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Time dependent density functional calculation of plasmon response in clusters

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We have introduced a theoretical scheme for the efficient description of the optical response of a cluster based on the time-dependent density functional theory. The practical implementation is done by means of the fully fledged time-dependent local density approximation scheme, which is solved directly in the time domain without any linearization. As an example we consider the simple Na_2 cluster and compute its surface plasmon photoabsorption cross section, which is in good agreement with the experiments.

Keywords: optical response of cluster, time-dependent density functional theory
PACC: 3640C, 6120L, 7115M

1. Introduction

Density functional theory (DFT)[1,2] for calculating ground-state properties of a many-electron system is one of the most successfully and widely used methods in the computational condensed-matter physics, materials science and quantum chemistry. One of the most widely used techniques employs the first-principle pseudopotential scheme based on the DFT in local density approximation (LDA). Unfortunately, the DFT is often considered to be inadequate to describe those problems, such as the excitation states, strongly correlated physics. A number of attempts has been made to overcome these major drawbacks ever since the inception of the formal DFT three decades ago.[3] Recently, the time-dependent density functional theory (TDDFT) has acquired the status of a formalism independent of the conventional time-dependent quantum mechanical methods to deal with the excitation states and the time evolution of quantum mechanical systems with high accuracy. For TDDFT early foundations were laid by Bloch who attempted to develop a time-dependent Thomas–Fermi method.[4] A time-dependent density functional variational approach was developed by Deb and Ghosh and by Bartolotti,[5,6] and subsequently generalized by Runge and Gross,[7] as well as by Dhara and Ghosh.[8] More recently, time-independent DFT approaches for excited states are also developed, e.g. the Kohn–Sham DFT extended to the individually excited state,[9] quantal density functional theory (Q-DFT) of singly or multiply excited bound nondegenerate states.[10] Presently, as a simplest level of approximation to the TDDFT, the time-dependent local density approximation (TDLDA) has been widely applied to describing the photoabsorption of atoms, molecules, solids, and clusters, starting with jellium model by Ekardt.[11,12]

Optical properties of metal clusters have been investigated theoretically and experimentally.[13–15] The photoabsorption spectra are a most prominent observable for the study of the structural properties of metallic clusters and have long been studied. The experiments using molecular-beam techniques and laser spectroscopy provide spectral profiles and absolute values for the absorption cross section. It is now possible to calculate the complex response of a small free cluster to an external field on a microscopic level. Here we demonstrate the validity of the procedure based on the TDLDA.

2. Theoretical framework

We give a brief summary about TDDFT, which is the basis of our electronic quantum mechanical calculations. In what follows we use the atomic units (a.u). Within the TDDFT, the physics of an interacting N-electron system is mapped to a model system of nonin-

teracting electrons with equivalent density and energy. The time-dependent density is obtained, in principle exactly, through a set of single-electron wavefunctions $\phi_j(\boldsymbol{r},t)$ which satisfy the time-dependent Kohn–Sham (TDKS) equation,[15]

$$\begin{aligned} i\frac{\partial}{\partial t}\phi_j(\boldsymbol{r},t) =& \hat{H}_{\mathrm{KS}}\phi_j(\boldsymbol{r},t) \\ =& \left(-\frac{\nabla^2}{2}+\upsilon_{\mathrm{eff}}[n](\boldsymbol{r},t)\right)\phi_j(\boldsymbol{r},t). \quad (1) \end{aligned}$$

The Kohn–Sham effective potential υ_{eff} is usually decomposed into an ionic background potential $\upsilon_{\mathrm{ion}} = \sum_I \upsilon_{\mathrm{ps}}(\boldsymbol{r}-\boldsymbol{R}_I)$ from the ionic core at positions $\{R_I\}$, an external force potential υ_{ext}, a Hartree part υ_{H} and a so-called exchange correlation (xc) potential υ_{xc},

$$\begin{aligned} \upsilon_{\mathrm{eff}}[n](\boldsymbol{r},t) =& \upsilon_{\mathrm{ion}}(\boldsymbol{r},t)+\upsilon_{\mathrm{ext}}(\boldsymbol{r},t) \\ &+\upsilon_{\mathrm{H}}[n](\boldsymbol{r},t)+\upsilon_{\mathrm{xc}}[n](\boldsymbol{r},t), \quad (2) \end{aligned}$$

where the electronic density n is given by $n(\boldsymbol{r},t) = \sum_{j=1}^{N}|\phi_j(\boldsymbol{r},t)|^2$, and the Hartree potential $\upsilon_{\mathrm{H}}[n](\boldsymbol{r},t)$ is defined as

$$\upsilon_{\mathrm{H}}[n](\boldsymbol{r},t) = \int \mathrm{d}^3r' \frac{n\left(\boldsymbol{r}',t\right)}{|\boldsymbol{r}-\boldsymbol{r}'|}. \quad (3)$$

The xc potential $\upsilon_{\mathrm{xc}}[n](\boldsymbol{r},t)$ is a functional of the time-dependent density and has to be approximated in practice. The simplest choice used in this work, i.e. the TDLDA, is defined as

$$\upsilon_{\mathrm{xc}}^{\mathrm{TDLDA}}[n](\boldsymbol{r},t) = \mathrm{d}\varepsilon_{\mathrm{xc}}^{\mathrm{hom}}(n)/\mathrm{d}n|_{n=n(\boldsymbol{r},t)}, \quad (4)$$

where $\varepsilon_{\mathrm{xc}}^{\mathrm{hom}}(n)$ is the xc energy density of the homogeneous electron gas, for which we use the parametrization of Perdew and Zunger.[16] Our norm-conserving pseudopotentials υ_{ps} in the fully separable forms are constructed following the method of Troullier and Martins.[17]

The TDKS equations are integrated with a simple second-order differencing (SOD) scheme,

$$\phi_j(t_{n+1}) = -2\mathrm{i}\Delta t\hat{H}_{\mathrm{KS}}(t_n)\phi_j(t_n)+\phi_j(t_{n-1}), \quad (5)$$

which is accurate to the second order of Δt. We use the technique of fast Fourier transform (FFT) to evaluate the kinetic Laplacian operator, which is quite efficient and accurate. Because of existence of the calculation error, the single-particle orbitals $\phi_j(\boldsymbol{r},t)$ are no longer orthogonal to each other and must, at least in principle, be reorthogonalized. In the SOD scheme, the error in the propagation accumulates in the phase of the wavefunction $\phi_j(\boldsymbol{r},t)$. The SOD propagator scheme has ever been used to describe the response of irradiated Na_2 cluster by strong ultrashort laser pulse.[18]

To calculate the photoabsorption cross section of a cluster, an external field, $\upsilon_{\mathrm{ext}}(\boldsymbol{r},t) = k_q\delta(t)\hat{\boldsymbol{D}}_q$ ($\hat{\boldsymbol{D}}_q$ denotes the dipole operator in the three orientations along the principal axes of cluster $\vec{e}_q(q=1,2,3)$) is applied instantaneously at $t=0$, producing an initial state for the time evolution[15]

$$\phi_j(\boldsymbol{r},t_0) = \mathrm{e}^{\mathrm{i}k_q r_q}\phi_j^{\mathrm{stat}}(\boldsymbol{r}), \quad (6)$$

where $\phi_j^{\mathrm{stat}}(\boldsymbol{r})$ are orbitals for the ground state of the cluster. For one-photon processes, one has to make sure that k_q is small enough so as to be in the regime of linear response, but it is, on the other hand, large enough to give a numerically stable signal. The ground-state electronic configuration and ionic coordinates are found with the Car–Parrinello scheme for structure optimization.[19] Then, we calculate the time evolution under this initial condition without any external fields. The dynamic polarizabilities as a function of time are obtained

$$\alpha_q(t) = -\frac{1}{k_q}\int \mathrm{d}^3r r_q\delta n(\boldsymbol{r},t), \quad (7)$$

where the induced density $-\delta n$ is defined as $\delta n(\boldsymbol{r},t) = n(\boldsymbol{r},t)-n(\boldsymbol{r},t_0)$. Spectral properties are related to the Fourier transform $\alpha_q(\omega)$, with

$$\alpha_q(\omega) = \int_0^T \mathrm{d}t\alpha_q(t)\,\mathrm{e}^{\mathrm{i}\omega t-\Gamma t/2}, \quad (8)$$

where Γ is a smoothing parameter. In order to obtain energy resolution of Γ, the time evolution T has to be $T \geq 2\pi/\Gamma$. Consequently, an average over the three excitations along the three principal axes of the cluster is obtained

$$\alpha(\omega) = (1/3)\sum_{q=1,2,3}\alpha_q(\omega). \quad (9)$$

Finally, the oscillator strength $\mathrm{d}f/\mathrm{d}\omega$, the photoabsorption cross section $\sigma(\omega)$, are related to the imaginary part of the dynamic polarizability $\mathrm{Im}\,\alpha(\omega)$,

$$\sigma(\omega) = \frac{2\pi^2e^2}{m_{\mathrm{e}}c}\frac{\mathrm{d}f}{\mathrm{d}\omega} = \frac{4\pi\omega}{c}\mathrm{Im}\,\alpha(\omega). \quad (10)$$

3. Results and discussions

In this part, we demonstrate the validity of the TDLDA model. Na_2 cluster is selected for two reasons: 1) The Na_2 cluster itself is interesting. It is

known that the cluster Na_2 absorbs visible light, but most of the energy is released. And the fluorescence is so strong that the optical pumping of Na_2 clusters can produce laser emission. 2) The Na_2 system is simple. We know that the clusters are formed by the loosely bound valence electrons and ionic cores which are composed of the more tightly bound electrons and atomic nuclei. The ionic cores may influence the optical response of the cluster directly, when the energy of a core-level excitation is comparable to the energy for collective motions of the delocalized electrons, the so-called core-polarization effect. In general, in sodium clusters, the energy of core response is much higher than that of the collective surface plasmon resonance. Therefore, the main influence of ionic cores can be regard as a confining background, which may be modelled by using pseudopotentials. The plasmon energy is almost carried totally by the valence electron interactions that are well described in the adiabatic TDLDA.

It has been observed that metal clusters can absorb light through the excitation in collective mode by the motion of electrons against the positive ionic background. This surface plasmon has been known from experiments on very large clusters previously, however, it could also be observed in the region of small clusters currently. According to the classical Mie theory, there is a single surface plasmon peak at the energy $\hbar\omega_{\rm p}/\sqrt{3}$, where $\hbar\omega_{\rm p} = \sqrt{4\pi\rho e^2/m_{\rm e}}$ is the energy of the volume plasmon in the bulk material (ρ is the electronic density and $m_{\rm e}$ is the free electron mass). Experimentally, surface plasma $\omega_{\rm s}$ shows a pronounced redshift from the classical Mie value, and the oscillator strengths of both volume plasma at $\omega_{\rm p}$ and the individual particle–hole excitations (Landau damping) are smaller by at least three orders of magnitude than the Mie value.

In Fig.1 (a) we show the fluctuation of the total energy using a SOD propagator in real time. Figure 1 (b) shows the dipole response $D_x(t) = \int {\rm d}^3 r x \delta n\,(\boldsymbol{r}, t)$ along x direction, the direction of the symmetry axis connecting two atoms. Figure 1 (c) is same as Fig.1 (b) but it is for the dipole response of $D_y(t)$ and $D_z(t)$ in other two directions orthogonal to the symmetry axis. Here, we use a small excitation $k_q \approx 5.8 \times 10^{-5}$/Bohr so that the Na_2 cluster has to stay in a linear regime. Then we can simulate the incoherent superposition of those modes from the three principal-axis orientations in only one TDLDA propagation by using an initial excitation $\boldsymbol{k}$ along the diagonal (1,1,1). After a thermalization time of 20 fs, the electron dynamics in the Na_2 cluster is propagated for 46 fs, which gives the photoabsorption cross section a resolution Γ of 0.14 eV.

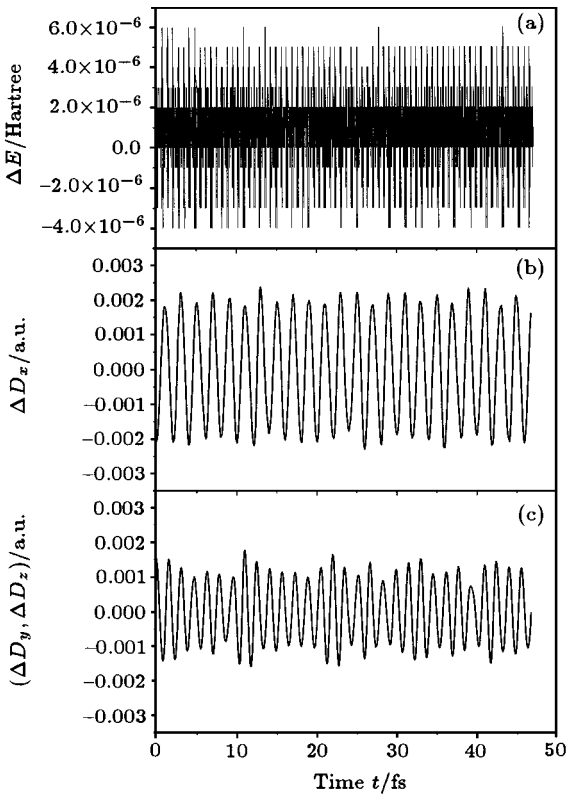


Fig.1. (a) The fluctuation of the total energy using a SOD propagator in real time; (b) the dipole response $D_x(t) = \int {\rm d}^3 r x \delta n\,(\vec{r}, t)$ along x direction, the direction of the symmetry axis connecting two atoms; c) same as b) but it is for dipole response $D_y(t), D_z(t)$ in the two directions orthogonal to the symmetry axis.

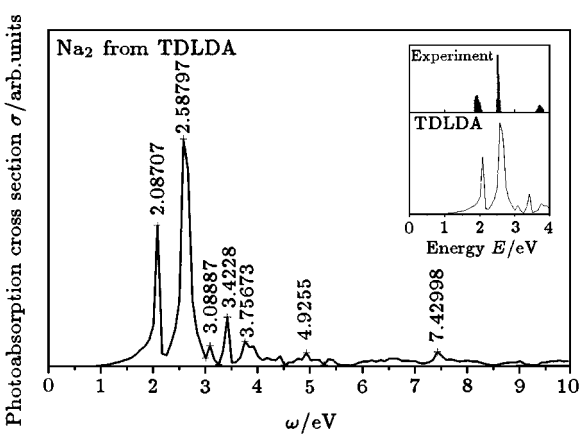


Fig.2. The photoabsorption cross section for Na_2 cluster obtained from the TDLDA.

The upper inset in Fig.2 shows the experimental photoabsorption cross section of the Na_2 cluster,

which is reproduced directly from Ref.[20]. The lower inset shows the photoabsorption cross section from our TDLDA calculations, which is plotted on the same scale. The experimental photoabsorption spectrum shows three collective excitation peaks around 1.9, 2.6 and 3.8 eV which belong to the $A^1\Sigma_u^+ \longleftarrow X^1\Sigma_g^+$, $B^1\Pi_u \longleftarrow X^1\Sigma_g^+$ and $C^1\Pi_u \longleftarrow X^1\Sigma_g^+$ transitions in the Na_2 cluster system. These three peaks are also produced by our TDLDA calculation to be 2.08707, 2.58797 and 3.7646 eV, respectively. The peak at 2.08707 eV is generated from the vibration mode parallel to the symmetry axis connecting two atoms. The peak at 2.58797 eV comes from vibration modes orthogonal to the axis, which is split by interference with a close particle–hole state. The smaller side peak of 3.08887 eV is the upper part of these modes. The peak of 2.08707 eV is substantially redshifted, compared with the typical 2.7–2.9 eV for spherical clusters. It is a trivial geometric effect in deformed clusters, so that in the elongated direction, here the axial orientation of the Na_2 cluster, the plasmon mode has a lower plasmon frequency. The peak at 3.7646 eV seems to produce a much larger split at 3.4228 eV. This split is also probably due to the interference of the particle–hole state whose energy is close to the plasmon resonance. It is interesting that there is a hint of ionization energy at 4.9278 eV for the process of $Na_2 \longrightarrow {Na_2}^+$ (for the ionization energy the calculated value $I_{\rm p}^{\rm LDA} = 5.0199$ eV from local density approximation is in agreement with experimental $I_{\rm p}^{\rm exp} = 4.87$ eV [21]). Since the ionic positions are fixed, the calculated finite width of the peak at $\omega_{\rm s}$ are only due to the resolution Γ and particle–hole excitations (Landau damping). Besides the difference from particle–hole states, our result is in good agreement with experiments. Our results follow perfectly the transition rules in the case of dipole radiation. The current TDDFT spectra do not provide information about the transitions between singlet and multiplet because the spin–orbit coupling effects are not included. In the case of Na_2 cluster the surface plasmon excitations are accurately given by the TDDFT calculations due to the following two reasons. Firstly, it is well known that the energy of the highest occupied orbital of Kohn–Sham DFT is the negative of the ionization energy.[22,23] Secondly, the excitations from the highest occupied orbital are found to be in excellent agreement with the differences of Kohn–Sham eigenvalues.[24] The TDLDA is entirely equivalent to the self-consistent first-order time-dependent perturbation theory around the LDA ground state in the limit of small amplitude of perturbation. The validity of TDDFT relies closely on the exactness of the selected exchange-correlation functionals. The present study demonstrates that the TDLDA collective model is capable of correctly describing the collective excitations, even in small cluster systems.

5. Conclusions and perspectives

Recent experimental developments lead cluster physics beyond the regime of linear response. Most theoretical descriptions of the induced nonlinear dynamics are based on the TDLDA and related scheme. We introduce the real-time TDLDA calculation for the photoabsorption cross section with the Na_2 cluster as an example, calculations are in good agreement with the experiments. Furthermore, TDLDA can work in many applications, such as ionization, energy balance, high-order harmonic generation, electron emission spectra, etc. However, because of the mean-field nature, TDLDA is still a tool which deserves further critical inspection and development. The present attention is focused on finding a scheme to include dynamic correlation effects and to embrace dissipation as well as fluctuations in TDDFT after the self-interaction and gradient corrections have been made in TDLDA.

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