Symmetry-breaking effects in bilayer graphene

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Introduction

In the recent years, materials based on carbon have caused considerable interest among researchers in both theory and application fields due to their special properties as well as potential to use them in nanotechnology. However, specific structures of carbon are often difficult to fabricate. Because of that some of them receive less attention than others until the techniques to produce them are finally developed. One of such carbon structure that gained more attraction after it was manufactured is graphene, i.e. a single layer of graphite.

Graphene is a two-dimensional layer of carbon atoms arranged in a hexagonal lattice (Fig. 1). Common graphite can be seen as stack of many graphene layers, and carbon nanotube is essentially rolled graphene sheet (in fact, some transport properties of nanotubes are caused by the structure of graphene and the confinement of the electrons [1]). So graphene can be considered as building block for other carbon-based materials, and as such an interesting object of investigation. Single-layer graphene was first produced in 2004 by Andre Geim's group [2]. Since then, the characteristics of the graphene as well as its possible applications have been widely studied.

Electronic properties of graphene and similar materials are relatively well known. Basic tight-binding calculations [3] show that overlapping p_z orbitals on neighboring carbon atoms develop into π and π^* bands, which become valence and conduction bands. These bands touch each other at the corner of hexagonal Brillouin zone (so-called K point). The energy at the touching point is equal to the Fermi energy, but the density of states there is zero, so one can call graphene a semimetal or a zero-band-gap semiconductor.

High expectations in field of atomic-scale technology are associated with bilayer graphene. The band structure of graphene is sensitive to the lattice symmetry. When two graphene sheets are arranged in the same fashion as in graphite (this is called Bernal stacking, [4]), the effects of sensitivity can be clearly observed. If the symmetry of the layers is broken, an energy gap between valence and conduction bands appears [4]. This can be done in several ways, such as applying electric field or doping one of the layers. Recent experiments show that these techniques can be used to control the width of emerging band gap [5], thus making it possible to construct a switch with a thickness of few atoms.

In this article we discuss the before-mentioned ways of symmetry breaking in bilayer graphene and the resulting electronic properties of the material. We performed accurate quantum mechanical simulations of graphene bandstructure under effect of electric field and n-type (potassium) doping, paying attention to the development of band gap and behaviour of Fermi level.

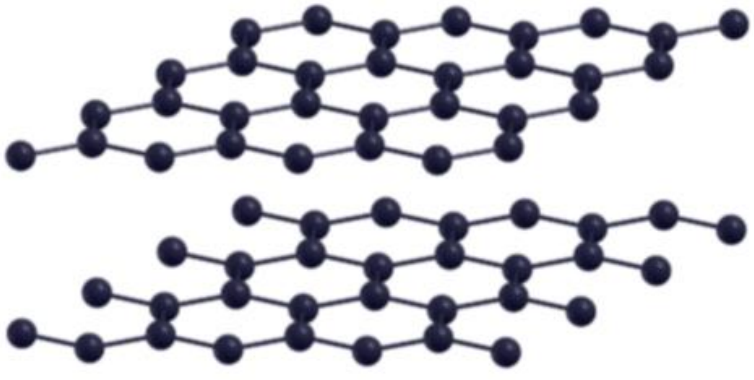

Fig. 1. Atomic structure of bilayer graphene

Methodology

The calculations have been performed using the *ab initio* total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) developed at the Institute für Materialphysik of the Universität Wien [6-9]. The simulations were run on Green and Mozart clusters at IFM, Linköpings Universitet.

VASP is built on the basis of density functional theory (DFT). DFT based computations are used widely in solid state physics and in most cases provide rather accurate results. DFT is a quantum mechanical method for calculating electronic structure in many-body systems [10]. Its underlying principle is the Hohenberg-Kohn-Sham theorem, stating that the ground-state energy of the system can be uniquely determined by its particle density ρ. Thus the problem of solving many-body Schrödinger equation can be replaced by the minimization of energy functional $E[\rho]$. A widely used approach to DFT is the Kohn-Sham equations that formally convert DFT to a single-particle theory with many-body effects included via the exchange-correlation term. The equations are usually solved by starting with initial guess for the particle density and iterating to get more accurate values (the procedure is called "self-consistency cycle").

In practical applications, additional approximations have to be made in order to solve these equations. Most important of them is the local-density approximation (which is used to determine the exchange-correlation energy). Another popular approach that makes solving differential KS equation easier is based on the concept of pseudopotentials. The main idea is that the inner electrons of the atoms are only little affected by chemical binding in molecules or solids in comparison to outer electrons. Thus their contribution can be approximated by a constant weak pseudopotential. The remaining valence electrons can be described by plane-wave basis sets. VASP mainly uses this method along with other approximations, including ultra-soft pseudopotentials and projected augmented waves [11,12].

Results

Distance between atoms in graphite layer a = 1.421 Å [13], and the interlayer spacing d = 3.354 Å [14]. We used these figures for the simulations of bilayer graphene. We also determined the spacing d for bilayer graphene as the distance for which the total energy of the system is minimal. Van der Waals forces that bind different layers of graphite are actually not well handled by VASP algorithms. Nevertheless, the minimum total energy was found at exactly the same distance.

First we performed calculations of double-layer graphene bandstructure (see Fig. 2) without any external factors. The results are shown in Fig. 3. Compared to the single-layer, each of the former valence and conduction bands split into two due to the interlayer interaction. The splitting of lower energy bands also exists but is hardly noticeable. Two of the new bands also meet around the K point at Fermi level E_F = -4,923 eV. In fact, the calculations suggest that bands have a tiny overlap of about 2,5 meV, and Fermi level is just above the crossing area. This well corresponds to experimental observations of Geim's group [2], which also propose that band overlap increases with the number of graphene layers.

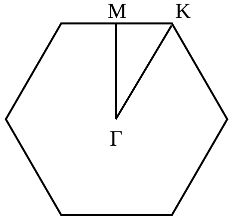

Fig. 2. Brillouin zone of the graphene in the momentum plane. Bandstructure was calculated along the indicated high-symmetry axes.

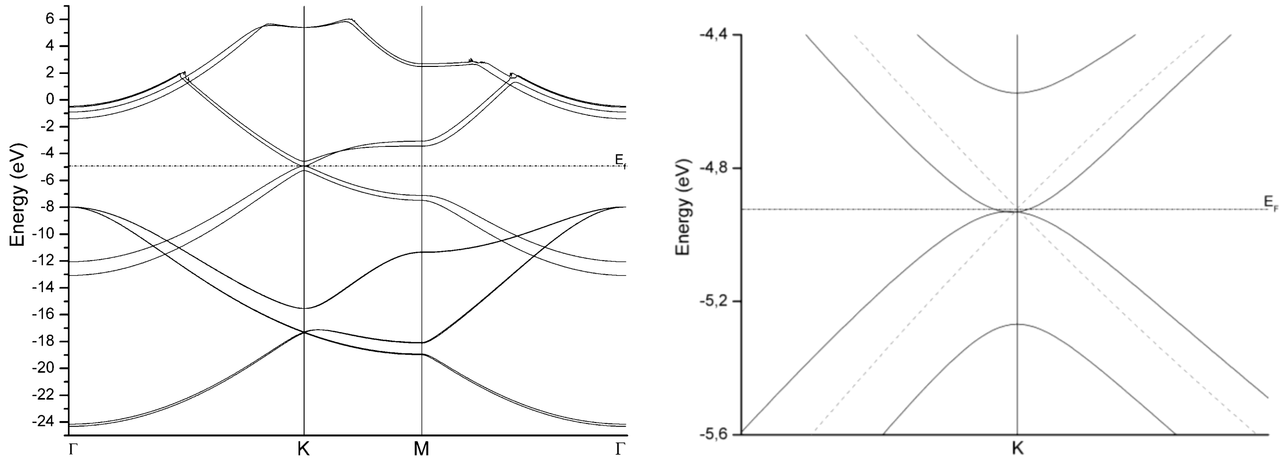

Fig. 3. Bandstructure of bilayer graphene. Picture on the right shows the area around the touching point of conduction and valence bands for single layer (dashed lines) and bilayer graphene.

Next we introduced an electric field into the system. As expected, it causes the energy gap between the meeting bands. The evolution of gap in respect of field strength is represented in Fig. 4. The results show the linear dependence which is close to the product of field strength E and interlayer distance d (that is, the drop of electric potential between layers). Simulations at higher fields confirm this assumption. For example, calculated band gap at the K point for E = 50 mV/Å equals to 168,5 meV, as compared to the potential difference E·d = 167,7 meV. However, when the field increases, the bands start to deviate from the smooth parabola-like form and develop a little kink, centered at K point. Possible reason for that could be change of electron mass because of electron-phonon interactions, as stated in [5]. Therefore, the minimal distance between bands at the corner of the kink is smaller than that at the K point.

The electric field does not change the value of Fermi level. Nevertheless, it causes neighboring bands to move into opposite directions, and at certain field strength (our calculations provide 6-7 mV/Å) Fermi level appears within the gap – graphene becomes an insulator.

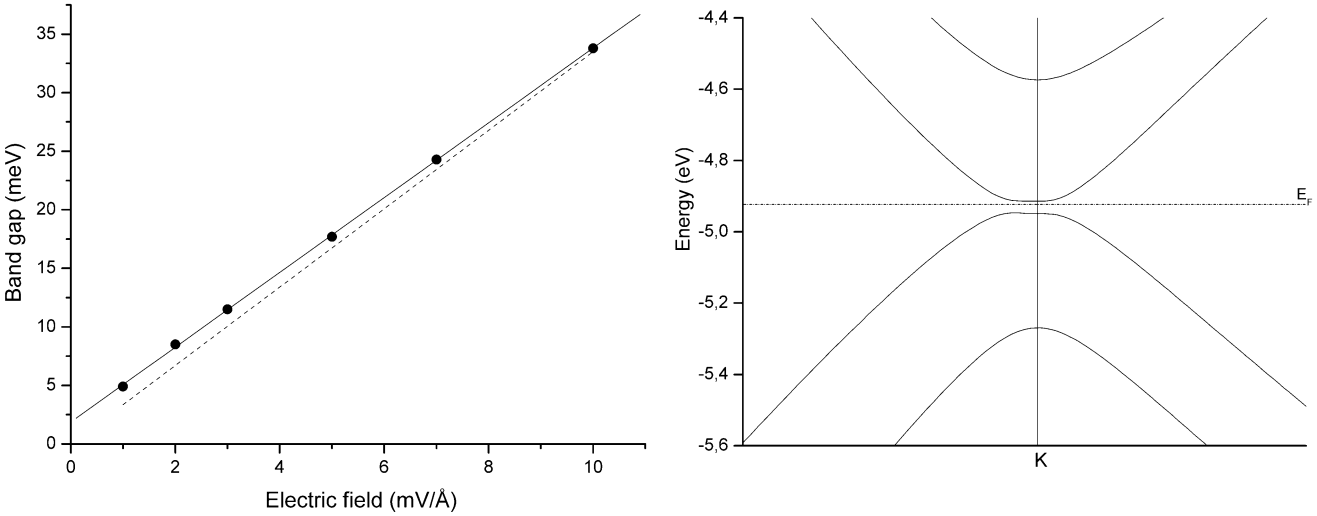

Fig. 4. Development of band gap under effect of electric field (left picture). Solid line is an approximation of the results. Dashed line marks the relationship Δε = E·d . The right picture shows the gap at the field equal 10 mV/Å.

In the second set of simulations we doped the upper layer of the graphene with potassium. The chosen concentrations of the dopant were 1 potassium atom for 36 and 144 carbon atoms, which corresponds to respectively 0,11 and 0,028 doping electron per unit cell. The position of K atom was determined by geometric relaxation; it ended up 2,65 Å above the upper layer, at the middle of the bond between two C atoms.

Doping the bilayer also resulted in a gap, but the distance between bands is considerably bigger and the kink is much deeper than those caused by the electric field. At the lower doping concentration, distance between bands is 0,27 eV at the middle and 0,21 eV at the corner of the concave. At the higher concentration the gap reaches 0,5 and 0,3 eV, respectively (Fig. 5). The behaviour is qualitatively the same as that observed experimentally by [5], although smaller doping levels were used in that experiment and narrower gaps were achieved. In this case, symmetry breaking is caused by a doping material, which donates its valence electrons to the upper layer.

Doping also affects Fermi level. Since density of states near the touching bands is small, the added charge causes substantial shift of the Fermi level in the direction of the upper energy bands (1,19 eV for doping concentration of 0,11 e^- per unit cell) [15,16]. So the metallic properties of the graphene increase.

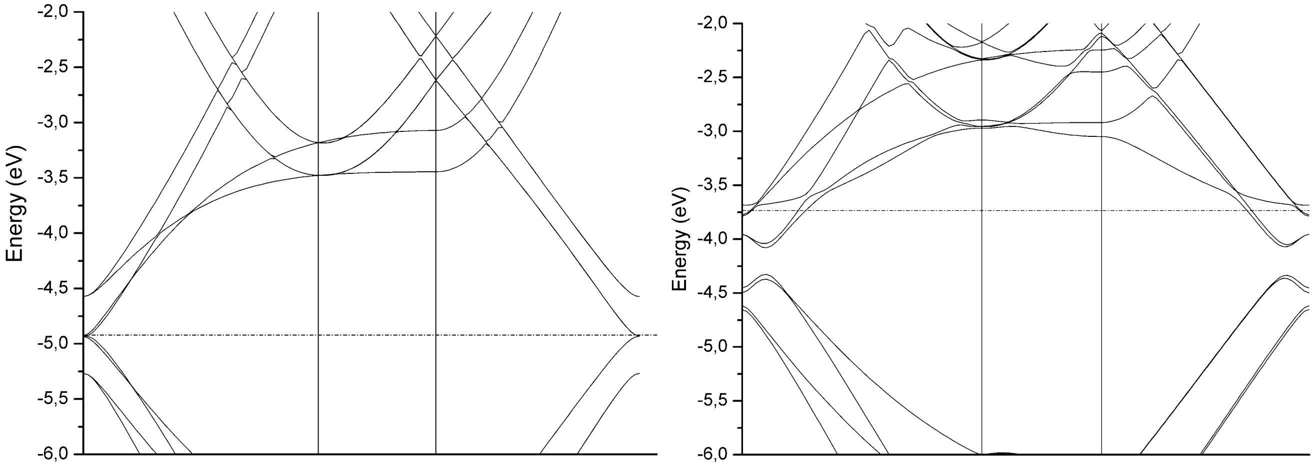

Fig. 5. Bandstructure of potassium doped bilayer graphene, compared to the undoped material (left picture). Doping level here is 0,11 electrons per unit cell.

To conclude, both symmetry-breaking techniques introduce an energy gap between conduction and valence bands of bilayer graphene. However, influence of them on Fermi level is different, and so should be the resulting electronic properties of the material.

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