Electronic excitation spectrum of metallic carbon nanotubes

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We have studied the discrete electronic spectrum of closed metallic nanotube quantum dots. At low temperatures, the stability diagrams show a very regular four-fold pattern that allows for the determination of the electron addition and excitation energies. The measured nanotube spectra are in excellent agreement with theoretical predictions based on the nanotube band structure. Our results permit the complete identification of the electron quantum states in nanotube quantum dots.

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Since their discovery [1] carbon nanotubes (NTs) have emerged as prototypical one-dimensional conductors [2]. At low temperatures, NT devices form quantum dots (QDs) where single-electron charging and level quantization effects dominate [2,3]. A continuous improvement in device fabrication and NT quality has enabled the recent observation of two-electron periodicity in 'closed' QDs [4] and four-electron periodicity in 'open' single- and multi-wall NT QDs [5,6]. Theoretically, the low-energy spectrum of single wall nanotube (SWNT) QDs has been modeled by Oreg et al., [8]. Experiments on open NT QDs are compatible with this model, but the presence of the Kondo effect and broadening of the energy levels prevents the observation of the full spectrum [7]. An analysis of the electronic excitations is therefore still lacking.

The two-fold degenerate, low-energy band structure of a metallic SWNT is schematically shown in Fig. 1a. Quantization along the nanotube axis leads to a set of single particle states that are equally spaced because of the linear dispersion relation [10]. The combination of the two bands and the spin yields a four-fold periodicity in the electron addition energy. The simplest model to describe QDs is the Constant Interaction (CI) model [11], which assumes that the charging energy is constant and independent of the occupied single particle states. To describe NT QDs the CI-model has been extended [8] to include five independent parameters: the charging energy $E_C$, the quantum energy level separation $\Delta$, the subband mismatch $\delta$, the exchange energy $J$, and the excess Coulomb energy $dU$. Fig. 1 illustrates the meaning of the last two parameters. An independent verification of the Oreg model [8] requires the observation of the ground state addition energies and of at least two excited states. Such a study has not been reported.

In this letter we investigate the excitation spectrum of closed SWNT QDs. Not only the ground but also the complete excited state spectrum of these QDs has been measured by transport-spectroscopy experiments, enabling us to determine all five parameters independently. With these, the remaining measured excitation energies are well predicted leading to a complete understanding of the spectrum, without adjustable parameters.

HiPco [12] and CVD [13] grown NTs were used for the fabrication of the devices. HiPco tubes were dispersed...
from a dichloroethane solution on an oxidized, p-doped Si substrate. The CVD nanotubes were grown from catalyst particles on predefined positions. Individual NTs were located by atomic force microscopy (AFM) with respect to predefined marker positions. Electrodes are designed on top of straight segments of NTs. The highly doped silicon is used as a backgate to change the electrostatic potential of the NT QD (see Fig. 1b). We have fabricated NT devices with lengths in between contacts, \( L \), varying from 100 nm to 1 \( \mu \)m.

Four-electron shell filling is observed in over 15 samples. In some cases the four-fold pattern extended over more than 60 electrons added to the QD. Figs. 1i-f show representative examples of Coulomb Blockade (CB) oscillations \[14\] in the linear response regime. Clearly, the Coulomb peaks are grouped in sets of four reflecting the two-fold character of the NT bandstructure.

In the following, we focus on three different devices exhibiting similar four-fold periodicity in CB oscillations. These samples (A, B and C) had high enough contact resistances so that not only the electron ground states but also their excited states could be resolved. Together they provide enough information to determine all the parameters in the model. We discuss the results of these three samples separately.

**Sample A** - This device is made from a HiPco NT \[12\] with \( L = 180 \) nm and a diameter of 1.1 nm as determined by AFM. It is contacted by evaporating Cr/Au (5/75 nm) electrodes. Fig. 2a shows the current, \( I \), as a function of source-drain bias voltage, \( V \), and gate voltage, \( V_G \). In the light-colored diamond-shaped regions, the current is blocked due to CB and the number of electrons is fixed. The clear four-fold periodicity makes it possible to assign the number of electrons in the last occupied shell. The sizes of the diamonds form an interesting pattern, namely a repetition of small/medium/small/big. This pattern is a consequence of the large subband mismatch compared to the exchange energy, as we show below.

The addition energy is defined as the change in electrochemical potential \( \Delta \mu_N \) when adding the \((N+1)\) charge to a quantum dot already containing \( N \) charges \[11\]. The addition energy is obtained by multiplying the diamond width, \( \Delta V_G \), by a conversion factor, \( \alpha \) \((\approx 0.017)\), which relates the gate voltage scale to the electrochemical potential \[14\].

The Oreg-model yields the following equations for the
addition energy of the N-th electron added [15]:
\begin{align}
\Delta \mu_1 &= \Delta \mu_3 = E_C + dU + J \quad (1) \\
\Delta \mu_2 &= E_C + \delta - dU \quad (2) \\
\Delta \mu_4 &= E_C + \Delta - \delta - dU. \quad (3)
\end{align}

To extract all five parameters, two more equations are needed. These are provided by the excitation spectrum. In Fig. 2c, we show the numerical derivative of Fig. 2a (i.e., the differential conductance) for the first group of four. Excited states of the electrons are visible for all diamonds. The value of a particular excitation energy equals the bias voltage at the intersection between the excitation line and the Coulomb diamond edge (see Fig. 2c). The green arrows in diamond one and two in Fig. 2c correspond to the first excitation for one and two electrons extra on the NT QD respectively. The theoretical values of these two energies are
\begin{align}
\Delta \mu_{1x} &= \delta \quad (4) \\
\Delta \mu_{2x} &= \delta - J - dU. \quad (5)
\end{align}

Equations (1)-(5) allow us to uniquely determine the five unknown parameters from the experimental data alone. We find $E_C = 4.3$ meV, $\Delta = 9.0$ meV, $\delta = 3.2$ meV, $J = 0.4$ meV and $dU \approx 0$ meV. The values of the parameters do not vary significantly between the different groups, as shown in Fig. 2d. The theoretically expected value for the level spacing is $\Delta = \hbar v_F/2L$ [3]. With $v_F = 8.1 \cdot 10^5$ m/s [14] and $L = 180$ nm, we find 9.3 meV in excellent agreement with the experimental value.

Figure 2d shows the calculated spectrum of the NT QD using the parameters deduced from the experiment. Some excitations are split by the exchange energy. The stars in the calculated spectrum correspond to the arrows in the experimental data. Green indicates the excitations used in the calculation whereas yellow denotes the predicted excited states. The calculated spectrum resembles the measured one strikingly well.

**Sample B** - This sample is CVD grown [13] with a diameter of 1.3 nm and $L = 500$ nm defined by Cr/Au contacts (5/40 nm). After contacting, the entire NT segment in between electrodes is suspended by etching away part of the SiO$_2$ [17]. We have measured the differential conductance, $dI/dV$, as a function of $V$ and $V_G$ at 300 mK (Fig. 3a). Again regular four-fold patterns are visible in the Coulomb diamonds.

The evolution of the Coulomb peaks as a function of the magnetic field (not shown here) gives information about the spin filling of the states [18]. We find that the filling is the same as sample A. Excited states of the QD are visible in all groups of four. The model parameters
have been extracted using the same analysis as described above. The result is shown in Fig. 3b. The average values are $E_C = 2.0$ meV, $\delta = 1.2$ meV, $J = 0.1$ meV, $dU = 0.2$ meV and $\Delta = 3.0$ meV. The value of $\Delta$ corresponds to a length of 440 nm [2], in good agreement with the NT length between contacts. Furthermore, in all groups of four at least one more excitation remains for a comparison between theory and experiment. In all cases we find good agreement [19].

Sample C- This NT is CVD grown [13] with a diameter of 2.7 nm and $L = 750$ nm. The contacts are made by evaporating Ti/Au (20/40 nm). Fig. 3 shows $dI/dV$ as a function of $V$ and $V_G$. A very regular pattern of Coulomb diamonds with four-fold periodicity is displayed together with the excited states. In addition, up to three inelastic co-tunneling lines [20] are visible (horizontal lines inside the Coulomb diamonds in Fig. 3c).

The observation of three equally sized small diamonds and the fact that the excitations have the same energy for all four charge states indicate that $\delta \approx J + 2dU$. We find $E_C = 6.6$ meV, $\Delta = 8.7$ meV, $\delta \approx J = 2.9$ meV, and $dU \approx 0$ meV. Theoretically a level separation of 8.7 meV indicates a NT QD length of $\sim 200$ nm, while the distance between contacts is 750 nm. This may suggest that sample C consists of a QD with NT leads connecting it to the contacts. This is consistent with the large value for $E_C$. Remarkably, all the predicted excitation lines are present in the spectrum [21]. Therefore all the electron states can be assigned (Fig. 3).

In summary, we have presented a complete analysis of the electronic spectrum in closed NT QDs. Samples with different lengths, production process (CVD and HiPco) and contact material all exhibit four-fold periodicity in the electron addition energy. The very regular Coulomb traces and stability diagrams enable the determination of the ground and excited state electron energies. Knowing precisely the spectrum of nanotube quantum dots is of fundamental importance in experiments involving the application of high frequency radiation such as photon-assisted tunneling and coherent control of the electron quantum states.

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