

Can ensemble density functional theory yield accurate double excitations?

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The recent use of a new ensemble in density functional theory (DFT) to yield direct corrections to the Kohn-Sham transitions yields the elusive double excitations that are missed by time-dependent DFT with the standard adiabatic approximation. But accuracies are lower than for single excitations, and formal arguments suggest that direct corrections at the exchange level should not be sufficient. We show that in principle, EDFT with direct corrections can yield accurate doubles and explain the error in naive formal arguments about TDDFT. Exact calculations and analytic results on a simple model, the Hubbard dimer, illustrate the results, showing that the answer to the title question is typically yes.

Time-dependent density functional theory (TDDFT) is a popular tool for calculating electronic excitations[1–4], 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, 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[6–8]. Unlike TDDFT, which employs linear response around the ground-state to deduce excitation energies, EDFT is based on a variational theorem for a decreasing set of eigenstates, from which transition frequencies can be deduced. Using the original ensemble of Gross, Oliveria, and Kohn (GOK) [6], 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[9], and in using the symmetry-adapted Hartree-exchange[10, 11], now referred to as the ensemble exact exchange (EEXX)[12]. Furthermore, new work in the generalized adiabatic connection, and the investigation of charge transfer within EDFT [13, 14], as well other recent contributions[15–18] have all been important to push EDFT forward. But these recent publications rarely focus on double excitations, except in Ref.[19].

In Ref.[19], an alternative ensemble (GOK II) was examined, which has several formal and practical advantages. Moreover, using the exact-exchange approximation above, and taking the weights of excited states to (almost) zero, Ref.[19] found a simple direct ensemble correction (DEC) to Kohn-Sham 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.

The present work addresses the question: Does the DEC method of Ref.[19] really produce a useful path toward calculating double excitations, or are their results more-or-less accidental, in the sense that there is no limit in which the method yields the right corrections to KS transitions? There are formal reasons for raising these concerns. In TDDFT correlation contributions to the XC kernel are needed to produce the frequency dependence required to generate double excitations. But the exchange correction used in DEC does not include correlation. So how can it yield accurate corrections?

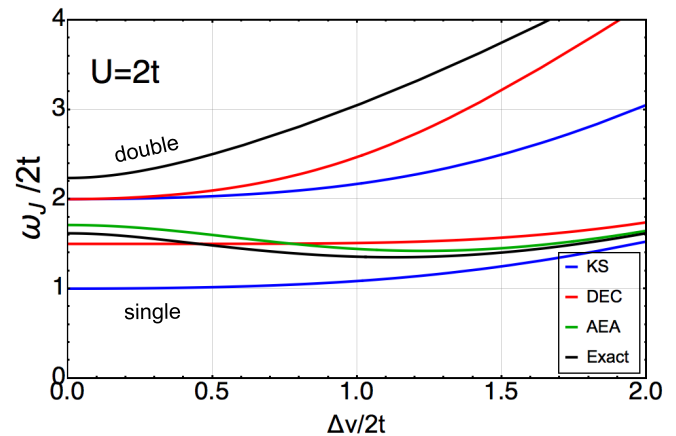


FIG. 1. Transition frequencies versus onsite potential difference for the weakly correlated Hubbard dimer at with $2t = 1$. The exact many body solution (black) for single (bottom four curves) and double excitation (top three curves) are compared against the Kohn Sham (KS), Adiabatically Exact Approximation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

We answer these questions with calculations on a simple model, the asymmetric Hubbard dimer, which provides explicit analytic results. 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. 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.

Görling-Levy (GL) perturbation theory [20] is the appropriate tool for studying excitations 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[20, 21]), one finds

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

where the KS energy of the J -th state is ϵ_J , v_{JJ} is the expectation value of the electron-electron repulsion operator minus the Hartree and exchange potentials [22], 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 [23].

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

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

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[23]. 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 TDDFT to extract double excitations. The approximate kernel of dressed TDDFT, which applies only to doubles that are strongly coupled to singles, uses the square of the exchange matrix element of the Hamiltonian, i.e., a second-order contribution [24, 25]. Thus, without correlation contributions, TDDFT cannot typically produce double excitations.

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 [6–8]. The GOK ensemble has weight w for the highest state, and all others 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 $E_{\text{HXC},\mathbf{w}}[n]$, 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 , with its slope related to transitions of the system. 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 [9]. Most recently, this ensemble exact exchange (EEXX) [12] has been shown to be the correct (energy-minimizing) choice to first-order in the interaction.

Ref.[19] 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:

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

where H_J is an exchange contribution depending only on the KS orbitals and energies of the J -th state (Eq.(9) of Ref.[19]). 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.

But the DEC/EEXX approximation of EDFT contains only a first order correction to the KS transition frequencies, and so cannot generate corrections that are second-order in the interaction (with fixed density). So, are the first-order corrections that it produces for multiple exci-

tations trivial or meaningful? And if meaningful, how do such corrections arise in TDDFT?

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 [26]. The dimer is likely the smallest meaningful model of interacting fermions, with a Hilbert space of just 6 states[27]. 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 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 [27], 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. A full discussion of how linear-response TDDFT works for the dimer has just been completed[23]. Recently, the dimer has been used to illustrate EDFT weight-dependence[28], novel approaches to band gaps[29], and approaches to noncollinear magnetism [30].

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 $U = 4t$. Any 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 well-known analytic results for the single (lower) and double (higher) excitations [23]. 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[27].

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[31]. 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), on opposite sites for the first excitation (and also not interacting), whereas for the double, both electrons are again 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 the response function is not a matrix but a single function [23] that vanishes at each excitation:

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

If f_{HXC} is ignored, transitions occur at $\omega = \omega_s$. If $f_{\text{HXC}}(\omega = 0)$ 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 $f_{\text{HXC}}(\omega = 0)$. This produces the green curve for the single excitation in Fig. (1). We see that AEA is extremely accurate (because correlation is weak), and becomes even more so as the asymmetry is increased. 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 [32]).

Next we apply EDFT to the dimer. The results for the single are well-known [33], because they can be extracted from a bi-ensemble of the ground and first excited states, and 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 Eq.(3) to the KS eigenstates of the Hubbard dimer, one finds:

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

which agree perfectly with Eq.(1), applied to the dimer and expressed in terms of the ground-state density [23]. 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

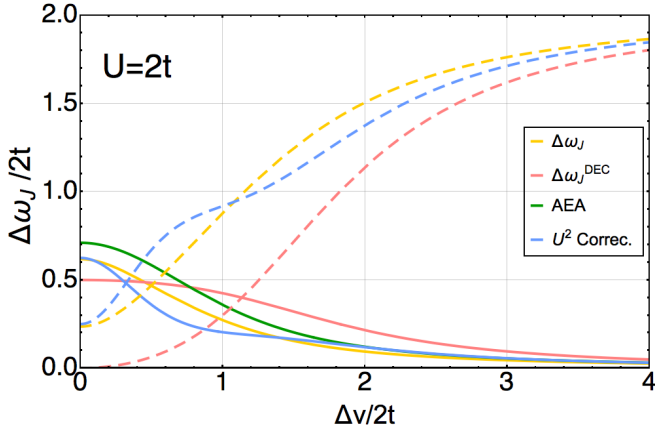


FIG. 2. Correction to the KS transitions of Fig. 1, both exact and various approximations, where solid lines are single excitations, dashed are double. The correction to the single turns off with increasing asymmetry, but not so the double excitation. The DEC/EEXX approximation correctly captures both effects. Also included is the leading correlation contribution, which further improves the results, when the system is weakly correlated.

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 the Hooke’s atom [19]. 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 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 [23]. 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.[23] to derive the next correction in powers of U (or λ), by converting Δv -dependence to Δn -

dependence, 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. [19]. 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.

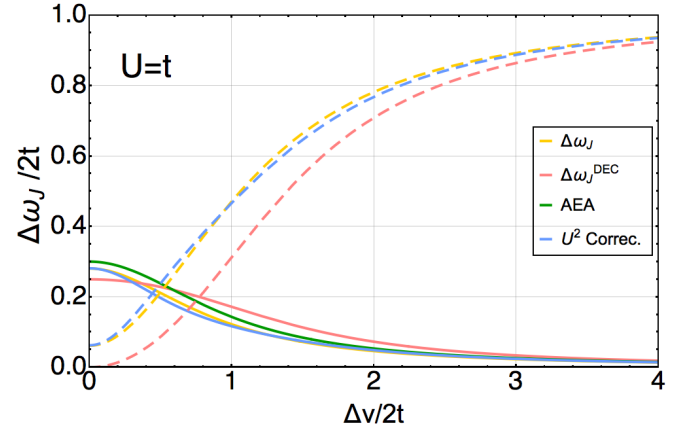


FIG. 3. Same as Fig. 2 but at a weaker correlation of $U = t$, showing that the DEC improves as correlation weakens, and the second order correction agrees even better.

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 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. Near $\Delta v = 0$, DEC fails completely, with equal corrections to the first and second excitation, making the gap precisely zero. This is where 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.[23], that for $\Delta v > U$, a system is always weakly correlated, no matter how large U is, as far as DFT is concerned.

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

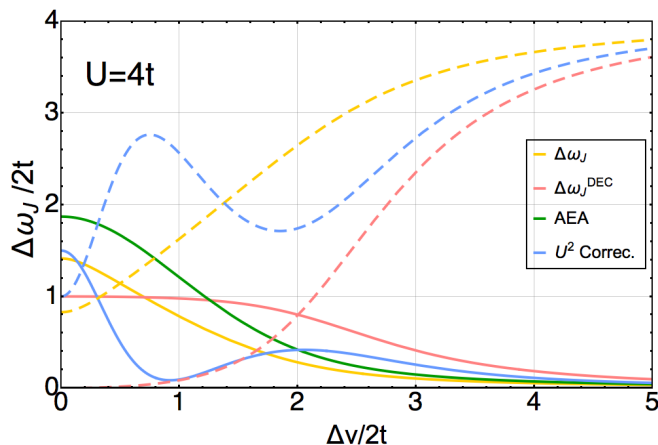


FIG. 4. Same as Fig. 2, but at a stronger correlation of $U = 4t$, showing the failure of DEC when correlation is strong. Here DEC fails for small Δv , but nonetheless agrees for both DEC and its second-order correction for large values of Δv , showing that the system becomes weakly correlated when asymmetry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

is more typical than either of those studied in Ref.[19], as all cases studied there involved double excitations in 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).

How would TDDFT capture these effects if correlation is included? Ref.[23] gives the answer for this model. There is a pole in the kernel that generates the double excitation. It has the form:

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

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.

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. A longer paper on the subject is in preparation.

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