A hybrid functional for the exchange-correlation kernel in time-dependent density functional theory

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A review of the approximations in any time-depedendent density functional calculation of excitation energies is given. The single-pole approximation for the susceptibility is used to understand errors in popular approximations for the exchange-correlation kernel. A new hybrid of exact exchange and adiabatic local density approximation is proposed and tested on the He and Be atoms.

I. INTRODUCTION

Ground-state density functional theory is well-established as an inexpensive alternative to traditional *ab initio* quantum chemical methods [1]. Now time-dependent density functional theory (TDDFT) is rapidly emerging as an inexpensive accurate method for the calculation of electronic excitation energies in quantum chemistry [2,3]. Calculation of dynamic response properties using TDDFT has a long history, since the pioneering work of Zangwill and Soven [4,5]. It is only relatively recently that attention has been focussed on the direct extraction of excitation energies [6–11]. Already, this method has been implemented in several quantum chemistry packages, such as deMon [12], Turbomole [13,14], ADF [15], and QCHEM [16]. Important calculations include the calculation of excited-state crossings in formaldehyde [12], excitations with significant doubly-excited character [16], the photospectrum of chlorophyll A [17], and the response of 2-D quantum strips [18].

How are excitation energies calculated using TDDFT? First, a self-consistent ground-state Kohn-Sham calculation is performed, using some approximation for the exchange-correlation energy E_{xc}, such as B3LYP [19] or PBE [20]. This yields a set of Kohn-Sham eigenvalues ϵ_i and orbitals ϕ_i. Even with the *exact* ground-state energy functional and potential, these eigenvalues are in general *not* the true excitations of the system, but are closely related. In a second step, the central equation of TDDFT response theory is solved, which extracts the true linear response function from its Kohn-Sham counterpart. This equation includes a second unknown functional, the exchange-correlation kernel $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$, which is the Fourier transform of the functional derivative of the *time-dependent* exchange-correlation potential. The poles of the exact response function are shifted from those of the KS function, and occur at the true excitations of the system. These steps are typically repeated for several nuclear positions.

The success of any density functional method, however, depends on the quality of the approximate functionals employed. The above calculation requires two distinct density functional approximations: one for the ground-state energy, which implies a corresponding approximation for the exchange-correlation potential $v_{xc}(\mathbf{r}) = \delta E_{xc}/\delta\rho(\mathbf{r})$, and a second for the exchange-correlation kernel. Most calculations now appearing in the chemical literature use the adiabatic local density approximation (ALDA) for f_{xc}. Adiabatic implies that the frequency-dependence of f_{xc} is ignored, and its $\omega = 0$ value used, and LDA implies $f_{xc}(\mathbf{r}, \mathbf{r}') = \delta v_{xc}(\mathbf{r})/\delta\rho(\mathbf{r}')$, where v_{xc} is the LDA potential from ground-state LDA calculations.

The more drastic of the two approximations is that for the ground-state. Very often, functionals which yield accurate ground-state energies have very poor-looking potentials. (How this can happen can be understood by considering the virial theorem, which relates energies to potentials [21]). These poor potentials then have in turn badly behaved virtual orbitals. In particular, local and semi-local approximations, i.e., generalized gradient approximations, fail to capture the correct asymptotic behavior of the potential, and many virtual states are not even bound. Even hybrid functionals, such as B3LYP [19] and PBE0 [22], do not much improve the asymptotic behavior, since they only mix a fraction of exact exchange. This restricts calculations within these approximations to only low-lying excitations. This difficulty is most pronounced in atoms, becomes smaller for bigger molecules, and is irrelevant for bulk solids. Recently [23], we have shown that even with approximations which are free from self-interaction error, such as exact exchange, or self-interaction corrected LDA, and which therefore reproduce the dominant part of the asymptotic decay of the potential, inaccuracies in the Kohn-Sham eigenvalues (mostly due to the incorrect position of the highest occupied level) dominate over any errors introduced in the second step, namely the correction of KS levels to the true levels.

The present work studies the accuracy of approximations to f_{xc} alone. This is because, for low-lying states, errors in f_{xc} must be disentangled from errors in the KS energy levels, and also because many people are working to improve approximations to the exact ground-state potential [24–26], which we hope will ultimately reduce those errors discussed above. Hence all our calculations are performed using the *exact* Kohn-Sham potentials of the He and Be atoms, for which we thank Cyrus Umrigar [27]. We study a variety of approximations to f_{xc}, all adiabatic. We focus especially on the spin-decomposition of such approximations, which determines the relative positions of singlet and triplet excitations in TDDFT. We use the single-pole approximation for the susceptibility to directly relate errors in f_{xc} to errors in excitation energies. We find that exact exchange works well for parallel spins, which determines the mean energy of the singlet and triplet, while the antiparallel contribution to f_{xc} determines their splitting, which is well-approximated in ALDA. With this insight, we construct a hybrid of exact exchange and ALDA, which greatly improves results for He, and moderately improves them for Be. We use atomic units ($e^2 = \hbar = m_e = 1$) throughout, except in Fig. 1.

II. METHODOLOGY

The basic response equation of TDDFT has the same form as that of time-dependent Hartree-Fock theory, or of the Random Phase Approximation, i.e.,

$$
\chi^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; \omega) = \chi_s^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; \omega)
$$
$$
+ \sum_{\sigma''\sigma'''} \int d^3 r'' \int d^3 r''' \, \chi_s^{\sigma\sigma''}(\mathbf{r}, \mathbf{r}''; \omega)
$$
$$
f_{HXC}^{\sigma''\sigma'''}(\mathbf{r}'', \mathbf{r}'''; \omega) \, \chi^{\sigma'''\sigma'}(\mathbf{r}''', \mathbf{r}'; \omega) \quad (1)
$$

where χ is the exact frequency-dependent susceptibility of the system, while χ_s is its Kohn-Sham analog, and $f_{HXC}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'| + f_{xc}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')$. The σ indices denote spin, i.e., $\sigma = \uparrow$ or $\downarrow$. By various means, the poles of χ as a function of ω can be found [7]. Our method for finding these poles is to consider only the discrete poles, i.e., those corresponding to bound states. In the particular case of a frequency-independent model for f_{xc}, we can show [23] that these poles occur at the eigenvalues of the matrix

$$
M_{qq'}^{\sigma\sigma'} = \delta_{qq'}^{\sigma\sigma'} \omega_{q\sigma} + \alpha_{q'\sigma'} \int d^3 r \int d^3 r' \, \Phi_{q\sigma}^*(\mathbf{r}) \times
$$
$$
f_{HXC}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') \Phi_{q'\sigma'}(\mathbf{r}') . \quad (2)
$$

For notational brevity, we have used double indices $q \equiv (j, k)$ to characterize the excitation energy $\omega_{q\sigma} \equiv \epsilon_{j\sigma} - \epsilon_{k\sigma}$ of the single-particle transition ($k\sigma \rightarrow j\sigma$). Consequently, we set $\alpha_{q\sigma} := f_{k\sigma} - f_{j\sigma}$, where $f_{k\sigma}$ is the occupation number of that orbital, and $\Phi_{q\sigma}(\mathbf{r}) = \varphi_{k\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r})$.

While we do include sufficient bound-state poles to converge to an accurate result, our method does neglect continuum contributions, and this effect will be discussed in the next section.

All approximations we study for f_{xc} are adiabatic. The most ubiquitous is ALDA (or more precisley, the adiabatic local spin density approximation) in which

$$
f_{xc}^{\sigma\sigma' \, ALDA}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \left. \frac{\partial^2 e_{xc}^{unif}(n_\uparrow, n_\downarrow)}{\partial n_\sigma \partial n_{\sigma'}} \right|_{n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}')} . \quad (3)
$$

Note that this leads to a completely short-ranged approximation to f_{xc}. Similarly, any adiabatic GGA approximation leads to an approximate f_{xc} which is almost as short-ranged.

A second distinct approximation to f_{xc} is in terms of its (usually) dominant exchange contribution. A highly accurate approximation to the exact exchange-only equations of ground-state density functional theory (the optimized effective potential equations) was introduced by Krieger, Li, and Iafrate [28]. This approximation has been extended to the time-dependent case [6]:

$$
f_x^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = -\delta_{\sigma\sigma'} \frac{\left| \sum_k f_{k\sigma} \varphi_{k\sigma}(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}') \right|^2}{n_\sigma(\mathbf{r}) |\mathbf{r} - \mathbf{r}'| n_\sigma(\mathbf{r}')} . \quad (4)
$$

This is exact for one electron, and for (spin-unpolarized) two-electron exchange. Note that this approximation has a long-ranged contribution, which can cancel exactly the direct hartree contribution to the matrix $\mathbf{M}$ in Eq. (2).

A third approximation which we tried is the self-interaction corrected (SIC) ALDA, which is simply the second functional derivative of the SIC-LDA energy:

$$
E_{xc}^{SIC-LDA} = E_{xc}^{LDA} + \sum_{i\sigma} (E_x[n_{i\sigma}] - E_{xc}^{LDA}[n_{i\sigma}]), \quad (5)
$$

where $n_{i\sigma} = |\varphi_{i\sigma}|^2$ is the density of a single-orbital, and $E_x[n_{i\sigma}]$ is the exact Hartree self-interaction energy of that orbital. This approximation should improve over ALDA, in avoiding spurious self-interaction errors, and over just exchange, by including some correlation.

III. DATA

In this section, we report calculations for the He and Be atoms using the exact ground-state Kohn-Sham potentials, the three approximations to the kernel mentioned in the previous section, and including many bound-state poles in Eq. (2), but neglecting the continuum. The technical details are given in Ref. [23]. Table I lists the results, which are compared with a highly accurate non-relativistic variational calculations [29,30] In each symmetry class (s, p, and d), up to 38 virtual states were

TABLE I. Singlet/triplet excitation energies in the helium and beryllium atoms, calculated from the exact Kohn-Sham potential by using approximate xc kernels (in millihartrees), and using the lowest 34 unoccupied orbitals of s and p symmetry for He, and the lowest 38 unoccupied orbitals of s, p, and d symmetry for Be. Exact values from Ref. [29] for He and from Ref. [30] for Be.

		Singlet/triplet shifts				
	ω_{KS}	ALDA	X	SIC	hybrid	exact
		Transitions from the 1s state in He atom				
2s	746.0	22/-11	20/-25	19/-16	14/-19	12/-18
3s	839.2	6.9/-2.4	5.8/-4.9	5.6/-3.6	5.1/-4.6	3.3/-4.2
4s	868.8	3.1/-0.9	2.5/-1.7	2.4/-1.3	2.4/-2.0	1.3/-1.6
5s	881.9	1.6/-0.4	1.3/-0.8	1.3/-0.6	1.3/-1.0	0.6/-0.8
6s	888.8	1.0/-0.3	0.8/-0.5	0.7/-0.4	0.8/-0.7	0.4/-0.5
2p	777.2	-0.8/-7.4	7.2/-8.4	6.1/ 0.2	2.7/-3.4	2.7/-6.6
3p	847.6	0.7/-1.9	2.5/-2.3	2.2/-0.5	1.4/-1.3	1.0/-2.0
4p	872.2	0.4/-0.7	1.1/-0.9	1.0/-0.2	0.6/-0.5	0.5/-0.8
5p	883.6	0.2/-0.4	0.6/-0.5	0.5/-0.1	0.4/-0.3	0.2/-0.4
6p	889.8	0.1/-0.3	0.3/-0.3	0.3/-0.1	0.2/-0.2	0.1/-0.3
err	57	32	31	29	12	-
		Transitions from the 2s state in Be atom				
3s	244.4	7.1/-5.7	10.9/-10.6	10.3/-1.4	6.6/-4.6	4.7/-7.1
4s	295.9	2.5/-1.6	3.6/-2.5	3.5/-0.6	2.6/-1.6	1.4/-2.0
5s	315.3	1.1/-0.7	1.7/-1.0	1.6/-0.3	1.2/-0.7	0.6/-0.9
6s	324.7	0.6/-0.4	0.9/-0.5	0.9/-0.2	0.7/-0.4	0.3/-0.5
2p	132.7	56/-42	55/-133	53/-53	10/-88	61/-32
3p	269.4	2.0/-4.3	6.4/-4.2	5.6/ 1.1	4.2/-2.8	4.8/-1.5
4p	304.6	0.3/-1.4	2.1/-1.2	1.9/ 0.3	1.3/-0.8	1.7/-4.1
5p	319.3	0.1/-0.6	1.0/-0.5	0.9/ 0.1	0.6/-0.2	0.2/ 0.0
6p	326.9	0.0/-0.4	0.5/-0.3	0.4/ 0.0	0.3/-0.2	0.1/-0.1
3d	283.3	-5.4/-2.8	1.8/-2.0	0.9/ 3.2	-1.4/ 1.2	10.3/-0.6
4d	309.8	-1.4/-1.1	0.8/-0.9	0.5/ 0.9	-0.2/ 0.6	3.6/-0.2
err	138	56	144	73	136	-
err'	45	41	37	44	29	-

calculated. The errors reported are absolute deviations from the exact values. The second error under the Be atom excludes the $2s \to 2p$ transition, for reasons discussed in the next section.

The effect of neglecting continuum states in these calculations has been investigated by van Gisbergen et al. [15], who performed ALDA calculations from the exact Kohn-Sham potential in a localized basis set. These calculations were done including first only bound states, yielding results identical to those presented here, and then including all positive energy orbitals allowed by their basis set. They found significant improvement in He singlet-singlet excitations, especially for $1s \to 2s$ and $1s \to 3s$. Other excitations barely changed. Assuming inclusion of the continuum affects results with other approximate kernels similarly, these results do not change the basic reasoning and conclusions presented below, but suggest that calculations including the continuum may prove to be more accurate than those presented here.

IV. SINGLE-POLE ANALYSIS

The simplest truncation of the eigenvalue equation (2) for the excitation energies is to ignore all coupling between poles, except that between a singlet-triplet pair. This is equivalent to setting $\langle q|f_{\mathrm{HXC}}|q'\rangle$ to zero, for $q \neq q'$. (We have dropped the spin-index on these contributions, since we deal only with closed shell systems). Then the eigenvalue problem reduces to a simple 2×2 problem, with solutions

$$\Omega_q^+ = \omega_q + 2\Re\langle q|f_{\mathrm{HXC}}|q\rangle$$
$$\Omega_q^- = \omega_q + 2\Re\langle q|\Delta f_{\mathrm{XC}}|q\rangle, \qquad (6)$$

where

$$f_{\mathrm{HXC}} = \frac{1}{4}\sum_{\sigma\sigma'} f_{\mathrm{HXC}}^{\sigma\sigma'} = \frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{2}\left(f_{\mathrm{XC}}^{\uparrow\uparrow} + f_{\mathrm{XC}}^{\downarrow\uparrow}\right),$$

$$\Delta f_{\mathrm{XC}} = \frac{1}{4}\sum_{\sigma\sigma'} \sigma\sigma' f_{\mathrm{HXC}}^{\sigma\sigma'} = \frac{1}{2}\left(f_{\mathrm{XC}}^{\uparrow\uparrow} - f_{\mathrm{XC}}^{\downarrow\uparrow}\right). \qquad (7)$$

Thus f_{HXC} is the spin-summed contribution, which contributes to χ, the spin-summed susceptibility, and therefore gives rise to the singlet level, while Δf_{XC} is the spin-flip contribution, also called $\mu_o^2 G_{\mathrm{XC}}$ in the theory of the frequency-dependent magnetization density [31]. Thus even within the SPA, the KS degeneracy between singlets and triplets is broken, and we identify Ω_q^- with the triplet. In Table II, we report results within the single-pole approximation.

At this point, we notice the very strong shift in the Be $2s \to 2p$ transition. This is due to the small magnitude of its transition energy, so that the pole of the $2p$ energy is very close to the pole of the $2s$ energy. Thus the single pole approximation is not expected to work well for this case, and it should be excluded from general statements based on the SPA.

A. Why are Kohn-Sham excitation energies so good?

We see throughout the data that the Kohn-Sham eigenvalues are always inbetween the exact singlet and triplet energy levels. The splitting is much larger for Be than for He, but this obervation is true in both cases. It has already been made by Filippi et al [32], and explained in terms of quasi-particle amplitudes [33]. Here, we use the single-pole approximation to analyze this result in terms of the known behavior of density functionals. From Eq. (6) we find that the mean energy is given by

$$\bar{\Omega}_q = \frac{1}{2}(\Omega_q^+ + \Omega_q^-) = \omega_q + \Re\langle q|\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{\mathrm{XC}}^{\uparrow\uparrow}(\mathbf{r},\mathbf{r}'|q\rangle,$$

$$(8)$$

3

TABLE II. Same as Table I, but within the single pole approximation.

	ω_{KS}	Singlet/triplet shifts			
	exact	ALDA	X	SIC	hybrid
Transitions from the $1s$ state in He atom					
$2s$	746.0	25.8/-10.3	22.7/-22.8	21.4/-14.7	18.0/-18.1
$3s$	839.2	6.6/-2.6	5.6/-5.5	5.3/-3.9	4.7/-4.5
$4s$	868.8	2.6/-1.0	2.2/-2.1	2.1/-1.5	1.8/-1.8
$5s$	881.9	1.3/-0.5	1.1/-1.1	1.0/-0.8	0.9/-0.9
$6s$	888.8	0.7/-0.3	0.6/-0.6	0.6/-0.4	0.5/-0.5
$2p$	777.2	-0.8/-7.0	7.8/-7.9	6.4/ 0.2	3.1/-3.1
$3p$	847.6	0.7/-2.0	2.4/-2.3	2.1/-0.5	1.4/-1.3
$4p$	872.2	0.4/-0.8	1.0/-1.0	0.9/-0.2	0.6/-0.6
$5p$	883.6	0.2/-0.4	0.5/-0.5	0.5/-0.2	0.3/-0.3
$6p$	889.8	0.1/-0.3	0.3/-0.3	0.2/-0.1	0.2/-0.2
err	57	34	32	31	15
Transitions from the $2s$ state in Be atom					
$3s$	244.4	8.2/-5.4	13.0/-9.5	12.2/-1.3	8.6/-5.1
$4s$	295.9	2.4/-1.6	3.5/-2.7	3.4/-0.6	2.4/-1.6
$5s$	315.3	1.0/-0.7	1.5/-1.1	1.4/-0.3	1.1/-0.7
$6s$	324.7	0.5/-0.4	0.7/-0.6	0.7/-0.2	0.5/-0.4
$2p$	132.7	75/-34	71/-65	67/-41	58/-52
$3p$	269.4	-0.4/-4.3	5.4/-4.7	4.5/ 0.6	2.3/-1.6
$4p$	304.6	-0.1/-1.5	1.7/-1.5	1.5/ 0.2	0.8/-0.6
$5p$	319.3	-0.1/-0.7	0.8/-0.6	0.7/ 0.1	0.4/-0.2
$6p$	326.9	-0.1/-0.4	0.4/-0.4	0.3/ 0.0	0.1/-0.2
$3d$	283.3	-5.0/-2.6	1.8/-1.9	1.0/ 3.4	-1.2/ 1.1
$4d$	309.8	-1.4/-1.1	0.8/ 0.0	0.6/ 0.8	0.3/ 0.6
err	138	61	79	60	55
err'	45	45	36	44	33

while the energy splitting is given by

$$\Delta\Omega_q = (\Omega_q^+ - \Omega_q^-) = 2\Re\langle q|\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{\mathrm{C}}^{\uparrow\downarrow}|q\rangle, \qquad (9)$$

since there is no exchange contribution to antiparallel f_{XC}. If we further define $\delta\Omega_q = \bar{\Omega}_q - \omega_q$ as the deviation of the mean energy from the Kohn-Sham level, we see that

$$|\delta\Omega_q| < \Delta\Omega_q/2 \qquad (10)$$

must be satisfied for the Kohn-Sham level to lie in between the singlet and triplet levels. Within the single-pole approximation, we have a very simple expression for the ratio of these two:

$$\frac{2\delta\Omega_q}{\Delta\Omega_q} = \frac{\Re\langle q|f_{\mathrm{HXC}}^{\uparrow\uparrow}|q\rangle}{\Re\langle q|f_{\mathrm{HC}}^{\uparrow\downarrow}|q\rangle} \qquad (11)$$

Consider first the He atom. For two electrons, $f_{\mathrm{x}}^{\uparrow\uparrow} = -1/|\mathbf{r}-\mathbf{r}'|$, exactly cancelling the Hartree term in Eq. (8), leaving only the parallel correlation contribution. (This is reflected in the X column on Table II, where the upshift of the singlet is equal to the downshift of the triplet.) Thus we find

$$\frac{2\delta\Omega_q}{\Delta\Omega_q} = \frac{\Re\langle q|f_{\mathrm{C}}^{\uparrow\uparrow}|q\rangle}{\Re\langle q|\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{\mathrm{C}}^{\uparrow\downarrow}|q\rangle} \qquad \text{(2el)} \qquad (12)$$

for two electrons in the single-pole approximation. It is well-known (see, e.g., Ref. [34]) that for ground-state energies, parallel correlation is much weaker than antiparallel, since antiparallel electrons are not kept apart by the exchange interaction. Thus this ratio is expected to stay well less than 1, as it does for all our He excitations. The effect of the single-pole approximation on this conclusion can be judged by studying the shift in the mean for the X results in Table I.

For Be, and any system with more than two electrons, there is still a good deal of cancellation of the exchange contribution with the direct contribution, but this cancellation is no longer exact. This can be seen in the Be results for X in Table II. By studying the form of f_{X} given in Eq. (4), we expect this remnant exchange contribution to be of order $O((N-2)/N^2)$ for unpolarized systems. Thus in exchange-dominated (i.e., high density or weakly correlated) systems, the direct Coulomb term in the denominator will be larger than any remnant exchange term in the numerator. On the other hand, in low-density or strongly correlated systems, if antiparallel correlation continues to dominate over parallel correlation, this ratio will still be less than one. We conclude that the Kohn-Sham levels will usually be close to the true excitations (of single-particle nature).

B. Relation of exact exchange to Görling-Levy perturbation theory

Both time-dependent DFT and Görling-Levy [35] perturbation theory are formally exact methods for extracting electronic excitation energies in density functional theory. In this section, we consider the expansion of the excitation energies in powers of the adiabatic coupling constant λ to first order. This procedure should give identical results in both theories. Recently, Filippi et al [32] have performed GL first order calculations for the He atom, using the exact Kohn-Sham potential. Their results are numerically identical to ours, using the exact exchange kernel, but only *within* the single-pole approximation, as given by Table II. Results calculated with the full (i.e., many poles) scheme, i.e., in Table I, differ slightly from theirs. This produces a paradox, in which the easier SPA is more accurate (apparently exact), while the more sophisticated treatment introduces errors.

The resolution of this paradox can be seen most easily in Eq. (1), the RPA-type equation for the susceptibility. Insertion of f_{X} alone (linear in λ) into these equations will lead to all powers of λ being present in the solution, since it is a self-consistent integral equation. This is most easily seen by iterating the equations. A simple way to recover the exact first-order GL result is by solving the
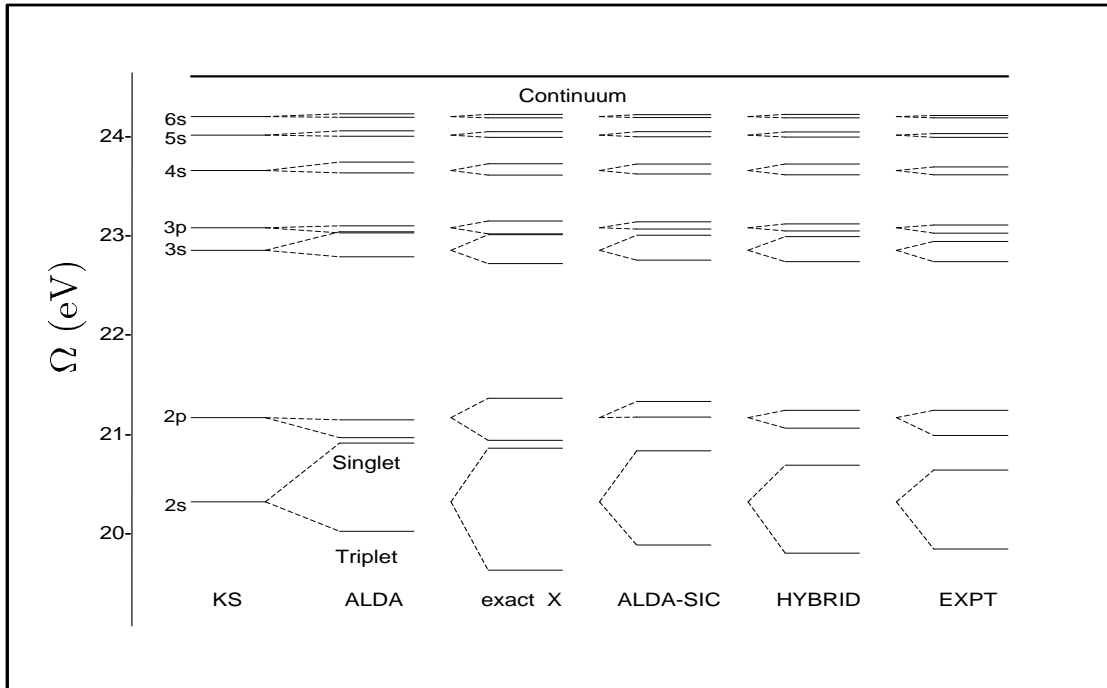
FIG. 1. *Excitation energies from the ground-state of He, including the orbital energies of the exact Kohn-Sham potential, the time-dependent spin-split correction calculated within four different functional approximations, and experimental numbers [38].*

equations with λf_{X}, and making λ very small, to find the linear contribution to the change in excitation energies. Insertion of $\lambda = 1$ into this result will yield the exact GL result.

A far simpler method is to use the single-pole approximation. To see why this works, consider Eq. (2), our matrix whose eigenvalues are at the excitation energies. Since f_{HXC} is at least first-order in λ, all off-diagonal contributions are of $O(\lambda)$. Thus to lowest order, the diagonal dominates, and the off-diagonal corrections contribute $O(\lambda^2)$ corrections. Retaining only diagonal contributions, i.e., the single-pole approximation, yields the exact result to first order in λ. A detailed functional derivation of this result has recently been given by Gonze and Scheffler [37].

C. A new hybrid functional for the kernel

To illustrate the importance of understanding the origin of errors in density functionals, we use the insight gained within the SPA in the previous sections to construct a hybrid functional for f_{XC}. We then apply this both within SPA and in the full calculation. Our original idea, as mentioned in section II, was to use a simple self-interaction correction to produce a better approximation than either exact exchange or ALDA, but the SIC results

of Tables I and II show this does not happen.

Consider Fig. 1, which illustrates the positions of energy levels in the different schemes for the He atom. Our first step is to consider the mean energies. As pointed out in subsection A, these are determined by the parallel contributions to f_{XC} and the Hartree term. We have already seen how these two terms cancel exactly at the exchange level, so that the mean energy is very good in such a calculation. In ALDA, the cancellation (exact for He) of the exchange contributions is lost. This can be seen in the large shifts in the ALDA mean energies in Table II and in Fig. 1. Furthermore, the remaining small parallel-spin correlation contribution can be expected to be grossly overestimated by ALDA, since LDA ground-state correlation energies are usually too large by a factor of 2 or 3. Unfortunately, even SIC-ALDA is not exact for two-electron exchange, and it also suffers from a poor mean energy. Thus we recommend using only exact exchange for the parallel-spin contribution.

On the other hand, the splitting is determined solely by anti-parallel correlation contributions, and the direct term. Thus, an exact exchange treatment misses entirely the significant anti-parallel correlation contribution. This error is highlighted by the far too large splittings in the exchange results in Tables I and II, implying significant cancellation between the direct and antiparallel correlation contributions. So here we advocate use of ALDA. Since the splitting depends on anti-parallel contributions to f_{XC}, but the SIC correction only applies to one spin at a time, SIC-ALDA has exactly the same splittings. Our recommended hybrid is therefore

$$f_{\mathrm{XC}}^{\uparrow\uparrow} = f_{\mathrm{X}}^{\uparrow\uparrow}, \qquad f_{\mathrm{XC}}^{\uparrow\downarrow} = f_{\mathrm{XC}}^{\uparrow\downarrow\ \mathrm{ALDA}}. \qquad (13)$$

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Results shown in Tables I and II indicate that this hybrid decreases almost all errors over either exact exchange or ALDA. On average, the decrease is by about a factor of 3 for the He atom, but much less for Be (about 40%). Notable exceptions are the triplet transitions to p states in He and in Be, where the error is increased.

V. CONCLUSIONS

We have shown how the results of TDDFT with approximate exchange-correlation kernel functionals may be understood in terms the well-known behavior of the ground-state functionals from which they are derived. We have shown in a simple case how a more accurate functional may be constructed from this insight. We regard this as an initial step toward an accurate approximation for f_{xc}. Another obvious analytic tool would be the direct adiabatic decomposition of f_{xc} in terms of λ, which has proved so successful in understanding the hybrids commonly used in ground-state calculations [39,40].

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