Excitation Energies from Time-Dependent Density-Functional Theory

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A new density-functional approach to calculate the excitation spectrum of many-electron systems is proposed. It is shown that the full linear density response of the interacting system, which has poles at the exact excitation energies, can rigorously be expressed in terms of the response function of the noninteracting (Kohn-Sham) system and a frequency-dependent exchange-correlation kernel. Using this expression, the poles of the full response function are obtained by systematic improvement upon the poles of the Kohn-Sham response function. Numerical results are presented for atoms.

The traditional density-functional formalism of Hohenberg, Kohn, and Sham [1,2] is a powerful tool in predicting ground-state properties of many-electron systems [3–5]. The description of excited-state properties within density-functional theory (DFT), however, is notoriously difficult. Several extensions of ground-state DFT have been devised to tackle excited states. They are based either on the Rayleigh-Ritz principle for the lowest eigenstate of each symmetry class [6–8] or on a variational principle for ensembles [9–12]. A serious difficulty is that, until today, very little is known on how the exchange-correlation (xc) energy functionals appearing in these approaches differ from the ordinary ground-state xc energy.

In this Letter we propose a different approach to the calculation of excitation energies which is based on a *time-dependent* (TD) version of DFT. TDDFT is by now a well-established theory: Hohenberg-Kohn and Kohn-Sham-type theorems have been proved [13,14] rigorous properties [15,16] and good approximations [17,18] of the TD xc potential have been found, and the formalism has been applied rather successfully to the linear and nonlinear photoresponse of a large variety of systems [19].

To extract excitation energies from TDDFT we exploit the fact that the frequency-dependent linear response of a finite interacting system has discrete poles at the excitation energies $\Omega_m := E_m - E_0$ of the unperturbed system. The idea is to calculate the shift of the Kohn-Sham orbital energy differences $\omega_{jk} := \epsilon_j - \epsilon_k$ (which are the poles of the Kohn-Sham response function) towards the true excitation energies Ω_m in a systematic fashion. To this end we first derive a formally exact representation of the linear density response $\rho_1(\mathbf{r}\omega)$ in terms of the Kohn-Sham response function and a frequency-dependent xc kernel, which will then be used to calculate the shifts of the poles.

We consider interacting many-electron systems subject to external potentials $v_{\text{ext}}(\mathbf{r}t) = v_0(\mathbf{r}) + v_1(\mathbf{r}t)$, where $v_0(\mathbf{r})$ denotes the static external potential of the unperturbed system (typically the nuclear Coulomb potential) and $v_1(\mathbf{r}t)$ is a time-dependent external perturbation. The unperturbed many-body state is assumed to be the *ground state* corresponding to $v_0(\mathbf{r})$. Then, trivially, the time-dependent density $\rho(\mathbf{r}t)$ is a functional of the external potential $\rho(\mathbf{r}t) = \rho[v_{\text{ext}}](\mathbf{r}t)$. The fundamental one-to-one correspondence between time-dependent densities and time-dependent potentials demonstrated by Runge and Gross [13] guarantees that the functional $\rho[v_{\text{ext}}]$ can be inverted, i.e., $v_{\text{ext}}(\mathbf{r}t) = v_{\text{ext}}[\rho](\mathbf{r}t)$. In terms of the two functionals $\rho[v_{\text{ext}}]$ and $v_{\text{ext}}[\rho]$, the density-density response function can be expressed as a functional derivative

$$\chi(\mathbf{r}t, \mathbf{r}'t') = \frac{\delta \rho[v_{\text{ext}}](\mathbf{r}t)}{\delta v_{\text{ext}}(\mathbf{r}'t')} \bigg|_{v_{\text{ext}}[\rho_0]} \quad (1)$$

to be evaluated at the *static* external potential corresponding to the unperturbed ground-state density ρ_0, i.e., $v_{\text{ext}}[\rho_0] = v_0$. The linear density response $\rho_1(\mathbf{r}t)$ to the perturbation $v_1(\mathbf{r}t)$ is then given by

$$\rho_1(\mathbf{r}t) = \int dt' \int d^3r' \, \chi(\mathbf{r}t, \mathbf{r}'t') v_1(\mathbf{r}'t') . \quad (2)$$

For *noninteracting* particles moving in some external potential $v_s(\mathbf{r}t)$, the Runge-Gross theorem holds as well. Therefore the functional $\rho(\mathbf{r}t) = \rho[v_s](\mathbf{r}t)$ can be inverted, $v_s(\mathbf{r}t) = v_s[\rho](\mathbf{r}t)$, and the Kohn-Sham response function, i.e., the density-density response function of noninteracting particles with unperturbed density ρ_0, is

$$\chi_s(\mathbf{r}t, \mathbf{r}'t') = \frac{\delta \rho[v_s](\mathbf{r}t)}{\delta v_s(\mathbf{r}'t')} \bigg|_{v_s[\rho_0]} . \quad (3)$$

Hence, each external potential v_{ext} uniquely determines a density $\rho[v_{\text{ext}}]$ which, in turn, uniquely determines another potential $v_s[\rho[v_{\text{ext}}]]$ such that the density of noninteracting particles moving in $v_s(\mathbf{r}t)$ is identical with the density of Coulomb-interacting particles moving in the external potential $v_{\text{ext}}(\mathbf{r}t)$. The potential $v_s(\mathbf{r}t)$ corresponding to a given $v_{\text{ext}}(\mathbf{r}t)$ is termed the time-dependent Kohn-Sham potential and is usually written as $v_s(\mathbf{r}t) = v_{\text{ext}}(\mathbf{r}t) + v_H(\mathbf{r}t) + v_{\text{xc}}(\mathbf{r}t)$, where $v_H(\mathbf{r}t) = \int d^3r' \, \rho(\mathbf{r}'t)/|\mathbf{r} - \mathbf{r}'|$ is the time-dependent Hartree potential (atomic units are used throughout) and v_{xc} denotes the time-dependent xc potential. Defining a time-dependent xc kernel by

$$f_{\text{xc}}[\rho](\mathbf{r}t, \mathbf{r}'t') := \delta v_{\text{xc}}[\rho](\mathbf{r}t)/\delta \rho(\mathbf{r}'t') \quad (4)$$

and employing the functional chain rule to calculate the response function (1),

$$\chi(\mathbf{r}t, \mathbf{r}'t') = \int d^3x \int d\tau \, \frac{\delta\rho(\mathbf{r}t)}{\delta v_s(\mathbf{x}\tau)} \frac{\delta v_s(\mathbf{x}\tau)}{\delta v_{\text{ext}}(\mathbf{r}'t')}\bigg|_{v_{\text{ext}}[\rho_0]}, \tag{5}$$

one obtains, by inserting Eqs. (3) and (4), a Dyson-type equation relating the noninteracting and interacting response functions to each other:

$$\chi(\mathbf{r}t, \mathbf{r}'t') = \chi_s(\mathbf{r}t, \mathbf{r}'t') + \int d^3x \int d\tau \int d^3x' \int d\tau' \, \chi_s(\mathbf{r}t, \mathbf{x}\tau)\left(\frac{\delta(\tau - \tau')}{|\mathbf{x} - \mathbf{x}'|} + f_{\text{xc}}[\rho_0](\mathbf{x}\tau, \mathbf{x}'\tau')\right)\chi(\mathbf{x}'\tau', \mathbf{r}'t'). \tag{6}$$

Multiplying both sides of Eq. (6) with $v_1(\mathbf{r}'t')$ and integrating over $\mathbf{r}'t'$ yields, by virtue of Eq. (2),

$$\rho_1(\mathbf{r}t) = \int dt' \int d^3r' \, \chi_s(\mathbf{r}t, \mathbf{r}'t')v_{s,1}(\mathbf{r}'t'), \tag{7}$$

with

$$v_{s,1}(\mathbf{r}t) = v_1(\mathbf{r}t) + \int d^3r' \, \frac{\rho_1(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} + \int d^3r' \int dt' \, f_{\text{xc}}[\rho_0](\mathbf{r}t, \mathbf{r}'t')\rho_1(\mathbf{r}'t'). \tag{8}$$

We emphasize that Eqs. (7) and (8), postulated in previous work [17,20,21], constitute an exact representation of the linear density response, i.e., the *exact* linear density response $\rho_1(\mathbf{r}t)$ of an interacting system can be written as the linear density response of a *noninteracting* system to the effective perturbation $v_{s,1}(\mathbf{r}t)$. Combining Eqs. (7) and (8) and taking the Fourier transform with respect to time, the *exact* frequency-dependent linear density response can be written as

$$\rho_1(\mathbf{r}\omega) = \int d^3r' \, \chi_s(\mathbf{r}, \mathbf{r}'; \omega)\left[v_1(\mathbf{r}'\omega) + \int d^3x\left(\frac{1}{|\mathbf{r}' - \mathbf{x}|} + f_{\text{xc}}[\rho_0](\mathbf{r}', \mathbf{x}; \omega)\right)\rho_1(\mathbf{x}\omega)\right]. \tag{9}$$

The Kohn-Sham response function $\chi_s(\mathbf{r}, \mathbf{r}'; \omega)$ is readily expressed in terms of the static unperturbed Kohn-Sham orbitals φ_j. For spin-saturated unperturbed states it is given by

$$\chi_s(\mathbf{r}, \mathbf{r}'; \omega) = 2\sum_{j,k}(n_k - n_j)\frac{\varphi_k^*(\mathbf{r})\varphi_j(\mathbf{r})\varphi_j^*(\mathbf{r}')\varphi_k(\mathbf{r}')}{\omega - \omega_{jk} + i\delta}, \tag{10}$$

where n_k, n_j are the Fermi-occupation factors (1 or 0). As a function of ω, χ_s has poles at the Kohn-Sham orbital-energy differences ω_{jk}. In order to calculate the shift towards the true excitation energy Ω we rewrite Eq. (9) as

$$\int d^3x\left[\delta(\mathbf{r} - \mathbf{x}) - \int d^3r' \, \chi_s(\mathbf{r}, \mathbf{r}'; \omega)\left(\frac{1}{|\mathbf{r}' - \mathbf{x}|} + f_{\text{xc}}[\rho_0](\mathbf{r}', \mathbf{x}; \omega)\right)\right]\rho_1(\mathbf{x}\omega) = \int d^3r' \, \chi_s(\mathbf{r}, \mathbf{r}'; \omega)v_1(\mathbf{r}'\omega). \tag{11}$$

Since the true excitation energies Ω are generally not identical with the Kohn-Sham excitation energies ω_{jk}, the right-hand side of Eq. (11) remains finite for $\omega \to \Omega$. The *exact* density response ρ_1, on the other hand, has poles at the true excitation energies $\omega = \Omega$. Hence the integral operator acting on ρ_1 on the left-hand side of Eq. (11) cannot be invertible for $\omega \to \Omega$ [22]. The true excitation energies Ω can therefore be characterized as those frequencies where the eigenvalues of this integral operator vanish or, equivalently, where the eigenvalues $\lambda(\omega)$ of

$$\int d^3r \int d^3r' \, \chi_s(\mathbf{x}, \mathbf{r}; \omega)\left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}}[\rho_0](\mathbf{r}, \mathbf{r}'; \omega)\right)\zeta(\mathbf{r}'\omega) = \lambda(\omega)\zeta(\mathbf{x}\omega) \tag{12}$$

satisfy $\lambda(\Omega) = 1$. This condition rigorously determines the true excitation spectrum of the interacting system at hand. So far, no approximations have been made. One possibility to actually calculate Ω is to expand all quantities appearing in Eq. (12) about one particular Kohn-Sham energy difference $\omega_\nu := \omega_{jk}$:

$$\chi_s(\mathbf{x}, \mathbf{r}; \omega) = 2\alpha_\nu \frac{\Phi_\nu(\mathbf{x})\Phi_\nu^*(\mathbf{r})}{\omega - \omega_\nu} + 2\sum_{\kappa \neq \nu}\alpha_\kappa \frac{\Phi_\kappa(\mathbf{x})\Phi_\kappa^*(\mathbf{r})}{\omega_\nu - \omega_\kappa + i\delta} + \cdots,$$

$$f_{\text{xc}}[\rho_0](\mathbf{r}, \mathbf{r}'; \omega) = f_{\text{xc}}[\rho_0](\mathbf{r}, \mathbf{r}'; \omega_\nu) + \frac{df_{\text{xc}}[\rho_0](\mathbf{r}, \mathbf{r}'; \omega)}{d\omega}\bigg|_{\omega_\nu}(\omega - \omega_\nu) + \cdots,$$

$$\zeta(\mathbf{x}\omega) = \zeta(\mathbf{x}\omega_\nu) + \frac{d\zeta(\mathbf{x}\omega)}{d\omega}\bigg|_{\omega_\nu}(\omega - \omega_\nu) + \cdots,$$

$$\lambda(\omega) = A(\omega_\nu)/(\omega - \omega_\nu) + B(\omega_\nu) + \cdots, \quad (13)$$

where the double index $\nu := (j, k)$ labels the single-particle transition ($k \to j$). Furthermore, we have defined $\Phi_\nu(\mathbf{r}) := \varphi_k(\mathbf{r})^* \varphi_j(\mathbf{r})$, and $\alpha_\nu := n_k - n_j$. Assuming that the true excitation energy Ω is not too far away from ω_ν it will be sufficient to consider only the lowest-order terms of the above Laurent expansions. Inserting the Laurent expansions of χ_s, f_{xc}, ζ, and λ into Eq. (12), the coefficients A and B are readily identified as $A(\omega_\nu) = M_{\nu\nu}(\omega_\nu)$ and

$$B(\omega_\nu) = \frac{dM_{\nu\nu}}{d\omega}\bigg|_{\omega_\nu} + \frac{1}{M_{\nu\nu}(\omega_\nu)}$$
$$\times \sum_{\kappa \neq \nu} \frac{M_{\nu\kappa}(\omega_\nu)M_{\kappa\nu}(\omega_\nu)}{\omega_\nu - \omega_\kappa + i\delta}, \quad (14)$$

where the matrix elements $M_{\kappa\nu}$ are

$$M_{\kappa\nu}(\omega) = 2\alpha_\nu \int d^3r \int d^3r' \, \Phi_\kappa^*(\mathbf{r})$$
$$\times \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}'; \omega) \right) \Phi_\nu(\mathbf{r}'). \quad (15)$$

The condition $\lambda(\Omega) = 1$ and its complex conjugate then lead, in lowest order, to

$$\Omega = \omega_\nu + \Re M_{\nu\nu}. \quad (16)$$

Since B involves a summation over an infinite set of single-particle transitions (including transitions to the continuum), it is difficult to calculate this term. In order to estimate the importance of this and higher-order contributions, we took a different route: Rather than expressing all quantities by Laurent expansions, we approximate the response function χ_s by a *finite* sum $\chi_s(\mathbf{x}, \mathbf{r}; \omega) \approx 2 \sum_\kappa^K \alpha_\kappa \Phi_\kappa(\mathbf{x}) \Phi_\kappa^*(\mathbf{r})/(\omega - \omega_\kappa)$. This leads to a $K \times K$ matrix equation whose solutions turn out to be rather close to the lowest-order results obtained from Eq. (16). This suggests that the sum of all higher-order terms of the Laurent expansion (13) gives only a small correction.

Apart from the truncations, two further approximations are necessary: (i) The frequency-dependent xc kernel f_{xc} has to be approximated. (ii) The static Kohn-Sham orbitals entering Eq. (16) have to be calculated with an *approximate* (static) potential $v_{\mathrm{xc}}^{\mathrm{stat}}$. As a test of the method, we have calculated the lowest excitation energies for the alkaline earth elements and the zinc series. Here, the $s\,^1S \to p\,^1P$ transitions under consideration are threefold degenerate in the magnetic quantum number m of the "final" state. In principle, for degenerate Kohn-Sham eigenvalues ϵ_j or ϵ_k the expansions about the corresponding Kohn-Sham pole yield matrix equations for the coefficients in Eq. (13) which can lead to several different corrections of a single ω_ν, thus describing the multiplet splittings. In our case, however, the three possible corrections are identical, as they should be. We have performed two calculations, both based on Eq. (16). The first one employs the ordinary local density approximation (LDA) for $v_{\mathrm{xc}}^{\mathrm{stat}}$ and the so-called TDLDA, also known as "adiabatic" LDA [23]

for f_{xc} (both using the parametrization of Vosko, Wilk, and Nusair [24]). The second calculation uses the x-only optimized effective potential (OEP) for $v_{\mathrm{xc}}^{\mathrm{stat}}$ in the approximation of Krieger, Li, and Iafrate (KLI) [25] and for f_{xc}

$$f_{\mathrm{xc}}^{\mathrm{OEP}}[\rho_0](\mathbf{r}, \mathbf{r}'; \omega) = -\frac{2|\sum_k n_k \varphi_k(\mathbf{r})\varphi_k^*(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|\rho_0(\mathbf{r})\rho_0(\mathbf{r}')}. \quad (17)$$

The latter is based on the recently proposed time-dependent OEP method [18] where the xc potential is an explicit functional of time-dependent orbitals. A calculation analogous to Eqs. (1)–(6) involving the derivatives $\delta v_{\mathrm{xc}}^{\mathrm{OEP}}/\delta\psi_j(\mathbf{r}t)$ shows that in the time-dependent OEP theory the crucial Eq. (6) holds for the quantity $f_{\mathrm{xc}}^{\mathrm{OEP}}$ defined through

$$\int_t^\infty dt' \int d^3r' \sum_{jk} \{\varphi_j(\mathbf{r})\varphi_j^*(\mathbf{r}')\varphi_k(\mathbf{r}')\varphi_k^*(\mathbf{r})e^{-i\omega_{jk}(t-t')}$$
$$\times [n_j f_{\mathrm{xc}}^{\mathrm{OEP}}(\mathbf{y}\tau, \mathbf{r}'t') - g_{\mathrm{xc}}^{(j)}(\mathbf{y}\tau, \mathbf{r}'t')] - \mathrm{c.c.}\} = 0, \quad (18)$$

where

$$g_{\mathrm{xc}}^{(j)}(\mathbf{y}\tau, \mathbf{r}'t') = \left[\frac{1}{2\psi_j^*(\mathbf{r}'t')} \frac{\delta v_{\mathrm{xc}}^{\mathrm{OEP}}(\mathbf{y}\tau)}{\delta\psi_j(\mathbf{r}'t')} \right]_{\psi_j(t)=\varphi_j e^{-i\epsilon_j t}}. \quad (19)$$

Equation (18) is formally identical with the integral equation for the time-dependent OEP xc potential [18] with $v_{\mathrm{xc}}^{\mathrm{OEP}}(\mathbf{r}'t')$ and $u_{\mathrm{xc}j}(\mathbf{r}'t')$ replaced by $f_{\mathrm{xc}}^{\mathrm{OEP}}(\mathbf{y}\tau, \mathbf{r}'t')$ and $g_{\mathrm{xc}}^{(j)}(\mathbf{y}\tau, \mathbf{r}'t')$, respectively. A simple analytical approximation to $v_{\mathrm{xc}}^{\mathrm{OEP}}$ is given by

$$v_{\mathrm{xc}}^{\mathrm{appr}}(\mathbf{r}t) = \sum_j \frac{|\psi_j(\mathbf{r}t)|^2}{2\rho(\mathbf{r}t)} [u_{\mathrm{xc}j}'(\mathbf{r}t) + u_{\mathrm{xc}j}'^*(\mathbf{r}t)], \quad (20)$$

where $u_{\mathrm{xc}j} = [\delta\mathcal{A}_{\mathrm{xc}}/\delta\psi_j(\mathbf{r}t)]/\psi_j^*(\mathbf{r}t)$, with the xc part $\mathcal{A}_{\mathrm{xc}}$ of the quantum mechanical action functional. Applying this approximation to (18), i.e., setting

$$f_{\mathrm{xc}}^{\mathrm{appr}}(\mathbf{y}\tau, \mathbf{r}'t') = \sum_j \frac{|\varphi_j(\mathbf{r})|^2}{2\rho(\mathbf{r})} [g_{\mathrm{xc}}^{(j)}(\mathbf{y}\tau, \mathbf{r}'t') + \mathrm{c.c.}]$$
$$(21)$$

and using the explicit analytical form (20) to evaluate (19), one arrives at the compact expression (17) if $\mathcal{A}_{\mathrm{xc}}$ is approximated by the TD Fock term (*TD x-only approximation*). In general, the Fourier transform of the xc kernel defined by Eq. (18) is frequency dependent (even in the TD x-only case), a feature which is not accounted for in the present treatment of this equation. However, for the special case of a two-electron system treated within TD x-only theory, Eqs. (17) and (20) are the *exact* solutions of the respective integral equations, as is easily checked.

In Table I the excitation energies calculated from Eq. (16) are compared with experimental values. The OEP values are clearly superior to the LDA results and are also better than the usual Δ_{SCF} values. The unoccupied orbitals and their energy eigenvalues are very sensitive to the behavior of the potential far from the nucleus. One major reason for the superiority of the OEP is the fact

TABLE I. The lowest $^1S \rightarrow {}^1P$ excitation energies of various atoms. The experimental values (first column) [30] are compared with results calculated from Eq. (16) within LDA and OEP (second and third columns, respectively) and with ordinary Δ_{SCF} values (fourth column). The corresponding Kohn-Sham orbital-energy differences ω_ν are shown in the last two columns (all values in rydbergs).

Atom	Ω_{exp}	Ω^{LDA}	Ω^{OEP}	$\Omega(\Delta_{SCF})$	ω_ν^{LDA}	ω_ν^{OEP}
Be	0.388	0.399	0.392	0.331	0.257	0.259
Mg	0.319	0.351	0.327	0.299	0.249	0.234
Ca	0.216	0.263	0.234	0.211	0.176	0.157
Zn	0.426	0.477	0.422	0.403	0.352	0.314
Sr	0.198	0.241	0.210	0.193	0.163	0.141
Cd	0.398	0.427	0.376	0.346	0.303	0.269

that it is self-interaction free and therefore has the correct $-1/r$ tail (while the LDA potential falls off exponentially). An important point is that the OEP decreases *correctly* for *all* orbitals. For this reason, the *x*-only OEP is also superior to the Hartree-Fock (HF) potential which is self-interaction free only for the occupied orbitals but not for unoccupied ones. As a consequence, HF orbital-energy differences are typically too large.

In spite of the fact that we focused on the situation of closed shells and singlet terms, the method is also capable of describing spin-flip processes and excitations in open-shell atoms, if a spin-dependent exchange-correlation kernel [26] is used. More detailed results for atoms as well as molecules will be presented elsewhere [27].

We emphasize that the calculation of excitation energies from Eq. (16) involves only *known ground-state* quantities, i.e., the ordinary Kohn-Sham orbitals and the corresponding Kohn-Sham eigenvalues. Thus our scheme requires only one self-consistent Kohn-Sham calculation, whereas the so-called Δ_{SCF} procedure involves linear combinations of two or more self-consistent total energies [7]. So far, the best results are obtained with the optimized effective potential for v_{xc}^{stat} in the KLI *x*-only approximation. Further improvement is expected from the inclusion of correlation terms [28,29] in the OEP. Work along these lines is in progress.

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