Spectral Correlation in Incommensurate Multi-Walled Carbon Nanotubes

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We investigate the energy spectra of clean incommensurate double-walled carbon nanotubes, and find that the overall spectral properties are described by the critical statistics similar to that known in the Anderson metal-insulator transition. In the energy spectra, there exist three different regimes characterized by Wigner-Dyson, Poisson, and semi-Poisson distributions. This feature implies that the electron transport in incommensurate multi-walled nanotubes can be either diffusive, ballistic, or intermediate between them, depending on the position of the Fermi energy.

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Carbon nanotubes have attracted great attention due to their remarkable electrical and mechanical properties. Many theoretical and experimental studies have demonstrated that single-walled nanotubes (SWNTs) exhibit ballistic electron conduction, and single-molecule devices utilizing semiconducting SWNTs have been realized. On the other hand, despite useful applications of multi-walled nanotubes (MWNTs), the transport properties of MWNTs are not well understood and even controversial; conductance measurements using scanning probe microscopy showed ballistic behavior, while magneto resistances measured for MWNTs on top of metallic gate indicated diffusive conduction.

In general, MWNTs have very complex electronic structure, so that a direct use of their transport properties is severely hindered. If concentric carbon shells are especially incommensurate, the Bloch theorem is no longer valid, and the Landauer formula for conductance is not applicable because it is difficult to count the number of conducting channels. In fact, several experiments on MWNTs indicated that carbon shells have often different periodicities. However, electronic structure calculations have been mostly focused for commensurate multi-walled nanotubes so far. Here, instead of directly calculating conductances, we investigate the spectral properties of energy levels in incommensurate MWNTs.

The spectral analysis of energy levels has proven to be a useful tool to probe the nature of eigenstates in disordered conductors. In the diffusive metallic regime, the statistics of spectral fluctuations is described by the Gaussian orthogonal ensemble (GOE) of random-matrix theory. In this regime, the distribution of energy spacings between nearest levels is well fitted by the Wigner-Dyson surmise of energy spacings

\[ P_{\text{GOE}}(s) = \frac{s}{4} \exp\left(-\frac{s^2}{4}\right), \]

where \( s \) is in units of mean level spacing \( \Delta \). In the insulating regime, where the energy levels are uncorrelated, \( P(s) \) is given by the Poisson distribution,

\[ P_{P}(s) = \exp(-s). \]

At the Anderson transition point, a critical statistics was found. The short-range level correlation has been later described by semi-Poisson distribution, which has now been an important issue in quantum chaos.

In this Letter we make a spectral analysis of the energy levels of clean incommensurate MWNTs, and find that the level statistics is similar to that of the Anderson metal-insulator transition. The energy spectra exhibit both the Wigner-Dyson and Poisson distributions depending on the position of the Fermi level. In addition, we demonstrate that incommensurate MWNTs have an intermediate regime, which satisfies the semi-Poisson statistics.

To investigate the spectral correlation, we consider double-walled carbon nanotubes (DWNTs), because the electrical conduction in MWNTs is believed to be governed by the outermost shells. We use a tight-binding model with one \( \pi \)-orbital per carbon atom, which successfully describes the electronic structure of DWNTs. The tight-binding Hamiltonian is given by

\[ H = \gamma_0 \sum_{i,j} c_i^\dagger c_j - W \sum_{i',j'} \cos(\theta_{i',j'}) e^{(\alpha-d_{i',j'})/\delta} c_{i'}^\dagger c_j, \]

where \( \gamma_0 = -2.75 \text{ eV} \) is the hopping parameter between intra-layer nearest neighbor sites, \( i \) and \( j \), and \( W = \gamma_0/8 \) is the strength of inter-wall interactions between inter-layer sites, \( i' \) and \( j' \), with the distance of \( d_{i',j'} \), and the cut-off for \( d_{i',j'} > 3.9 \text{ Å} \). Here \( \theta_{ij} \) is the angle between two \( \pi \)-orbitals, \( c_{ij} \) is the annihilation operator of an electron on site \( i' \), \( a = 3.34 \text{ Å} \) is the distance between two carbon walls, and \( \delta = 0.45 \text{ Å} \).

To extract the fluctuations from the level sequence, it is customary to map the real energy spectra \( \{\epsilon_i\} \) onto the unfolded spectra \( \{E_i\} \) through \( E_i = N(\epsilon_i) \), where \( N(\epsilon_i) \) is the number of levels up to \( \epsilon_i \) and the overline denotes its broadened value. Here we use the Gaussian broadening scheme for averaging the energies.
After unfolding, we obtain the distribution \( P(s) \) as a function of nearest energy spacing, \( s_i = E_i - E_{i-1} \) (the mean level spacing of the unfolded spectra equals 1), and the number variance \( \Sigma(L) = \langle (n(L,E) - L)^2 \rangle \), which represents the variance of the number of levels in the interval \( (E - L/2, E + L/2) \), i.e., \( n(L,E) = N(E + L/2) - N(E - L/2) \). The bracket \( \langle \cdots \rangle \) denotes the average around the energy \( E \) on an energy window much larger than the mean level spacing but much smaller than \( E \).

The two shells of DWNTs are incommensurate if the ratio of the unit cell lengths along the tube axis is irrational. We test many incommensurate DWNTs, where both the shells are metallic or semiconducting, a semiconducting shell is inside a metallic tube, and vice versa. The diameters of the inner and outer tubes are 1.5 and 2.2 nm, respectively, and the nanotube length is set to be about 53 nm. We find the spectral properties are similar for all the incommensurate DWNTs with different helicities. (See the \( P(s) \) in Figure 1.) Since the spectral properties are similar for all the tubes considered here, from here on, we only present the spectral properties of the \( (16,5)/(23,8) \) DWNT where the semiconducting \( (16,5) \) single-walled tube is aligned inside the metallic \( (23,8) \) tube. In the inset of Figure 1, \( \Sigma(L) \) is also shown for the \( (16,5)/(23,8) \) nanotube. We find that \( P(s) \) and \( \Sigma(L) \) cannot be described by the Poisson distribution or GOE, but, they are well described by the semi-Poisson (SP) distribution:

\[
P_{SP}(s) = 4s \exp(-2s) \tag{2}
\]

\[
\Sigma_{SP}(L) = \frac{L}{2} + \frac{1}{8}(1 - e^{-4L}) \tag{3}
\]

The SP distribution is defined by removing every other level from an ordered Poisson sequence and turned out to be a reference point for the critical statistics of several disordered systems like the Anderson model at mobility edge, and also of other systems without disorder such as pseudo-integrable quantum billiards.

While \( P(s) \) carries information on short-range correlation in the energy spectra, \( \Sigma(L) \) contains rather long-range correlation. Usually \( \Sigma(L) \) indicates a deviation from the universal value for large \( L \), thus, the particle dynamics becomes nonuniversal at short time scale. For large \( L \), the spectral correlation is not universally semi-Poisson but depends on the helicity of nanotubes. The deviation from the SP distribution gives useful information: the linear behavior for large \( L \), i.e., \( \Sigma(L)/L \to \chi \), represents the level compressibility, and for disordered metals \( \chi \) was shown to be

\[
\chi = \frac{1}{2}(1 - \frac{D_2}{d}) \tag{4}
\]

where \( D_2 \) is the multifractal exponent of the inverse participation ratio and \( d \) is the spatial dimension. Here \( D_2/d \) is related to the ’probability of return’

\[
p(t) \propto t^{-D_2/d} \tag{5}
\]

Our incommensurate DWNT behave as a two-dimensional systems \( (d = 2) \) with off-diagonal disorder, which has a mixed boundary between periodic and hard-wall conditions. From the inset in Figure 1 we estimate \( D_2/d \) to be about 0.32 for the DWNT considered here. While \( p(t) \propto t^{-d/2} \) in normal diffusion, our system exhibits anomalous diffusion, which was also found by previous wavepacket spreading calculations.

The SP distribution in Figure 1 is mostly contributed by the Fermi level increases, we find similar statistics for the energy states from 0.08 to 1.3 eV, and exhibits the Poisson distribution, indicating that the energy levels are uncorrelated. Single-wall nanotubes, which are constituents
of the DWNT, are approximately described in terms of $P_F(s)$ and $\delta(s)$. In this case, the delta-function peak results from the doubly degenerate states due to inversion symmetry. If inter-wall interactions are absent in the DWNT, a superposition of two independent spectra of the nanotube constituents is also described by the Poisson and delta functions.

When inter-wall interactions break the degeneracy, smearing out the delta-function peak, $P(s)$ is still Poisson-like, as shown in Fig. 2(a), implying that the energy mixing between the two carbon shells is insignificant for low energies. In the low energy regime, it is useful to use the Landauer formula,

$$G = \frac{2e^2}{h} \sum_i T_i(E_F),$$

where $T_i(E_F)$ is the transmission probability of the channel $i$ obtained from the band structure calculations at the Fermi energy $E_F$. Our results infer that quantized conductances observed in MWNTs may be due to the fact that the Fermi level is close to the charge neutrality point, $E_F \approx 0$. However, it is usually very difficult to find experimentally the location of the Fermi level.

As the Fermi level is shifted further, since the mean level spacing becomes smaller and the inter-wall interaction matrix elements become more significant, the inter-wall interactions induce a more significant mixing of the energy levels between the carbon shells. For higher energy states, we find that $P(s)$ follows the SP distribution, as shown in Figs. 2(b) and (d). The quantum conductance in this regime still remains a challenging problem. In particular, it is a nontrivial but important task to find the tube length dependence of quantum conductance in this regime. Recent calculations showed negligible inter-wall tunneling currents for the tube length of 1 µm, but it is questionable whether one can use the Bardeen’s formalism for DWNTs where the coherent back-tunneling between carbon shells is non-negligible. According to the weak localization formula, $\delta \sigma \propto -\int dt \rho(t)$, with Eq. 6, conductances may depend on the tube length. However, the weak localization formula considers only the interference of the pair of time-reversal paths, which is not guaranteed in the critical regime.

In Fig. 2(c), one can see that the critical statistics evolves to the GOE as going to the higher energy region, where $P(s)$ is quite close to the Wigner-Dyson surmise. We also find the GOE-like statistics for both $P(s)$ and $\Sigma(L)$ in all the incommensurate DWNTs tested here. The appearance of the GOE-like behavior indicates that all the symmetries except for time-reversal symmetry are effectively broken, and the corresponding electron motion is ergodic. In this regime, the conductivity of MWNTs may be described by the weak localization theory. One should also note that the weak localization theory is applicable for energies higher than those in the first critical regime, because the sequence of statistics with increasing energy is Poisson $\rightarrow$ SP $\rightarrow$ GOE $\rightarrow$ SP.

In MWNTs on top of metallic gates, the details of contacts, local excessive charges, and depletion of charge carriers may change the position of the Fermi level. Based on our results, we guess that in conductance measurements, the Fermi level is shifted to the GOE regime or to the critical regime (close to the GOE) where conductivity is properly described by the weak localization formula.

The calculated variances over every 1000 consecutive levels are compared with the densities of states for two different DWNTs in Fig. 3. The size of fluctuations of the level spacing is dictated by the spectral statistics;

$$\langle (s-\langle s \rangle)^2 \rangle = \frac{\int ds (s-1)^2 P(s)}{\int ds P(s)} = 1, \quad \frac{1}{2}, \quad \frac{4}{\pi} - 1 \quad (\text{Poisson, SP, GOE}).$$

It is expected that the effect of inter-wall interactions on the level spacing is most significant when the mean level spacing $\Delta$ is minimum near $E = \pm \gamma_0 = \pm 2.75eV$, where the maximum DOS occurs on a graphene sheet. One can see $\langle (s-\langle s \rangle)^2 \rangle = \frac{4}{\pi} - 1 \approx 0.27$ near $E = \pm \gamma_0 = \pm 2.75eV$, which is a signature of GOE distribution. The variances larger than 1 near $E = 0$ are due to the fact that $P(s)$ is not completely Poisson-like because the degenerate levels of each nanotube layer are not completely lifted up.

We find that a transition from the Poisson-like to SP-like statistics occurs at lower energies as the diameter of nanotubes increases. One of the reasons for this trend seems that the DOS is enhanced for nanotubes with larger diameters. The transition energy is close to 1 eV.
in the (43,8)/(51,9) DWNT with the outer and inner diameters of 4.4 and 3.7 nm, respectively, while it is higher than 1 eV for the (16,5)/(23,8) tube with the diameters of 2.2 and 1.5 nm, as shown in Fig. 3. Since experimentally measured diameters of MWNTs are often in the range of 10 nm, we expect that the crossover of spectral statistics occurs at energies lower than 1 eV.

Very recently, Kociak and his co-workers measured the conductance of a DWNT whose two tubes have a gap and showed linear conductance near the Fermi level. The linear conductance or a finite DOS near the Fermi level indicates that the Fermi level indeed can be shifted far from the charge neutral point.

Finally, we point out that the spectral statistics might be probed through conductance measurements in the Coulomb blockade regime. The temperature should be low enough to ensure that $k_B T < U, \Delta$, where $U$ is the charging energy of nanotube dot. In the resonant tunneling regime, where electron tunnels through one quantum level, if electron-electron interactions are not too strong, the conductance peak spacing with varying the gate voltage provides information on the single-particle energy spacing.

In conclusion, we have shown that the spectral statistics of incommensurate double-walled nanotubes follows the Poisson, GOE, or SP distribution, depending on the energy window, while the overall states are well described by the SP distribution. This results indicate that the nature of electron transport in multi-walled nanotubes can be either ballistic, diffusive, or critical, depending on the position of the Fermi level. It is questioned whether the usual weak localization correction is relevant to existing experiments. The Coulomb blockade oscillation in nanotube dots is suggested to investigate the spectral statistics in this work.

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