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Infrared absorption spectra of few-layer graphenes studied by first principles calculations

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ABSTRACT

The infrared (IR) absorption spectra of the undoped, the hole- and electron-doped few-layer graphene (FLG) with layer number of $N = 1, 2, 3$ have been calculated using the density functional theory in the local density approximation. It is found that in contrast with the featureless optical spectrum of the undoped monolayer graphene, the undoped AB-stacking bilayer and trilayer graphenes exhibit interesting rich IR spectra, e.g., the peaks and jumps in their IR spectra, which are caused by the coupling between different layers. And clear characteristic peaks, lying at different energies, exist in the IR spectra of the hole- or electron-doped bilayer and trilayer graphenes due to the asymmetrical band structures. Beside, based upon their different IR spectra, a powerful experimental tool has been proposed to identify accurately the layer number and doping type of the FLGs.

1. Introduction

Graphene is a two-dimensional (2D) flat monolayer composed of carbon atoms arranged in a honeycomb network, which can be used as a basic building block for all other graphitic materials. In 2004, a single graphene sheet was successfully isolated in experiment, and the free-standing monolayer graphene (MLG) was made experimentally in succession [1]. Since then, other few-layer graphenes (FLGs) are also obtained in recent years. Because of the graphene's unusual mechanical and electronic properties, a lot of experimental and theoretical researches had been made in the past several years on its growth [2], band structures [3–6], electronic excitations [7–10], transport properties [11–17], optical spectra [18,19], and phonons [20], which have already shown a lot of new physics and potential applications for nanoelectronic and nanoelectromechanical devices.

A graphite crystal is a vertical stack of the hexagonal graphene sheets along their c-axis, coupled by weak van der Walls interaction. It is known that there are three different stacking ways for the graphene layers, which are simple hexagonal, orthorhombic, and rhombohedral, forming the AA-, AB-, ABC-stacked graphites, respectively. The natural graphite usually adopts the AB-stacking sequence, showing a nonvanishing density of states (DOS) at its Fermi energy [21]. FLG is a stack of graphite sheets with thickness less than 50 nm. In Fig. 1(a), we show the geometrical structure of the ABA-stacked three-layer graphene (TLG), for which there exist two inequivalent atoms, A_i and B_i, in a primitive cell of each graphene.

For a single graphene sheet (or the MLG), its perpendicular p_z orbitals on the sheet induce two linear energy bands crossing at its Fermi energy E_F, leading to a zero-gap semiconductor with a vanishing DOS at the E_F. The FLG with their layer number $N \geqslant 2$ can also be considered as a 2D semimetal. But, the interlayer interaction destroys the symmetry and isotropy of their energy bands, making the original linear bands become the parabolic ones, which also remarkably causes a weak overlap between the valence and conduction bands in the bilayer graphene (BLG).

In contrast with the extensive studies on the FLGs' electrical properties, there are less experimental and theoretical studies on their optical properties, especially their IR ones [22–24], which, however, are important for understanding their electronic structures and excited-state properties. For example, the IR spectroscopy is a powerful tool to get information of their low-lying energy excitations. Early in 2006, Lu et al. [21] studied the low-

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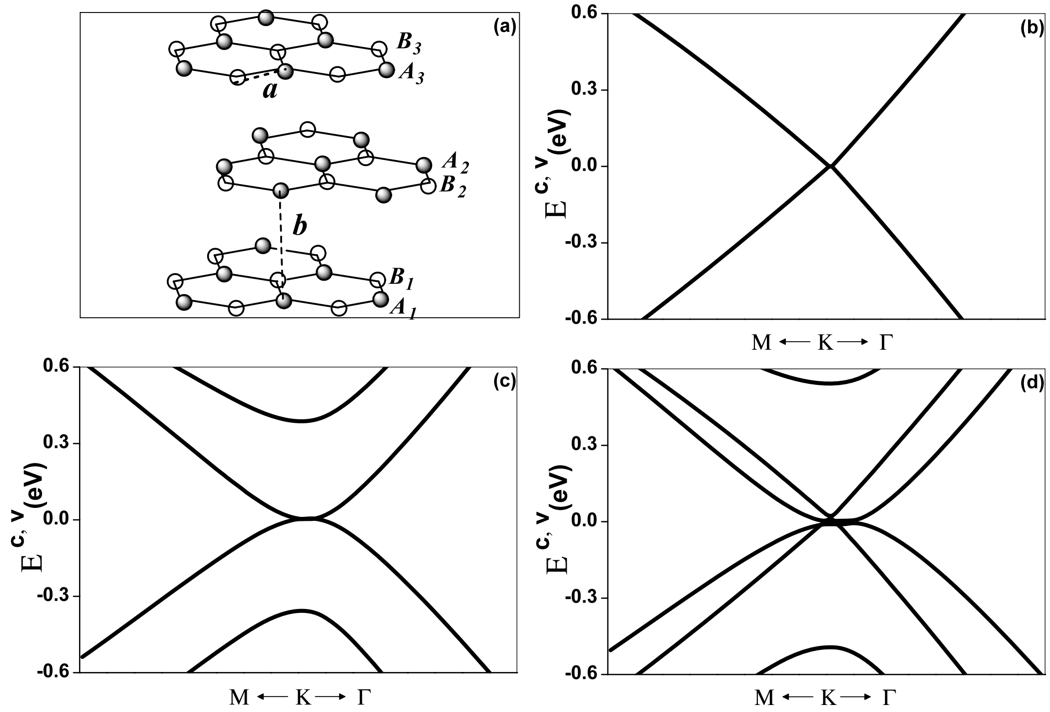

Fig. 1. (a) Schematic of the AB-stacked 3-layer graphene. Here, a is the C–C bond length in the graphene, b is the distance between two nearest neighbor (n.n.) graphene layers. Low-energy dispersions of the AB-stacking N-layer graphenes are shown in: (b) $N = 1$, (c) $N = 2$, and (d) $N = 3$.

energy electronic and optical properties of AB-stacking undoped FLG with layer number $N = 1$–4 by the tight-binding (TB) model. Experimentally, Wang et al. [25] measured the FLGs' IR spectroscopy, finding the strong interband transitions in the hole-doped (p-doped) MLG and BLG, which can be substantially modified by electrical gating. Therefore, the FLGs' strong and layer-dependent optical spectra, controllable by a simple electrical gate, hold promise for their new applications in the IR optics and optoelectronics. Lately, Li et al. [26] and Kuzmenko et al. [27], observed significant asymmetry in the optical conductivity of BLG upon electrostatic doping of electrons and holes by infrared spectra. More recently, Zhang et al. [28] and Mak et al. [29] directly observed an electric-field induced band gap in carrier-doped bilayer graphene by infrared spectroscopy.

Therefore, from a theoretical point of view, it is also interesting to study the IR spectra of the doped FLGs, and compare them with the experimental observations. In addition, as we know, due to the development of density functional theory (DFT) during the last two decades, the *ab initio* methods can be used to calculate many physical properties with unprecedented accuracy. Moreover, compared with TB method, the *ab initio* calculation has the advantage of their high transferability and predictive power because the TB calculations mostly rely on some parameters. So, it is natural and necessary to do the DFT calculations on the IR spectra of the FLGs, especially the doped FLGs.

Thus, in this Letter, we perform the first-principles calculations on the IR absorption spectra of the undoped, hole- and electron-doped FLGs with layer number of $N = 1, 2, 3$, and study in detail their dependence on the layer number, doping type, and the interlayer interaction.

2. Theory and computational details

2.1. Theory of optical absorption

By diagonalizing the Hamiltonian matrix, the energy dispersion $E(\vec{k}, j)$ and the related eigenfunction $|\psi(\vec{k}, j)\rangle$ can be obtained, where j represents the unoccupied (occupied) state. Furthermore, the IR absorption properties of a FLG can be studied by the imaginary part of the frequency-dependent dielectric function:

$$\varepsilon''(\omega) = \frac{1}{\Omega}\left(\frac{2\pi e}{m_e \omega}\right)^2 \sum_{j_1, j_2,} 2w_{\vec{k}} \left|\langle \psi(\vec{k}, j_1)\big|\hat{\hat{E}} \bullet \hat{\hat{P}}\big|\psi(\vec{k}, j_2)\rangle\right|^2 \times \delta\left[E(\vec{k}, j_1) - E(\vec{k}, j_2) - \omega\right] \qquad (1)$$

which is suitable for the zero temperature. The indices $j_1 = 1, 2, \ldots, N$ and $j_2 = -1, -2, \ldots, -N$ denote respectively the conduction and valence subbands, counted from the E_F. $\hat{\hat{E}}$ is the polarization direction of the photon, and $\hat{\hat{P}}$ the electron momentum operator. Under $\hat{E}_x \parallel \hat{x}$ ($\hat{E}_y \parallel \hat{y}$), the electrons could be excited from the occupied valence π bands to the unoccupied conduction π^* bands. At zero temperature ($T = 0$ K), only inter-π-band excitations can occur. The excitation energy is $\omega_{ex} = E(\vec{k}, j_1) - E(\vec{k}, j_2)$ because photon's momentum is almost zero, and hence the optical selection rules is $\Delta\vec{k} = 0$.

2.2. Computational details

We have used the total-energy plane-wave pseudopotential method in the local density approximation (LDA) with the Ceperley–Alder exchange correlation. The Vienna *ab initio* simulation package (VASP) [30] is employed. The interaction between the ions and electrons is described by the highly accurate full-potential projected augmented wave (PAW) [30–32], which can give a more accurate and reliable result than the ultrasoft potential. In our calculations, the $2s$ and $2p$ orbitals of the carbon atom are treated as valence orbitals, and a large plane-wave cutoff 500 eV is used throughout.

A supercell geometry is adopted, so that the FLG is aligned in a hexagonal supercell, with the closest distance between the adjacent FLGs being at least 10 Å along the stacking direction, which is taken along the z direction. And a uniform grid of $n \times n \times 1$