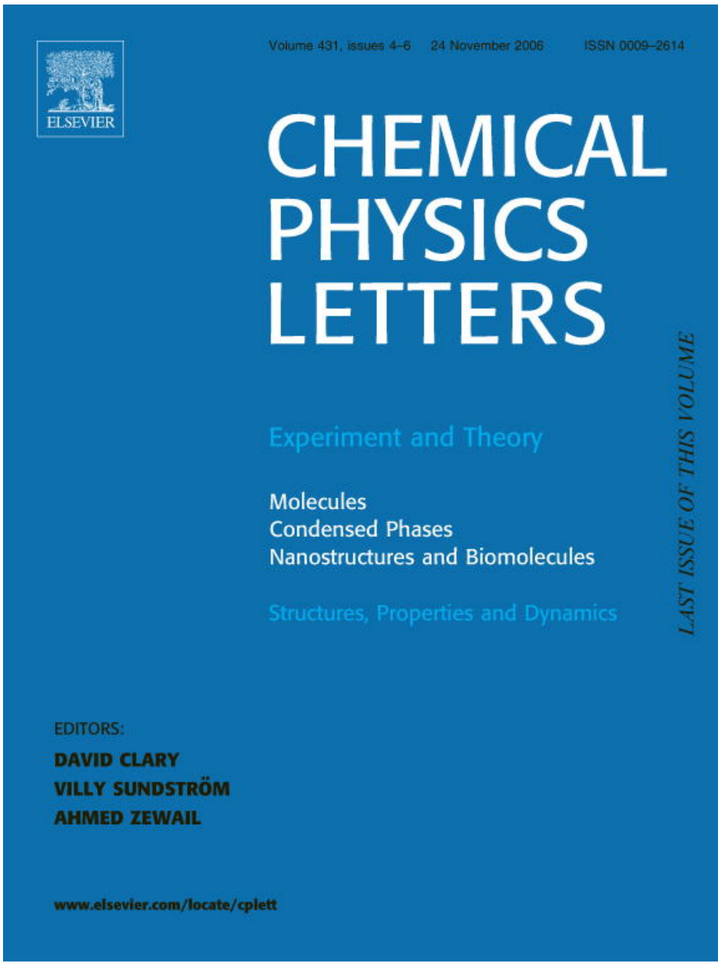

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A new challenge for time-dependent density functional theory

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Abstract

The quantum defect is an excellent tool to study errors in excitation energies obtained with *ab initio* methods. We perform a quantum defect analysis of the s, p, and d Rydberg states of Be with accurate ground state Kohn–Sham potentials. The s- and p-quantum defects are well described by the ALDA, but it fails badly for the d-quantum defect. This failure is not clear from the excitation energies alone and it provides a new challenge for functional development in time-dependent density functional theory.

1. Introduction

Time-dependent density functional theory (TDDFT) [1] has become a popular method for calculating excitation energies of atoms, molecules, clusters, and solids [2,3]. In many common situations, it yields transition frequencies with errors below 0.2 eV, and properties of excited states are obtained with an accuracy comparable to that of ground state DFT.

As any theory is increasingly applied, the limitations of its approximations are discovered [3]. An early limitation for TDDFT was due to the poor asymptotic behavior of potentials in approximations to ground state DFT. This problem was overcome by the development of asymptotically corrected potentials [4–7]. Later, it was found that adding an asymptotic tail to the LDA potential, without any modification in the inner region, gives very accurate results [8]. Another limitation was that within the adiabatic approximation, double excitations are missed by TDDFT. It was shown by Maitra et al. that this problem can be overcome with a frequency dependent exchange-correlation (xc) kernel [9,10]. A still open question is how to obtain charge-transfer excitations within TDDFT. An empirical approximation of the xc-kernel has been designed as a step to overcome this problem [11].

In this letter, we report a new and surprising failure of present TDDFT calculations. While previously hinted at in the literature, our recently developed quantum defect analysis (QDA) for atoms [12] makes it very clear that this is a qualitative failure. Essentially, as the angular-momentum change grows, TDDFT with the adiabatic local density approximation (ALDA), gives worse and worse transition energies. For s → d transitions, including TDDFT xc-contributions is much worse than ignoring them altogether!

2. Theory

For closed shell atoms and for any spherical one-electron potential that decays as $-1/r$ at large distances, the bound-state transitions form a Rydberg series with frequencies:

$$\omega_{nl} = I - \frac{1}{2(n-\mu_{nl})^2} \tag{1}$$

where I is the ionization potential, and μ_{nl} is called the quantum defect [13]. We use atomic units ($e^2 = \hbar = m_e = 1$) throughout. For real atoms, quantum defects depend only weakly on the principal quantum num-

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ber n for large n and converge to a finite value in the limit $n \to \infty$.

The quantum defect is a smooth function of energy, and is well approximated a polynomial of some low order p:

$$\mu^{(p)}(E) = \sum_{i=0}^{p} \mu_i E^i, \quad E = \omega - I. \tag{2}$$

Thus we calculate transition frequencies, extract the quantum defect via Eq. (1) and plot them as a function of E. When we fit our quantum defect values to Eq. (2), we optimize the fit over the entire range of excitation energies, not just around $E = 0$ (the μ_i are simply related to the a, b, and c coefficients in Refs. [14,15]).

For the TDDFT part, we solve the linear response equations as derived by Casida [16]. Such a TDDFT calculation consists of two parts. First the ground state KS orbitals and KS orbital energies are determined with DFT. For He and Be, nearly exact potentials have been developed by Umrigar et al. (He [17] and Be [18]), and we use these potentials for the ground state. In this way, we eliminate any error due to the underlying ground state KS potential. In the second part of the calculation (the TDDFT part), we do perturbation theory on the ground state results. This means solving Casida's equations, and we use the ALDA xc-kernel in all cases. We also include results in the Hartree approximation, equivalent to setting the xc-kernel to zero. In this approximation triplet values correspond to the bare KS orbital energy differences, as the Hartree interaction involves no spin flips.

3. Computational details

For the calculation of KS orbital energies and TDDFT excitation energies, we used the Amsterdam Density Functional program package ADF (http://www.scm.com). The numerical integration accuracy was set to 12 significant digits, and the convergence criterion in the self-consistent procedure for the solution of the KS equations was set to 10^{-12}. We reached convergence with a large even tempered basis set with primitive basis functions including f functions and a fit set including g functions.

In order to map the accurate potentials onto the integration grid of ADF we performed a cubic spline interpolation between the available data points. We confirmed the quality of our ground state KS results by comparing the ADF orbital energies with orbital energies obtained with an optimized potential model (OEP) program developed by Engel (engel@th.physik.uni-frankfurt.de [19,20]). This program is basis set independent, works with a radial grid, and both the energies and the potentials are optimized in a self-consistent way. For this code, the accurate potentials do not need to be interpolated. We obtained ground state orbitals energies with ADF that were identical to the ones obtained with the OEP code at least up to five digits (in a.u.).

In order to obtain the coefficients in Eq. (2) for He, we included states up to $n = 6$ in case of the ALDA and $f_{xc} = 0$ calculations, up to $n = 10$ in case of the accurate wave function reference data, and up to $n = 7$ for the KS values. For Be we included states up to $n = 6$ in case of ALDA and $f_{xc} = 0$ calculations, up to $n = 8$ in case of the experimental reference data, and up to $n = 9$ for the KS values.

4. Results

Van Gisbergen et al. first calculated transitions from the accurate Be KS potential [21] using the ALDA kernel and reported tables with transitions. If the same data is cast into a quantum defect and plotted as function of energy, systematic errors in the transition energies are revealed and more insight in the results is obtained. Since Rydberg energies get closer together with higher energies, the absolute error that is made in the excitation energies by approximate methods will get smaller. This obscures the true accuracy of approximate methods. The quantum defect does not suffer from this problem since it amplifies the small differences between approximate and true results at higher energies.

The continuous lines in all graphs that we show correspond to the fitted quantum defect values. The coefficients used to obtain the continuous quantum defect, using Eq. (2), are reported in Ref. [12] for the s- and p-cases. We show the s-quantum defect of Be in Fig. 1. The dashed line with open triangles shows the scattering from the ground state KS potential, which lies neatly between the experimental singlet (closed squares) and triplet (open squares) values. We note how large the quantum defects are. We see from Eq. (1) that a quantum defect of 1 means (for single-particle scattering) that the deviation from $-1/r$ is so big that the energy of a particular transition to a state with quantum number n corresponds exactly to the energy of that transition in a hydrogen atom to a final state with quantum number $n' = n - 1$. Inclusion of only Hartree

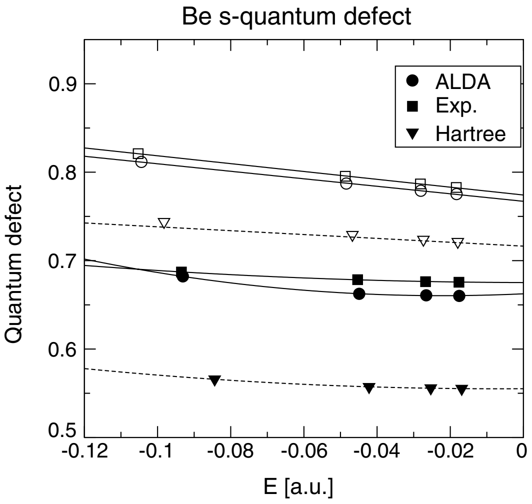

Fig. 1. Hartree and ALDA singlet and triplet s-quantum defects of Be, compared with experimental values [22]. The closed symbols correspond to singlet values, the open symbols correspond to triplet values.

effects shifts this line down to the closed triangles for the singlet, but leave the triplets unchanged. Finally, the ALDA xc-kernel shifts both of these Hartree results upward to the circles. The ALDA accounts for more that 80% of the error of the Hartree approximation.

We next show the p-quantum defect in Fig. 2. In this case we are seeing a lot more structure and the ALDA slightly overestimates the curvature of the quantum defect correction in this case. This produces the largest errors for the most negative energies (i.e. the lowest transitions). When E goes to zero all quantum defect values get close together except for the singlet Hartree values which underestimate the experimental results. The triplet Hartree results are a good approximation to the experiment. Here ALDA clearly overestimates the correction to $\mu(0)$. This is not a large problem for lower transitions, but causes the $E \to 0$ results to be worse than bare Hartree. In fact, the KS values lie in between the experimental singlet and triplet values until $n = 6$. It can be seen from the graph that they do seem to get below the experimental singlet and triplet results for $n > 6$. Indeed, for $n = 7$, both the singlet and triplet experimental quantum defects (0.3616 and 0.3676, respectively) lie above the KS value of 0.3550. So here we have an example where the quantum defect of the bare KS orbital energy differences does not lie between the experimental singlet and triplet values.

We also performed calculations on higher s → d transitions that have not been studied previously. We show the d-quantum defect of Be in Fig. 3 and that of He in Fig. 4. For Be we first note that the KS curve lies, as before, between the singlet and triplet. But in this case it is much closer, and parallel to, the triplet curve. In this case the Hartree approximation does rather well, by shifting the singlet curve about halfway towards the experiment, while not moving the triplet. But the ALDA curves are a disaster. For the singlet, the ALDA correction is in the wrong direction! For the triplet the correction is in the right direction, but it is too large by a factor of about four. We find similar results in case of He (Fig. 4). First of all, the KS curve lies below the singlet and triplet curves for all n values studied. Again it is close to the triplet curve, the singlet Hartree curve underestimates the reference curve. The ALDA correctly shifts both singlet and triplet curves upward, but the shift is too large for the singlet, again leading to a dramatic overestimation.

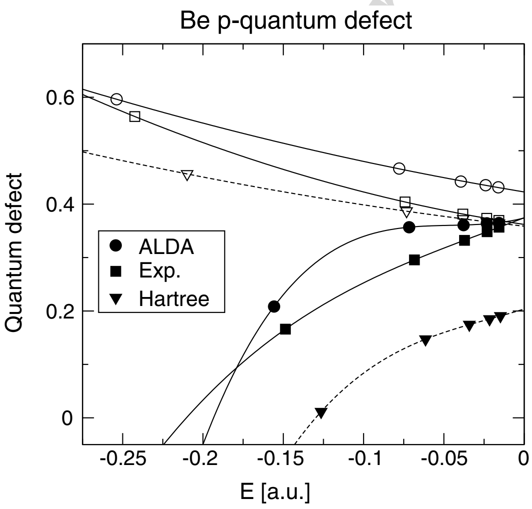

Fig. 2. Hartree and ALDA singlet and triplet p-quantum defects of Be, compared with experimental values [22]. The closed symbols correspond to singlet values, the open symbols correspond to triplet values.

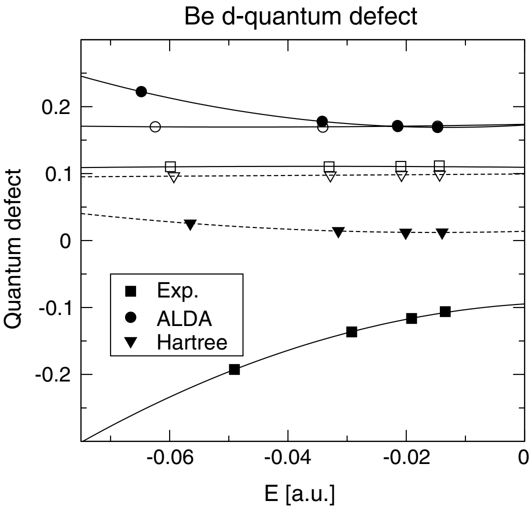

Fig. 3. Hartree and ALDA singlet and triplet d-quantum defects of Be, compared with experimental values [22]. The closed symbols correspond to singlet values, the open symbols correspond to triplet values.

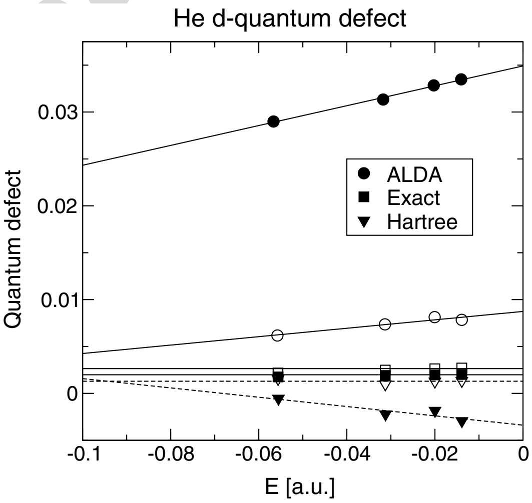

Fig. 4. Hartree and ALDA singlet and triplet d-quantum defects of He, compared with accurate wave function results [23] (labeled 'Exact'). The closed symbols correspond to singlet values, the open symbols correspond to triplet values.

We show the coefficients of the d-quantum defect corresponding to the fit of Eq. (2) in Table 1. Apart from the coefficients we also give the 'Max. AE' in this tables, by which we mean the maximum absolute error between the fitted values and the true quantum defect values. In all cases we stopped adding coefficients to the fit expansion

Table 1
We give the coefficients of the expansion of the singlet and triplet d-quantum defect of He and Be

Atom	Reference[a]		$f_{xc} = 0$		ALDA	
	Singlet	Triplet	Singlet	Triplet	Singlet	Triplet
He						
μ_0	0.0020	0.0026	−0.0034	0.0013	0.0349	0.0087
μ_1			−0.0496		0.1059	0.0449
Max. AE	0.0002	0.0005	0.0006	0.0003	0.0002	0.0003
Be						
μ_0	− 0.0947	0.1094	0.0138	0.0994	0.1725	0.1736
μ_1	0.5636	−0.0810	0.2353	0.0554	0.5291	0.1699
μ_2	−29.2439	−1.1540	7.8553		20.0356	1.7686
Max. AE	0.001	0.001	0.0003	0.0002	0.0000	0.0008

The ionization energy of He is 0.9037 a.u., and that for Be is 0.3426 in all cases.

[a] Accurate wave function results for He from Ref. [23] and experimental data for Be from Ref. [22].

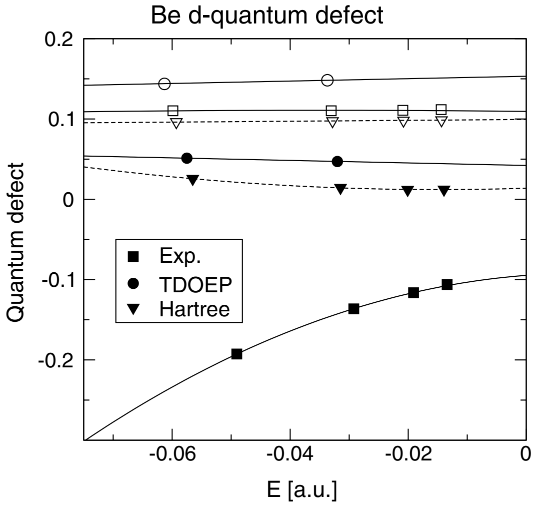

Fig. 5. Hartree and TDOEP singlet and triplet d-quantum defects of Be, compared with experimental values [22]. The closed symbols correspond to singlet values, the open symbols correspond to triplet values.

until this error was smaller than 0.001, or when adding more coefficients no longer reduced the error. We see that three coefficients are enough in all cases to completely describe the quantum defect. The ALDA estimate for the $E = 0$ quantum defect (μ_0) is close to the exact data for $l = 0$, 1, but not for $l = 2$ and we also see that the $E = 0$ quantum defect is not always between the exact singlet and triplet values.

Thus in case of the d-quantum defect, including the ALDA kernel within TDDFT worsens the results instead of improving it. In the mid 1980s a similar failure of the LDA was observed in the case of transfer energies [24,25]. It was found that sp transfer energies in first row atoms and sd transfer energies in 3d atoms are underestimated by the local spin-density approximation (LSD). The source of the error was linked to the fact that the LSD is unable to properly take into account the nodal structure of the orbitals. The failure of the ALDA that we observe here may be related to the LSD problem, but the methodology here is very different. In TDDFT, we extract transitions by using linear response, while in order to obtain transfer energies, one subtracts total energy differences.

To test the effect of including orbital dependence in the kernel we extracted quantum defect values from the exchange-only OEP calculations of Petersilka et al. [26]. They did not do full time-dependent OEP, instead they use the approximate PGG kernel [27]. We show results in Fig. 5. The errors are similar to those of ALDA, but considerably quantitatively smaller. A full OEP calculation might do better still.

Acknowledgement

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