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Oscillator strength distribution of C_{60} in the time-dependent density functional theory

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ABSTRACT

An oscillator strength distribution of the fullerene C_{60} molecule is calculated in the time-dependent density functional theory. A real-time method is employed to obtain the spectrum of a wide energy region extending up to 120 eV. The orbitals are expressed on the uniform grid points in the three-dimensional Cartesian coordinates inside a large cubic box area. The calculated distribution shows an intense peak centered at around 20 eV, accompanying a number of sharp structures on it up to 35 eV. Absolute values and gross features of the oscillator strength distribution are in reasonable agreement with measurements.

1. Introduction

The optical properties of C_{60} molecule have been intensively investigated right after the discovery of this novel molecule [1]. Reflecting a high spatial symmetry of this molecule, the spectrum below the ionization threshold is rather simple and is characterized by the three peaks corresponding to the $\pi-\pi^*$ excitations [2–7]. A sum of the oscillator strength of these bound excitations amounts to less than 10, out of total number of valence electrons, 240. Hence most of the oscillator strength distributes above the ionization threshold, as in other organic molecules.

Several groups have reported measurements of the oscillator strength distribution of C_{60} molecule for a wide energy region through photoabsorption, photoionization, and electron energy loss measurements [8–17]. The cross section is characterized by the intense peak structure centered around 20 eV. Several additional peaks are also observed up to 35 eV [13,15–17]. There has been a controversy about the absolute value of the photoabsorption cross-section. Berkowitz made a careful examination of the absolute value by the sum rule analysis [12]. Recently, Kafle et al. have made a reevaluation of several measurements using the reliable data of the C_{60} vapor pressure, and have reported an oscillator strength distribution for a wide energy region which satisfies the Thomas–Reiche–Kuhn sum rule [17].

There have been several attempts to obtain the oscillator strength distribution of C_{60} in the first-principles calculations. One of the present authors previously reported the first-principles calculation of the oscillator strength distribution of C_{60} in the time-dependent density functional theory (TDDFT) [18,19], A real-time method was employed to obtain the oscillator strength distribution for a wide energy region. In these calculations, the obtained distribution above the ionization threshold appears jagged because of the too small spatial area adopted in the calculation. Alasia et al., Westin et al., and Tsolakidis et al. also reported the first-principles calculation of the optical absorption spectrum [20–22]. Colavita et al. reported a calculation of the oscillator strength distribution which is smooth above the ionization threshold. They have found an interesting fact that there appear very sharp structures in the oscillator strength distribution up to 40 eV above the threshold [23]. However, the calculation by Colavita et al. did not include the dynamical screening effect which should be significant for a large molecule.

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In this paper, we will report the oscillator strength distribution of C_{60} in the TDDFT. The calculation is achieved in a much wider spatial area than that in the previous calculation [18,19]. Such calculations have come to be feasible by employing the massively parallel supercomputer. Introducing an absorbing potential outside the molecule, we can describe the outgoing boundary condition for emitted electrons accurately. Therefore, the obtained oscillator strength distribution is a fully convergent one in the TDDFT, for a given density functional and for a fixed ion geometry.

The organization of this paper is as follows: in Section 2, we present our formalism. In Section 3, we present the calculated oscillator strength distribution. We also discuss the dependence of the results on the density functionals adopted, a comparison with measurements, and a comparison with previous theoretical calculations. In Section 4, a summary will be presented.

2. Formulation

2.1. Real-time method

We employ the real-time method which is suitable to calculate the oscillator strength distribution for a wide energy region. A detailed explanation of the real-time method is found in Ref. [24]. We here briefly explain the method.

We solve the following time-dependent Kohn–Sham (TDKS) equation in the time-domain,

$$i\hbar\frac{\partial}{\partial t}\psi_i(\vec{r},t)=\left\{-\frac{\hbar^2}{2m}\nabla^2+V_{\rm ps}(\vec{r})+V_{\rm ext}(\vec{r},t)-iW_{\rm abs}(r)+\int d\vec{r}'\frac{e^2}{|\vec{r}-\vec{r}'|}n(\vec{r}',t)+\mu_{\rm xc}[n(\vec{r})]\right\}\psi_i(\vec{r},t), \quad (1)$$

$$n(\vec{r},t)=2\sum_i|\psi_i(\vec{r},t)|^2, \quad (2)$$

where $V_{\rm ps}(\vec{r})$ is the electron–ion potential, $\mu_{\rm xc}[n(\vec{r},t)]$ is the exchange–correlation potential, $-iW_{\rm abs}(r)$ is the absorbing potential, and $V_{\rm ext}(\vec{r},t)$ is the external perturbing potential.

We treat σ and π electrons explicitly, 240 electrons in total for C_{60} molecule. There are 120 spatial orbitals $\psi_i(\vec{r},t)$, accordingly, occupied by the spin up and down electrons. For an interaction between the valence electrons and the core ions, we employ the norm-conserving pseudopotential of Troullier–Martin's type [25] with a separable approximation [26].

To calculate the dipole response of the molecule, we apply an instantaneous dipole distortion. To be specific, we employ the following external perturbation potential,

$$V_{\rm ext}(\vec{r},t)=-\hbar kz\delta(t), \quad (3)$$

where k is the parameter which specifies the magnitude of the distortion. Before this distortion is applied at $t=0$, the molecule is in the ground state described by the static Kohn–Sham orbitals $\phi_i(\vec{r})$. The impulsive dipole distortion results in the multiplication of the plane wave to the orbital wave functions,

$$\psi_i(\vec{r},t=0_+)=e^{ikz}\phi_i(\vec{r}). \quad (4)$$

This is an initial condition for the time evolution calculation with Eq. (1). We then evolve the system without any external potential, and calculate the dipole moment as a function of time,

$$d(t)=\int d\vec{r}n(\vec{r},t)z. \quad (5)$$

The oscillator strength distribution is then obtained by taking a Fourier transformation of the dipole moment,

$$\frac{df(E)}{dE}=\frac{2mE}{\pi k\hbar^3}{\rm Im}\int_0^T dtw(t)d(t)e^{iEt/\hbar}, \quad (6)$$

where $w(t)$ is the filter function which is introduced to reduce the numerical noise originated from the finite period of the time evolution. In the following calculation, we employ the following function if not specified otherwise,

$$w(t)=1-3\left(\frac{t}{T}\right)^2+2\left(\frac{t}{T}\right)^3. \quad (7)$$

We note that this filter function does not change the total oscillator strength in the calculation, since it does not change the slope at $t=0$, $(d/dt)w(t)=0$ at $t=0$.

We place an absorbing potential, $-iW_{\rm abs}(r)$, outside the molecule. This potential absorbs the electron flux emitted from the molecule and accounts approximately for the outgoing boundary condition. The performance of the absorbing potential is discussed in detail in Ref. [27]. A practical shape of the potential will be given later.

2.2. Numerical details

To describe the Kohn–Sham orbitals, $\psi_i(\vec{r},t)$, we employ a uniform grid representation in the three-dimensional Cartesian coordinate. To describe the continuum effect accurately for emitted electrons, it is necessary to solve the TDKS equation in a sufficiently large spatial area. In our calculations below, we typically employ a cubic spatial area of 80 a.u. side, with a grid spacing of 0.5 a.u. Then the total number of the grid points is $160^3=4{,}096{,}000$. This is much larger than that in the previous calculation reported in Ref. [19] where the number of grid points was about 65,000.

We employ a massively parallel supercomputer to make the present calculation feasible. We have developed and employed an efficiently parallelized computational program to solve the TDKS equation in which the spatial area is divided into a number of rectangular parallelepipeds. We typically employ 512 processors in parallel, dividing the cubic area of 80 a.u. side into 512 small cubes of 10 a.u. side.

The geometry of C_{60} is set to be C–C distances of 1.457 Åfor single and 1.384 Åfor double bonds, respectively. For all calculations in this paper, the ion position is fixed during the time evolution. To evolve the wave function, we employ a fourth order Taylor expansion method [18]. The time step is taken to be $\Delta t/\hbar=9.92\times10^{-4}\ {\rm eV}^{-1}$ and the number of typical time steps is 25,000. Thus the total duration of the time evolution is $T/\hbar=25{,}000\times9.92\times10^{-4}=24.8\ {\rm eV}^{-1}$.

Regarding the absorbing potential, we employ a linear function in radial coordinate [27],

$$-iW_{\rm abs}(r)=-iW_0\frac{r-R}{\Delta R}\quad(R<r). \quad (8)$$

The absorbing potential is placed outside of a radius $R=21.1$ a.u. The strength and thickness of the absorbing potential is set $W_0=4$ eV and $\Delta R=18.9$ Å, respectively. We have confirmed that the calculated oscillator strength distribution is not sensitive to the detailed choice of these parameters.

The distortion parameter k in Eq. (3) is taken to be $k=0.001$ Å^{-1}.

3. Results

3.1. Oscillator strength distribution

In the real-time method, we first calculate the dipole moment as a function of time after an impulsive distortion of the molecule. We show the calculated dipole moment, $d(t)$, in Fig. 1. We then take a Fourier transformation of the dipole moment to obtain the