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Accurate double excitations from ensemble density functional calculations

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The recent use of a new ensemble in density functional theory (DFT) to produce direct corrections to the Kohn-Sham transitions yields the elusive double excitations that are missed by time-dependent DFT (TDDFT) with the standard adiabatic approximation. But accuracies are lower than for single excitations, and formal arguments about TDDFT suggest that a correction kernel is needed. In principle, ensemble DFT with direct corrections at the exchange level must yield accurate doubles in the weakly correlated limit. We illustrate with exact calculations and analytic results on the Hubbard dimer. We also explain the error in formal arguments in TDDFT. *Published by AIP Publishing.*
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I. INTRODUCTION

Time-dependent density functional theory (TDDFT) is a popular tool for calculating electronic excitations¹⁻⁴ but with current approximations, has some severe limitations. Within the adiabatic approximation used in almost all practical calculations and all standard codes, double (and multiple) excitations are entirely missed by TDDFT.⁵ While in some cases these can be recovered in an ad-hoc fashion using dressed TDDFT,^{6,7} which approximates the frequency dependence, there is no general procedure for capturing these relevant excitations.

On the other hand, ensemble DFT (EDFT) is almost as venerable, but is much less used.⁸⁻¹⁰ Unlike TDDFT, which employs linear response around the ground-state to deduce excitation energies, EDFT is based on a variational theorem of ground and excited states (with monotonically decreasing weights), from which individual transition frequencies can be deduced. Using the original ensemble of Gross, Oliveria, and Kohn (GOK),⁸ there has been much formal progress over three decades, but accurate approximations have been difficult to develop. An important step forward came with the identification of ghost-interaction errors and their removal in the work of Papaconstantinou, Gidopoulos, and Gross,¹¹ and in using the symmetry-adapted Hartree-exchange,^{12,13} now referred to as the ensemble exact exchange (EEXX).¹⁴ Furthermore, new work in the generalized adiabatic connection and the investigation of charge transfer within EDFT,^{15,16} as well other recent contributions,¹⁷⁻²⁰ have all been important to push EDFT forward. But these recent publications rarely focus on double excitations, except in Ref. 21.

In Ref. 21, an alternative ensemble (GOK II) was examined, which has several formal and practical advantages. The GOK ensemble has the same weight for each state,

except for its highest multiplet, while the GOK II ensemble also has the same ensemble weight for each state, except for its ground state. Moreover, using the exact-exchange approximation (EEXX) mentioned and taking the weights of excited states to (almost) zero, Ref. 21 found a simple direct ensemble correction (DEC) to Kohn-Sham (KS) transition frequencies, analogous to expressions in TDDFT. Preliminary tests on atoms and a simple model (1D Hooke's atom) showed that, for single excitations, results were comparable to or better than standard TDDFT results. More importantly, double excitations were predicted by the new method, but substantially less accurately than for singles in every case.

While Ref. 21 made progress in understanding EDFT, both in developing the theory and testing it on atoms and a model system, it left an important question unanswered. All test cases had single excitations close to the double excitations and were chosen to ensure that this was the case. This is the condition needed to apply dressed TDDFT, but is not generic. Moreover, in these tests, the accuracy of the double excitations from EDFT was about half of that when compared to single excitations.

It has long been claimed that, by truncating the response equations of linear-response TDDFT with the exchange kernel, the results agree exactly with DFT perturbation theory, both for two electrons²² and more generally.²³ But for two electrons, the exchange kernel is frequency-independent and so cannot produce double excitations. The frequency-dependence needed to produce double excitations requires correlation contributions to the kernel in TDDFT.²⁴ This would imply that double excitations require some correlation contribution to be accurate. But the DEC/EEXX approximation in EDFT is a purely exchange term, so how can it produce these double excitations?

The present work addresses the following question: Does the DEC method of Ref. 21 really produce a useful path toward calculating double excitations, or are their results more-or-less

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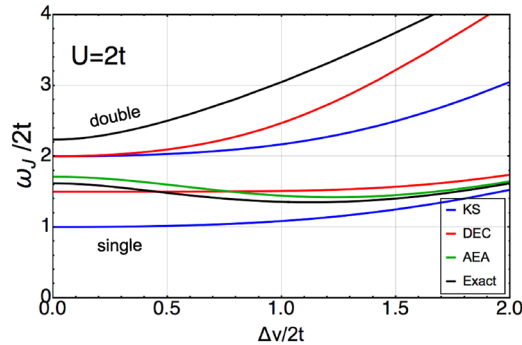


FIG. 1. Transition frequencies versus onsite potential difference for the weakly correlated Hubbard dimer at $2t = 1$. The exact many body solution (black) for single (bottom four curves) and double excitation (top three curves) is compared against the Kohn Sham (KS), Adiabatically Exact Approximation (AEA), and Direct Ensemble Correction (DEC).

accidental? More precisely, is there any limit in which their method becomes exact for double excitations?

We answer these questions with calculations on a simple model, the asymmetric Hubbard dimer, which provides explicit analytic results, and an in depth analysis of the errors that is not currently possible on larger, more realistic systems. Our principal results are shown in Fig. 1 and described in detail within. While DEC in EDFT and adiabatic TDDFT both yield accurate results (but not everywhere) for the first single excitation, only DEC makes a prediction for the double and is typically accurate for weakly correlated systems. We find a substantial exchange correction to the Kohn-Sham transition of the double-excitation, except in the symmetric case. We also explain the connection with TDDFT and the relation among various expansions in powers of the coupling constant. Finally, we explain why correlation is needed to find double (and multiple) excitations in TDDFT, but not in EDFT.

II. BACKGROUND

A. Görling-Levy perturbation theory

Görling-Levy (GL) perturbation theory²⁵ is the appropriate tool for studying the coupling-constant dependence of individual eigenenergies in DFT for weakly correlated systems. Expanding the energy of the J -th many-body state in powers of λ , the electron-electron repulsion, while keeping the density fixed (the adiabatic connection^{25,26}), one finds

$$E_J = E_J^{(0)} + \lambda \Delta v_{JJ} + \lambda^2 \left(\sum_{J' \neq J} \frac{|v_{c,J'J}|^2}{E_{J'}^{(0)} - E_J^{(0)}} - v_{c,J,J} \right), \quad (1)$$

where $E_J^{(0)}$ is the sum of the KS eigenvalues of the occupied orbitals in the J th many body state, v_{JJ} is the expectation value of the electron-electron repulsion operator minus the Hartree and exchange potentials,²⁷ and $v_{c,J,J}$ is the expectation of the 2nd-order correlation potential. Here we label excitations by the level of the excitation of the adiabatically connected KS determinant relative to the occupation of the KS ground state.²⁴

B. Time-dependent DFT

TDDFT yields transition frequencies via linear response. The exact density-density response function is

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \sum_{J \neq 0} \frac{m_J(\mathbf{r}) m_J^*(\mathbf{r}')}{\omega - \omega_J + i0_+} + c.c. (\omega \rightarrow -\omega), \quad (2)$$

where $m_J(\mathbf{r}) = \langle 0 | \hat{n}(\mathbf{r}) | J \rangle$, $\hat{n}(\mathbf{r})$ is the density operator, and transitions occur at its poles.³ The KS counterpart is its value when $\lambda \rightarrow 0$, keeping the density fixed. Then the wavefunctions become single Slater determinants (typically), and the difference in the inverse of the two response functions is called the Hartree-exchange-correlation kernel.²⁴ Because the density is a single-particle operator, $m_J^{(0)}(\mathbf{r}) = 0$ unless J is a single-particle excitation, i.e., double excitations do not appear in the KS response. If the kernel is then approximated as frequency-independent (called the adiabatic approximation), it does not affect the pole-structure, so the approximated response has only single excitations. In the specific case of two electrons whose ground-state is a singlet, the exchange kernel is static. Thus, correlation effects (at least second-order in λ) are needed in the TDDFT kernel to extract double excitations. In the approximate kernel of dressed TDDFT, which applies only to doubles that are strongly coupled to singles, the Hamiltonian is evaluated between KS determinants,^{28,29} yielding a numerator in the approximate kernel that is second-order in the electron-electron repulsion.

In a generic electronic system, there are many more double excitations than single excitations, and these doubles may or may not be strongly coupled to a particular single excitation. However, in Coulomb systems, there are strong patterns in the positioning of excitations in the spectrum. For example, all double excitations in the He atom are in fact auto-ionizing resonances in the continuum. For small molecules, double excitations that are optically allowed are often close to a single excitation, and for these, the theory of dressed TDDFT yields a practical approach, and hence, there are more results for such double excitations using TDDFT in the literature and only those cases were studied in Ref. 21. The conundrum about this state of affairs is very simple. If double excitations have contributions to first-order in the coupling-constant, then why are correlation contributions needed in the TDDFT kernel in order to find them?

C. Ensemble DFT

Ensemble DFT is based on a variational principle for ensembles that are a mixture of the lowest M electronic eigenstates, for a chosen set of weights $\mathbf{w} = \{w_J\}_{J=0 \dots M-1}$ that are normalized and monotonically decreasing. Just as in ground-state DFT, one can define $F_{\mathbf{w}}[n]$ which, when added to the external potential and minimized over (ensemble) densities, yields the ensemble energy.⁸⁻¹⁰ The GOK ensemble has weight w for the highest state, and all others are chosen equal. One can also define an ensemble KS system of non-interacting electrons by using the same ensemble and the correct minimizing ensemble density. The change in $F_{\mathbf{w}}$ between interacting and non-interacting defines the ensemble Hartree-exchange-correlation energy $E_{HXC,\mathbf{w}}[n]$, whose

functional derivative yields the corresponding contribution to the KS potential.

One complication of EDFT is that a range of values of w is allowed (as long as normalization is possible), and the total energy of the system E_w is exactly linear with respect to w , so its slope is related to the transition frequencies of the system. For a bi-ensemble of a ground and first excited state, the slope is simply the transition frequency between them. In practice, almost all approximations lead to non-linear behavior with w , leading to different predictions depending on the value of w chosen. The (traditional) Hartree energy, being quadratic in the density, has unphysical cross terms proportional to $w_J w_{J'}$, which are referred to as ghost interaction errors. The careful removal of these errors from Hartree and exchange together yields greatly increased accuracy.¹¹ Most recently, this ensemble exact exchange (EEXX)¹⁴ has been shown to be the correct (energy-minimizing) choice to first-order in the interaction.

Reference 21 used an alternative ensemble suggested by GOK (called GOK II), in which each state in the ensemble has weight w , except the ground state. They also considered the limit as $w \rightarrow 0$, thereby using only the slope around $w = 0$, yielding a unique answer that is simply a correction to the ground-state KS transitions; i.e., there is no need to do an additional self-consistent cycle for $w \neq 0$. Finally, they also noted that, for the GOK II ensemble, within EEXX, this direct energy correction requires only energy differences between the level of interest and the ground state (and not all intervening states, as is otherwise the case). Plugging in the EEXX into the DEC approximation and in the absence of degeneracies,

$$\Delta\omega_J^{EEXX} = \lambda(H_J - H_0), \quad (3)$$

where H_J is an exchange contribution depending only on the KS orbitals and energies of the J th state [Eq. (9) of Ref. 21]. They also calculated both single and double excitations for a series of atoms and ions and for the 1D Hooke's atom. In all cases, the DEC/EEXX yielded single excitations with accuracy comparable to that of TDDFT with standard approximations, while double excitations were also predicted, but with less accuracy. The errors were ascribed to correlation effects missed by DEC/EEXX.

D. Hubbard dimer

The Hubbard model is a paradigm of strongly correlated physics and typically consists of an infinite lattice, with hopping and site-interaction terms.³⁰ The dimer is likely the smallest meaningful model of interacting fermions, with a Hilbert space of just 6 states.³¹ It mimics strong correlation effects of bond stretching, but is not a quantitatively accurate model for any first-principle Hamiltonian. In its usual form, it is a simplified version of a minimal-basis model of two electrons on two atoms, with one basis function per atom. The Hamiltonian is

$$\hat{H} = -t \sum_{\sigma} (\hat{c}_{1\sigma}^{\dagger} \hat{c}_{2\sigma} + h.c.) + U \sum_i \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow} + \sum_i v_i \hat{n}_i. \quad (4)$$

Here t is the electron hopping energy, U is the repulsion between the particles in each site, and the symmetry of the

dimer is controlled by the potential difference, $\Delta v = v_2 - v_1$, and the density is characterized by a single number, $\Delta n = n_1 - n_2$. The Hubbard dimer is extremely useful for understanding ground-state DFT,³¹ especially when correlations are strong, and extensions and variations have been used in many time-dependent problems to understand TDDFT. Its value comes from the ability to solve most problems analytically. Because the double excitation in the dimer is never close to the single excitation, dressed TDDFT cannot be applied.²⁴ A full discussion of how linear-response TDDFT works for the dimer has just been completed.²⁴ Recently, the dimer has been used to illustrate EDFT weight-dependence,³² novel approaches to bandgaps,³³ and approaches to noncollinear magnetism.³⁴

III. THEORY

Above, we have given three different formalisms that yield excitation energies with different types of DFT theories. If implemented exactly, they must all yield the same answers. Moreover, the transition frequencies, when expanded in powers of the electron-electron coupling constant, must be the same, term-by-term. However, when approximations are used, such as EEXX in DEC or the adiabatic approximation in TDDFT, there is no such guarantee.

The simplest to compare are the GL perturbative expansion and the DEC in EDFT. If the EEXX truly yields the exact exchange contribution to any excitation, it must agree with GL to first-order in the coupling constant, for any excitation. In Ref. 21, it was referred to as symmetry-eigenstate Hartree-exchange, as a sensible choice was made for the ensemble eigenstates. It has since been argued¹⁴ that this choice minimizes the ensemble energy and so should always yield the correct answer (to leading order in the coupling constant).

Below, we confirm that indeed all three approaches agree for the Hubbard dimer, finding the next corrections and explaining the complexities of the kernel in TDDFT that are needed to recover this result.

IV. RESULTS

Here, we study only singlet states, avoiding the complexities of spin-flipping transitions. There are then only 2 transitions, one to a single and one to a double excitation (the nature of a transition is determined by adiabatically turning off the interaction and labelling it based on its KS determinant). There are two parameters: Δv measures the degree of asymmetry, while U measures the strength of the interaction. When $\Delta v = U = 0$, the dimer is a symmetric tight-binding problem. When $\Delta v/(2t)$ grows large, the dimer is highly asymmetric, with both particles mostly on one site (in the ground state); when $U/(2t)$ grows large, the dimer has strong correlation effects, just like when a bond is stretched, and many ground-state density functional approximations fail. For $\Delta v = 0$, the expansion about weak correlation diverges at $U = 4t$, while the λ -dependence is found by replacing U by λ for a fixed Δn .

Many of the most important results of this study appear in Fig. 1. The solid black lines are the analytic results for the single (lower) and double (higher) excitations.^{24,31,35,36} The value $U = 2t$ is chosen to be a significant correlation strength, but still in the weakly correlated regime. The blue lines are the corresponding KS transitions, with the double at exactly twice the single. These are the exact KS transitions, meaning the transitions between occupied and unoccupied KS orbitals of the exact ground-state KS potential, found from the functional derivative of the exact ground-state XC energy.³¹

There are many lessons in this figure. As is typical for weakly correlated systems, the KS transition frequencies are a reasonable zero-order approximation to the exact optical excitations.³⁷ We define $\Delta\omega_J = \omega_J - J\omega_s$ as the difference between the exact and KS transition frequency. We also note that the accuracy of the KS transitions is not uniform with Δv . At $\Delta v = 0$ (the symmetric case), $\Delta\omega_2 < \Delta\omega_1$. But, as Δv grows, and especially when $\Delta v > U$, the single excitation energy curve approaches its KS alterego, but the double excitation does not. This is because, in the charge transfer regime when $\Delta v > U \gg 2t$, both electrons are on the same site for the ground state (e.g., site 1) and on opposite sites for the first excitation (and also not interacting), whereas for the double, both electrons are again on one site (site 2). The reverse is true for the Mott-Hubbard regime, defined for the region of $U \gg \Delta v \gg 2t$.

Next we consider TDDFT within the adiabatically exact approximation (AEA). The extremely small Hilbert space means that the response function is not a matrix but a single function²⁴ that vanishes at each excitation,

$$\chi^{-1}(\omega) = \chi_S^{-1}(\omega) - f_{HXC}(\omega). \quad (5)$$

If f_{HXC} is ignored, transitions occur at $\omega = \omega_s$. If $f_{HXC}(\omega = 0)$ is used (AEA), it shifts the positions of the single excitations, but still misses all higher excitations. This is the best possible performance of the adiabatic approximation because we used the exact ground state functional to determine $f_{HXC}(\omega = 0)$. This produces the green curve for the single excitation in Fig. 1. We see that AEA is extremely accurate and becomes even more so as the asymmetry is increased. Notice that the AEA becomes accurate as correlations weaken because the coefficient of the numerator of the pole in $f_{XC}(\omega)$ is of the order $O(\lambda^2)$, so its effect on the position of the single excitation vanishes²⁴ as $\lambda \rightarrow 0$. But there is no analogous curve for the double excitation, as there is no way to access the double within linear-response TDDFT without a frequency dependent kernel. (Even higher-order perturbation theory can at most yield doubles that are twice the singles, which would not be accurate.³⁸)

Next we apply EDFT to the dimer. The results for the ground state and first single excitation are well known^{31,36} because they can be extracted from a bi-ensemble of the ground and first excited states, where there is no difference between the GOK and GOK II ensembles. But to extract the double excitation, we use a three state GOK II ensemble. Applying the DEC/EEXX to the GOK II ensemble, with the exact KS eigenstates of the Hubbard dimer, i.e., Eq. (3), we find

$$\Delta\omega_1^{DEC} = \frac{U}{2} \left(1 - \frac{\Delta n^2}{4} \right), \quad \Delta\omega_2^{DEC} = \frac{U}{2} \Delta n^2. \quad (6)$$

These results agree perfectly with Eq. (1), applied to the dimer and expressed in terms of the ground-state density.²⁴ These yield the red lines in Fig. 1.

To analyze and expand on these results, in Fig. 2, we directly plot $\Delta\omega_J$ for each transition. This is the true measure of the quality of an approximate treatment of excitations, as the KS transitions are determined entirely by ground-state DFT. We use the single as a test case, as the analytic results are already known. The DEC/EEXX curves are comparable to those of the AEA TDDFT, doing better for $\Delta v < 2t$, but worse as the asymmetry increases, similar to its performance for both atoms and Hooke's atom.²¹ As $\Delta v \rightarrow \infty$, $\Delta n \rightarrow 2$, turning off the corrections to the single.

Now we focus on the main interest, the double excitation. Here DEC/EEXX yields no correction at $\Delta v = 0$, but everywhere else reduces the error of the KS transition, but with substantially greater error than for the single. This is consistent with the earlier results, but can we discern here if this is accidental or not? To do this, we take an advantage of the model's simplicity and the many results that are already known. One peculiarity is that, performing a many-body expansion for fixed Δv as a function of U , one finds that the double excitation has no first-order correction, i.e., correction to the tight-binding result is of order U^2 .²⁴ This would appear to make it useless for our purposes. However, ω_s , by virtue of its dependence on the ground-state density, *does* have a first-order correction in λ , which means that $\Delta\omega_2$ is also first-order and is correctly captured by the DEC/EEXX approximation, as shown. This correction happens to vanish at $\Delta v = 0$. (This means that studying only the symmetric dimer would produce qualitatively incorrect conclusions on this point.)

Because of the simplicity of the model, we can use the results of Ref. 24 to derive the next correction in powers of U (or λ), by converting Δv -dependence to Δn -dependence,

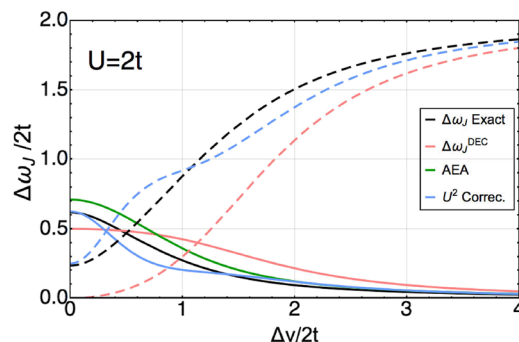


FIG. 2. Correction to the KS transitions of Fig. 1, both exact and various approximations, where solid lines are single excitations and dashed lines are double. The correction to the single turns off with increasing asymmetry, but not so for the double excitation. The DEC/EEXX approximation correctly captures both effects. Also included is the leading correlation contribution (blue), which further improves the results, when the system is weakly correlated. Here the black $\Delta\omega_J$ curves correspond to the exact result (see text for details), the pink $\Delta\omega_J^{DEC}$ curves are for the DEC/EEXX, the green curve is for the AEA, and the blue curves are for the second order corrections.

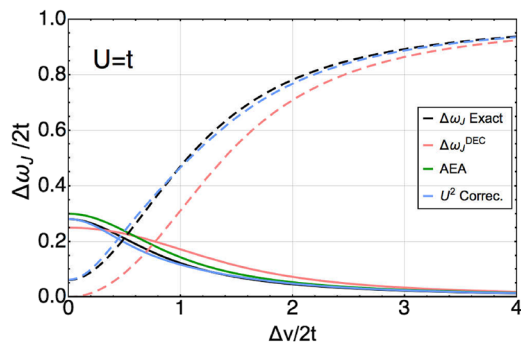


FIG. 3. The same as Fig. 2, but at a weaker correlation of $U = t$, showing that the DEC improves as correlation weakens, and the second order correction agrees even better.

yielding

$$\begin{aligned}\Delta\omega_1^{(2)} &= \frac{\sqrt{4 - \Delta n^2}(4 - 13\Delta n^2 + 3\Delta n^4)U^2}{64(2t)}, \\ \Delta\omega_2^{(2)} &= \frac{\sqrt{4 - \Delta n^2}(4 + 11\Delta n^2 - 3\Delta n^4)U^2}{32(2t)}.\end{aligned}\quad (7)$$

Note that these corrections *cannot* be deduced from the DEC/EEXX of Ref. 21 since by definition, the DEC/EEXX contains no correlation and therefore no higher order corrections. These are shown in Fig. 2 and (almost) everywhere reduce the error of DEC, as expected in the weakly correlated regime. Moreover, they do produce great improvement in the double at $\Delta v = 0$, and so provide a benchmark for correlation corrections to DEC/EEXX. Finally, we note that these corrections would be extremely difficult to calculate for a system with an *ab initio* Hamiltonian, as they require knowing the exact ground-state, the exact Kohn-Sham eigenstates, and performing second-order Görling-Levy perturbation theory on those states.

To make sure our understanding is correct, in Fig. 3, we show the results when $U = t$, i.e., the same system but with weaker correlation. Now the second-order correction is almost perfect everywhere, showing that the perturbation theory is converging. Moreover, the absolute errors in DEC have halved but remain large out to about $\Delta v = 2U$. In our last figure, Fig. 4, we show what happens as GL perturbation theory begins to fail.

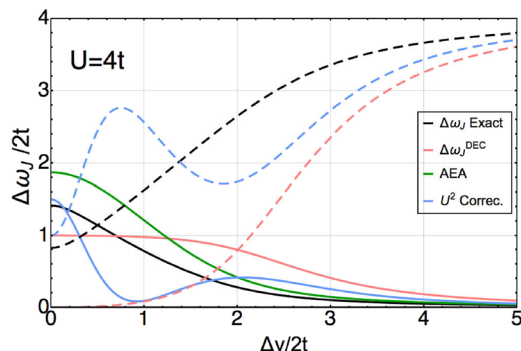


FIG. 4. The same as Fig. 2, but at a stronger correlation of $U = 4t$, showing the failure of DEC when correlation is strong. Here DEC fails for small Δv , but nonetheless agrees for both DEC and its second-order correction for large values of Δv , showing that the system becomes weakly correlated when asymmetry dominates over correlation strength.

Near $\Delta v = 0$, DEC fails completely, with equal corrections to the first and second excitation, making the gap precisely zero. This is where the convergence of perturbation theory breaks down, and the KS transitions are not a good starting point. However, even here, for $\Delta v \gg U$, the gap is much larger, and both single and double corrections become accurate. This is consistent with the claims of Ref. 24 that for $\Delta v > U$, a system is always weakly correlated, no matter how large U is, as far as DFT is concerned.

V. DISCUSSION

So what can we conclude from this very simple model? The most important thing is that, generically, the DEC/EEXX approximation yields a meaningful and non-zero correction to a double excitation, producing the exact linear term in the GL perturbation for fixed density. In special cases where this term vanishes identically, it is of course useless. In some ways, our case is more typical than either of those studied in Ref. 21, as all cases studied there involved double excitations in the regions of the energy spectrum with single excitations nearby (where dressed TDDFT could be applied), but here we have a double excitation without a single nearby (and hence dressed TDDFT would not work).

To understand why TDDFT linear response requires a correlation kernel to capture an exchange contribution, it is crucial to understand that an expansion of the kernel in the coupling-constant is not a meaningful concept. Consider how would TDDFT capture these effects if correlation is included? Reference 24 gives the answer for this model. There is a pole in the kernel that generates the double excitation. It has the form

$$f_{HXC}(\omega) \approx \frac{a}{\omega - \omega_p}.\quad (8)$$

Now, both the numerator and ω_p have expansions in powers of λ . While ω_p contains all orders, a starts at second-order. It is meaningless to speak of an expansion of the kernel in powers of λ , as this expansion always fails as ω approaches the pole. Both the numerator and the transition frequencies have well-behaved expansions in powers of λ and can be usefully approximated in a power series when the system is weakly correlated, but the kernel in TDDFT never does. The arguments of Refs. 23 and 22 focus on the denominator alone, neglecting the requirement of having a non-zero numerator to the order given and so are only correct for single excitations.

Although the Hubbard dimer is not a quantitative model of anything, it roughly approximates a minimal basis model for a diatomic with two valence electrons. In the symmetric case, this would correspond to H_2 . As the bond is stretched, $t \rightarrow 0$, but U and Δv remain finite, so $U/(2t)$ and $\Delta v/(2t) \rightarrow \infty$. For H_2 , by symmetry, $\Delta v = 0$, and this may present special difficulties for DEC/EEXX, as the linear contribution might be unusually small. On the other hand, for LiH, it should work well.

Finally, while this model may appear overly simple, its great power lies in the ability to show transparently what is going on. It clearly demonstrates that EDFT *can* accurately capture double excitations, even when using an EEXX

approximation, with no correlation. It would be highly non-trivial (and time consuming) to perform all these TDDFT and EDFT calculations on more realistic systems and impossible to write down and examine the behavior of analytic expressions.

ACKNOWLEDGMENTS

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