Excitations in Time-Dependent Density-Functional Theory

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An approximate solution to the time-dependent density-functional theory response equations for finite systems is developed, yielding corrections to the single-pole approximation. These explain why allowed Kohn-Sham transition frequencies and oscillator strengths are usually good approximations to the true values, and why sometimes they are not. The approximation yields simple expressions for Görling-Levy perturbation theory results, and a method for estimating expectation values of the unknown exchange-correlation kernel.

Traditional density-functional theory (DFT) is a popular and efficient method for the calculation of ground-state properties of interacting many electron systems [1]. There exist several extensions of the basic formalism that allow extraction of excited-state properties. One popular approach is via *time-dependent* DFT (TDDFT), in which the interacting system in a time-dependent external field is mapped exactly to a noninteracting time-dependent Kohn-Sham system with the same time-dependent density [2]. If a weak time-dependent electrical field is considered, this leads [3] to a Dyson-like response equation for the exact susceptibility of the interacting electronic system. For finite systems, discrete poles of this susceptibility occur at the true transition frequencies, and the strengths of these poles are related to oscillator strengths. Solution of these equations has been implemented in several quantum chemical packages, and excitation spectra of many molecules have been calculated and reported in numerous papers (see the references in Ref. [4]). Once an accurate ground-state Kohn-Sham potential is used, transition frequencies are typically within about 0.2 eV of experiment. Oscillator strengths are usually good in these calculations (within a factor of 2), but not always. There are considerable subtleties in applying TDDFT to extract the optical response of solids [5].

The benefit of using TDDFT to extract optical spectra is that it combines moderate accuracy with inexpensive calculation, just as in the ground-state case. But even beginning from an *exact* ground-state KS potential, the spectrum still depends on the unknown exchange-correlation (XC) kernel, i.e., the functional derivative of the time-dependent XC potential. This is often approximated by the crude but reliable adiabatic local-density approximation (ALDA). These TDDFT calculations compare very favorably with configuration-interaction singles calculations, the only alternative that is comparable in computational cost [6]. Higher level calculations, such as more complete configuration-interaction, Bethe-Salpeter, or quantum Monte Carlo, can be made more accurate, but

cost more, limiting their use to smaller systems. TDDFT has recently been applied to electron-transfer problems in biological systems [7].

Although TDDFT methodology has been implemented and is being used widely, understanding of its accuracy and reliability, as well as its relation to other methods, has been slow. The relation to first-order Görling-Levy (GL) perturbation theory has been found [8,9], as well as the connection with the *GW* approximation [8]. The extreme case of stretched H_2 has recently been studied by several authors [10–12], although this also represents difficulties for the ground-state theory [13]. By using a matrix formulation of Casida [14], the present paper shows how, when the excitations of a system are discrete, an approximate solution, that can be made arbitrarily accurate, can be used to understand and explain many trends in the results of TDDFT calculations.

To demonstrate our results, we apply them to the prototype systems of the He and Be atoms. We chose these because their exact ground-state KS potentials are known [15], and because their lowest allowed transitions are characteristic of two distinct classes of interest: In the He atom the $1s$ to $2p$ singlet transition is at 21.22 eV, while the KS transition, i.e., the energy difference between the $1s$ and $2p$ ground-state KS orbital energy levels, is 21.15 eV, less than 0.1 eV smaller. On the other hand, in the Be atom, the $2s$ to $2p$ level singlet transition is at 5.3 eV, but in the KS case it is at 3.6 eV. We explain below the fundamental difference between these two systems, and why the KS eigenvalues are a good approximation in the first case, but a poor approximation in the second. Furthermore, the oscillator strength for the $1s$ to $2p$ transition in the He atom is 0.27, but 0.32 in the exact KS case. Thus the oscillator strength of the He atom KS system is close to the true one, but noticeably less close than the transition frequency. Finally, the $2s$ to $2p$ oscillator strength in the Be atom is 1.37, but 2.54 for the corresponding Kohn-Sham system, far closer than one would expect, given the error in transition frequencies. We discuss why.

We denote the exact KS eigenvalues as ϵ_i and orbitals as $\phi_i(\mathbf{r})$. Casida [14] has written the TDDFT response equations as an eigenvalue equation for the square of the transition frequencies,

$$\sum_{q'} \tilde{\Omega}_{qq'}(\omega) v_{q'} = \Omega v_q, \tag{1}$$

where q is a double index, representing a transition from occupied KS orbital i to unoccupied KS orbital a, $\omega_q = \epsilon_a - \epsilon_i$, $\Omega = \omega^2$, and $\Phi_q(\mathbf{r}) = \phi_i^*(\mathbf{r})\phi_a(\mathbf{r})$. The matrix is

$$\tilde{\Omega}_{qq'}(\omega) = \delta_{qq'}\Omega_q + 2\sqrt{\omega_q \omega_q'}\langle q|f_{\mathrm{HXC}}(\omega)|q'\rangle, \tag{2}$$

where

$$\langle q|f_{\mathrm{HXC}}(\omega)|q'\rangle = \int d^3r \int d^3r' \Phi_q^*(\mathbf{r})f_{\mathrm{HXC}}(\mathbf{r},\mathbf{r}',\omega)\Phi_{q'}(\mathbf{r}'). \tag{3}$$

In this equation, f_{HXC} is the Hartree-exchange-correlation kernel, $1/|\mathbf{r}-\mathbf{r}'| + f_{\mathrm{XC}}(\mathbf{r},\mathbf{r}',\omega)$, where f_{XC} is the unknown XC kernel. A self-consistent solution of Eq. (1) yields the excitation energies ω and the oscillator strengths can be obtained from the eigenvectors [14].

It has been noticed that the KS transition frequencies are often "good" approximations to the true frequencies [16,17]. If the transition frequencies and oscillator strengths are expanded in powers of the coupling constant λ, as in GL perturbation theory [18], the zero-order values are the Kohn-Sham values [19]. In Eq. (3), we see that, if f_{HXC} is small, i.e., if the system is sufficiently weakly correlated, this is correct. We show below that this is *not* the reason why the KS values are good approximations in many systems, such as the He atom, and is especially untrue when the ground state has a near degeneracy, such as for the Be atom.

Our approximate solution relies on the fact that $\langle q|f_{\mathrm{HXC}}|q'\rangle$ decays rapidly with distance from the diagonal, because the overlap of increasingly different orbitals decays by cancellation of oscillations. To zero order, we ignore all off-diagonal elements, finding the small-matrix approximation (SMA) [20],

$$\Omega^{\mathrm{SMA}} = \Omega_q + 2\omega_q\langle q|f_{\mathrm{HXC}}(\omega_q)|q\rangle. \tag{4}$$

The original single-pole approximation (SPA) [3] can be viewed as a special case of SMA when the shift from the KS value is small,

$$\begin{aligned} \omega &= \sqrt{\Omega_q + 2\omega_q\langle q|f_{\mathrm{HXC}}|q\rangle} \\ &= \omega_q + \langle q|f_{\mathrm{HXC}}(\omega_q)|q\rangle + \cdots, \end{aligned} \tag{5}$$

exact to first order in GL perturbation theory [8].

To go beyond SPA, we use a continued-fraction method [21] for inverting a matrix with a dominant diagonal, as it allows for direct resummation of parts of the perturbation expansion. Truncating the expansion at second order in the off-diagonal matrix elements,

$$\Omega = \Omega_q^{\mathrm{SMA}} + \sum_{q'\neq q} \frac{4\omega_q \omega_{q'}|\langle q|f_{\mathrm{HXC}}(\omega_q^{\mathrm{SMA}})|q'\rangle|^2}{\Omega_q^{\mathrm{SMA}} - \Omega_{q'}^{\mathrm{SMA}}}. \tag{6}$$

This is a key result of this paper, leading to many conclusions. First, it yields the exact GL perturbative expression to second order in λ. Expanding $f_{\mathrm{HXC}} = \lambda f_{\mathrm{HX}} + \lambda^2 f_{\mathrm{C}}^{[2]} + \cdots$, we find

$$\omega = \omega_q + \lambda\langle q|f_{\mathrm{HX}}(\omega_q)|q\rangle + \lambda^2\delta\omega_q^{(2)}, \tag{7}$$

where the second-order shift consists of four terms:

$$\begin{aligned} \delta\omega_q^{(2)} = {} & \langle q|f_{\mathrm{C}}^{[2]}(\omega_q)|q\rangle + 2\sum_{q'\neq q} \frac{\omega_{q'}|\langle q|f_{\mathrm{HX}}(\omega_q)|q'\rangle|^2}{\Omega_q - \Omega_{q'}} \\ & + \langle q|f_{\mathrm{HX}}(\omega_q)|q\rangle\langle q|\frac{\partial f_{\mathrm{HX}}}{\partial\omega}(\omega_q)|q\rangle \\ & - \frac{|\langle q|f_{\mathrm{HX}}(\omega_q)|q\rangle|^2}{2\omega_q}, \end{aligned} \tag{8}$$

by consistently treating the relation between ω and λ to second order.

For the ground-state energy, the second-order correction has been identified as playing a key role in constructing accurate functionals, especially in cases of strong static correlation [22]. It is likely to play a similar role for excitations, and can be easily extracted from Eq. (7).

Second, we may now deduce precisely when SPA (or SMA) is valid. Defining the shift from the KS value as

$$\Delta\Omega_q = \Omega - \Omega_q, \tag{9}$$

we rewrite Eq. (6) in the following suggestive form:

$$\Delta\Omega_q = \Delta\Omega_q^{\mathrm{SMA}}\left\{1 + \sum_{q'\neq q} \frac{\Delta\Omega_{q'}^{\mathrm{SMA}}}{\Omega_q^{\mathrm{SMA}} - \Omega_{q'}^{\mathrm{SMA}}}\frac{|M_{qq'}|^2}{M_{qq}M_{q'q'}}\right\}, \tag{10}$$

where $M(\omega_q)_{qq'} = \langle q|f_{\mathrm{HXC}}(\omega_q)|q'\rangle$. A simple estimate of the size of this correction can be given by assuming $M_{qq'} \sim \sqrt{M_{qq}M_{q'q'}}$, a very good approximation for these systems. Then the SMA is valid when

$$\sum_{q'\neq q} \frac{\Delta\Omega_{q'}^{\mathrm{SMA}}}{\Omega_q^{\mathrm{SMA}} - \Omega_{q'}^{\mathrm{SMA}}} \ll 1, \tag{11}$$

i.e., the SMA shift need only be small on the scale of the separation between transition frequencies. Thus, even when the corrections to KS transition frequencies are *large*, SMA remains valid if the poles are well separated.

In the special case when the SMA correction is small compared to a KS transition itself, this result simplifies to

$$\sum_{q'\neq q} \frac{\langle q|f(\omega_q)_{\mathrm{HXC}}|q'\rangle}{\omega_q - \omega_{q'}} \ll 1. \tag{12}$$

For example, the allowed transitions from the ground state of the He atom are listed in Table I. Comparing

TABLE I. Exact results for the He and Be atoms, using numerically exact ground-state Kohn-Sham potentials.

Atom	Transition	Frequency (eV)			Oscillator strength	
		KS[a]	SMA[b]	Exact	KS	Exact[c]
He	$1s \rightarrow 2p$	21.15	21.23	21.22	0.3243	0.2762
	$1s \rightarrow 3p$	23.06	23.10	23.09	8.47(−2)	7.34(−2)
	$1s \rightarrow 4p$	23.73	23.75	23.75	3.41(−2)	2.99(−2)
	$1s \rightarrow 5p$	24.04	24.05	24.05	1.71(−2)	1.50(−2)
	$1s \rightarrow 6p$	24.21	24.22	24.22	9.8(−3)	8.6(−3)
Be	$2s \rightarrow 2p$	3.61	4.95	5.28	2.5422	1.3750
	$2s \rightarrow 3p$	7.33	7.39	7.46	3.79(−2)	9.01(−3)
	$2s \rightarrow 4p$	8.29	8.31	8.33	2.06(−2)	2.3(−4)
	$2s \rightarrow 5p$	8.69	8.70	8.69	1.08(−2)	8.1(−4)
	$2s \rightarrow 6p$	8.90	8.90	8.90	6.3(−3)	7.5(−4)

[a]Exact values published previously [17].
[b]Hybrid SPA results from Ref. [9], converted to SMA.
[c]He numbers are from Ref. [23] and Be numbers are from Ref. [24].

KS transition frequencies with physical ones, we find them good to within less then 0.1 eV. This implies all matrix elements $\langle q|f_{HXC}|q'\rangle$ are small, and SPA is valid. Calculations within ALDA for this case [10] show no difference between full solution of the response equations and the SPA result. The column marked SMA lists SMA results with our best estimate of f_{HXC} for this case, a hybrid of exact exchange with ALDA antiparallel correlation [9]. For the transition to $2p$, the exact exchange result is 21.37 eV [25], showing that there must be substantial cancellation by correlation effects. For this system and others like it, GL perturbation theory converges slowly, while our expansion converges rapidly.

Our other prototype is the excitations from the ground state of the Be atom. For the $2s \rightarrow 2p$ transition, the expectation value of f_{HXC} is relatively large. We expect SMA to work quite well for that transition, but less well for others, since the one strong transition contributes to the correction in Eq. (10), especially having a small denominator. This is born out by the frequency results in Table I. Within ALDA [10], the SMA transition is at 5.27 eV, but the full calculation is 5.08 eV.

In the SMA, in which off-diagonal elements are neglected, the eigenvectors in Eq. (1) remain unit vectors, and the oscillator strengths retain their KS values. When we include the change due to the off-diagonal elements to leading order, we find

$$f = \frac{2}{3}\left(\omega_q \vec{\mu}_q^2 + \sum_{q' \neq q} \frac{4\langle q|f(\omega_q)_{HXC}|q'\rangle \omega_q \omega_{q'} \vec{\mu}_q \vec{\mu}_{q'}}{\Omega_q^{SMA} - \Omega_{q'}^{SMA}}\right). \quad (13)$$

Here $\vec{\mu}_q$ denotes the KS dipole matrix element. Our first conclusion from this important result is that it contains the exact GL expression for oscillator strengths to first order in λ, by ignoring the correlation kernel. The sum is rapidly converging, as the matrix element decays rapidly

with principal quantum number. Using f_X for the He atom, the corrections of Eq. (13), summed over only bound-bound transitions, reduce the oscillator strength by 11%, whereas the exact answer is 15% lower than the KS value. The remaining reduction is due to either correlation effects or transitions to the continuum.

If we estimate off-diagonal elements with geometric means of diagonal elements, we find

$$f \sim f_q\left(1 + 2\sum_{q' \neq q} \frac{\sqrt{\Delta\Omega_q^{SMA} \Delta\Omega_{q'}^{SMA}}}{\Omega_q^{SMA} - \Omega_{q'}^{SMA}} \sqrt{\frac{f_{q'}}{f_q}}\right). \quad (14)$$

The effect of off-diagonal matrix elements is to mix various KS oscillator strengths. For the dominant transition, if Eq. (11) is satisfied for excitation energies, it is also satisfied for oscillator strengths. The correction to an oscillator strength is first order in the off-diagonal matrix element, as opposed to the second-order correction to the SMA transition-frequency shift. Thus, fractional corrections to KS oscillator strengths will generally be larger than those to SMA shifts. So even with large SMA shifts, the associated oscillator strengths can be good.

The oscillator strengths of the He and Be atoms confirm our previous conclusions. For the well-separated transitions (He atom), the KS oscillator strengths are close to the true oscillator strengths, but not as close as the transition frequencies. The deviations estimated in Eq. (14) are consistent with those of the transition frequencies. Similarly, in the case of the Be atom, we see that the $2s \rightarrow 2p$ KS oscillator strength is good to within a factor of 2, because the corrections due to other transitions are quite mild. On the other hand, the higher transitions have KS oscillator strengths that are an order of magnitude different from the true ones, because of the huge corrections due to the first transition.

Ours is not an accurate numerical solution of the TDDFT response equations, but is rather a method for understanding results. Our explanation of the accuracy of the KS optical response, in terms of the TDDFT corrections to it, contrasts nicely with the wave function explanation of Ref. [17]. For example [10], the He oscillator strengths within ALDA are good to within 5%. The present work shows that this reflects the accuracy of $\langle q | f_{HXC}^{ALDA} | q' \rangle$ for these transitions.

Thus far, we have focused on approximate solutions of the TDDFT response equations for the exact ground-state KS potential. In practice, this potential is approximated. Local-density and generalized-gradient approximations have potentials that are too shallow, so that Rydberg states are not bound. This can be corrected by some addition of the correct asymptotic behavior [26], or by use of an orbital-dependent functional [27–29], whose derivative yields an accurate potential at large distances. From accurate calculations on the He and Be atoms, we find the principal effects of using either exchange-only or self-interaction-corrected local-density potentials to be a shift in the orbital energies, numerically identical to the error in the ionization potential. But the KS dipole matrix elements are extremely accurate in these approximate potentials, so that the dominant error in oscillator strengths comes from the errors in eigenvalues. Thus, current technology allows accurate calculation of KS oscillator strengths.

We conclude with an observation that should be useful for development of approximations to f_{XC}. In cases where poles are well separated and SMA is valid, as can be determined by comparing oscillator strengths, the difference between KS transition frequencies and physical ones yields an exact expectation value of f_{HXC}, to *all* orders in coupling constant λ. This would provide an invaluable benchmark for testing approximate XC kernels, similar to the widespread use exact XC potentials have enjoyed in the ground-state case [15].

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