, where the H subscript stands for HOMO of the atom. When we consider the closed-shell molecule composed of the two atoms at large separation, the ground-state KS potential develops a step between the atoms, that exactly lines up the atomic HOMOs [23, 26]. To see this, consider the Kohn-Sham wavefunction Φ_0 for the molecule. This is the doubly-occupied bonding orbital:

$$\begin{aligned}\Phi_0 &= \phi_0(\mathbf{r}_1)\phi_0(\mathbf{r}_2)\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)/\sqrt{2}\,, \text{ with}\\ \phi_0(\mathbf{r}) &= \left(\phi_1(\mathbf{r})+\phi_2(\mathbf{r})\right)/\sqrt{2(1+S_{12})} \qquad (10)\end{aligned}$$

where S_{12} is the overlap integral $\int \phi_1(\mathbf{r})\phi_2(\mathbf{r})d^3r$, exponentially small in the separation R. In the limit of large separation, $\phi_{1,2}$ denotes the occupied atomic orbital of atom 1(2). Inserting ϕ_0 into the KS equation, while recognizing that near each atom, the orbital must reduce to that atom's atomic HOMO, with the appropriate orbital energy, one sees that the exchange-correlation potential must develop a step of size $|I_2 - I_1|$ between the atoms; raising the potential of the atom with the larger ionization energy. A simple 1-d example is given in Fig. 1 where each "atomic nucleus" is an Eckart potential. The potential eventually goes back down to zero on the right-hand-side. (A similar picture for two delta-function "nuclei" can be found in Ref. [23]). The step renders the HOMOs of each atom degenerate, and is necessary to prevent dissociation into fractionally charged species [17]. If they were not exactly lined up, then one could lower the energy of the system by transferring a fraction of charge from one of the atoms to the other, contradicting the charge neutrality that is observed in nature. This phenomenon is closely related to the derivative discontinuity discovered in the 80's [17, 23–26]. It is important to note that the step is present in exact DFT and is approximated in spatially-nonlocal approximations such as exact-exchange [18, 27] Most common approximate potentials, such as LDA, garner only local or semi-local density information, and so do not display the step.

The fact that in exact DFT the atomic HOMO's become degenerate has an apparently drastic consequence

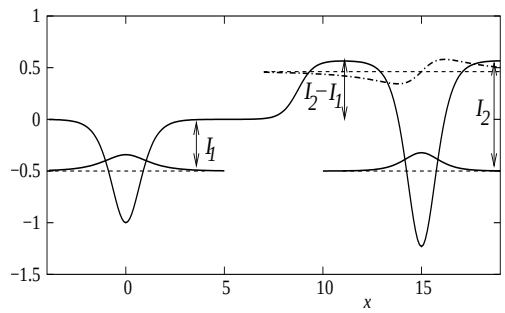

FIG. 1: The 2-electron KS potential for two widely separated "Eckart" atoms, $V_{\rm ext}(x) = 1/\cosh^2(x) + 1.8/\cosh^2(x-15)$. The highest occupied orbitals of each atom are shown solid, and the first excited state of the right-hand atom is shown in dash-dot.

for CT excited states: Whereas a (semi-)local DFT approximation would yield a finite KS transition energy, albeit underestimated, the *exact* KS system yields *zero* energy for charge transfer between the atoms!

The Kohn-Sham energies are poor because, in this case, the KS description is fundamentally different from the interacting system. The KS ground-state involves each electron delocalized over both atoms, whereas the true wavefunction has one atom on each. We shall come back to this point shortly.

The alignment of the atomic HOMO's leads to three nearly degenerate singlet two-electron KS states, whose spatial parts are:

$$\begin{aligned}\Phi_0 &= \phi_0(\mathbf{r}_1)\phi_0(\mathbf{r}_2)\\ \Phi_q &= \left(\phi_0(\mathbf{r}_1)\bar{\phi}_0(\mathbf{r}_2) + \bar{\phi}_0(\mathbf{r}_1)\phi_0(\mathbf{r}_2)\right)/\sqrt{2}\\ \Phi_D &= \bar{\phi}_0(\mathbf{r}_1)\bar{\phi}_0(\mathbf{r}_2) \qquad (11)\end{aligned}$$

where ϕ_0 is the bonding orbital of Eq. (10), and $\bar{\phi}_0$ is the antibonding orbital

$$\bar{\phi}_0 = \left(\phi_1 - \phi_2\right)/\sqrt{2(1-S_{12})}\,. \qquad (12)$$

At large separations the "singly-excited" Φ_q is slightly higher in energy than Φ_0 by tunnel splittings between the atomic orbitals, and the "doubly-excited" Φ_D higher again; the orbital energy of the antibonding state is at $\bar{\omega} \sim \exp(-R)$, where R is the separation between the atoms. The proximity of Φ_q and Φ_D to Φ_0 is a signature of the static correlation in the ground-state.

Before discussing the implication of this static correlation for TDDFT, we first show that the electron interaction splits the degeneracy between the Kohn-Sham states, recovering states of CT nature and approximations for their energies. We assume that the tunnel-splittings are much smaller than the energy-splitting from the electron-electron interaction, and that the basis of the three states, Eqs. (11), has negligible couplings to all other KS excitations. To simplify the discussion, we choose $I_2 > I_1$. Diagonalizing the true Hamiltonian in this basis, yields the three states:

(i) the Heitler-London ground-state $\Psi_0 = (\phi_1(\mathbf{r})\phi_2(\mathbf{r}') + \phi_2(\mathbf{r})\phi_1(\mathbf{r}'))\sqrt{2}$
(ii) charge-transfer excited state from atom 2 to atom 1: $\Psi_{2\to 1} = \phi_1(\mathbf{r})\phi_1(\mathbf{r}')$. This has energy, relative to the Heitler-London state,

$$\omega_1 = I_2 - A_1 - 1/R \tag{13}$$

where $A = A_{\rm S} + A_{\rm XC}^{\rm approx}$, with

$$A_{\rm XC}^{\rm approx} = -\int d^3r \int d^3r' \phi_H(\mathbf{r})^2 \phi_H(\mathbf{r}')^2 V_{\rm ee}(\mathbf{r}-\mathbf{r}') \tag{14}$$

Here $V_{\rm ee}$ is the electron-electron interaction, $V_{\rm ee} = 1/|\mathbf{r}-\mathbf{r}'|$. For later purposes, the subscript H stands for the highest occupied orbital of the atom; for one-electron atoms, it simply indicates the occupied atomic orbital on the atom. Note also that for open-shell atoms, $A_{\rm S} = I = -\epsilon_H$.
(iii) charge-transfer excited state from atom 1 to atom 2: $\Psi_{1\to 2} = \phi_2(\mathbf{r})\phi_2(\mathbf{r}')$, of energy

$$\omega_2 = I_1 - A_2 - 1/R \tag{15}$$

Thus, the correct nature of the ground-state, and CT states with the correct form of energy (c.f. Eq. 7), including an approximation for the exchange-correlation contribution to the electron affinity, are recovered.

In a sense, accounting for the electron-interaction undoes the static correlation in the system. Because of the step in the potential, and the consequent nearly degenerate triple of KS determinants, the ground-state problem resembles the well-known homonuclear dissociation problems of ground-state DFT [28, 29], where the dissociation limit is incorrect because the KS ground-state involves mixing ionic combinations into the true neutral Heitler-London form. Static correlation was an important agent above in treating the perturbation: The Hamiltonian can always be written in terms of the KS Hamiltonian $H_{\rm S}$, as $H = H_{\rm S} + V_{\rm ee} - v_{\rm H} - v_{\rm XC}$. For any two-electron system, as we have here, $v_{\rm X} = -v_{\rm H}/2 \sim O(\lambda)$, where λ is the interaction strength. Typically the correlation potential is $O(\lambda^2)$, appearing at the next order of interaction strength, but when there is static correlation, it is much stronger: $v_{\rm C}$ cancels $v_{\rm H} + v_{\rm X}$ and adds the step, yielding

$$\begin{aligned} v_{\rm HXC}(\mathbf{r}) &= 0\,, \text{ for } \mathbf{r} \text{ near atom 1} \\ &= I_2 - I_1\,, \text{ for } \mathbf{r} \text{ near atom 2} \end{aligned}$$

This must be so in order for the KS equation for the molecular orbital ϕ_0 to reduce to that for the atomic orbital $\phi_{1,2}$, respectively, near atom 1 and atom 2. We discuss how static correlation affects the exchange-correlation kernel of TDDFT in the next section.

We now consider the approximate result for $A_{\rm XC}$, Eq. (14). The derivation neglected all KS states except for the three in the basis (11): the approximation thus becomes exact when the basis is truly isolated, or in the limit of weak interaction so that the higher-lying KS states are not appreciably mixed in. A simple example for which the exact affinity at all interaction strengths is easily calculable, is that of a fermion in one dimension living in a delta-function well (i.e. a one-dimensional H atom). It is a standard textbook problem to find the only bound-state of the well. The electron affinity can be obtained by subtracting its ground-state energy from that of two interacting fermions in the well. When their interaction is a delta-function repulsion of strength λ:

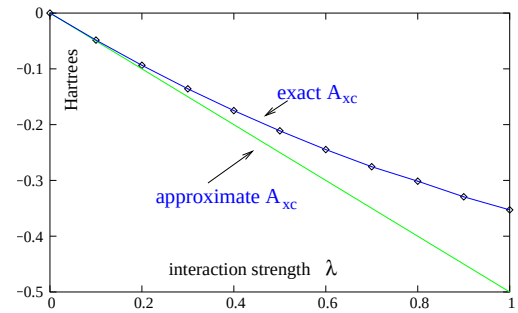

FIG. 2: Exchange-correlation contribution to the electron affinity of a fermion in a δ-well: exact (extracted from Ref. [30]) and approximate (Eq. 14)

$$H = -\sum_i^2 \frac{1}{2}\frac{d^2}{dx_i^2} - \sum_i^2 \delta(x_i) + \lambda\delta(x_1 - x_2)\,, \tag{16}$$

the ground-state energy has an exact solution [30]. (Atomic units are used throughout the paper). In figure 2, the exact $A_{\rm XC}$ has been plotted from $A_{\rm XC} = E(1) - E(2) - A_{\rm S} = -E(2) - 2I$, where the ground-state energy for two fermions, $E(2)$, is obtained from Ref. [30], and that for one fermion is $E(1) = -A_{\rm S} = -I = -0.5H$. Comparing this with the approximation from Eq. (14), where ϕ_H is the textbook solution for the orbital in the one-fermion problem, we see that, as expected, the approximation becomes exact in the weak interaction limit.

This result for $A_{\rm XC}$ is consistent with a perturbative analysis of $E(N) - E(N+1)$. Consider adding one electron to an $N = 1$-species. In an unrelaxed approximation, the extra electron plops into the same spatial orbital as the first. A perturbative approximation for the electron affinity is obtained from calculating the difference in the Hamiltonians of the 2-electron and 1-electron system, in the unrelaxed doubly-occupied orbital. One finds exactly the result, Eq. (14).

Although our results so far have been derived for charge transfer between two one-electron species, it is straightforward to show that they hold for charge-transfer between two general open-shell species. There the KS molecular HOMO sits atop a spin-paired KS determinant, containing all the inner orbitals of both atoms.

So far, we have examined the exact ground-state KS potential for a closed shell molecule composed of two open-shell species, and found that the step in between the species leads to a near zero value for charge-transfer in

the Kohn-Sham system. We showed that the static correlation is broken by the electron-electron interaction, and how the latter allows us to recapture the true ground-state and excited charge-transfer states, together with an approximation for the exchange-correlation electron affinity.

IV. THE EXCHANGE-CORRELATION KERNEL FOR CHARGE-TRANSFER

How does the static correlation in the ground-state affect the TDDFT description of charge-transfer? In TDDFT, the exchange-correlation kernel must play the role of the diagonalization of the previous section in salvaging the CT energies from their near zero KS value. We now examine what the nature of the exact $f_{\rm XC}$ must be, and the signatures of static correlation in the kernel.

Consider the KS response function, $\chi_{\rm S}(\mathbf{r},\mathbf{r}',\omega)$. We may write this as

$$\chi_{\rm S}(\mathbf{r},\mathbf{r}',\omega) \approx \frac{2\bar{\omega}}{\omega^2-(\bar{\omega})^2} X_{\rm S}(\mathbf{r},\mathbf{r}',(\omega)) \tag{17}$$

where we include only the contribution to Eq. (2) from the antibonding transition, valid in the limit that the KS bonding-antibonding pair is well-separated from the higher KS transitions. The assumption is that to lowest order in the interaction strength, the interacting charge-transfer states arise from this transition only. This is analogous to the approximation of restricting to the 3×3 subspace when we considered diagonalization. The numerator $X_{\rm S}(\mathbf{r},\mathbf{r}',(\omega)) = \left(\phi_1^2(\mathbf{r})-\phi_2^2(\mathbf{r})\right)\left(\phi_1^2(\mathbf{r}')-\phi_2^2(\mathbf{r}')\right)/4 + O\left((\omega^2-\bar{\omega}^2)\Delta_{\rm S}/[\bar{\omega}(\omega^2-\Delta_{\rm S}^2)]\right)$, where $\Delta_{\rm S}$ is the frequency of the next highest KS transition.

Notice that $\chi_{\rm S}$ vanishes exponentially with separation of the atoms due to the exponential dependence of the tunnel splitting $\bar{\omega}$ on separation. This can be understood from $\chi_{\rm S} = \frac{\delta n}{\delta v_{\rm S}}(\omega)$: the perturbation at $\bar{\omega}$ excites the antibonding transition, whose density difference from the bonding orbital's is exponentially small with separation.

Now we turn to the interacting response function, $\chi(\mathbf{r},\mathbf{r}',\omega)$, which is a sum over all excitations of the interacting system. As in the KS case, we zoom into the excitations that describe charge transfer:

$$\chi(\mathbf{r},\mathbf{r}',\omega) \approx \frac{2\omega_1}{\omega^2-\omega_1^2} X_1(\mathbf{r},\mathbf{r}',(\omega)) + \frac{2\omega_2}{\omega^2-\omega_2^2} X_2(\mathbf{r},\mathbf{r}',(\omega)) \tag{18}$$

Within the isolated basis approximation, $X_1(\mathbf{r},\mathbf{r}',(\omega)) = X_2(\mathbf{r},\mathbf{r}',(\omega)) = 2\phi_1(\mathbf{r})\phi_2(\mathbf{r})\phi_1(\mathbf{r}')\phi_2(\mathbf{r}') + O(1/\Delta)$. Again the response function vanishes exponentially with separation, but this time because the CT transitions have exponentially weak oscillator strength due to overlap between widely separated spatial regions: in the orbital product $\phi_1(\mathbf{r})\phi_2(\mathbf{r})$, each orbital is exponentially small as a function of atomic separation R in the places where the other is finite. The inverse functions, χ^{-1} and $\chi_{\rm S}^{-1}$, are therefore both exponentially large as a function of separation R (*not* to be confused with the finite behaviour as a function of $|\mathbf{r}-\mathbf{r}'|$).

We note that we are retaining backward transitions in the expressions above: these are "small-matrix approximations" rather than "single-pole approximations" that include only the forward transition. The latter is not valid here because the antibonding transition frequency is very small: the backward transition is of almost the same magnitude as the forward, so should not be neglected. The single-pole approximation is only valid when the shift from the KS energy is small [11]: here, the shift is the entire CT energy, since the KS transition energy is near zero (i.e. exponentially small in the separation).

As we saw in the diagonalization procedure, the CT transitions of the interacting system arise from the KS subspace of bonding and antibonding orbitals. In the diagonalization procedure, the number of states was preserved: the three KS 2-electron singlet molecular determinants of Eq. (11), composed of the bonding and antibonding orbitals, were rotated by the electron-electron interaction into the Heitler-London ground-state and CT states onto each of the two atoms. The picture is somewhat different in the response functions. Here the space is of excitations out of the ground-state, so in the interacting case there are two (one to each CT state). But the KS response function has only the single-excitation (corresponding to $\Phi_0 \to \Phi_q$ of Eq. (11)): double excitations cannot appear in the KS response function because the numerator involves the one-body density operator, which connects only states differing in one orbital (see also Ref. [14]). It is the job of the exchange-correlation kernel, $f_{\rm XC}$ to generate an extra pole, and also to mix them. Specifically,

$$f_{\rm HXC}(\omega) = \chi_{\rm S}^{-1}(\omega) - \chi^{-1}(\omega)$$
$$= \frac{1}{2}\left(\frac{(\omega^2-\bar{\omega}^2)}{\bar{\omega}} X_{\rm S}^{-1} - \frac{(\omega^2-\omega_1^2)(\omega^2-\omega_2^2)}{\omega_2(\omega^2-\omega_1^2)+\omega_1(\omega^2-\omega_2^2)} X_1^{-1}\right) \tag{19}$$

Due to the f-sum rule, in the limit of the isolated basis,

$$\bar{\omega} X_{\rm S} = \omega_1 X_1 + \omega_2 X_2 \approx (\omega_1+\omega_2) X_1 \tag{20}$$

we find $X_1^{-1} = (\omega_1+\omega_2)X_{\rm S}^{-1}/\bar{\omega}$. Finally, we require that a dressed small-matrix approximation, arising from plugging Eq. (19) into Eq. (5) yields the true transition frequencies $\omega=\omega_1$ and $\omega=\omega_2$ as solutions. This fixes $[q|X_{\rm S}^{-1}|q] = 1/2$, and our expression for the kernel becomes:

$$\bar{\omega}[q|f_{\rm HXC}(\omega)|q] = \omega_{av}^2 + \frac{\omega_1\omega_2-\bar{\omega}^2}{4} + \frac{\omega_1\omega_2\omega_{av}^2}{\omega^2-\omega_1\omega_2} \tag{21}$$

for the KS transition q =bonding→anti-bonding orbital, and where $\omega_{av} = (\omega_1+\omega_2)/2$. This, with ω_1 and ω_2 given by Eqs. (13), (14),and (15), gives the exact exchange-correlation kernel matrix element in terms of KS quantities, in the limit that the charge-transfer states are isolated from the other transitions, in that coupling to them

can be neglected. Notice the strong non-adiabaticity in the exact kernel, manifest by the pole in the denominator on the right-hand-side.

In the usual presentations of the TDDFT charge-transfer problem, the failure is due to the vanishing overlap between the occupied orbital, on one atom, and the unoccupied one on the other atom, widely separated. This means that $q = \phi_i \phi_a$ vanishes exponentially with separation. This does not occur in the exact analysis of CT between open shells presented here: here the occupied orbital is the bonding orbital and the unoccupied is the anti-bonding orbital, so their overlap goes as $(\phi_1^2 - \phi_2^2)/2$ where ϕ_1 is the atom 1's HOMO (or LUMO) and ϕ_2 is atom 2's HOMO (or LUMO). Although the overlap remains finite, the matrix element $[q|f_{\rm HXC}|q]$ diverges exponentially with interatomic separation R, as $1/\bar{\omega}$, as can be seen from Eq. (21).

A divergence of $f_{\rm HXC}$-matrix elements has previously been found in H_2 dissociation [29], where the the lowest singlet-singlet KS transition energy vanishes with separation, while the true energy approaches a finite number; the step in the KS potential for our heteroatomic molecules leads to a similar feature raising its head again here, but now with the kernel being strongly frequency-dependent. Also, the CT treatment in Ref. [4] utilized an empirically determined kernel that displays also exponentially large behaviour as a function of atomic separation.

V. DISCUSSION AND OTHER IMPLICATIONS OF STATIC CORRELATION

By considering electron transfer between two one-electron species at long-range, we investigated how charge-transfer is captured in the exact KS system. The bare KS energies for CT approach zero exponentially with the separation of the species, but including the electron-electron interaction, splits the near-degeneracy and recaptures finite CT energies of the correct form. We derived the form of the TDDFT exchange-correlation kernel, Eq. (21), that becomes exact in the limit that the charge-transfer states are isolated from all the other excitations in the system. The main features of the kernel are (i) a strong frequency-dependence, due to the mixing in of the double excitation to the antibonding KS state, and (ii) a dependence on the inverse tunnel splitting between the two species, that goes exponentially with their separation.

A crucial feature of the exact KS system in this paper is the step between the two widely separated species. This gives rise to static correlation in the ground-state, and hence the strong frequency-dependence and exponential-dependence on the atomic separation of the $f_{\rm XC}$ matrix element, discussed above. Not only does it play a vital role in the description of CT states, but it also has very interesting, and unexplored, effects on other excitations of a long-range heteroatomic molecule. For example, higher atomic excitations become KS resonances, as illustrated in Figure 1. Here two one-dimensional "Eckart atoms" are shown: the second excited state of the atom on the right can tunnel out of the barrier presented by the step. The acrobatics the exchange-correlation kernel must perform in order to turn such a resonance back into a bound state of the true system, will be pursued in future work.

Another interesting consequence of the step is that for *every* single excitation out of the HOMO bonding orbital, $\phi_0 \to \phi_a$, there is a nearly degenerate double-excitation, $(\phi_0, \phi_0) \to (\bar{\phi}, \phi_a)$, where the other electron occupying the HOMO is excited to the antibonding orbital, separated in energy only by the tunnel-splitting. Doubles are absent in the KS response [14], but they are essential in this case for a correct prediction of the nature and energy of the interacting state: for example, it is needed to lead to a charge-neutral excited state on each atom [31]. The presence of double excitations immediately leads to poles in the frequency-dependence of the exchange-correlation kernel [14]; the static correlation implies the poles are ubiquitous and will be investigated in future work.

Acknowledgement This work is supported in part by the American Chemical Society's Petroleum Research Fund and the Research Foundation of CUNY.

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