Ab Initio Excitation Spectra and Collective Electronic Response in Atoms and Clusters

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We implement the linear response theory within the time-dependent local density-functional formalism (TDLDA) to calculate excitation energies and photoabsorption spectra of atoms and clusters. The calculated *ab initio* spectra are in very good agreement with experiment. Along with the exact TDLDA formalism, we consider several approximate expressions for the electronic transition energies. The analysis of the spectra calculated with different levels of approximation indicates the important role of the collective electronic excitations in atoms and clusters. [S0031-9007(99)08543-9]

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The theoretical background for calculating ground state properties of many-electron systems is now well established. One of the most widely used techniques employs the first principles pseudopotential formalism [1] based on the density-functional theory (DFT) in the local density approximation (LDA) [2]. Excited state properties, however, still present a challenge for computational methods. Accurate calculations for the excitation energies and absorption spectra require highly sophisticated techniques, such as the configuration-interaction (CI) method [3], or Green's function methods based on Hedin's GW approximation [4]. While these methods provide good agreement with experiment [5–8], they are very computationally demanding.

Recently developed linear response theory within the time-dependent density-functional formalism provides a new tool for calculating excited state properties [9]. This method, known as the time-dependent LDA (TDLDA), allows one to compute the true excitation energies from the conventional, time-independent Kohn-Sham transition energies and wave functions. Presently, only a few attempts of TDLDA calculations for a limited number of systems are available, and the existing results are controversial. Rubio *et al.* [10] and Pacheco and Martins [11] reported an excellent agreement with experiment for the TDLDA absorption spectra of several metallic clusters. On the other hand, Petersilka *et al.* [12] claimed that TDLDA fails to predict the correct excitation energies for alkaline-earth atoms due to the inaccuracy of the local density approximation for the excited states.

In this paper, we address the existing controversy. Our calculations indicate that the reported disagreement between theoretical and experimental transition energies is a consequence of using in Ref. [12] an inaccurate formula to compute electronic excitations. When the collective electronic excitations are included into the calculations exactly, we find the TDLDA excitation energies and absorption spectra to be in very good agreement with experiment. In fact, our exact TDLDA spectra stand well in comparison with the other theoretical spectra obtained with more complicated CI and GW methods [5,7], requiring at the same time lower computational effort.

We implemented the TDLDA formalism entirely in real space within the higher-order finite difference pseudopotential method [13]. The time-independent exchange-correlation term was approximated with the Perdew-Zunger parametrization of the Ceperley-Alder functional, which was slightly adjusted to ensure two continuous derivatives for the correlation energy [14]. The real-space pseudopotential code represents a natural choice for implementing TDLDA due to the real-space formulation of the general TDLDA theory. With other methods, such as the plane-wave approach, TDLDA calculations typically require an intermediate real-space basis [15], which complicates calculations and may introduce an extra error. Our direct real-space approach simplifies implementation and allows us to perform the complete TDLDA response calculation in a single step.

A complete analysis of the general TDLDA formalism can be found elsewhere [9,12]. The excited state properties are derived within the time-dependent DFT as a linear response to an applied periodic perturbation. The system response is described by means of the coupling matrix, which can be used to calculate the true electronic excitations. In the adiabatic approximation the coupling matrix $K_{ij\sigma,kl\tau}$ is given by

$$K_{ij\sigma,kl\tau} = \iint \phi^*_{i\sigma}(\mathbf{r})\phi_{j\sigma}(\mathbf{r})\left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{\partial v^{\mathrm{xc}}_{\sigma}(\mathbf{r})}{\partial\rho_{\tau}(\mathbf{r}')}\right) \times \phi_{k\tau}(\mathbf{r}')\phi^*_{l\tau}(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'. \quad (1)$$

The matrix indices i, j, σ in the above expression correspond to the occupied states, unoccupied states, and the spin index, respectively; $\phi(\mathbf{r})$ are the Kohn-Sham one-electron wave functions, and $v^{\mathrm{xc}}(\mathbf{r})$ is the LDA exchange-correlation potential. The TDLDA electronic transition energies Ω_n can be obtained from the solution of the eigenvalue problem [9]:

$$[\omega^2_{ij\sigma}\delta_{ik}\delta_{jl}\delta_{\sigma\tau} + 2\sqrt{f_{ij\sigma}\omega_{ij\sigma}}\,K_{ij\sigma,kl\tau}\sqrt{f_{kl\tau}\omega_{kl\tau}}]\mathbf{F}_n = \Omega^2_n\mathbf{F}_n\,, \quad (2)$$

where $\omega_{ij\sigma} = \epsilon_{j\sigma} - \epsilon_{i\sigma}$ are the Kohn-Sham transition energies, and $f_{ij\sigma} = n_{i\sigma} - n_{j\sigma}$ are the differences between the occupation of the i and j states. So far, no approximation other than the adiabatic local density approximation has been made. The exact solution of the matrix equation (2) fully incorporates the collective electronic excitations.

Along with the exact TDLDA formalism, we consider two approximate expressions for the excitation energies. For simplicity, we will assume a spin-unpolarized case, i.e., $f_{ij\uparrow} = f_{ij\downarrow} = f_{ij}$, although all results can be easily generalized for any spin configuration. Let us make the assumption that the coupling between different one-electron transitions is weak. Under this assumption we can neglect all matrix elements with $i \neq k$ and $j \neq l$. The only remaining off-diagonal elements of the coupling matrix $K_{ij\sigma,kl\tau}$ are now generated by the spin index, and Eq. (2) reduces to a series of independent 2×2 matrix equations. Solving for the transition energies, we obtain

$$\Omega_{ij} \approx \sqrt{\omega_{ij}[\omega_{ij} + 2f_{ij}(K_{ij\uparrow,ij\uparrow} \pm K_{ij\uparrow,ij\downarrow})]}\,. \qquad (3)$$

Equation (3) gives two solutions for each Ω_{ij}; one with the plus sign describes transitions to the singlet excited state, and the other with the minus corresponds to the triplet transitions. This approximation can be viewed as an attempt to correct Kohn-Sham excitation energies individually without including collective electronic effects. Assuming that TDLDA corrections to the Kohn-Sham transition energies are relatively small, we can further simplify Eq. (3) by taking a linear expansion around ω_{ij}:

$$\Omega_{ij} \approx \omega_{ij} + f_{ij}(K_{ij\uparrow,ij\uparrow} \pm K_{ij\uparrow,ij\downarrow})\,. \qquad (4)$$

Equation (4) is identical to the approximate TDLDA formula derived in Ref. [12].

TABLE I. The singlet $^1S \rightarrow {}^1P$ excitation energies of close-shell atoms (in eV). The energies calculated with different levels of TDLDA approximation [Eqs. (2)–(4)] are compared to the experimental values [16] and the usual Kohn-Sham transition energies ω^{KS}. In case of Zn and Cd atoms the d-shell electrons were explicitly included into pseudopotential calculations.

Atom	Experiment	Eq. (2)	Eq. (3)	Eq. (4)	ω^{KS}
Be	5.28	4.94	5.07	5.43	3.50
Mg	4.34	4.34	4.56	4.76	3.39
Ca	2.94	3.22	3.36	3.56	2.39
Sr	2.69	2.96	3.10	3.28	2.22
Zn	5.79	5.71	6.30	6.54	4.79
Cd	5.41	5.10	5.60	5.86	4.12

To assess the accuracy of the TDLDA formalism, we first computed the excitation energies for several closed shell atoms. In Table I we include the $^1S \rightarrow {}^1P$ singlet transition energies calculated with different levels of TDLDA approximation. The analysis of the data in Table I leads us to the following conclusions: First, although all three TDLDA equations improve upon Kohn-Sham transition energies, the values obtained through the full matrix diagonalization [Eq. (2)] are clearly the best. In the latter case, the experimental and theoretical values agree within 5%–10% for all atoms. Second, the discrepancy between the exact [Eq. (2)] and the approximate [Eq. (3)] TDLDA excitation energies shows the important role of the collective electronic effects. The electronic correlations are particularly large in the case of Zn and Cd, where they are caused by d levels which are close in energy. Third, the excitation energies calculated with the linear expansion formula [Eq. (4)] almost exactly reproduce the numbers reported for the TDLDA energies in Ref. [12]. The poor agreement between these values and experiment has been explained in Ref. [12] by the fact that LDA is not accurate for the unoccupied orbitals, which affects the calculated transition matrix elements. In particular, the authors of Ref. [12] have attributed this discrepancy to the "wrong" asymptotic tail behavior of the LDA potential (which decays exponentially, whereas the exact potential should fall off as $1/r$). However, our present calculations demonstrate that the observed discrepancy should be attributed to the inaccuracy of Eq. (4) itself. As such, we find that the asymptotic behavior of the potential is not as important for the excited state properties, as it had been previously thought [12,17].

In Table II we compare the singlet $^1S \rightarrow {}^1P$ and triplet $^1S \rightarrow {}^3P$ atomic transition energies, calculated with several different techniques. The comparison indicates that TDLDA transition energies are generally in better agreement with experiment than the values obtained with either the optimized effective potential (OEP) or the ordinary self-consistent field (SCF) method [12]. The singlet OEP excitation energies in Table II are almost as accurate as the energies calculated with TDLDA. However, TDLDA values for the triplet transitions are much better than the OEP triplet energies due to the fact that the exchange-only OEP method does not account for the correlation effects,

TABLE II. The comparison between singlet and triplet excitation energies for atoms, calculated with TDLDA [Eq. (2)], optimized effective potential, and ordinary self-consistent field method [12]. The values for the experimental triplet transitions represent the average over different spin-orbit components. All values are in eV.

Atom	Transition	Experiment	TDLDA	OEP	SCF
Be	$^1S \rightarrow {}^1P$	5.28	4.94	5.33	4.50
	$^1S \rightarrow {}^3P$	2.72	2.45	1.88	2.46
Mg	$^1S \rightarrow {}^1P$	4.34	4.34	4.45	4.07
	$^1S \rightarrow {}^3P$	2.72	2.79	2.05	2.80
Ca	$^1S \rightarrow {}^1P$	2.94	3.22	3.18	2.87
	$^1S \rightarrow {}^3P$	1.89	1.93	1.22	1.96
Sr	$^1S \rightarrow {}^1P$	2.69	2.96	2.86	2.62
	$^1S \rightarrow {}^3P$	1.82	1.82	1.10	1.84
Zn	$^1S \rightarrow {}^1P$	5.79	5.71	5.74	5.48
	$^1S \rightarrow {}^3P$	4.05	4.27	3.40	4.30
Cd	$^1S \rightarrow {}^1P$	5.41	5.10	5.11	4.71
	$^1S \rightarrow {}^3P$	3.88	3.69	2.87	3.70

which play a significant role for the triplets [18]. The TDLDA values for both singlets and triplets are also superior to the ordinary self-consistent excitation energies. At the same time the TDLDA method is more efficient than the regular SCF approach, since TDLDA requires only one self-consistent calculation to obtain the complete excitation spectrum.

Next, we applied the TDLDA technique to calculate absorption spectra of atomic clusters. We chose sodium clusters as well-studied objects, for which accurate experimental measurements of the absorption spectra are available [19]. Since the wave functions for the unoccupied electron states are very sensitive to the boundary conditions, TDLDA calculations need to be performed within a relatively large boundary domain. For sodium clusters we used a spherical domain with a radius of 25 a.u. and a grid spacing of 0.9 a.u. We carefully tested convergence of the calculated excitation energies with respect to these parameters and the number of unoccupied states included in the calculations.

The calculated absorption spectra for the first three closed shell clusters Na_2, Na_4, and Na_8 are shown in Fig. 1. Of the three different TDLDA expressions, only the spectra calculated with the exact formula given by Eq. (2) agree with experiment. The large discrepancy between the exact [Fig. 1(d)] and the approximate [Fig. 1(c)] TDLDA spectra implies a substantial contribution to the absorption from the collective electronic excitations. The role of the collective effects increases with increasing the cluster size. When all electronic correlations are included, the agreement between TDLDA and experiment is remarkable. The exact TDLDA correctly reproduces the experimental spectral shape, and the calculated peak positions agree with experiment within 0.1–0.2 eV. The comparison with other theoretical work demonstrates that our TDLDA absorption spectra computed with the exact Eq. (2) are almost as accurate as the available CI spectra [5]. Furthermore, the TDLDA spectrum for the Na_4 cluster seems to be in better agreement with experiment than the GW absorption spectrum calculated in Ref. [7].

Finally, we applied TDLDA to calculate the static polarizabilities of atomic clusters. The mean static polarizability α is related to the absorption properties through the perturbation theory expression:

$$\alpha = \sum_n \frac{F_n}{\Omega_n^2}, \qquad (5)$$

where F_n is the oscillator strength and Ω_n is the transition energy. We used Eq. (5) and the TDLDA values for F_n and Ω_n to compute the polarizabilities of sodium and silicon clusters (Table III). It is well known that for the regular Kohn-Sham transition energies the perturbation formula Eq. (5) substantially overestimates polarizabilities [20]. The data in Table III indicate that polarizabilities calculated from approximate TDLDA spectra [Eq. (3)] are also considerably

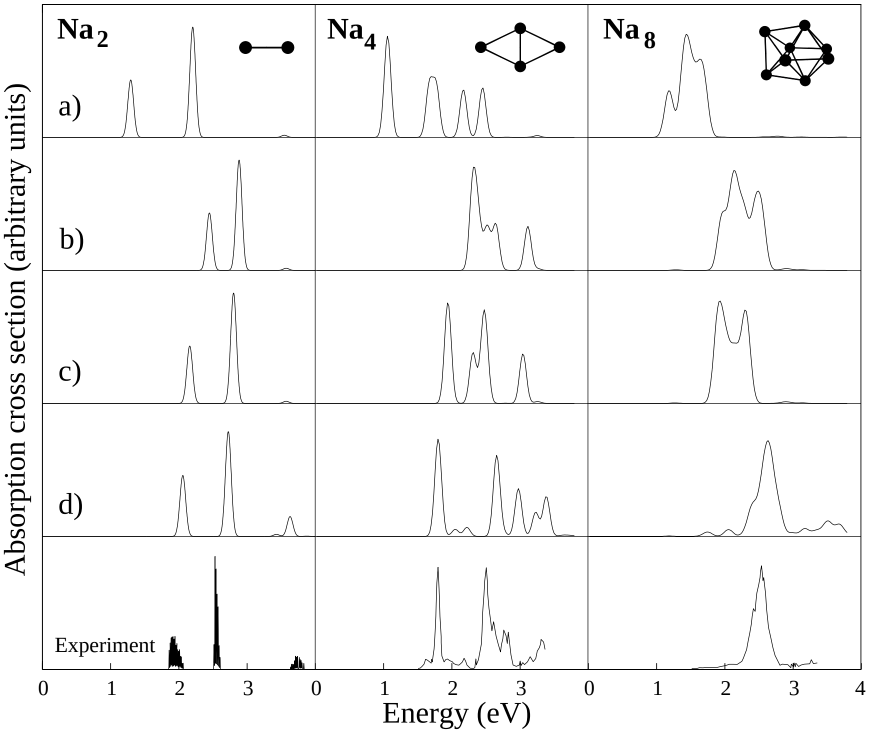

FIG. 1. The calculated and experimental absorption spectra of sodium clusters. (a) The regular Kohn-Sham absorption spectra. The other plots show the TDLDA spectra calculated with Eq. (4) (b), Eq. (3) (c), and Eq. (2) (d). The experimental spectra are adapted from Ref. [19]. All calculated spectra have been broadened by 0.06 eV to simulate finite temperature.

TABLE III. Mean static polarizabilities (Å^3/atom) of atomic clusters. The first and second columns list polarizabilities calculated according to Eq. (5), with the transition energies and oscillator strengths given by Eq. (3) and Eq. (2), respectively. The last column shows polarizabilities calculated by the finite-field method [21].

Cluster	Eq. (3)	Eq. (2)	Finite field
Na_2	17.0	17.8	18.1
Na_4	20.5	19.1	19.3
Na_8	23.2	14.6	14.7
Si_3	9.25	5.13	5.22
Si_4	9.40	4.99	5.07
Si_5	11.41	4.75	4.81
Si_6	9.97	4.40	4.46
Si_7	10.97	4.32	4.37

overestimated. On the other hand, polarizabilities computed with the transition energies and oscillator strengths obtained from the exact solution of Eq. (2) are in excellent agreement with the polarizabilities calculated using the finite-field method [21]. These results present additional evidence of a large contribution to the absorption spectra of clusters from the collective electronic effects. Only the exact TDLDA formula which accounts for all electronic correlations provides accurate values for the polarizability. As such, Eq. (5) represents a good test for the calculated absorption spectra, which can be particularly important when the direct experimental measurements of the photoabsorption are not available.

In conclusion, we have implemented the linear response theory within the time-dependent density-functional formalism and the local density approximation to calculate excitation energies and photoabsorption spectra of atoms and clusters. The calculated *ab initio* TDLDA spectra were found to be in very good agreement with experiment. The comparison of the spectra calculated with the exact and the approximate TDLDA expressions indicates the important role of the collective electronic excitations in atoms and clusters.

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