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Dynamic Hyperpolarizability Calculation without Basis Functions

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We have developed a real-space computational method for linear and nonlinear dynamic polarizabilities in the time-dependent density-functional theory. In the method, we employ the uniform three-dimensional Cartesian grid representation without introducing any basis functions. The spatial convergence is controlled by the two intuitive parameters, the spatial volume and the spacing of grid points. As an illustrative example, we present a calculation of C_{60} polarizabilities convergent with respect to the spatial parameters.

Keywords: hyperpolarizability; time dependent density functional theory; real space method; higher order finite difference method; C_{60}

INTRODUCTION

In calculating linear and nonlinear optical properties of molecules, careful examinations are required in choosing a basis set as well as incorporation of the correlation effects. In this report, we present a new method to calculate linear and nonlinear dynamic polarizabilities in which the response equations are solved on discrete spatial grid points in the three-dimensional Cartesian coordinate without introducing any basis functions.

Our method is based on the time-dependent local-density approximation (TDLDA), which is an extension of the static density functional theory so as to treat electronic dynamics such as excitations and collisions.[1] The TDLDA method has been successfully applied to optical absorption of molecules and clusters [2,3,4] in the adiabatic local-density approximation where the same exchange-correlation potential as the static case is employed for time-dependent dynamics.

the plane wave e^{ikz} where k is a small distortion parameter. We calculate the real-time evolution with this initial condition and obtain the polarization in time, $p_z(t) = \int d\vec{r} z \rho(\vec{r}, t)$. The frequency-dependent linear dipole polarizability $\alpha(\omega)$ is then obtained through the Fourier transformation, $\alpha_{zz}(\omega) \propto \int dt e^{-i\omega t} p_z(t)$. From single real-time calculation, we can thus obtain whole spectrum at once.

Though the real-time method is quite useful for the linear response, the extension to the nonlinear response seems to be difficult, since we have to calculate responses many times to external fields with different time profiles. Instead we have developed a multiple iterative method to solve the nonlinear response equation at a fixed frequency.

The general framework of the nonlinear response in the TDLDA is presented by Senatore and Subbaswamy.[5] Since the essence of our method is included in the computation of the linear response, we explain our method for this case.

For a dipole external field, the self-consistent equation for the first order transition density $\rho^{(1)}(\vec{r})$ is derived from the time-dependent Kohn-Sham equation (1) as

$$\rho^{(1)}(\vec{r}) = \int d\vec{r}_1 \chi_0^{(1)}(\vec{r}, \vec{r}_1; \omega) h^{(1)}(\vec{r}_1), \tag{2}$$

$$h^{(1)}(\vec{r}) = z + \int d\vec{r}' v(\vec{r} - \vec{r}') \rho^{(1)}(\vec{r}'), \tag{3}$$

where the electron-electron interaction is the sum of the Coulomb and exchange-correlation potentials.

$$v(\vec{r} - \vec{r}') = \frac{e^2}{|\vec{r} - \vec{r}'|} + \frac{\delta\mu}{\delta\rho} \delta(\vec{r} - \vec{r}'). \tag{4}$$

$\chi_0^{(1)}(\vec{r}, \vec{r}'; \omega)$ is the independent particle response function written in terms of the ground state Kohn-Sham orbitals satisfying $h_0 \phi_i = \epsilon_i \phi_i$ with static Kohn-Sham Hamiltonian h_0 as

$$\begin{aligned} \chi_0^{(1)}(\vec{r}, \vec{r}'; \omega) &= \sum_i \phi_i^*(\vec{r}) \phi_i(\vec{r}') G(\vec{r}, \vec{r}'; \hbar\omega + \epsilon_i) \\ &\quad + \phi_i(\vec{r}) \phi_i^*(\vec{r}') G(\vec{r}', \vec{r}; -\hbar\omega + \epsilon_i), \end{aligned} \tag{5}$$

where $G(\vec{r}, \vec{r}', E)$ is the single-electron Green's function defined by $G(\vec{r}, \vec{r}', E) = \sum_i \phi_i(\vec{r}) \phi_i(\vec{r}') / (E - \epsilon_i)$.

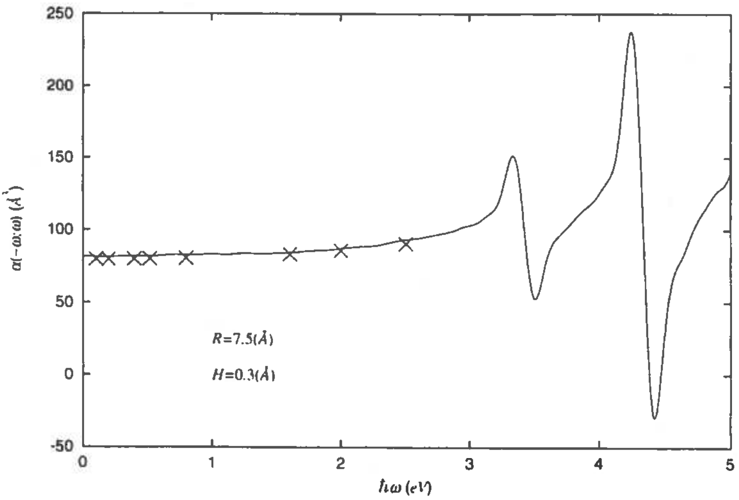

FIGURE 1 Linear polarizability $\alpha(\omega)$ of C_{60} molecule calculated by the real-time method (solid line) and the real-space response function method (crosses).

polarizability for a whole spectral region are obtained at once, from a time evolution of a long period. We calculated up to $T/\hbar = 40\text{eV}^{-1}$ with the time step of $\Delta T/\hbar = 0.001\text{eV}^{-1}$. In the real-space response function calculation, the calculation is achieved for every fixed frequency. The calculation for a single frequency costs, however, much less than the real-time calculation for a long period. The crosses in Fig.1 shows the real-space calculation employing the same grid points as in the case of the real-time calculation.

We may check the convergence of the calculation by changing the sphere radius and grid spacing in the real-space calculation. The convergence of the linear polarizability with respect to the sphere radius is shown in Fig.2. The grid spacing is set to 0.3Å which we checked to be fine enough. The frequency of the external field is fixed at $\hbar\omega = 0.52\text{eV}$. The ground state Kohn-Sham calculation is convergent with the sphere of 6-7Å radius. The convergence of the linear polarizability is achieved with a similar radius.

We calculate the second hyperpolarizability of C_{60} with the same grid points, and the result is shown in Fig.3. We see that the larger radius is required to obtain convergent result for the hyperpolarizability than to obtain the linear polarizability. This is similar to the usual observation that wider basis functions are required for hyperpolarizability calculation than for linear polarizability.

The converged values for the static α and γ in our method are 79.6Å^3 and 55.7×10^{-36}esu, respectively. With the same exchange-correlation potential (VWN[11]), they are reported to be 82.5Å^3 and 14.0×10^{-36}esu in the basis function method.[12] Though the linear polarizbilities coincide to each other with good accuracy, our converged value of γ is larger than that of Ref.[12] by about 20%. This difference is larger than that suggested in Ref.[12], where possible increase was estimated to be 5-10% by increasing their basis functions.

The frequency dependence of γ at low frequency region is known to be parameterized as

$$\gamma(-3\omega;\omega,\omega,\omega) = \gamma(0;0,0.0)(1 + 12A\omega^2). \qquad (6)$$

We obtained the coefficient A by a fitting procedure, $A = 22.6 \pm 0.3$ a.u., which is quite close to the value reported in Ref.[12], $A = 23.0 \pm 0.2$ a.u., in spite of the rather large difference for the static γ.

SUMMARY

We have developed a numerical method to calculate linear and nonlinear polarizabilities of molecules without basis functions in the time-dependent local-density approximation. The response equations as well as the Kohn-Sham equation are solved by discretizing the three-dimensional Cartesian coordinates into uniform grids. The spatial convergence is controlled by the two intuitive parameters, the volume of the spatial area and the grid spacing of the uniform mesh. We developed a multiple iterative method to solve the equation for transition density, avoiding explicit constructions of the response function and Green's function. As an example, we show calculation of linear and nonlinear dynamic polarizabilities of C_{60} molecule convergent with respect to the spatial parameters.

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