Spin-Multiplet Energies from Time-Dependent Density-Functional Theory

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Abstract

Starting from a formally exact density-functional representation of the frequency-dependent linear density response and exploiting the fact that the latter has poles at the true excitation energies, we develop a density-functional method for the calculation of excitation energies. Simple additive corrections to the Kohn-Sham single-particle transition energies are derived whose actual computation only requires the ordinary static Kohn-Sham orbitals and the corresponding eigenvalues. Numerical results are presented for spin singlet and triplet energies.

1 Introduction

In recent years, density-functional theory (DFT) [1, 2, 3, 4, 5] has enjoyed increasing popularity in the field of quantum chemistry. The computational simplicity of the Kohn-Sham scheme and the availability of reliable exchange-correlation (xc) functionals allow accurate calculations even for very large systems [6, 7]. The traditional density functional formalism of Hohenberg, Kohn and Sham [1, 2] is mainly a ground-state theory. In view of the advantages of DFT, a generalization allowing the calculation of excitation spectra is highly desirable, especially since most experimental data are obtained by spectroscopical techniques. One might be tempted to interpret the Kohn-Sham single-particle energy differences as excitation energies. This interpretation, however, has no rigorous basis and in practice the Kohn-Sham orbital energy differences deviate by 10–50% from the true excitation energies. Another deficiency of the Kohn-Sham orbital energy spectrum is the fact that it shows no multiplet-splittings.

To deal with excited states, several extensions of ground-state DFT have been proposed which rely either on the Rayleigh-Ritz principle for the lowest eigenstate of each symmetry class [8, 9, 10] or on a variational principle for ensembles [11, 12, 13, 14, 15, 16]. A practical difficulty of these approaches is that the respective xc energy functionals depend on the symmetry labels of the state considered or on the particular ensemble. Until today, little is known about the explicit form of these

excited-state xc functionals although significant progress has recently been made in the ensemble formalism [17, 18, 19, 20, 21, 22].

In this article we are going to elaborate on a different approach [23, 24, 25] to the calculation of excitation energies which is based on *time-dependent* density-functional theory (TDDFT) [26]. In the linear response regime TDDFT has been applied rather successfully to the photo-response of atoms and molecules [27, 28, 29, 30, 31]. Dynamical hyperpolarizabilities have also been calculated [32] and first applications beyond the perturbative regime have emerged [33, 34, 35]. For a recent review of TDDFT and its applications, see [36].

To calculate excitation energies from TDDFT we use the fact that the frequency-dependent linear density response of a finite system exhibits discrete poles at the true (correlated) excitation energies of the unperturbed system. It can be shown [23] that the exact linear density response of an interacting system can be written as the linear density response of a noninteracting (Kohn-Sham) system to an effective perturbation. The basic idea is to use this formally exact representation of the frequency-dependent linear density response to calculate the shifts of the Kohn-Sham orbital energy differences (which are the poles of the Kohn-Sham response function) towards the true excitation energies in a systematic way. This programme has recently been carried out [23] rather successfully to the calculation of singlet excitation energies. The purpose of the present article is to extend the scheme to incorporate spin degrees of freedom. This will allow us to calculate the excitation energies of spin multiplets.

2   Method

The frequency-dependent linear density response $n_{1\sigma}(\mathbf{r}, \omega)$ of interacting electrons with spin σ to a frequency-dependent perturbation $v_{1\nu}(\mathbf{y}, \omega)$ is usually written in terms of the full response function $\chi_{\sigma\nu}$ as

$$n_{1\sigma}(\mathbf{r}, \omega) = \sum_\nu \int d^3y \, \chi_{\sigma\nu}(\mathbf{r}, \mathbf{y}; \omega) v_{1\nu}(\mathbf{y}, \omega) \,. \tag{1}$$

Alternatively, the exact frequency-dependent spin-density response can be calculated (self-consistently) from

$$n_{1\sigma}(\mathbf{r}, \omega) = \sum_\nu \int d^3y \, \chi_{\mathrm{s}\,\sigma\nu}(\mathbf{r}, \mathbf{y}; \omega) v_{\mathrm{s}\,1\nu}(\mathbf{y}, \omega) \tag{2}$$

as the response of noninteracting (Kohn-Sham) particles subject to the effective potential

$$v_{\mathrm{s}\,1\nu}(\mathbf{y}, \omega) = v_{1\nu}(\mathbf{y}, \omega) + \sum_{\nu'} \int d^3y' \left(\frac{1}{|\mathbf{y} - \mathbf{y}'|} + f_{\mathrm{xc}\,\nu\nu'}(\mathbf{y}, \mathbf{y}'; \omega) \right) n_{1\nu'}(\mathbf{y}', \omega) \,. \tag{3}$$

Here the spin-dependent exchange-correlation kernel f_{xc} is given by the Fourier transform of

$$f_{\mathrm{xc}\,\sigma\sigma'}(\mathbf{r}, t, \mathbf{r}', t') := \left. \frac{\delta v_{\mathrm{xc}\sigma}[n_\uparrow, n_\downarrow](\mathbf{r}, t)}{\delta n_{\sigma'}(\mathbf{r}', t')} \right|_{n_{0\uparrow}, n_{0\downarrow}} \tag{4}$$

with respect to $(t - t')$. The proof that Eqs. (2) - (4) represent the *exact* linear spin-density response of the interacting system is based on the spin-dependent generalization [37] of TDDFT. The argument follows step by step the proof for the spin-independent case given in Ref. [23] and will therefore not be repeated here. The response-function χ_s of the Kohn-Sham system can be expressed in terms of the unperturbed static Kohn-Sham spin orbitals $\phi_{j\sigma}$ as

$$\chi_{s\,\sigma\sigma'}(\mathbf{r},\mathbf{r}';\omega) = \delta_{\sigma\sigma'} \sum_{j,k} (f_{k\sigma} - f_{j\sigma}) \frac{\phi_{j\sigma}(\mathbf{r})\phi_{k\sigma}^*(\mathbf{r})\phi_{j\sigma}^*(\mathbf{r}')\phi_{k\sigma}(\mathbf{r}')}{\omega - (\epsilon_{j\sigma} - \epsilon_{k\sigma}) + i\eta} \tag{5}$$

where $f_{k\sigma}$, $f_{j\sigma}$ are the Fermi-occupation factors (1 or 0). The summations in (5) run over all unperturbed Kohn-Sham orbitals, including the continuum states. Note that the Kohn-Sham response function (5) is diagonal in the spin variable and exhibits poles at frequencies $\omega_{jk\sigma} \equiv \epsilon_{j\sigma} - \epsilon_{k\sigma}$ corresponding to Kohn-Sham single-particle excitations within the same spin space. In order to calculate the shifts towards the true excitation energies Ω of the interacting system, we rewrite Eq. (2) as

$$\sum_{\nu'} \int d^3y' \left(\delta_{\sigma\nu'}\delta(\mathbf{r} - \mathbf{y}') - \sum_{\nu} \int d^3y\, \chi_{s\,\sigma\nu}(\mathbf{r},\mathbf{y};\omega) \left(\frac{1}{|\mathbf{y} - \mathbf{y}'|} \right. \right.$$
$$\left. \left. + f_{xc\,\nu\nu'}(\mathbf{y},\mathbf{y}';\omega) \right) \right) n_{1\nu'}(\mathbf{y}',\omega) = \sum_{\nu} \int d^3y\, \chi_{s\,\sigma\nu}(\mathbf{r},\mathbf{y};\omega) v_{1\nu}(\mathbf{y},\omega)\,. \tag{6}$$

In general, the true excitation energies Ω are not identical with the Kohn-Sham excitation energies $\omega_{jk\sigma}$. Therefore, the right-hand side of Eq. (6) remains finite for $\omega \to \Omega$. Since, on the other hand, the *exact* spin-density response $n_{1\sigma}$, has poles at the true excitation energies Ω, the integral operator acting on $n_{1\sigma}$ on the left-hand side of Eq. (6) cannot be invertible for $\omega \to \Omega$. This is easily seen by reductio ad absurdum: Assuming the inverse operator existed, its action on both sides of Eq. (6) would result in a finite right-hand side for $\omega \to \Omega$ in contradiction to the fact that $n_{1\sigma}$, remaining on the left-hand side, has a pole at $\omega = \Omega$.

Consequently, the true excitation energies Ω are characterized as those frequencies where the integral operator acting on the spin-density vector in Eq. (6) is not invertible or, equivalently, where the eigenvalues of this operator vanish. If the delta-function in Eq. (6) is integrated out the true excitation energies Ω are those frequencies, where the eigenvalues $\lambda(\omega)$ of

$$\sum_{\nu'} \int d^3y' \sum_{\nu} \int d^3y\, \chi_{s\sigma\nu}(\mathbf{r},\mathbf{y};\omega) \left(\frac{1}{|\mathbf{y} - \mathbf{y}'|} + f_{xc\,\nu\nu'}(\mathbf{y},\mathbf{y}';\omega) \right) \gamma_{\nu'}(\mathbf{y}',\omega) =$$
$$\lambda(\omega)\gamma_\sigma(\mathbf{r},\omega) \tag{7}$$

satisfy

$$\lambda(\Omega) = 1\,. \tag{8}$$

This condition rigorously determines the true excitation spectrum of the interacting system considered.

For notational convenience, we introduce double indices $q \equiv (j, k)$ so that $\omega_{q\sigma} \equiv \epsilon_{j\sigma} - \epsilon_{k\sigma}$ denotes the excitation energy of the single-particle transition $(j\sigma \to k\sigma)$. Moreover, we define

$$
\begin{align}
\Phi_{q\sigma}(\mathbf{r}) &:= \phi_{k\sigma}(\mathbf{r})^* \phi_{j\sigma}(\mathbf{r}) , \tag{9} \\
\alpha_{q\sigma} &:= f_{k\sigma} - f_{j\sigma} \tag{10}
\end{align}
$$

and set

$$
\xi_{q\sigma}(\omega) := \sum_{\nu'} \int d^3 y' \int d^3 y \, \Phi_{q\sigma}(\mathbf{y})^* \left(\frac{1}{|\mathbf{y} - \mathbf{y}'|} + f_{\mathrm{xc}\,\sigma\nu'}(\mathbf{y}, \mathbf{y}'; \omega) \right) \gamma_{\nu'}(\mathbf{y}', \omega) . \tag{11}
$$

With these definitions, Eq. (7) takes the form

$$
\sum_q \frac{\alpha_{q\sigma} \Phi_{q\sigma}(\mathbf{r})}{\omega - \omega_{q\sigma} + i\eta} \xi_{q\sigma}(\omega) = \lambda(\omega) \gamma_\sigma(\mathbf{r}, \omega) . \tag{12}
$$

Solving this equation for $\gamma_\sigma(\mathbf{r}, \omega)$ and reinserting the result on the right-hand side of Eq. (11) leads to

$$
\sum_{\sigma'} \sum_{q'} \frac{M_{q\sigma\, q'\sigma'}(\omega)}{\omega - \omega_{q'\sigma'} + i\eta} \xi_{q'\sigma'}(\omega) = \lambda(\omega) \xi_{q\sigma}(\omega) . \tag{13}
$$

Here we have introduced the matrix elements

$$
M_{q\sigma\, q'\sigma'}(\omega) = \alpha_{q'\sigma'} \int d^3 r \int d^3 r' \, \Phi_{q\sigma}^*(\mathbf{r}) \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\mathrm{xc}\,\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; \omega) \right) \Phi_{q'\sigma'}(\mathbf{r}') . \tag{14}
$$

Note that the summation in Eq. (13) extends over all single-particle transitions $q'\sigma'$ between occupied and unoccupied Kohn-Sham orbitals, including the continuum states. Up to this point, no approximations have been made. In order to actually calculate $\lambda(\omega)$, the eigenvalue problem (13) has to be truncated in one way or another. One possibility is to expand all quantities in Eq. (13) about one particular KS-orbital energy difference $\omega_{p\tau}$:

$$
\begin{align}
\xi_{q\sigma}(\omega) &= \xi_{q\sigma}(\omega_{p\tau}) + \left. \frac{d\xi_{q\sigma}(\omega)}{d\omega} \right|_{\omega_{p\tau}} (\omega - \omega_{p\tau}) + \dots \tag{15} \\
\lambda(\omega) &= \frac{A(\omega_{p\tau})}{\omega - \omega_{p\tau}} + B(\omega_{p\tau}) + \dots \tag{16}
\end{align}
$$

The matrix elements with $\omega_{p\tau} \neq \omega_{q'\sigma'}$ can be expanded into a Taylor series

$$
\frac{M_{q\sigma\, q'\sigma'}(\omega)}{\omega - \omega_{q'\sigma'} + i\eta} = \frac{M_{q\sigma\, q'\sigma'}(\omega_{p\tau})}{\omega_{p\sigma} - \omega_{q'\sigma'} + i\eta} + \frac{d}{d\omega} \left[\frac{M_{q\sigma\, q'\sigma'}(\omega)}{\omega - \omega_{q'\sigma'} + i\eta} \right]_{\omega_{p\tau}} (\omega - \omega_{p\tau}) + \dots \tag{17}
$$

whereas, for $\omega_{p\tau} = \omega_{q'\sigma'}$, the matrix elements have to be represented by a Laurent series

$$
\frac{M_{q\sigma\, q'\sigma'}(\omega)}{\omega - \omega_{q'\sigma'} + i\eta} = \frac{M_{q\sigma\, q'\sigma'}(\omega_{p\tau})}{\omega - \omega_{p\tau} + i\eta} + \left. \frac{dM_{q\sigma\, q'\sigma'}(\omega)}{d\omega} \right|_{\omega_{p\tau}} + \dots \tag{18}
$$

Inserting Eqs. (15) - (18) in Eq. (13) the coefficients A and B are readily identified. If the pole $\omega_{p\tau}$ is non-degenerate one finds:

$$
A(\omega_{p\tau}) = M_{p\tau\, p\tau}(\omega_{p\tau}) \tag{19}
$$

4

and

$$B(\omega_{p\tau}) = \left.\frac{dM_{p\tau p\tau}}{d\omega}\right|_{\omega_{p\tau}} + \frac{1}{M_{p\tau p\tau}(\omega_{p\tau})} \sum_{q'\sigma'\neq p\tau} \frac{M_{p\tau\, q'\sigma'}(\omega_{p\tau})M_{q'\sigma'\,p\tau}(\omega_{p\tau})}{\omega_{p\tau} - \omega_{q'\sigma'} + i\eta}\,. \qquad (20)$$

The corresponding eigenvector (in lowest order) is given by

$$\xi_{q\sigma} = \frac{1}{A(\omega_{p\tau})}M_{q\sigma\, p\tau}(\omega_{p\tau})\xi_{p\tau} \qquad (21)$$

with $(p\tau)$ fixed. The number $\xi_{p\tau}$ is free and can be chosen to properly normalize the vector ξ.

If the pole $\omega_{p\tau}$ is $\wp$-fold degenerate,

$$\omega_{p_1\tau_1} = \omega_{p_2\tau_2} = \ldots = \omega_{p_\wp\tau_\wp} \equiv \omega_0\,, \qquad (22)$$

the lowest-order coefficient A in Eq. (16) is determined by the following matrix equation

$$\sum_{k=1}^{\wp} M_{p_i\tau_i\, p_k\tau_k}(\omega_0)\xi^{(n)}_{p_k\tau_k} = A_n(\omega_0)\xi^{(n)}_{p_i\tau_i}\,, \quad i = 1\ldots\wp\,. \qquad (23)$$

In general, one obtains $\wp$ different eigenvalues $A_1 \ldots A_\wp$. Then the remaining components of the corresponding eigenvectors $\xi^{(n)}$ can be calculated from

$$\xi^{(n)}_{q\sigma} = \frac{1}{A_n(\omega_0)} \sum_{k=1}^{\wp} M_{q\sigma\, p_k\tau_k}(\omega_0)\,\xi^{(n)}_{p_k\tau_k}\,, \qquad (24)$$

once the eigenvalue problem (23) has been solved. Assuming that the true excitation energy Ω is not too far away from ω_0 it will be sufficient to consider only the lowest-order terms of the above Laurent expansions. In particular, we set

$$\lambda_n(\omega) \approx \frac{A_n(\omega_0)}{\omega - \omega_0}\,. \qquad (25)$$

The condition (8) and its complex conjugate, $\lambda^*(\Omega) = 1$, then lead, in this order, to a compact expression for the excitation energies:

$$\Omega_n = \omega_0 + \Re A_n(\omega_0)\,. \qquad (26)$$

This is the central result of our analysis. Eq. (26) shows that a single KS pole can lead to several many-body excitation energies. The corresponding oscillator strengths can be obtained [25] from the eigenvectors $\xi^{(n)}$ and the KS oscillator strengths.

3 Application to closed-shell systems

In this section, we will apply the above formalism to systems with spin-unpolarized ground states. For these systems, the Kohn-Sham orbital eigenvalues are degenerate with respect to the spin variable, which implies a lack of spin-multiplet structure in the Kohn-Sham spectrum. In the following, we demonstrate how this is restored by

the lowest-order corrections (26). Assuming that there are no further degeneracies besides the spin degeneracy, Eq. (23) reduces to the following (2×2) eigenvalue problem:

$$\sum_{\sigma'=\uparrow,\downarrow} M_{p\sigma p\sigma'}(\omega_0)\xi_{p\sigma'}(\omega_0) = A\xi_{p\sigma}(\omega_0) \,. \tag{27}$$

For spin-saturated systems, one finds $M_{p\uparrow p\uparrow} = M_{p\downarrow p\downarrow}$ and $M_{p\uparrow p\downarrow} = M_{p\downarrow p\uparrow}$, so that the eigenvalues of Eq.(27) are given by

$$A_{1,2} = M_{p\uparrow p\uparrow} \pm M_{p\uparrow p\downarrow} \,. \tag{28}$$

By Eq. (26), the resulting excitation energies are:

$$\Omega_1 = \omega_0 + \Re\left\{M_{p\uparrow p\uparrow} + M_{p\uparrow p\downarrow}\right\} \tag{29}$$

$$\Omega_2 = \omega_0 + \Re\left\{M_{p\uparrow p\uparrow} - M_{p\uparrow p\downarrow}\right\} \,. \tag{30}$$

Inserting the explicit form of the matrix elements (14) one finds

$$\Omega_1 = \omega_0 + 2\Re \int d^3r \int d^3r' \, \Phi_p^*(\mathbf{r}) \left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}';\omega_0)\right) \Phi_p(\mathbf{r}') \tag{31}$$

$$\Omega_2 = \omega_0 + 2\Re \int d^3r \int d^3r' \, \Phi_p^*(\mathbf{r})\mu_0^2 G_{\mathrm{xc}}(\mathbf{r},\mathbf{r}';\omega_0)\Phi_p(\mathbf{r}') \tag{32}$$

where

$$f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}';\omega) = \frac{1}{4}\sum_{\sigma,\sigma'=\pm 1} f_{\mathrm{xc}\sigma\sigma'}(\mathbf{r},\mathbf{r}';\omega) \tag{33}$$

and

$$G_{\mathrm{xc}}(\mathbf{r},\mathbf{r}';\omega) = \frac{1}{4\mu_0^2}\sum_{\sigma,\sigma'=\pm 1} (\sigma\cdot\sigma')f_{\mathrm{xc}\sigma\sigma'}(\mathbf{r},\mathbf{r}';\omega) \,; \tag{34}$$

μ_0 denotes the Bohr magneton. For simplicity, we have dropped the spin index of $\Phi_{p\sigma}$ in Eqs. (31) and (32). (This is possible only if the unperturbed KS ground-state determinant is spin-saturated since, in this case, $\phi_{j\uparrow}(\mathbf{r}) = \phi_{j\downarrow}(\mathbf{r})$ for all j.)

The quantity G_{xc} gives rise to exchange and correlation effects in the Kohn-Sham equation for the linear response of the frequency-dependent magnetization density $m(\mathbf{r},\omega) = \mu_0(n_\uparrow(\mathbf{r},\omega) - n_\downarrow(\mathbf{r},\omega))$ [37].

The fact that the magnetization density response naturally involves spin-flip processes, suggests that Ω_2 represents the spin triplet excitation energies of many-electron systems with spin-saturated ground states. The corresponding spin singlet excitation energies, on the other hand, are given by Ω_1. This assignment will be given further support by the numerical results presented in the next section.

4   Results and Discussion

Apart from the truncation of the expansions (15) - (18), two further approximations are necessary in the described TDDFT-calculation of excitation energies:

(i) The frequency-dependent xc kernels f_{xc} and G_{xc} have to be approximated.

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(ii) The static Kohn-Sham orbitals entering Eqs. (31) and (32) through Eq. (9) have to be calculated with an *approximate* (static) potential $v_{\text{xc}}^{\text{stat}}$.

As an application of the method, we consider the lowest excitation energies of the alkaline earths and the elements of the zinc series. Here, in addition to the degeneracy with respect to the spin index, the $s \to p$ transitions under consideration are threefold degenerate in the magnetic quantum number m of the "final" state. Hence, we have six degenerate poles and Eq. (23) is a (6×6) eigenvalue problem. In our case, however, the matrix $M_{p_i \tau_i \, p_k \tau_k}$ in Eq. (23) consists of three identical (2×2) blocks, leading only to two distinct corrections, independent of m, as it should be. The resulting triplet states are still degenerate with respect to the total angular momentum quantum number because the spin-orbit coupling is not accounted for in the non-relativistic Kohn-Sham equations.

In tables 1 - 4 we show excitation energies calculated from Eqs. (31) and (32). The calculation of Table 1 employs the ordinary local density approximation (LDA) for $v_{\text{xc}}^{\text{stat}}$ (using the parametrization of Vosko, Wilk and Nusair [38]) and the so-called 'adiabatic' LDA (ALDA) for the xc kernels:

$$f_{\text{xc}}^{\text{ALDA}}[n_0](\mathbf{r}, \mathbf{r}'; \omega) = \delta(\mathbf{r} - \mathbf{r}') \frac{\partial^2}{\partial \rho^2} \left. \left(\rho \epsilon_{\text{xc}}^{\text{hom}}(\rho, \zeta) \right) \right|_{(\rho = n_0(\mathbf{r}),\, \zeta = 0)} \tag{35}$$

and [39]

$$G_{\text{xc}}^{\text{ALDA}}[n_0](\mathbf{r}, \mathbf{r}'; \omega) = \delta(\mathbf{r} - \mathbf{r}') \frac{1}{\mu_0^2 n(\mathbf{r})} \frac{\partial^2}{\partial \zeta^2} \left. \left(\epsilon_{\text{xc}}^{\text{hom}}(\rho, \zeta) \right) \right|_{(\rho = n_0(\mathbf{r}),\, \zeta = 0)} . \tag{36}$$

For the xc energy per particle, $\epsilon_{\text{xc}}^{\text{hom}}$, of the homogeneous electron gas and its second derivative with respect to the relative spin polarization $\zeta := (n_\uparrow - n_\downarrow)/n$, also called the xc-contribution to the "spin-stiffness coefficient", we use the parametrization of Ref. [38].

The calculation of Table 2 uses the x-only optimized effective potential (OEP) for $v_{\text{xc}}^{\text{stat}}$ in the approximation of Krieger, Li and Iafrate [40] and for f_{xc} the kernel

$$f_{\text{xc}}^{\text{TDOEP}}[n_0](\mathbf{r}, \mathbf{r}'; \omega) = - \frac{2 \left| \sum_k f_k \phi_k(\mathbf{r}) \phi_k^*(\mathbf{r}') \right|^2}{|\mathbf{r} - \mathbf{r}'| \, n_0(\mathbf{r}) \, n_0(\mathbf{r}')} , \tag{37}$$

which is based on the time-dependent OEP method in the x-only approximation [23, 41].

The mean absolute deviation from the experimental singlet spectrum for the excitation energies calculated from Eq. (31) is 36 mryd for the pure LDA calculation of Table 1 and 11 mryd for the x-only OEP calculation of Table 2.

In Table 3 we show the results of a "hybrid" calculation (OEP+ALDA) which employs the x-only OEP for $v_{\text{xc}}^{\text{stat}}$ and the ALDA (including local exchange *and* correlation terms) for the xc kernels. The results of this calculation are of similar quality as the x-only OEP calculation of Table 2. The mean absolute deviation from experiment is 15 mryd. Thus, for the singlet spectrum, the OEP values are

clearly superior to the LDA results and are also better than the usual LDA-Δ_{SCF} values, which deviate on the average by 27 mryd from the experimental data. This can be traced back to the sensitivity of the unoccupied orbitals and their energy eigenvalues to the asymptotic behavior of the Kohn-Sham potential. One major reason for the superiority of the optimized effective potential is the fact that it is self-interaction free and therefore has the correct $-1/r$ tail (while the LDA potential falls off exponentially). We note in passing that since the optimized effective potential decreases correctly for *all* orbitals, it is also superior to the Hartree-Fock (HF) potential which is self-interaction free only for the occupied orbitals but not for the unoccupied ones. Consequently, HF orbital-energy differences are typically too large.

The triplet spectrum obtained from Eq. (32) within the LDA deviates on the average from experiment by 9 mryd, which is slightly better than the mean absolute deviation of 10 mryd of the LDA-Δ_{SCF} spectrum. However, in spite of the fact that the OEP provides self-interaction free orbitals, it reproduces the triplet spectrum less accurately: the average deviation from experiment is 55 mryd, as can be seen from Table 2. This is a consequence of the fact that we have employed the time-dependent *x-only* approximation for the kernel $f_{\text{xc}\,\sigma\sigma'}$. This approximation neglects the correlation between electrons of antiparallel spin and leads to an xc kernel which is diagonal in spin space. Accordingly, from Eqs. (33) and (34), we have within the x-only TDOEP

$$G_{\text{xc}}^{\text{TDOEP}}[n](\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{\mu_0^2} f_{\text{xc}}^{\text{TDOEP}}[n](\mathbf{r}, \mathbf{r}'; \omega) \, . \tag{38}$$

We expect that the OEP triplet energies can be improved considerably by adding appropriate correlation terms [42, 43] to the TDOEP xc kernels. This expectation is backed by the observation that when the x-only OEP approximation of $v_{\text{xc}}^{\text{stat}}$ is combined with a local density prescription (ALDA) for exchange *and* correlation in the xc kernels f_{xc} and G_{xc}, the triplet spectrum is reproduced fairly well by Eq. (32). This can be seen from Table 3, where the calculated triplet spectrum deviates on the average by 15 mryd from the experimentally measured one.

To complete the discussion of the various approximate xc functionals employed, we list the singlet-triplet separations for the lowest $S \to P$ transitions of the alkaline earth elements and the zinc series in Table 4. Obviously, by calculating $\Omega_1 - \Omega_2$ from Eqs. (31) and (32), the Kohn-Sham excitation energies ω_0 and hence all the errors contained in the Kohn-Sham eigenvalues cancel out. Again, the mean absolute deviation δ from experiment clearly shows that singlet-triplet splittings are well reproduced only if correlation is included in the xc *kernels*. The best results are obtained when the ground-state potential is self-interaction free (OEP+ALDA).

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5 Summary and Conclusion

We have developed a formally exact scheme of calculating excitation energies from TDDFT. Within that scheme, we arrived at compact *approximate* expressions for the excitation energies which performed quite well in practical calculations of singlet and triplet excitations. The calculation involves only *known ground-state* quantities, i.e., the ordinary static Kohn-Sham orbitals and the corresponding Kohn-Sham eigenvalues. Thus the scheme described here 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 [9].

In spite of the fact that we focused our attention to the lowest transition energies of closed shell systems, and spin-multiplets, the method is also capable of dealing with spatial multiplets, higher excitations and open-shell systems. Work along these lines is in progress.

6 Acknowledgments

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Atom	State	Ω_{exp}	Ω^{LDA}	$\Omega(\Delta_{\mathrm{SCF}})$	ω_0^{LDA}
Be	$^1P_1$	0.388	0.399	0.331	0.257
	$^3P_0$	0.200			
	$^3P_1$	0.200	0.192	0.181	0.257
	$^3P_2$	0.200			
Mg	$^1P_1$	0.319	0.351	0.299	0.249
	$^3P_0$	0.199			
	$^3P_1$	0.199	0.209	0.206	0.249
	$^3P_2$	0.200			
Ca	$^1P_1$	0.216	0.263	0.211	0.176
	$^3P_0$	0.138			
	$^3P_1$	0.139	0.145	0.144	0.176
	$^3P_2$	0.140			
Zn	$^1P_1$	0.426	0.477	0.403	0.352
	$^3P_0$	0.294			
	$^3P_1$	0.296	0.314	0.316	0.352
	$^3P_2$	0.300			
Sr	$^1P_1$	0.198	0.241	0.193	0.163
	$^3P_0$	0.130			
	$^3P_1$	0.132	0.136	0.135	0.163
	$^3P_2$	0.136			
Cd	$^1P_1$	0.398	0.427	0.346	0.303
	$^3P_0$	0.274			
	$^3P_1$	0.279	0.269	0.272	0.303
	$^3P_2$	0.290			

Table 1: *The lowest $S{\to}P$ excitation energies of various atoms. The experimental values (first column) [44] are compared with results calculated from Eq. (31) for the singlet and from Eq. (32) for the triplet (second column) and with ordinary LDA-Δ_{SCF} values (third column). The LDA was employed for $v_{\mathrm{xc}}^{\mathrm{stat}}$ and the ALDA for the xc kernels. The corresponding Kohn-Sham orbital-energy differences ω_0 are shown in the last column (All values in rydbergs).*

Atom	State	Ω_{exp}	Ω^{OEP}	$\Omega(\Delta_{\mathrm{SCF}})$	ω_0^{OEP}
Be	$^1P_1$	0.388	0.392	0.331	0.259
	$^3P_0$	0.200			
	$^3P_1$	0.200	0.138	0.181	0.259
	$^3P_2$	0.200			
Mg	$^1P_1$	0.319	0.327	0.299	0.234
	$^3P_0$	0.199			
	$^3P_1$	0.199	0.151	0.206	0.234
	$^3P_2$	0.200			
Ca	$^1P_1$	0.216	0.234	0.211	0.157
	$^3P_0$	0.138			
	$^3P_1$	0.139	0.090	0.144	0.157
	$^3P_2$	0.140			
Zn	$^1P_1$	0.426	0.422	0.403	0.314
	$^3P_0$	0.294			
	$^3P_1$	0.296	0.250	0.316	0.314
	$^3P_2$	0.300			
Sr	$^1P_1$	0.198	0.210	0.193	0.141
	$^3P_0$	0.130			
	$^3P_1$	0.132	0.081	0.135	0.141
	$^3P_2$	0.136			
Cd	$^1P_1$	0.398	0.376	0.346	0.269
	$^3P_0$	0.274			
	$^3P_1$	0.279	0.211	0.272	0.269
	$^3P_2$	0.290			

Table 2: *The lowest S→P excitation energies of various atoms. The experimental values (first column) [44] are compared with results calculated from Eq. (31) for the singlet and from Eq. (32) for the triplet (second column) and with ordinary LDA-Δ_{SCF} values (third column). The x-only optimized effective potential was used for $v_{\mathrm{xc}}^{\mathrm{stat}}$ and the approximate TDOEP kernels (37), (38). The corresponding Kohn-Sham orbital-energy differences ω_0 are shown in the last column (All values in rydbergs).*

Atom	State	Ω_{exp}	$\Omega^{\mathrm{OEP+ALDA}}$	$\Omega(\Delta_{\mathrm{SCF}})$	ω_0^{OEP}
Be	$^1P_1$	0.388	0.398	0.331	0.259
	$^3P_0$	0.200			
	$^3P_1$	0.200	0.196	0.181	0.259
	$^3P_2$	0.200			
Mg	$^1P_1$	0.319	0.329	0.299	0.234
	$^3P_0$	0.199			
	$^3P_1$	0.199	0.196	0.206	0.234
	$^3P_2$	0.200			
Ca	$^1P_1$	0.216	0.236	0.211	0.157
	$^3P_0$	0.138			
	$^3P_1$	0.139	0.129	0.144	0.157
	$^3P_2$	0.140			
Zn	$^1P_1$	0.426	0.417	0.403	0.314
	$^3P_0$	0.294			
	$^3P_1$	0.296	0.280	0.316	0.314
	$^3P_2$	0.300			
Sr	$^1P_1$	0.198	0.211	0.193	0.141
	$^3P_0$	0.130			
	$^3P_1$	0.132	0.117	0.135	0.141
	$^3P_2$	0.136			
Cd	$^1P_1$	0.398	0.370	0.346	0.269
	$^3P_0$	0.274			
	$^3P_1$	0.279	0.239	0.272	0.269
	$^3P_2$	0.290			

Table 3: *The lowest S→P excitation energies of various atoms. The experimental values (first column) [44] are compared with results calculated from Eq. (31) for the singlet and from Eq. (32) for the triplet (second column) and with ordinary LDA-Δ_{SCF} values (third column). The x-only optimized effective potential was used for $v_{\mathrm{xc}}^{\mathrm{stat}}$ and the ALDA (including exchange and correlation terms) for the xc kernels. The corresponding Kohn-Sham orbital-energy differences ω_0 are shown in the last column (All values in rydbergs).*

Atom	J	EXP	LDA	OEP	OEP+ALDA	Δ_{SCF}
Be	0	0.188				
	1	0.188	0.207	0.253	0.202	0.150
	2	0.188				
Mg	0	0.120				
	1	0.120	0.142	0.175	0.133	0.094
	2	0.120				
Ca	0	0.077				
	1	0.077	0.118	0.144	0.107	0.067
	2	0.076				
Zn	0	0.132				
	1	0.130	0.164	0.172	0.136	0.087
	2	0.126				
Sr	0	0.067				
	1	0.066	0.105	0.129	0.094	0.058
	2	0.062				
Cd	0	0.124				
	1	0.119	0.158	0.165	0.131	0.074
	2	0.108				
δ			0.033	0.057	0.018	0.028

Table 4: *Singlet-triplet separations for the lowest $S \rightarrow P$ transitions of various atoms calculated with different approximations of the xc-functionals (see text) in comparison with experimental values [44] (EXP). J is the total angular momentum quantum number of the triplet state. δ denotes the mean absolute deviation of the calculated values from the experimental ones (All values in rydbergs).*