SPIN CONFIGURATIONS IN CARBON NANOTUBES*

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The theory of a Coulomb blockade phenomenon in carbon nanotubes is briefly reviewed and its experimental consequences are discussed. This review is based on the joint paper Y. Oreg, K. Byczuk, B.I. Halperin, *Phys. Rev. Lett.* **85**, 365 (2000).

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1. Introduction

The physics of mesoscopic systems is being very actively studied theoretically and experimentally during the last 15 years. Such an active research has become possible when experimentalists invented and developed new methods of growing crystals which enable them to produce quasi-two- or quasi-one-dimensional structures as well as so called quantum dots which can be thought of as zero dimensional systems [1]. This huge progress in mesoscopic experimental physics was also possible when new classes of materials were found. For example, carbon nanotubes attract continuous attention of researchers [2].

In mesoscopic systems, when the number of particles is very far from infinite one should not expect to have sharp phase transitions. However, the microscopic forces which usually trigger the phase transitions in macroscopic systems are present in mesoscopic systems as well, and under certain conditions their effects can be even amplified. In such circumstances one can observe and study new phenomena which might disappear in the thermodynamic limit.

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In the present contribution to this School on "Quantum Phase Transitions in High Energy and Condensed Matter Physics" we are going to review briefly our theory concerning the Coulomb blockade phenomenon in the metallic carbon nanotubes. Here, we will focus on one particular physical effect which can be seen only in a finite length system with quantized energy levels. Using physical arguments we explain here how one can add many electrons into the carbon nanotubes with the same spins but the total spin of the electrons in the system fluctuates only between zero, one-half, and one. Calculational details have been presented in our recent paper [3], which an interested reader is referred to for further details.

2. Coulomb blockade

Metallic wires of macroscopic size (few centimeters) usually conduct an electric current according to the Ohm's law, *i.e.* the current I is proportional to an applied bias voltage V, *i.e.* $I = G\,V$, where G is the conductance of the sample. When the sizes of the sample decrease to few nanometers length, but the system still contains a large number of the itinerant electrons, the macroscopic electrical current can still flow but the Ohm's law is not obeyed [1]. Instead of the current proportional to the transport voltage V, one observes step-like jumps in the current-voltage characteristics. In other words, the conductance $G = dI/dV$ is not a constant but has peaks at finite values of V. These steps and peaks are experimental manifestations of the *Coulomb blockade* phenomenon [1].

The Coulomb blockade may be observed if the following conditions are satisfied: (a) the system must be small enough so that the charging energy $E_{\rm C} = e^2/2C$ (the energy needed to change the number of the electrons in the system by one) is larger then the energy of the thermal fluctuations $E_{\rm T} = k_{\rm B}T$ in the system (C is the classical capacitance and $k_{\rm B}T$ is temperature in the energy units). The distance between the Coulomb blockade peaks is determined by this charging energy. Note that for a metallic sphere of the radius $R = 10$ nm the capacitance $C = 4\pi\varepsilon_0 R$ is about 10^{-18} F and hence $E_{\rm C}$ is of the order of few meV; (b) the system is well isolated from the pads so that the number of the electrons is constant and can be considered as a good quantum number characterizing the system (the proper description of the system is obtained by using the canonical partition function). Quantitatively, the contact tunneling resistance $R_{\rm T}$ must be much larger then the quantum resistance $R_{\rm Q} = h^2/e$. The current flow through such a closed system, in contrast to open systems, is due to a quantum-mechanical tunneling of the single electrons through the contacts.

3. Mesoscopic ferromagnetism

Some good metals like iron or nickel are ferromagnet, *i.e.* these systems have finite magnetic moments below a certain critical temperature. Ferromagnetism of the itinerant electrons is a manifestation of the electron–electron interaction in the system combined with the Pauli exclusion principle. The finite magnetic moment of the system survives in the thermodynamic limit [4].

Small, mesoscopic systems, though not magnetic in the thermodynamic limit, may possess certain kind of a magnetism with non zero effective magnetic moments. The ground state spin of the electrons can fluctuate between zero and some finite value because of mechanisms which are similar to mechanisms leading to the Hund's rule in atomic physics [5].

4. Carbon nanotubes

Carbon nanotubes are elongated fullerens 1–100 μm long. They can be viewed as cylinders with surfaces made of graphite layers. Depending on the direction in which the graphite layer is wrapped up, the carbon nanotube can be either metallic or semi conducting [2].

The metallic carbon nanotubes can be used as mesoscopic wires to conduct a current. However, since they are very small (with a large charging energy) and the contacts with the electrodes are rather poor, at very low temperatures they conduct a current in agreement with the Coulomb blockade theory. Applying a very small transport voltage V and changing the gate potential V_{g} (on an electrode which is not directly coupled with the nanotube) one can observe discrete conductance peaks for such V_{g} that the total energy of N and $N+1$ electrons in the system is the same.

According to the quantum charging model (including both the charging effects and quantized one-particle energy levels in a finite system) when the external magnetic field B is applied each conductance peak should split up as a function of B [6]. This corresponds to different energies which are needed to add (or remove) electrons with either a spin up or a spin down respectively.

Such a behavior was not observed in experiment [7]. Instead, there has been seen eight successive Coulomb peaks going up with changing the magnetic field B, which may be interpreted that all eight electrons entering the carbon nanotube had the same spin up. However, now a puzzling problem has arrived: how this would be possible if the carbon nanotube, similarly to a parent graphite material, is not a ferromagnet.

5. Carbon nanotubes in external potential

In our paper (with Oreg and Halperin) we have provided microscopic explanation of this experiment as well as constructed a Hartree–Fock model which predicts different spin configurations in the metallic carbon nanotube [3].

The central point in our theory is how a non-uniform external electrostatic potential influence the single-electron states in the two one-dimensional bands crossing the Fermi level in the metallic carbon nanotube. Note that because of the finite length of the nanotube these one dimensional bands have discrete quantized levels (with a typical mean distance between them $\Delta = 0.5$ meV), which are populated by the electrons according to the Pauli principle.

The uniform gate potential applied to the nanotube shifts all levels in the same way. However, we found theoretically that when the gate potential has a non-uniform component (affecting only a part of the carbon nanotube) apart from this uniform shift there is also a relative shift of the levels belonging to the two different bands. In other words, changing V_{g} the distance between the two given levels from the two different bands changes and eventually the levels even cross each other. Microscopic derivation of this result based on the Thomas–Fermi approach is presented in our paper [3].

This is a very plausible scenario regarding to the geometrical configuration in the experiment [7]. Namely, the nanotube was deposited on two metallic electrodes with distance between them about 200 nm. The gate electrode was far apart about 200 μm away. If we suppose that the two electrodes, which were in contact with the nanotube, were grounded then the potential felt by the electrons in the nanotube just on the top of these electrodes had to be approximately zero. On the other hand, in the slit between the electrodes, the electrons had to feel the potential proportional to V_{g}. Hence, effectively the entire potential shape acting on the tube had a shape of a hat, so it could not be uniform in space.

6. Exchange interaction in carbon nanotubes

In the last section we have considered the single-particle states in the carbon nanotubes neglecting the Coulomb interaction between the electrons. However, the electrostatic interaction is, of course, present in these systems and it turns out to be very important [2].

Within the Hartree–Fock approximation [3], the effect of the electron–electron interaction appears in two very different ways. First of all, there is a contribution to the total ground state energy due to so called direct interaction. This direct interaction has a momentum transfer $k = 0$ and, therefore, corresponds to the classical charging energy E_{c} of the system. In addition to

that, there is also an exchange interaction and an exchange energy contribution. The exchange interaction has a higher momentum transfer $2k_{\mathrm{F}}$, where k_{F} is the Fermi vector in these one-dimensional systems. This exchange interaction favors the parallel spin configuration between the electrons. The carbon nanotubes would have the ferromagnetic ground state if the exchange interaction energy J were larger then the mean level spacing between the quantized single-particle levels. In other words, the energy gain due to the ferromagnetic polarization of the electron spins would be larger than the loss in the kinetic energy due to the occupation of the higher energy levels. This corresponds to the *Stoner criterion* in a finite system. However, as we have examined theoretically in [3], it is not the case in the carbon nanotubes. Moreover, there are no experimental evidences for the ferromagnetic instability in the carbon nanotubes [2].

7. Internal spin flips in carbon nanotubes induced by gate potential

The exchange interaction energy J is smaller than the mean level spacing Δ in the carbon nanotubes [3]. However, as we have discussed in Section 5 the actual distance between the quantized levels changes as a function of the non-uniform gate potential. Imagine now, that ε_{B} is the highest doubly occupied level in the nanotube and ε_{A} is the lowest unoccupied one. They belong to the different symmetry bands coming from the bonding and the anti bonding orbitals along the nanotube circumference. If $\varepsilon_{\mathrm{A}} - \varepsilon_{\mathrm{B}} > J$ then the level ε_{B} is doubly occupied by two electrons in a singlet state. However, if $\varepsilon_{\mathrm{A}} - \varepsilon_{\mathrm{B}} < J$ then the most stable configuration would be a triplet state with two electrons with parallel spins occupying ε_{A} and ε_{B} levels. These two situations are shown schematically in Fig. 1. It means that

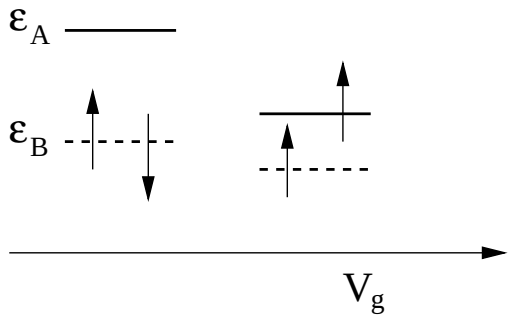

Fig. 1. The relative distance between ε_{A} and ε_{B} levels changes when the non-uniform gate potential V_{g} increases. If $\varepsilon_{\mathrm{A}} - \varepsilon_{\mathrm{B}} > J$ then the lower ε_{B} level is doubly occupied and the total spin is zero. However, when $\varepsilon_{\mathrm{A}} - \varepsilon_{\mathrm{B}} < J$ then the two levels are single occupied and the total spin is one.

changing the gate potential we can change the relative distance between the quantized levels and as a result the total spin of the nanotube with even number of electrons can vary between zero and one (*cf.* Fig. 1). Note that applying the external probe on the charge degrees of freedom one can control the spin degrees of freedom in the metallic carbon nanotubes.

8. Carbon nanotubes and Coulomb blockade

In the Coulomb blockade regime when we sweep the gate potential we change the number of the electrons in the nanotube by one: $N-1 \to N \to N+1 \to N+2$, *etc.* If now other parameters, for example the charging energy, are properly matched such that additions of the extra electrons happen when two ε_{A} and ε_{B} levels are close to each other then the spins of all

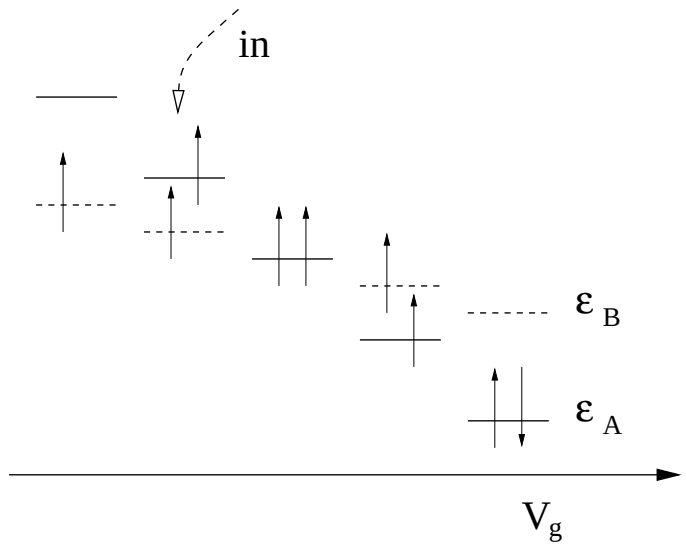

Fig. 2. The cartoon explaining the single-electron tunneling into the metallic carbon nanotube and the internal spin-flip transition. For properly matched microscopic parameters of the system the additional electron can tunnel in if ε_{A} and ε_{B} levels are close to each other ($\varepsilon_{\mathrm{A}} - \varepsilon_{\mathrm{B}} < J$). Then the extra electron must have the same spin as the electron already present there and the total spin rises from $1/2$ to 1. While increasing V_{g}, the two levels approach each other, cross each other, and eventually come apart. When $|\varepsilon_{\mathrm{A}} - \varepsilon_{\mathrm{B}}| > J$ then the more stable configuration is the one in which the lowest (ε_{A}) level is doubly occupied and the total spin is zero. Note, that we have silently assumed the existence of a spin-relaxation mechanism, *e.g.* the spin-orbit coupling due to the metallic electrodes, which equilibrates the system.

incoming electrons are the same[1]. The effect of the exchange interaction is enhanced because the actual ratio $J/(\varepsilon_{\mathrm{A}} - \varepsilon_{\mathrm{B}})$ is large for particular V_{g} values. However, due to the internal spin flips, which are induced by the changing V_{g}, the total spin changes from one to zero. So we can have the following sequence: $S_{\mathrm{total}} : 0 \to 1/2 \to 1 \Rightarrow 0 \to 1/2 \to 1 \Rightarrow 0$, *etc.*, where $(\to)$ means that the extra electron is added to the nanotube with spin one-half and $(\Rightarrow)$ means the internal transition with flipping one spin. The cartoon picture of this process is shown in Fig. 2.

This model explains the experimental findings in [7]. It also predicts another possible behavior of the Coulomb blockade peaks with respect to the external magnetic field. For example, few electrons can enter the tube with spins up, then few others can enter with alternating spins up and down, and finally few electrons can enter with spins down. But during the entire time the total spin changes only between zero, one-half and one. Similar non-intuitive behavior of the peak evolutions in the carbon nanotube has been observed recently by the same group [8].

9. Conclusions

In the present paper we have shortly reviewed our theory [3] concerning the Coulomb blockade phenomena in the metallic carbon nanotubes. We have discussed how the external potential can influence the single-particle states in the carbon nanotubes and how the competition between the actual distance between the quantized one-particle energy levels and the exchange interaction leads to the internal spin transitions in these systems. Our theoretical model explains the puzzling experimental findings in [7] and predicts other possible results some of which have been observed recently [8].

We conclude that although the exchange interaction in the carbon nanotubes is too small to trigger the paramagnetic–ferromagnetic phase transition, its effects can be amplified by the gate electrode and the conducting pads leading to new and interesting experimental behaviors.

[1] "Matching the other parameters" is a subtle issue here because, of course, we cannot control them intentionally. They, as for example the charging energy, are randomly distributed around some mean values. So, as usually in mesoscopic experiments, the results can change from a sample to a sample or from an experimental set-up to an experimental set-up. And rather one should ask about statistical behaviour: how often a given observation appears and how often and how long it is reproducible for a given set-up.

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