Ab-initio study of electronic properties of a two-dimensional array of carbon nanotubes

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Ab-initio study of electronic properties of a two-dimensional array of carbon nanotubes

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Abstract. The equilibrium geometry and electronic band structure of a planar array of carbon nanotubes are studied with the use of the Quantum Espresso code - a plane-wave realisation of the density functional theory (DFT). The many-electron correlations and van der Waals corrections are taken into account. The optimal distance between nanotubes in the array corresponding to the minimum of the total energy of the system is found. A strongly anisotropic hyperbolic dispersion is demonstrated for low-energy charge carriers in an array of quasi-metallic (15,0) carbon nanotubes with the optimal inter-tube separation governed by van der Waals forces.

1. Introduction

Graphene-based nanomaterials have attracted great attention due to their unique electronic and mechanical properties. Graphene sheet rolled into a cylindrical shape forms a structure called carbon nanotube (CNT) [1]. CNTs manifest drastically different electronic properties from being a metal or a very narrow-gap semiconductor (quasi-metal) to a mid-gap semiconductor depending on their chiral vector - the way they are rolled.

Ab-initio methods are widely used for modeling electronic properties of single nanotubes with different chirality and more complex systems constructed on the basis of CNTs [2,3]. Moreover, such structures are extensively studied experimentally. For example, results of experimental studies of self-assembled horizontally aligned carbon nanotube arrays were recently published [4]. Such structures show great potential as building blocks for transparent displays, nanoelectronics, quantum lines, field emission transistors, super-strong tethers, aeronautics and astronics materials, and even space elevators. Recently, a giant optical absorption peak corresponding to inter-subband transitions has been observed in a film of highly-aligned for the excitation polarized normal to the tubes [5].

In this paper, we have estimated using DFT calculations the optimal distance between zigzag quasi-metallic (15,0) CNTs assembled in a perfect two-dimensional (2D) array, see Fig.1. We have calculated the electronic band structure of the corresponding CNT array for the bands closest to the Fermi level.

2. Computational details

The ab-initio calculations of the band structure and optimal distance between CNTs in the array were performed employing an ultra-soft pseudo-potential and a plane-wave basis in the Quantum Espresso package [6]. Quantum Espresso is based on the first principles density functional theory which allows the calculation of ground state properties of rather complex systems.

At the first stage we made an optimization of the spatial geometry of a planar array of (15,0) zigzag CNTs using the well-known generalized gradient approximation (GGA) for exchange-correlation potential - Perdew, Burke and Ernzerhof (PBE) functional [7] with and without the van der Waals (vdW) correction. The vdW interaction was included by the use of the method of Grimme (PBE-D2) [8]. The calculations were done for different inter-tube separations.

At the second stage, the band structure of the (15,0) CNT array was calculated using the PBE-D2 approach for an optimal distance *d*, which was found in the first stage. In order to get accurate results, the plane-wave cut-off was set to a high value of 800 eV, for which the structural relaxations and the electronic energies fully converged. A Gaussian smearing for the occupations was used with a smearing width of 0.01 eV. We performed a convergence test with respect to the number of k-points in the Monkhorst-Pack grid 10×10×1.

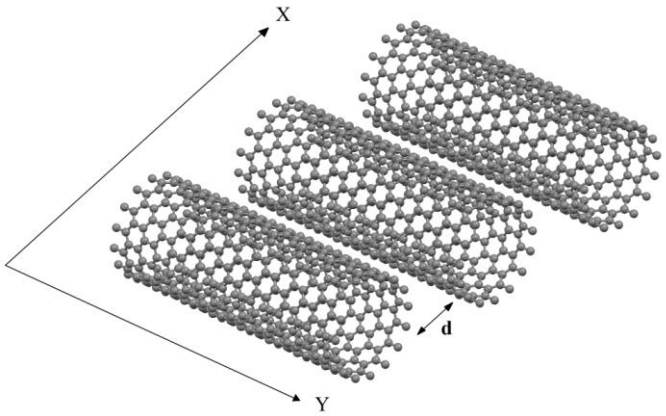

Figure 1. Horizontally aligned array of carbon zigzag nanotubes (15,0) separated by distance d between walls of tubes. The diameter of (15,0) CNT is 22.2 a.u.

3. Results

In this section we present the results of our calculations of the optimal inter-nanotube distance *d* and the electronic band structure of an array composed of (15,0) CNTs separated by this optimal distance.

To model a planar array, we used a hexagonal lattice with a separation of 60 atomic units (a.u.) between layers and 60 carbon atoms per unit cell. A diameter of an (*m,n*) CNT can be computed in a.u. as $D = 1.48\sqrt{m^2 + n^2 + \mathrm{mn}}$, where *n* and *m* are the integer components of the chiral vector [9]. For a (15,0) CNT the diameter is equal to *22.2* a.u.

3.1. Optimal distance

The calculated dependence of the total energy of the unit cell of the (15,0) CNT array on distance *d* between the carbon nanotube walls for PBE and PBE-D2 approaches is shown in Fig. 2.

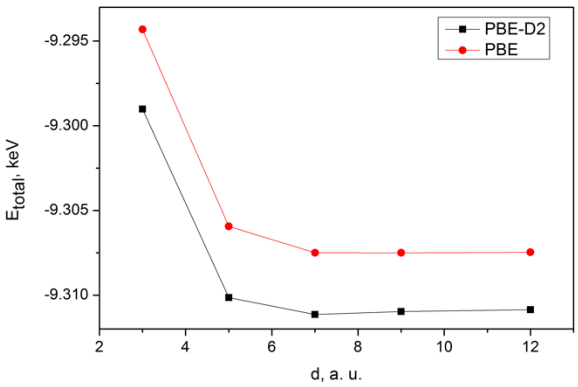

Figure 2. Dependence of the total energy on the distance between the nanotube walls obtained with PBE-D2 approach (lower curve) and PBE exchange-correlation potential (upper curve).

The optimal distance between nanotubes should correspond to the minimal value of the total energy of the system. It is interesting that the PBE approach (upper curve in the Fig. 2) is not enough to obtain the minimum in the dependence of the total energy on the distance. Taking into account the vdW correction (lower curve in the Fig. 2) leads to the appearance of the minimum and the optimal distance between nanotubes, respectively.

Finally, the results obtained with the PBE-D2 approach can be approximated by the Lennard-Jones potential (see Fig.3): $V(d) = \Delta E \left[\left(\frac{d_0}{d}\right)^{12} - 2\left(\frac{d_0}{d}\right)^{6} \right]$, where $\Delta E = 0.41$ eV is the depth of the Lennard-Jones potential, and d_0 corresponds to the total energy minimum.

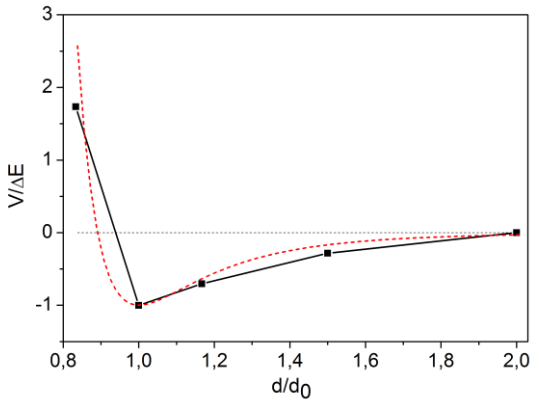

Figure 3. Dependence of total energy of the system (solid curve) and Lennard-Jones potential V with corresponding parameters (dashed curve) in units of depth of the potential well ΔE=0.41 eV of CNTs array unit cell on the normalized distance between nanotube walls (d_0=6 a.u.) obtained with PBE-D2.

3.2. Electronic band structure

The calculated band structure of a (15,0) CNT array along tube axis for $k_x = 0$ is shown in Fig. 4 (a). It is well known that an isolated (15,0) zigzag carbon nanotube has a small band gap, which is equal to 0.029 eV [10], and all its bands are doubly degenerate. It can be seen from Fig. 4 (a) that for the array of these nanotubes the degeneracy is removed, and the band gap for $k_y = 0$ and $k_x = 0$ is equal to 0.12 eV.

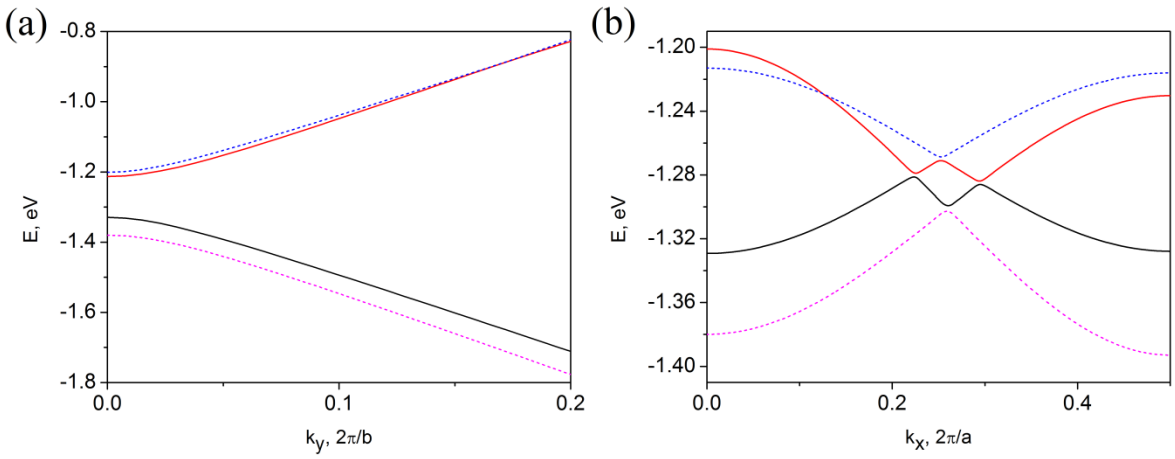

Figure 4. Electronic band structure of an array of (15,0) zigzag nanotubes separated by d=6 a.u. obtained with the PBE-D2 approach: (a) along the tube axis; (b) in the direction normal to the tube axis. The wave vectors are given in reciprocal space units.

For a 2D array of nanotubes, the electronic dispersion in the direction normal to the tube axis can also be calculated, see Fig. 4 (b). As can be seen from this figure, the band gap collapses away from the $k_x = 0$ point and the considered 2D material is in fact a metal. Finally, the two-dimensional dispersion for the bands closest to the Fermi level has saddle points, as can be seen from the Fig.4 (b). It means that the considered array represents a hyperbolic material for charge carriers.

4. Conclusion

We have found that a planar array of (15,0) zigzag CNTs separated by an optimal distance governed by van der Waals forces has a strongly anisotropic hyperbolic dispersion for its low-energy charge carriers. Thus, we have predicted a new type of hyperbolic van der Waals material with a rich energy spectrum promising interesting physical effects and optoelectronic applications.

5. Acknowledgements

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