Spin configurations of carbon nanotube in a nonuniform external potential

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We study, theoretically, the ground state spin of a carbon nanotube in the presence of an external potential. We find that when the external potential is applied to a part of the nanotube, its variation changes the single electron spectrum significantly. This, in combination with Coulomb repulsion and the symmetry properties of a finite length armchair nanotube induces spin flips in the ground state when the external potential is varied. We discuss the possible application of our theory to recent measurements of Coulomb blocked peaks and their dependence on a weak magnetic field in armchair carbon nanotubes.

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Carbon nanotubes have attracted continuous attention since their discovery. Their unique mechanical and electrical properties enable to design and build several systems, some may be used for practical applications. When they are rolled up in a certain way the electron states near the Fermi level have a one-dimensional (1D) character. The Coulomb interaction between the electrons in low-dimensional systems, especially in 1D, affects significantly the physical properties of the electrons. Indeed, power law behavior of the tunneling conductance was found experimentally. Recently, Coulomb blockade peaks were investigated in a single-electron transport experiments through short (~0.2–3 μm) isolated metallic nanotubes.

In the experiments of Tans et al. (I) and Cobden et al. (II) the spin direction of the additional electrons entering into the tube, as an external gate potential is varied, was determined various methods. Within the framework of the “orthodox theory”, where effects of the Coulomb interaction are modeled as a constant charging energy, one expects that the electrons will occupy states in pairs of spin up and spin down. The last level is singly or doubly occupied depending on the parity of the total number of electrons in the system. In that case, successive electrons entering the nanotube at a low magnetic field should have opposite spins. This behavior was observed in II, but in I eight successive electrons entered the tube with parallel spins. Shorter parallel spin (PS) sequences were reported in Ref. III.

The purpose of the present note is to explore one possible mechanism for PS sequences to occur. The essential feature is the existence of two (or more) families of single-electron states in the nanotube, which respond differently to the applied gate voltage $V_g$, and can cross (or nearly cross) at certain values of $V_g$. Electron-electron interactions can then cause spin flips (i.e., internal transitions) which can lead to PS sequences under proper conditions, as was noted in I. We point out that this can occur in ideal defect-free armchair nanotubes, as well as in nanotubes with sufficient disorder that states at the Fermi energy are localized in different regions of the tube.

For an infinite armchair nanotube, for a given wavevector parallel to the tube, there are two energy bands of different symmetry, which we designate as $B$ and $A$, distinguishing states which are bonding or anti-bonding for adjacent carbon atoms around the circumference of the tube. As we show below, levels from the $B$ and $A$ bands respond differently to a gate potential which is nonuniform along the tube axis. We assume here ideal reflecting boundary conditions at the ends of the nanotube, which preserve the symmetry, so that the discrete single particle levels from the two bands can actually cross each other as the gate potential is varied. (See Fig. II.) If there is weak mixing between bands on reflection from a tube end, or due to interactions with the substrate, near-crossings can still occur, and our conclusions will be unaltered.

Assume now, for example, that there are $2N$ particles in the nanotube and that the last $B$-level below the Fermi energy is occupied by two electrons with total spin 0. As the nonuniform potential (induced by the gate) is decreased an $A$-level crosses the highest (doubly) occupied $B$-level at the point $F1$ in Fig. I. In analogy to the first Hund’s rule for partially filled (degenerate) shell in an atom, the two electrons form a many-body ground state with a maximum possible spin. They occupy the $A$- and the $B$-levels near $F1$ point with total spin one as long as the energy difference between the levels is smaller than the energy gain due to the electron–electron interaction. There is a gain in the interaction energy because: (i) the direct interaction between the two electrons in the same state is stronger then the direct interaction between the electrons in different states; and (ii) electrons occupying different levels can minimize their interaction energy by maximizing the total spin, thereby allowing a maximally antisymmetric coordinate wave function, and gaining the negative exchange energy.

Now, assume that the nanotube initially has $2N−1$ particles where only the last state is singly occupied so that the total spin is 1/2. The $2N$th electron enters the system at such a gate potential that the ground state with total spin one is formed. Then, as the nonuniform potential is changed further a spin flip occurs and the
spin of the system drops to zero before the \((2N + 1)th\) electron enters into the nanotube. In this scenario both the \(2Nth\) and the \((2N+1)th\) electrons raise the total spin of the system by \(1/2\). But due to the internal spin flip the total spin of the system is not larger then one. The entry points of such a scenario are depicted in Fig. 1 by black triangles. We show below that a necessary condition for mixing between the \(A\) and \(B\) bands at the damaged tube-ends.) By contrast, in I, the nanotube lies on the top of a Si/SiO\(_2\) substrate with two thick Al/Pt electrodes, and it was suggested \([1]\) that the nanotube is unbroken in that area. The length of the conducting part of the nanotube \((L \sim 3 \mu m)\) is then larger than the gap between the electrodes \((d \sim 0.2 \mu m)\). The contact electrodes screen the potential applied to the gate, so that only the nanotube section above the electrode gap is affected by the gate. Thus, in I, the external potential due to the gate is not uniform. Relative motion of the \(A\) and \(B\) bands is thus possible, which can lead to spin flips.

We turn now to a description of our model calculation. The energy due to the interaction between the electrons is calculated within the Hartree-Fock theory. We assume that the electrons occupy the single particle states in the presence of a self-consistent external potential on the tube \(\phi(x)\), where \(x\) is the coordinate along the nanotube. The total ground state energy in this approximation is given by

\[
E\{\{N_{\mu\sigma}\}\} = \sum_{\mu,\sigma, l} \epsilon_{l\mu}[\phi] n_{l\mu\sigma} - \hbar \sum_\mu (N_{\mu\uparrow} - N_{\mu\downarrow}) + \frac{1}{2} U_c \left[ \sum_{\mu,\sigma} n_{\mu\sigma} - 2N_{\text{ion}} - N_0 \right]^2 + \delta U \sum_{\mu, l} n_{l\mu\uparrow} n_{l\mu\downarrow} + J \sum_{\mu, \mu'} N_{\mu\uparrow} N_{\mu'\downarrow},
\]

where a discrete level \(\epsilon_{l\mu}[\phi]\) corresponds to the \(lth\) eigenenergy in the band \(\mu = A, B\) of the nanotube in the presence of the space-dependent potential. (The band energies are defined such that the Fermi level is zero for a neutral nanotube with \(\phi = 0\).) The occupation of the state \(|\mu\sigma\rangle\), is \(n_{\mu\sigma} = 0\) or 1 and \(N_{\mu\sigma} = \sum_l n_{l\mu\sigma}\), where \(\sigma = \uparrow, \downarrow\). The term proportional to magnetic field \(h = g\mu_B H/2\) is the Zeeman energy, and \(N_{\text{ion}}\) is the number of carbon atoms. The constant \(N_0\) is a continuous parameter, dependent on the work functions of the nanotube and the contact electrodes, which we choose so that the chemical potential is zero in the equilibrium state when the contacts and gate electrodes are grounded. The values of the charging energy \(U_c\), the excess interaction of two electrons occupying the same level \(\delta U\), and the exchange parameter \(J\) are found by considering the real electron-electron interaction in the nanotube.

Generically, the interaction contains a long-range part, which influences mainly \(U_c\), and a short-range part due to the local interaction when two electrons occupy a \(p\)-orbital of the same carbon atom. The amplitude of this Hubbard-like term is approximately \(U_H \approx 15 \text{ eV} [1]\). The behavior of the long-range part is sensitive to the screening by the metallic electrodes. The interaction in the section of the nanotube, which is on the metallic electrodes is screened by the image charges in the metal and falls off like \(R^2/r^3\) for distances \(r\) much larger then the

![FIG. 1.](image)

**FIG. 1.** (a.) (Top) Evolution of the discrete single-particle levels of an armchair nanotube when a nonuniform electrostatic potential \(\phi(x)\) on the tube is varied (by changing the voltage, \(V_g\), on the gate electrode). The dashed lines represent the (anti-bonding) \(A\)-band, while the dashed-dot lines represent levels in the (bonding) \(B\)-band. The descending solid-line represents the highest occupied level for a tube with a fixed even number \(2N\) electrons. Heavy portions of the curve show where the highest state is doubly occupied \((S = 0)\), while lighter regions near the crossing points \(F1, F2, F3\), show where two states are singly occupied \((S = 1)\) due to the electron-electron interaction. Similar \(S = 1\) states will occur for \(2N + 2\) electrons near the crossing points \(f1\) and \(f2\). For odd-electron number, however, such as \(2N + 3\), no spin-flips occur and the highest filled states follows the trajectory indicated by the heavy dashed and dot-dashed lines. Note that \(S = 1\) states do not occur near the crossing points \(N1\) and \(N2\). (b.) (Bottom) The spin \(S\) of the system for fixed numbers of the electrons in the system when \(V_g\) is varied. Electrons added at the black triangles would have spins \(+1/2\) while those added at the white triangles would have alternating \(+1/2\) spins.

The change of the relative positions of the \(B\)- and \(A\)-levels is the presence of a nonuniform gate potential along the nanotube. In II Chromium-Gold contacts are deposited on the top of a rope with nanotubes, and probably break it. As a result, the only active part of the nanotube is between the electrodes and is exposed to an almost uniform gate potential. (Also, there is likely to be strong
nanotube radius $R$. We find the following values for the interaction parameters \cite{2}:

$$3.94 \ [5.04] > U_c / \Delta > 1.14 \ [1.34],$$

$$\delta U / \Delta = 0.11 \ [0.22], \quad J / \Delta \geq 0.22 \ [0.44] , \quad (2)$$

for \((10,10) \ [(5,5)]\) armchair nanotubes, respectively, where $\Delta = \pi \hbar v_F / L$ with $v_F = 8.1 \times 10^5 m/s$ is the level spacing at the Fermi energy in each band. The lower bound on $U_c$ is for the screened interaction and the upper bound is for the unscreened interaction. (Higher order correlation effects between the electrons may renormalize the parameters of the problem \cite{12}.) We have checked numerically that the long-range part of the interaction does not influence $J$ and $\delta U$ significantly and that the effect of a nonuniform potential, which changes the self-consistent wave functions, is also negligible for the parameter regions we consider below.

In order to find the evolution of the levels near the Fermi energy when the potential on the gate electrode $V_g$ is changed, we denote the self-consistent nonuniform potential on the nanotube by $\phi(x)$, and the energy of the last occupied level in band $\mu$ by $\epsilon_\mu$. In the Thomas-Fermi approximation the total number of states in band $\mu$ up to energy $\epsilon$ is:

$$N_\mu[\epsilon, \phi] = \int_{-\infty}^{\epsilon} d\epsilon' \int dx \rho_\mu[\epsilon' + \phi(x)]$$

(3)

where $\rho_\mu(\epsilon)$ is the density of states in band $\mu$. An application of a potential $V_g$ on the gate electrode changes both $\phi(x)$ and $\epsilon_\mu$ but does not change the number $N_\mu(\epsilon, \phi)$ which by definition equals $l$. Thus for a fixed $l$ we find (by formally expanding $N_\mu$ with respect to both its arguments)

$$\frac{\partial \epsilon_\mu}{\partial V_g} \approx -\frac{\int dx \rho_\mu[\epsilon_\mu + \phi_0(x)] \frac{\partial \phi(x)}{\partial V_g}}{\int dx \rho_\mu[\epsilon_\mu + \phi_0(x)]}$$

(4)

where $\phi_0(x)$ is the self-consistent potential on the tube for $V_g = 0$. To model the situation in Fig. 1 we take $\phi_0(x)$ to be a constant $\phi_0 = 0.3 V$ in the regions on top of the contacts but zero over the gap, while $\partial \phi(x) / \partial V_g$ is equal to a constant $c$ over the gap and zero in the regions over the contacts. For the tight-binding-band approximation to an armchair nanotube we may write:

$$\rho_\mu(\epsilon) \propto 1 / \left[ 1 - \frac{(\epsilon - \epsilon_0)}{(2\gamma)} \right]^2$$

(5)

where $\epsilon_0$ is the Fermi level and $\gamma = 2.7 eV$ is a quarter of the width of the (extended) bands in the nanotube. Thus for $\phi_0 \ll \gamma$ we find:

$$\frac{\partial \epsilon_\mu}{\partial V_g} \approx -c \frac{d}{L} \left[ 1 \pm \left( 1 - \frac{d}{L} \right) \phi_0 \right] / 3\gamma ,$$

where $+[-]$ refers to the $A[B]$ band. The value of the constant $c$ is mainly determined by the ratio of $d$ to the distance of the nanotube from the gate electrode. Based on a crude model of the geometry in Fig. 1, we estimate that for $V_g = \pm 4 V$ the potential on the tube is of order $\pm 0.1 V$ which gives $c \approx 0.02 \ [12] .

Using the picture described above, we find that $\epsilon_\mu[V_g]$ in Eq. (1) is given up to additive constants by:

$$\epsilon_\mu[\phi] = l\Delta - cV_g(\alpha + \beta), \quad \epsilon_0[\phi] = l\Delta - cV_g\beta,$$

(6)

where $\alpha \approx 0.005$ and $\beta \approx 0.065$ for $d/L = 1/15$. The slope of the levels from $A$-band (dashed lines in Fig. 1) is $\alpha + \beta$ and the slope of the levels from $B$-band (dashed-doted lines) is $\beta$.

Having crude estimations for the parameters of the model \cite{1} we can find a set of conditions under which a sequence of consecutive electrons will enter into the nanotube with PS. Fig. 1 shows the evolution of the ground state spin with a fixed number of particles when the gate potential increases. The width $\Delta V$ where the ground state has spin one depends on the values of $\alpha$ and $\beta$ as well as on the interaction parameters $U_c$ and $J$.

In order to find an example of sufficient conditions to have a PS sequence when electrons enter into the nanotube we first set $J = 0$ and $\delta U \ll \Delta$. For a fixed even number $2N$ of particles we find, after analyzing the evolution of the highest occupied level (bold line in Fig. 1a), that a spin flip occurs whenever an empty $A$-level crosses an occupied $B$-level. These crossing points are marked by $F_1, F_2, F_3$. Notice that if point $F_1$ occurs at a value $eV_g = 0$, then $f_1$ and $N1$ occur at $eV_g = \Delta/\alpha$, point $F_2$ occurs at $cV_g = 2\Delta/\alpha$, etc. We find that the following conditions are sufficient for a PS sequence: (i) $N_0$ is such that the initial Fermi energy is near the crossing point $F_1$; (ii) the $(2N+2)$th electron enters at $\delta V_g$ corresponding to points $f_1, f_2, ...$ at which spin flips occur in the case of $2N + 2$ electrons in the system; and (iii) the $(2N+1)$th electron does not enters at $cV_g$ corresponding to the points $F_2, F_3, ...$. We note that it is possible to find other sufficient conditions for a PS sequence, here we give one example. Since, with the assumptions $J = 0$ and $\delta U \ll \Delta$, electron entries occur when the distance of the line $F_1 \rightarrow f_1 \rightarrow F_2 \rightarrow f_2 \ldots$ from the Fermi level is equal to the charging energy $U_c$, we find that (i), (ii) and (iii) are fulfilled when:

$$\begin{align}
(i) \quad N_0' & \equiv (N_0 - k) \ mod 4 = 0, \\
(ii) \quad U_c' / \Delta & = (1/2) [n + (\beta/\alpha)(2n + 1)] , \\
(iii) \quad U_c' / \Delta & \neq m(1 + 2\beta/\alpha).
\end{align}$$

(7)

where $n$, $m$ and $k$ are integers, while $k$ is a large real number, proportional to $L$, whose value depends on details of the system. Since $N_0'$ is very sensitive to details, it may be considered a random number, different for every nanotube. If $\alpha/\beta$ and $N_0'$ satisfy the conditions (i)-(iii) we obtain an infinite sequence of PS electron entries. Conditions (i) and (ii) may be slightly relaxed when a finite $\delta U$ is included; in order to find a finite PS sequence.
in that case the actual $U_c$ in Eq. (1) has to be in a vicinity $\delta U$ of $U_c^*$ given in Eq. (5), and condition (i) needs to be satisfied with an accuracy of order $\delta U / \Delta$. However, finite $\delta U$ makes the condition (iii) somewhat more difficult to fulfill. Even with the inclusion of a finite $J$ it is possible to find, as shown in Fig. 2g, a set of parameters that give a PS sequence.

We note that by increasing the value of $h$ by an amount of order $\Delta$, one can convert a sequence of up spin entries, as in (a), to a sequence of down-spin entries as in (c) [2]. This is consistent with experimental results in I.

In Figure 1, of I, internal transitions of the nanotube appear as discontinuities of slope in the boundaries of the regions in the plane of bias voltage and gate voltage where conductance is inhibited by a Coulomb barrier. In our model, the relative change in slope on transition from an $A$-level to a $B$-level should be $\alpha/\beta$, or about 7%. In I, however, the changes observed are much larger than this. Such large changes may be more easily explained if there are localized states at the Fermi energy, due to disorder, which could then respond quite differently to the gate or bias voltages [3]. On the other hand, slope changes observed in Ref. [1], for a different nanotube, were smaller, of order 20%, and might possibly be consistent with our model of a perfect nanotube.

In conclusion, we presented a model of the armchair carbon nanotube in a nonuniform external potential and elucidated a microscopic mechanism for internal transitions in which spin flips occur. This mechanism could lead to electrons entering in parallel spin sequences, as was observed in I, and is consistent with the lack of these in II. We note that a sequence of parallel spin entries occur when few special conditions are fulfilled, in most cases one or more are not fulfilled and there is alternate or irregular spin sequence. However, there is a finite probability, that could be increased with the proper choice of gate configurations (that control the model parameters), to find a long sequence of parallel spins entries.

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FIG. 2. Evolution of the total spin $S$, under a non-uniform potential, whose maximum value on the nanotube is $cV_g$. Various cases are shown, with $\delta U = 0.2\Delta$ and with other parameters as given in the inset. The total spin $S = 0, 1/2$ or 1, is shown by the thin solid lines. Tick marks on the thick horizontal lines show the entry points of electrons. The $x$-axis is the product $\beta cV_g$, in units of the level spacing $\Delta$. A small magnetic field $h = 0.001\Delta$ was included.

To illustrate how the PS scenario works, we have calculated numerically the addition spectrum and the total spin of the ground states as a function of the maximum voltage on the nanotube, $cV_g$, that varies with the potential on the gate electrode. Results are shown in Fig. 2 for few selected sets of parameters, which are listed in the inset. Case (a) corresponds to an ideal situation when all electrons enter with the same (up) spin; in case (c) all the electrons enter with spin down. In case (b) $N_0$ is in-between the ideal matching conditions and the spin sequence is alternating. These three examples have $J = 0$ and parameters corresponding to $n = 0$ in condition (iii). Cases (d)-(f) correspond to $n = 1$. We see that by changing slightly the model parameters we can get PS series, alternating spins, and transitions between them. Finally in case (g) we show that even with finite $J$ it is possible to get a PS sequence.
Entering of consecutive electrons with parallel spins could be explained if the ground state spin of the nanotube was large, but it can be ruled out because (i) bulk graphite layers are not spin polarized and (ii) it does not give an explanation for the different in the experimental results of I and II.

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