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Symmetric and asymmetric dispersion relation in graphene

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Abstract. The standard tight-binding dispersion relation for graphene and carbon nanotubes has an electron-hole symmetry. This symmetry has not been observed experimentally until recently. We discuss here the effect of the overlap between π-orbitals at neighbouring sites, belonging to different sublattices, on the dispersion relation. The e-h asymmetry increases with the degree of overlap, although this effect is visible only for energy bands far from the Fermi level. We estimate the observable effects of this asymmetry on the DOS which could be observed in conductivity measurements and explain the symmetry found in the experiment. The degree of the overlap determines also the magnitude of the magnetic moment induced in the nanotube by the Aharonov-Bohm magnetic flux.

1. Introduction

Carbon nanotubes belong to the most promising materials for nanotechnology. It is therefore worthwhile to investigate their properties in detail. In calculations involving the dispersion relation of nanotubes it is commonly assumed that they inherit the standard tight-binding dispersion of graphene, and the periodic conditions around the nanotube quantize the momenta, forming energy bands [1]. In calculations concerning small nanotubes their curvature must also be taken into account. Its main consequences are a change in the angle between neighbouring π-bonds, in their length, and in the degree of $\sigma - \pi$ hybridization. It has been theoretically predicted and confirmed experimentally [2] that the curvature opens a band gap at the Fermi level. This gap decreases with increasing nanotube radius and almost vanishes at $d \approx 1.5$nm.
In the present paper we will investigate another contribution to the tight-binding model which is important also in large nanotubes. It is usually assumed that the π orbitals on the two sublattices of graphene do not intersect and the energy spectrum has the electron-hole symmetry. However it was found that in graphene the neighbouring π orbitals overlap, which removes the electron-hole symmetry of the spectrum. We present below a short study of the effect which this modification of the standard tight-binding Hamiltonian may have on transport and magnetic properties of carbon nanotubes.

2. Dispersion relation

On graphene plane we work in the basis $\mathbf{T}_1 = \sqrt{3}e_x$, $\mathbf{T}_2 = (\sqrt{3}/2)e_x + (3/2)e_y$. In this basis the dispersion relation without overlap on the adjacent carbon sites is

$$E_S(\mathbf{k}) = \pm\gamma\sqrt{1 + 4\cos^2\left(\frac{\sqrt{3}}{2}k_x\right) + 4\cos\left(\frac{\sqrt{3}}{2}k_x\right)\cos\left(\frac{3}{2}k_y\right)}. \tag{1}$$

The subscript S stands for "symmetric" and γ is the hopping integral for graphene, which is most often assumed to have the value 2.5, 2.7 or 3 eV, depending on the authors.
In real graphene the wavefunctions on neighbouring atoms always overlap, although this overlap may be small. In order to take this effect into account, a mixing between electrons from the two sublattices must be introduced. It may be expected that bonding states will not be as profitable in energy as they were without overlap – and vice versa, the antibonding states will have to overcome the natural tendency of the wavefunctions to overlap. Indeed, calculations confirm this intuition, yielding [1]

$$E_A(\mathbf{k}) = \frac{\epsilon_{2p} \mp \gamma|E_S(\mathbf{k})|}{1 \pm s|E_S(\mathbf{k})|}, \tag{2}$$

where s is the value of the overlap, ϵ_{2p} is the electron's on-site energy and the A subscript stands for "asymmetric". Following [1], we assume $s = 0.129$. The difference between the symmetric and asymmetric dispersion is shown in Fig. 1. In both cases the momentum spectrum remains

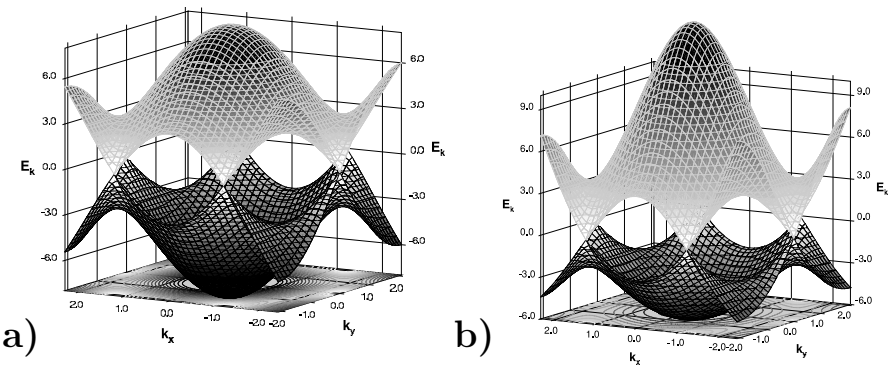

Figure 1. The dispersion relation of graphene. a) symmetric, without considering the overlap, and b) asymmetric, with overlap $s = 0.129$ as in [1]. Note the flattening of the valence band, not so favourable energetically anymore, and the elongation of the conduction band.

the same, determined by the transverse and longitudinal boundary conditions.

$$\mathbf{k} \cdot \mathbf{C}_h = k_C C_h = 2\pi l_c, \qquad \mathbf{k} \cdot \mathbf{L} = k_L L = 2\pi l_l, \qquad l_c, l_l \in \mathbb{Z}, \tag{3}$$

where $\mathbf{C}_h$ is the circumference (or the chiral vector) of the nanotube, and $\mathbf{L}$ is its length. The energy bands and the density of states are different in the two cases. Close to the Fermi surface, where the denominator in Eq. (2) is close to 1, the overlap does not result in a visible difference (see Fig. 2), but far from the Fermi level it is clearly different whether the dispersion takes into account the overlap or not.

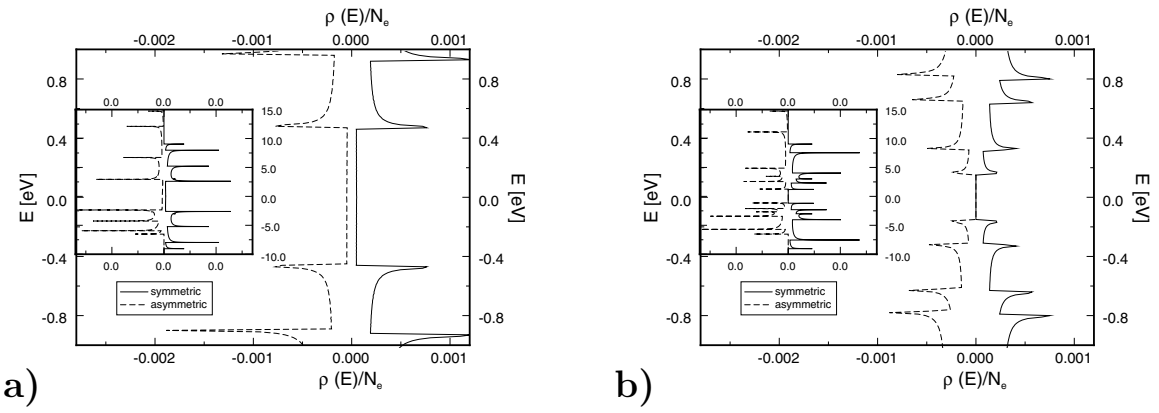

Figure 2. The density of states in a) metallic and b) semiconducting carbon nanotube, both in symmetric and asymmetric case. The top plots are in the full range of energies for small (3,3) metallic and (3,2) semiconducting tubes, for the sake of clarity. The bottom plots show the density of states of realistic, (20,20) and (20,19) nanotubes close to the Fermi level, in the range (-1eV, 1eV).

3. π overlap in transport experiments

In the CN's, as in graphene, there are only two Fermi points. Moreover, due to the small size of nanotubes, the energy gaps between individual one-dimensional energy subbands are large. These two features justify the treatment of nanotubes as one-dimensional wires with two conducting channels. In the Landauer-Büttiker formalism the (undoped) nanotube conductance of thermally activated electrons is [3]

$$G_{act}(T) = \frac{2e}{h} \sum_{i=1,2} |t_i|^2 \frac{2}{exp(\Delta E_i/kT) + 1}, \tag{4}$$

where $|t_i|^2$ are the transmission probability in the i-th channel and ΔE_i is the energy gap of the i-th subband at the Fermi level. In 2004 the group from Delft found a perfect symmetry between hole and electron energy levels in a semiconducting nanotube [4]. The experiment was performed in a standard quantum dot device setup, with the nanotube lying across two electrodes. The quantum dot differential conductance plots showed the electron-hole symmetry for the doping with up to 20 electrons/holes. This remarkable result, obtained in a transport experiment, probes the effective doping range of $\approx (-0.15, 0.15)$eV. The density of states, obtained numerically, of a CN whose size corresponds to that of the CN used in the experiment is plotted in the bottom part of Fig. 2b, in the range (-1eV,+1eV). It is clear that the visible deviation from symmetric DOS appears only when the doping exceeds $\sim \pm 0.5$eV. Thus it follows from our calculations that e-h symmetry is preserved for small doping, in agreement with the Delft experiment [4]. The asymmetry of the spectrum due to the overlap can be revealed at larger doping and, consequently, the overlap of the π-orbitals at adjacent carbon sites can be determined.

4. π overlap and the orbital magnetic moments

Due to their cylindrical topology carbon nanotubes in magnetic fields parallel to the nanotube axis display the Aharonov-Bohm effect. One of its manifestations are the persistent currents [5]. The change of phase of the electron running clockwise around the tube and of the electron

running anticlockwise produces a shift in their momenta, resulting in a nonequilibrium between currents carried by electrons with k_C and $-k_C$. The net current carried by all the electrons in the system does not decay provided that $\Delta E_g > kT$, where ΔE_g is the energy gap at the Fermi level, therefore it is called 'persistent'.
Persistent currents run perpendicular to the axis of the system, and they are not transport currents – their origin is purely topological. As they run around a closed loop, they induce an orbital magnetic moment in the nanotube. This magnetic moment determines the magnetic response of a nanotube in parallel magnetic field. This magnetic moment depends on the value of the flux penetrating the nanotube and it is given by [6]

$$\mu_{orb}(\phi, T) = -\pi R^2 \frac{\partial F(\phi, T)}{\partial \phi} = -\pi R^2 \sum_{\mathbf{k}} \frac{\partial E_{\mathbf{k}}(\phi)}{\partial \phi} f_{FD}(E, \mu_{chem}, T), \tag{5}$$

where F is the free energy, μ is the chemical potential, ϕ is the magnetic flux penetrating the nanotube, and $f_{FD}(E, \mu_{chem}, T)$ is the Fermi-Dirac distribution function.
Our theoretical calculations [6] show also that in nanotubes with shifted Fermi level (due to electron or hole-doping) the response varies depending on the amount of doping (cf. Fig. 3). This variation changes when the overlap is taken into account. The boundaries between dark and bright regions correspond to paramagnetic jumps in the persistent current, present when there are occupied electron states at the Fermi level. The values of doping and magnetic flux at which these jumps occur reflect the geometry of the Brillouin zone of the nanotube and the features of the dispersion relation. However, the response at slight doping is again nearly e-h symmetric, with differences seen only at larger values of doping, especially in the hole-doping (lower) region of the plot. The fundamental difference between transport phenomena and persistent currents

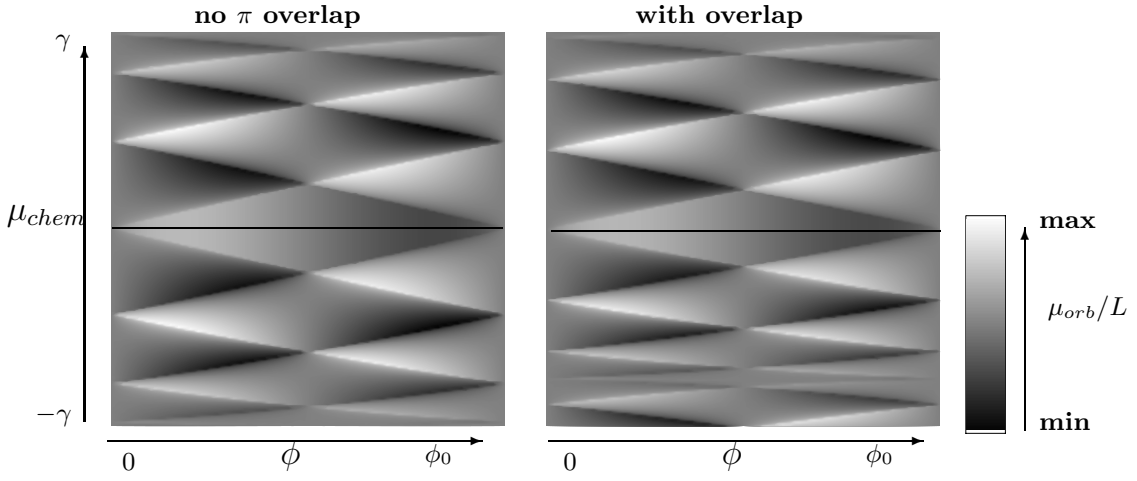

Figure 3. The magnetic moments (greyscale) dependence on ϕ and μ_{chem} in an armchair (7,7) nanotube at $T = 0$K and the doping in the range $(-\gamma, +\gamma)$.

is that the latter contain contributions from all states in the Brillouin zone, also those deep below the Fermi level. Thus, even though the pattern of the magnetic response does not yield information about the size of the overlap, its amplitude does. The amplitude of the magnetic moment for a metallic (20,20) and semiconducting (20,19) nanotube with and without overlap are presented in Table 1. It is plain to see that since $\partial E/\partial k_C$ is smaller in the asymmetric case, the individual currents are diminished and the amplitude of the magnetic moment can drop by a factor of 3 as compared to the symmetric case. As till now there is no conclusive

Table 1. Amplitude of the magnetic moments in undoped metallic (20,20) and semiconducting (20,19) nanotubes ($L = 0.1\mu m$) with symmetric and asymmetric dispersion relation. $T = 0$K.

CN type	μ_0 - symmetric	μ_0 - asymmetric
metallic	$85\mu_B$	$28\mu_B$
semiconducting	$52\mu_B$	$15\mu_B$

experiment measuring the magnetic moment, we cannot state which relation is better suited for CN's. However, the calculated differences of μ_{orb} for the two models are remarkable and when they are measured they could give us information about the precise value of the π orbital overlap in carbon nanotubes.

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