Photoabsorption Spectra of Graphitic Nanostructures by Time-Dependent Density-Functional Theory *

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Photoabsorption spectra of graphitic ribbons (GR) and triangular graphitic flakes (TGF) are investigated by time-dependent density-functional theory calculations within a real-time scheme. Major peaks in the low-energy region of the spectra are attributed to the π–π* electronic transitions. The peak of the strength function appears at 3.0 eV owing to π–π* transitions via edge states for a TGF with hydrogen (H) termination and at 6.0 eV owing to π–π* transitions at the Γ point for GR with H termination. Small structures in the strength function emerge at 0 ~ 2 eV for both graphitic structures after extraction of H atoms. The new structures are found to originate from the electronic transitions between dangling-bond states. Thus, the present study shows that the electronic states unique to nanoscale graphitic structures can be captured in the optical absorption spectra. [DOI: 10.1380/ejssnt.2005.439]

Keywords: Time-dependent density-functional theory; Electron density, excitation spectra calculations; graphite; Nano-films, stacks, and other nano materials;

I. INTRODUCTION

Carbon nanostructures have attracted much attention from both scientific and technological viewpoints. In particular, fullerenes show various electronic and magnetic properties depending on the materials encapsulated in the clusters. Carbon nanotubes are now key nanomaterials for nanometer-scale devices and future applications. Fullerenes or carbon nanotubes are formed of graphitic sheets of the sp² network, which are essentially responsible for numerous novel features of these nanostructures that have been observed in the last two decades. A graphitic ribbon, which is a graphene sheet with a finite width (edges), is theoretically known to exhibit remarkable physical properties [1–5] that are not expected to appear for either carbon nanotubes or fullerenes with closed structures. Graphitic ribbons have a π bond, a dangling bond, or edge states depending on their atomic geometry and the presence of hydrogen (H) termination.

Very recently, edge states of graphitic sheets with zigzag-shaped edges have also been observed in a scanning tunneling microscopy (STM) study [6]. We thus predict that these electronic states that are unique to graphitic nanostructures are also captured in optical absorption spectra, because the dangling bond and edge states have energies close to the Fermi level and π–π* transitions are likely to occur in these systems. This is the background for our first-principles study of photoabsorption of graphitic nanostructures.

Many interesting physical properties such as optical absorption, dynamical dielectric function and response to time-dependent fields are attributed to the electron excited states. While a conventional density-functional theory (DFT) is a powerful tool for calculating electronic states, it is limited to ground state properties. Thus the DFT method is not suitable for investigating the quantitative properties of the optical spectra originating from the electronic excitations. To go beyond the DFT, we adopted a time-dependent density-functional theory (TDDFT) [7] within a real-time scheme [8–11] in this study. The TDDFT method is known to be the most reliable method for addressing the problems associated with electronic excitations. For instance, the TDDFT correctly evaluates the excitation energies, which are substantially underestimated by the DFT.

Our objectives in this study are to check whether the electronic states that are characteristic of the graphitic nanostructures with zigzag edges are visible in the optical absorption spectra and to elucidate the correlation between the excitation spectra and the electronic states.

The TDDFT as a computational method and graphitic nanostructures as models adopted in this study are described in Sec. II. The results on absorption spectra of triangular graphitic flakes (TGF) and graphitic ribbons (GR), and the physical interpretation are provided in Sec. III. A summary is given in Sec. IV.

II. METHOD AND MODEL

We carried out time-dependent density-functional theory (TDDFT) calculations within the real-time scheme [8–11] to investigate the photoabsorption spectra of nanographitic structures. The TDDFT is a powerful computational method [8–14] for calculating the excited states or dynamical response of many-electron systems and has also been successfully applied to various nonequilibrium electron dynamics phenomena.

First, we determined the electronic ground-states in the absence of an external field by the conjugate gradient method in the conventional density-functional theory (DFT) calculations, before seeking to clarify the time evolution of the wave function under an external field. We employed the norm-conserving pseudopotentials of NCPS97 [15] based on the Troullier-Martins algorithm [16] and the Ceperley-Alder functional [17, 18] for the local-density approximation with the Perdew-Zunger parametrization [19].

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Next, in the simulation, an external field is turned on instantaneously at \( t = 0 \). Atomic units (\( e^2 = \hbar = m = 1 \)) are used throughout the present article. We apply an external potential of \( V_{\text{ext}}(\vec{r}, t) = k \mu \delta(t) \), \((k = E_\mu, \mu = x, y, z, E_\mu \) is the electric field in the \( \mu \) direction) to the ground-state electron density to induce the dynamical dipole response [9–11]. This potential is useful for determining the optical spectrum, because the potential form includes all frequency components and thus the spectrum of dipole response over the entire frequency region is obtained at once. The initial wave function is modified by giving a momentum \( k \) to electrons as
\[
\phi_i(\vec{r}, +0) = e^{-ik\mu} \phi_i(\vec{r}, 0). \tag{1}
\]
Finally, the time evolution of electron density is obtained by solving the time-dependent Kohn-Sham equation,
\[
\frac{\partial}{\partial t} \phi_\mu(\vec{r}, t) = H_{\text{KS}}(t) \phi_\mu(\vec{r}, t), \tag{2}
\]
\[
\alpha(\vec{r}, t) = 2 \sum |\phi_\mu(\vec{r}, t)|^2. \tag{3}
\]
In solving Eq. (2) we have adopted the fourth-order Taylor expansion method under the assumption that the Hamiltonian is invariant during the time step \( \Delta t \). Although this approximation breaks the unitarity condition for the time evolution, the normalization condition for the electron number meets the required accuracy in the present simulation with a rather short time interval.

The dynamical polarizability in the time representation is obtained at each time step as
\[
\alpha_\mu(t) = -\frac{1}{\hbar} \int d\vec{r} \mu \delta n(\vec{r}, t), \quad \mu = x, y, z, \tag{4}
\]
where \( \delta n(\vec{r}, t) \) is defined as \( \delta n(\vec{r}, t) = n(\vec{r}, t) - n(\vec{r}, 0) \). The dynamical polarizability in the energy representation is the Fourier transform of Eq. (4),
\[
\alpha_\mu(\omega) = \int_0^T dt \alpha_\mu(t)e^{i\omega t}, \quad \mu = x, y, z. \tag{5}
\]
A smoothing parameter \( \Gamma \) is introduced and the time evolution up to \( T \geq 2\pi/\Gamma \) is calculated to obtain \( \alpha_\mu(\omega) \) in the energy resolution of \( \Gamma \). The dipole strength function \( S_\mu(\omega) \), which is proportional to the absorption cross section, is obtained from the imaginary part of the polarizability,
\[
S_\mu(\omega) = \frac{2\omega}{\pi} \Im \alpha_\mu(\omega), \quad \mu = x, y, z. \tag{6}
\]
In this study, we investigate two types of graphitic nanostructure as shown in Fig. 1. One is (a) a TGF, [20] which is a finite-sized cluster and the other is (b) a GR of an infinite length (periodic structure) in one direction; however, both have a common property in that all their edges have a zigzag shape. The reason why we have chosen these structures is that both have zigzag-shaped edges and are good model-systems to explore the effect of hydrogen termination on optical properties. The unit cell is the region surrounded by the dashed lines in Fig. 1(b). Open circles and closed circles denote carbon atoms and hydrogen atoms, respectively. The external field is applied to the structures in the \( x \) and \( z \) directions for (a) and in the \( y \) and \( z \) directions for (b). The real-space DFT method is employed for the calculation of (a) TGFs and Fourier-space DFT with super-slab geometry is employed for (b) GRS. See the Refs. [21–23] for the details of methods used in the different calculation spaces.

Here, we summarize the computational details of the present calculations. The cell size and the mesh size in the real-space DFT calculations are 30 \( \AA \times 30 \AA \times 13 \AA \) and 0.265 \( \AA \), respectively. The second-order differential operator in the kinetic energy is approximated by employing a 9-point formula. The unit cell size is 2.5 \( \AA \times 20.0 \AA \times 10.0 \AA \) and the cutoff energy is 44 Ry in the Fourier-space DFT calculations. We choose 16 \( k_\parallel \) points in the first Brillouin zone for GRS. The time step \( \Delta t = 0.02 \) a.u., simulation time \( T = 600 \) a.u. (\( 1.45 \times 10^{-14} \) sec.), and smoothing parameter \( \Gamma = 0.3 \) eV are used in the calculation of the time evolution of the wave function.

### III. RESULTS AND DISCUSSION

First, we describe the results obtained on the photoabsorption spectra (strength functions, Eq. (6)) of TGFs. The calculated strength functions of TGFs are shown in Fig. 2 (a) for a H-terminated TGF and in Fig. 2(b) for a TGF without H termination. The solid line and dashed line denote \( S_x(\omega) \) and \( S_z(\omega) \), i.e., the spectra generated by the external field along \( x \) and \( z \) directions, respectively. We focus on and discuss three features in these spectra: (i) \( S_x(\omega) \) is negligibly small up to 10 eV, indicating a large energy gap. (ii) Large peaks appear at around 3–5 eV. (iii) A shoulder structure emerges at 0–2 eV in the spectrum of the TGF without H termination (Fig. 2(b)) that is absent in that with H termination (Fig. 2(a)).

We can predict the physical origins of these features, using the electronic structures in the ground state, namely molecular energy levels, orbitals, and dipole-transition probabilities evaluated by the DFT calculations, although the highest occupied molecular orbital (HOMO) energy and the lowest unoccupied molecular orbital (LUMO) energy gap and the excitation energies are underestimated by the DFT. The molecular orbital energies are given in Fig. 3(a) for a H-terminated TGF and in Fig. 3(b) for a TGF without H termination. The wave functions of HOMO energy levels of the two cases are drawn on the
right side of each energy diagram. All orbitals except those around the HOMO level that are dangling-bond (DB) states (σ nature) in Fig. 3(b) are π states having amplitudes along the z direction perpendicular to the molecular plane. Since the dipole-transition probabilities along the z direction, |⟨π|z|π⟩|^2 and |⟨σ|z|σ⟩|^2 are zero and |⟨π|z|σ⟩|^2 are quite small in the low-energy region, S_z(ω) becomes small. This is the reason for feature (i).

(ii) Large peaks at around 3∼5 eV are attributed to the π-π* transitions. In particular, the peak at 3 eV in Fig. 2(a) is found to be caused by transitions from the states at -6.1 eV to the LUMO level just above the HOMO level by 0.03 eV (almost degenerate) or from the HOMO level to the states at -2.4 eV (see Fig. 3(a)). An interesting thing to note here is that the distributions of the wave functions of the HOMO (and LUMO) states (see the right panel in Fig. 3(a)) are very similar to those of edge states of zigzag GRs[1–3]. Thus, the peak at 3 eV is an indication of the edge state of a finite-sized cluster. A discussion regarding the edge states is given later in this section. (iii) A shoulder in the low-energy region of 0∼2 eV in Fig. 2(b) stems from the transitions between the DB states at ∼6 eV in Fig. 3(b). The wave functions of the DB states are localized at edges as shown in the right panel of Fig. 3(b). The reason for the small amplitudes of the spectra, i.e., not a peak but a shoulder, is that many DB states exist close to each other with small energy differences. (Note the energy difference ω is in the numerator of Eq. (6)). Thus, the physical origins of the three main features in the spectra of Fig. 2 have been revealed.

Next, we discuss the absorption spectra of GRs. The strength functions of GRs are shown in Fig. 4(a) for a H-terminated case and in Fig. 4(b) for a GR without H termination. The solid line and dashed line denote S_y(ω) and S_z(ω), respectively. S_y(ω) is the spectrum generated by the external field perpendicular to the ribbon axis. The main features of these spectra are very similar to those of TGFs discussed above except for some quantitative differences, and the physical origins of the features are also found to be close to those of the features of TGF spectra by considering the electronic band structures of GRs. The band structures are shown for a H-terminated GR in Fig. 5(a) and for a GR without H termination in Fig. 5(b). The wave function at the Fermi level of X point, which has been defined as an edge state [1–3] (π nature), is drawn on the right side of Fig. 5(a), and that at the Fermi level of the X point, which is called a DB state [4] (σ nature) is drawn on the right side of Fig. 5(b).

(i) The reason why S_z(ω) is negligibly small in the low-energy region up to ∼10 eV is the same as that in the case of TGFs. (ii) The origin of the prominent peaks at ∼6 eV in either Fig. 5(a) or 5(b) resides in the π-π* transitions at Γ points. This reason is also similar to that of (ii) in the case of TGFs. A small peak at ∼1 eV...
eV in Fig. 4(b) originates from the transition from the occupied DB state to unoccupied DB states at Γ points. A similar feature is also seen in (iii) the shoulder structure at 0~2 eV in Fig. 2(b). There is a small difference between the spectra of TGFs and GRs: A gradual increase in the strength in the low-energy region of 0~5 eV in Fig. 4(a) (the ripple structure appears owing to a finite number of \(k\) sampling) is not seen in Fig. 2(a). This is attributed to the \(\pi-\pi^*\) transitions between the central two bands when \(k_x\) decreases from the \(X\) point toward the Γ point in Fig. 5(a).

A brief summary of the properties obtained is as follows. In addition to large peaks due to typical \(\pi-\pi^*\) transitions, the characteristic structures of the spectra in the low-energy region are reflected by the transitions between edge states for GRs (edge-like states for TGFs) and those between DB states for either GRs or TGFs. It is noted that these structures that are unique to graphitic nanostructures in the low-energy region of the strength function would be more pronounced in the spectra of the imaginary part of the dynamical polarizability function (see Eq. (6)).

**IV. CONCLUSION**

In conclusion, we investigated the photoabsorption spectra of graphitic ribbons and triangular graphitic flakes by the TDDFT calculations within a real-time scheme. The peaks and structures associated with the \(\pi-\pi^*\) transition via edge states appear in the low-energy region of the strength function if the edges are terminated with hydrogen. New signatures emerge at 0~2 eV in the spectra after extracting hydrogen atoms from the edges of either structure. The physical origin of the new features is found to be transitions between the dangling bond states. Therefore, the present results have shown that electronic structures unique to graphitic nanostructures can be detected in photoabsorption spectra.

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