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Abstract
Time-dependent density functional theory (TDDFT) has become a standard tool for
investigation of electronic excited states. However, for certain types of electronic excitations,
TDDFT is known to give systematically inaccurate results, which has been attributed to the
insufficiency of conventional exchange–correlation functionals, such as the local density
approximation (LDA). To improve TDDFT performance within LDA, a modified linear
response (MLR) scheme was recently proposed, in which the responses from not only the
ground state, but also the intermediate excited states are taken into account. This scheme was
shown to greatly improve TDDFT performance on the prediction of Rydberg and
charge-transfer excitation energies of molecules. Yet, for a validation of this TDDFT-MLR
scheme for excitation energies, there remain issues to be resolved regarding Rydberg transitions
of single atoms before going to larger systems. In the present work, we show an adapted
algorithm to construct the intermediate excited states for rare-gas atoms. With the technique,
Rydberg transition energies can be well decoded from LDA, as will also be shown in the
application of the TDDFT-MLR scheme to other types of atoms.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Density functional theory (DFT) [1, 2] has become the
most successful method for calculating ground-state properties
of condensed matter. This success is largely rooted in
the simplicity of conventional exchange–correlation (xc)
functionals, such as the simplest local density approximation
(LDA). LDA also plays an important role for calculations
of excited-state properties within the framework of time-
dependent density functional theory (TDDFT) [3–5], which
has emerged as a reliable standard tool for the investigation
of excited-state properties in recent years. Time-dependent
LDA (TDLDA) is often formulated in real time, which
facilitates the calculation of excited-state dynamics [6–8]. To
calculate optical spectra, TDDFT is usually combined with
linear response (LR) theory: Given a weak instantaneous
perturbation, the Kohn–Sham wavefunctions are propagated

for a sufficiently long time, and then the density (or dipole)
response is obtained and analyzed to give excitation energies.
This approach has demonstrated that TDLDA is able to give
good results for large systems in a computationally efficient
way [9–11].

In quantum chemistry, TDDFT-LR is preferably formu-
lated in the frequency domain, without explicitly propagating
Kohn–Sham wavefunctions. The calculation of excitation
energies is recast into a pseudoeigenvalue problem, known as
the Casida equation in the matrix form [12, 13]. Due to its
efficiency for small and medium-sized molecular systems, this
approach has been widely implemented in standard quantum
chemistry packages. Extensive calculations show that it can
generally give good predictions on valence excitation energies.
However, for Rydberg and charge-transfer excitations, there
is systematic underestimation of excitation energies from
TDDFT. The topic of how to improve TDDFT performance

on these problematic excitations has been the focus of wide attention. In most studies, effort has been concentrated to develop xc functionals with correct long-range behaviors. The typical recipe is the asymptotic correction of local xc potentials at large distances to show $-\frac{1}{r}$ behavior of the exact xc potential [14–17]. TDDFT performance has been improved by these methods, nevertheless, adjustable parameters are often introduced and a unified treatment has not been drawn up yet.

In our previous works, we have examined the above problems of TDDFT from a different point of view. That is, we try to improve the TDDFT methodology on how to calculate excitation energies from the LR scheme. In TDDFT within ordinary LR, the excitation energies are obtained from the response of the ground state to the applied perturbation. In contrast to this scheme, we presented a modified LR (MLR) scheme: responses from not only the ground state but also the intermediate excited states should be taken into account and the final result is an average of excitation energies from these responses. This scheme was shown to greatly improve TDDFT performance on the prediction of Rydberg and charge-transfer excitation energies of molecules [18, 19], and its efficiency is further demonstrated in calculating nonadiabatic couplings in molecular systems [20, 21], without any correction to the LDA functional.

Apart from the molecular systems, the application of TDDFT-MLR to atomic systems has not been done yet. Although it is anticipated that this can be done in a straightforward way, such an application is not necessarily trivial, concerning some arguments on the performance of LDA. The xc hole of the uniform electron gas is used as model for the exact hole in LDA. In the bonding region between two atoms, the LDA model hole resembles the exact exchange hole, which becomes more isotropic than in the separated atoms: The centered LDA exchange hole is a better approximation for the more homogeneous molecular density than for the more inhomogeneous density of atoms [22]. Therefore, there remains work to be done for the validation of TDDFT-MLR/LDA for single atoms, as done in molecular systems.

In the present paper, we report our recent calculation results of atomic excitation energies by TDDFT-MLR/LDA for various types of atoms. Except for rare-gas atoms, which need an adapted algorithm to construct intermediate excited states, all calculation procedures are kept the same as in the molecular systems. Our result will show that the TDDFT-MLR scheme achieves good accuracy for both valence and Rydberg transitions in all the atomic cases studied in this work.

2. Methodology

2.1. TDDFT-LR: Formulation of response from the ground state

In TDDFT-LR, a weak perturbation is applied to the ground state of the Kohn–Sham system and the response is examined. For real perturbations $\delta \mathbf{v}_{\text{appl}}(\omega)$, the Casida formalism [12, 13]

gives the real part of the density matrix $\delta \mathbf{P}(\omega)$ as

$$
\sum_{kl\tau}^{f_{k\tau}-f_{l\tau}>0} \left[\delta_{\sigma,\tau} \delta_{i,k} \delta_{j,l} \frac{\epsilon_{i\sigma}-\epsilon_{j\sigma}}{f_{i\sigma}-f_{j\sigma}} - 2K_{ij\sigma,kl\tau} \right.
$$
$$
\left. - \omega^2 \frac{\delta_{\sigma,\tau} \delta_{i,k} \delta_{j,l}}{(f_{i\sigma}-f_{j\sigma})(\epsilon_{i\sigma}-\epsilon_{j\sigma})} \right] (\text{Re}\,\delta P_{kl\tau})(\omega)
$$
$$
= \delta v_{ij\sigma}^{\text{appl}}(\omega), \tag{1}
$$

where $f_{i\sigma}$ and $\epsilon_{i\sigma}$ are, respectively, the occupation number and eigenenergy of the ith orbital with spin σ in the unperturbed ground state. The coupling matrix $\mathbf{K}$ has a Coulombic and an xc part. From the pole condition of $\delta \mathbf{P}(\omega)$, we get the following Casida equation,

$$
\mathbf{\Omega} \mathbf{F}_I = \omega_I^2 \mathbf{F}_I, \tag{2}
$$

where the eigenvalue ω_I^2 is the squared excitation energy of transition I, and the matrix element of $\mathbf{\Omega}$ is

$$
\Omega_{ij\sigma,kl\tau} = \delta_{\sigma,\tau} \delta_{i,k} \delta_{j,l} (\epsilon_{l\tau}-\epsilon_{k\tau})^2 + 2\sqrt{(f_{i\sigma}-f_{j\sigma})(\epsilon_{j\sigma}-\epsilon_{i\sigma})}
$$
$$
\times K_{ij\sigma,kl\tau} \sqrt{(f_{k\tau}-f_{l\tau})(\epsilon_{l\tau}-\epsilon_{k\tau})}. \tag{3}
$$

2.2. TDDFT-MLR: Formulation of responses from the intermediate excited states

In TDDFT-MLR, the responses from not only the ground state but also intermediate excited states are taken into account. The average excitation energy can be approximated from the calculation of the mid-excited state (Slater transition state), in which a half electron is promoted from the donor orbital to the acceptor one. The original Casida equation is general enough to treat fractional occupation number and in principle ready to be used for MLR calculations. On the other hand, to circumvent the case that the expression inside the square root in equation (3) could be negative in mid-excited states, we use the separation procedure $\epsilon_{l\tau} - \epsilon_{k\tau} > 0$ instead of $f_{k\tau} - f_{l\tau} > 0$ in equation (1) and then derive the pseudoeigenequation in a similar way while using the nonsymmetric form of the $\mathbf{\Omega}$ matrix [19],

$$
\Omega_{ij\sigma,kl\tau}^m = \delta_{\sigma,\tau} \delta_{i,k} \delta_{j,l} (\epsilon_{j\sigma}^m - \epsilon_{i\sigma}^m)^2
$$
$$
+ 2(f_{i\sigma}^m - f_{j\sigma}^m)(\epsilon_{j\sigma}^m - \epsilon_{i\sigma}^m) K_{ij\sigma,kl\tau}^m, \tag{4}
$$

which holds for arbitrary occupation number difference.

Since TDDFT-MLR uses the mid-excited state as the reference state, it is often questioned on its similarity to the Slater transition state method. An analysis of equation (4) reveals that the MLR scheme imposes a TDDFT correction to the Slater transition state method and is more rigorous in general cases. Even if the off-diagonal elements of $\mathbf{\Omega}$ is small, there can still be a considerable correction to the bare eigenenergy difference in the diagonal elements. On the other hand, there are often cases where TDDFT-MLR and the Slater method give similar results. An example are the doublet–doublet transitions without involving degenerate orbitals. In such conditions, $f_{i\sigma}^m = f_{j\sigma}^m$ (=0.5) and the result of TDDFT-MLR becomes equivalent to that of the Slater method.

Table 1. Singlet–singlet excitation energies (in eV) of alkaline earth atoms by different methods: TDDFT-LR within LDA, TDDFT-LR within asymptotic-corrected (AC) LDA, the Slater transition state method within LDA, and TDDFT-MLR within LDA. Each transition is labeled as valence (V) or Rydberg (R) in character. Experimental energies are taken from [30]. LR/AC-LDA results are taken from [17].

Atom	Transition	LR/LDA	LR/AC-LDA	Slater/LDA	MLR/LDA	Expt.
Be	V: $2s \rightarrow 2p$	4.95	4.84	3.52	4.68	5.28
	R: $2s \rightarrow 3s$	5.55	6.38	6.69	6.74	6.78
	R: $2s \rightarrow 3p$	5.93	6.98	7.33	7.35	7.46
Mg	V: $3s \rightarrow 3p$	4.43	4.37	3.50	4.27	4.35
	R: $3s \rightarrow 4s$	4.71	5.45	5.46	5.50	5.39
Ca	V: $4s \rightarrow 3d$	1.87	1.73	2.16	2.28	2.71
	V: $4s \rightarrow 4p$	3.24	3.24	2.48	3.15	2.93
	R: $4s \rightarrow 5s$	3.74	4.22	4.11	4.15	4.13

Table 2. Doublet–doublet excitation energies (in eV) of alkali metal atoms. Each transition is labeled as valence (V) or Rydberg (R) in character. Experimental energies are taken from [30].

Atom	Transition	LR/LSDA	MLR/LSDA	Expt.
H	R: $1s \rightarrow 2s$	7.29	9.75	10.20
	R: $1s \rightarrow 2p$	7.49	9.99	10.20
	R: $1s \rightarrow 3s$	7.47	11.78	12.09
Li	V: $2s \rightarrow 2p$	2.00	1.87	1.85
	R: $2s \rightarrow 3s$	3.03	3.35	3.37
	R: $2s \rightarrow 3p$	3.36	3.79	3.83
Na	V: $3s \rightarrow 3p$	2.22	2.19	2.10
	R: $3s \rightarrow 4s$	2.92	3.18	3.19
	R: $3s \rightarrow 3d$	3.19	3.79	3.62

3. Results and discussions

Calculation of atomic excitation energies are carried out using the ABINIT code [23, 24] in the framework of the planewave pseudopotential approach, in which our MLR scheme has been implemented within adiabatic LDA/LSDA. We use the Perdew–Wang 92 functional [25], which is a reparametrization of the Ceperley–Alder data [26]. The Troullier–Martins (TM) pseudopotentials [27] generated by Khein and Allan, with the inclusion of nonlinear core correction [28], as well as Hartwigsen–Goedecker–Hutter (HGH) pseudopotentials [29], are used for various atomic species. Since Rydberg states are spatially extended, it is necessary to use sufficiently large supercells. It is worth emphasizing that not only accuracy but also SCF convergence of mid-excited states can be worse with insufficient supercells. Due to the fact that upper Rydberg states might require larger supercell sizes, we have used a size range of 30–50 Bohr in our calculations.

3.1. Singlet–singlet transitions

In table 1 we list calculation results of singlet–singlet transitions in the alkaline earth atoms Be, Mg and Ca by various methods: TDDFT-LR within LDA and asymptotic-corrected LDA, the Slater transition state method within LDA, and TDDFT-MLR within LDA. It is noted that the calculated results are vertical excitation energies, i.e., atomic positions are fixed during the electronic excitation. In molecular systems, experimental vertical excitation energies have to be calculated from spectroscopic constants, while for single atoms this work is removed and a direct comparison is available.

The comparison shows that the TDDFT-LR/LDA results are relatively good for valence excitations, but not for Rydberg transitions. Contrarily, the Slater method gives good results for Rydberg transitions, but not for valence excitations, as discussed in our previous work on the basis of the approximate excitation energies from the ΔSCF method [18]. In contrast, TDDFT-MLR/LDA achieves good accuracy for both valence and Rydberg excitations. The accuracy is comparable to that of asymptotically-corrected LDA calculations, although in our case we do not impose any correction to the LDA functional.

3.2. Doublet–doublet transitions

In table 2 we list calculation results of TDDFT-LR and MLR within LSDA, together with the experimental data, for doublet–doublet transitions in alkali metal atoms H, Li and Na. All transitions in the hydrogen atom are Rydberg transitions: The transition energies are severely underestimated by ordinary LR, while greatly improved by the MLR scheme. For lithium and sodium atoms, excitation energies of the Rydberg transitions above the valence excitations are not so severely underestimated but still improved by TDDFT-MLR. It is worth mentioning that the Slater transition state method gives results very similar to those of TDDFT-MLR, suggesting that the TDDFT correction to the Slater method is rather small for these doublet–doublet transitions.

3.3. Transitions in rare-gas atoms

The previous calculations of atomic excitation energies are performed by using the calculation procedures the same as in molecular systems. However, for rare-gas atoms, it is found that the scheme of constructing the mid-excited state of singlet–singlet excitations in general atomic and molecular systems, as represented by the s_1 state in figure 1, cannot be straightforwardly applied. Instead, the other one in figure 1, the m_1 state, should be used. Conceptually, the s_1 state can be regarded as the linear combination of two m_1 states (corresponding to the promotion of either a spin-up or spin-down electron, respectively). Therefore, it is the mimic of the eigenfunction of $\hat{S}^2$ when the total spin $S = 0$. For general singlet–singlet excitations, the s_1 state would be the natural choice for the mid-excited state. It is known to be higher in energy than the m_1 state [31]. However, the unique closed-shell structure of the rare-gas atoms makes the s_1
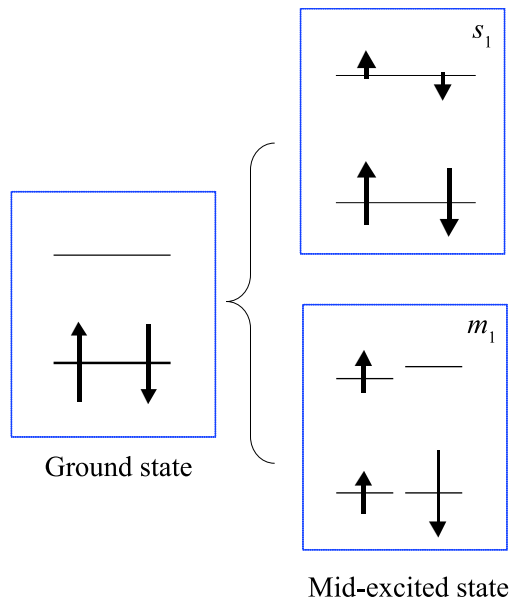
Figure 1. Schematic view of the mid-excited states of the singlet–singlet excitations. The s_1 state is constructed by equally promoting the spin-up and spin-down electrons to the acceptor orbital with a total amount of one half, while the m_1 state is by solely promoting a half spin-up (or equivalently, spin-down) electron with the use of the spin-unrestricted formalism.

Figure 2. Atomic excitation energies of He, calculated by TDDFT-LR within LDA and asymptotically correct LB94 functionals, the Slater transition state method within LDA (using the s_1 state), as well as TDDFT-MLR within LSDA (using the m_1 state).

Figure 3. Dependence of the $2p \rightarrow 3s$ transition energy of Ne on the cutoff energy of the HGH pseudopotential.

state (obtained from self-consistent calculations within LDA) have too many excited-state components to stand for the mid-excited state. This can be understood from the performance of the Slater transition state method within LDA for rare-gas atoms, as shown in figure 2, in which we compare the theoretical and experimental atomic excitation energies of He. The plot indicates that the energies computed by the Slater method, which is the bare eigenenergy difference of the s_1 state, appear to be considerably overestimated. This is rather different from its behavior in other cases of either atomic or molecular systems. The peculiar behavior of rare-gas atoms is also reported in the literature. It is pointed out that the rare-gas atoms are not a fully representative testing ground for the calibration of new xc functionals for the calculation of polarizabilities [32]. Bearing this in mind, we adapt our MLR scheme to utilize the m_1 state for rare-gas atoms. By doing this, our TDDFT-MLR values within LSDA show good accuracy on predicting excitation energies of He, as compared to the experimental data or the energies from asymptotically accurate LB94 potentials.

Calculation of excitation energies of rare-gas atoms involves more subtleties. The closed-shell structure of these atoms might require 'hard' pseudopotentials with high cutoff energies to construct the mid-excited states. In figure 3 the dependence of the $2p \rightarrow 3s$ transition energy of Ne on the cutoff energy of the HGH pseudopotential is shown. The difference between results of 100 Hartree and 150 Hartree is still ∼0.05 eV, thus a high cutoff energy is required for accurate results. We have also tested the soft TM pseudopotential of Ne and found the difference can be as large as ∼0.5 eV. In comparison, the conditions of pseudopotentials are not so strict
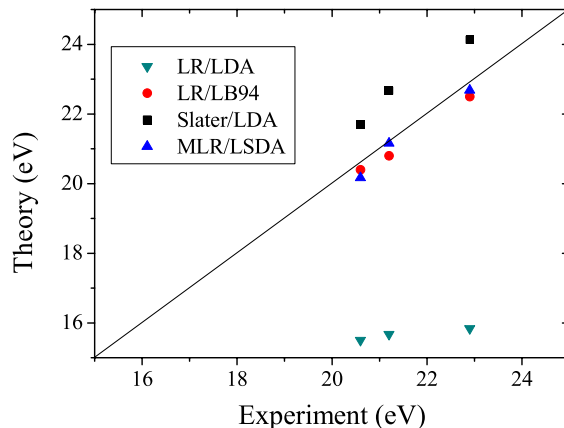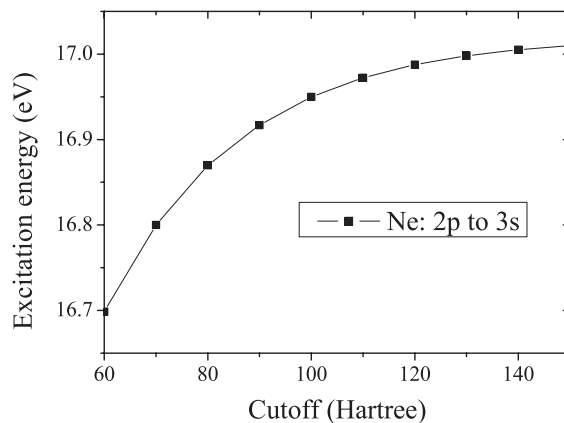
for He and Ar atoms. We have used the TM pseudopotential with a 30 Hartree cutoff for He, and the HGH pseudopotential with a 70 Hartree cutoff for Ar. In table 3 we list the calculation results for He, Ne and Ar. The Slater/LDA method systematically overestimates excitation energies, while our MLR/LSDA scheme achieves the same-level accuracy as that of the LB94 functional. The working mechanism of the m_1 state in MLR still needs to be explored and might be important for reducing the ambiguity in MLR.

4. Conclusion

We present calculations of atomic excitation energies by time-dependent density functional theory within modified linear response, using a local (spin) density approximation. Similar features are observed in single atoms as in molecular systems: good performance of modified linear response is shown for either valence or Rydberg transitions. For rare-gas atoms, we present an adapted algorithm to construct intermediate excited states, due to their unique closed-shell structures. Finally we would like to point out that because

Table 3. Singlet–singlet excitation energies (in eV) of rare-gas atoms. All transitions are Rydberg (R) in character. Experimental energies as well as calculation results by TDDFT-LR within LB94 are taken from [17].

Atom	Transition	Slater/LDA	LR/LB94	MLR/LSDA	Expt.
He	R: 1s → 2s	21.69	20.4	20.17	20.6
	R: 1s → 2p	22.67	20.8	21.16	21.2
	R: 1s → 3s	24.13	22.5	22.68	22.9
Ne	R: 2p → 3s	17.67	17.3	17.01	16.7
	R: 2p → 3p	19.66	19.0	19.09	18.7
	R: 2p → 4s	20.55	20.0	19.93	19.7
Ar	R: 3p → 4s	11.89	11.6	11.54	11.6
	R: 3p → 4p	13.48	13.3	13.15	13.1

of the simplicity of the modified linear response scheme, we anticipate further applications to condensed systems with localized states, such as the excitations of semiconductor defects or surface/adsorbate systems.

Acknowledgments

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