I. Introduction

Quantum interference (QI) in electron transport of single-molecule devices is a phenomenon that takes place when two or more pathways of electrons are in phase or out of phase. In clear contrast with the double-slit interference of light or electrons for which the interference patterns are observed in real space, quantum interference in electron transport studied here happens in the energy space and is typically accompanied by the increase or decrease of the transmission function in a certain energy range. In particular, the case of destructive quantum interference (DQI) is characterized by a sharp dip in the transmission function, which leads to a decrease of transmission by several orders of magnitude. In comparison, constructive quantum interference (CQI) leads to an increase of transmission, but with a theoretical upper limit of 4-fold conductance enhancement expected for a two-pathway system. For this reason, most attention has been paid to DQI since it introduces a strong signal that can be much more easily detected. Accompanied by the absence or presence of DQI, the corresponding molecular devices may present two states with a great difference in the conductance. This will find important applications in various fields, such as molecular switches, logic gates, data storage, field effect transistors, sensors, molecular thermoelectric devices and even molecular isomer identification. Consequently, it has attracted intensive attention in recent years.

The study of quantum interference in single-molecule devices dates back to Joachim et al.’s work in which it was proposed that for the benzene molecular junction with a meta...
connection configuration, it will present a sharp dip in the transmission function but not for the ortho and para configurations, and the sharp dip arises from DQI. This prediction was proved later by experimental work. Soon after that, DQI was observed in many systems, such as cross-conjugated molecules, polycyclic aromatic hydrocarbons (PAHs), aromatic molecules with heteroatoms, supramolecular systems, tetraionic cyclophane circuits, and even single perovskite quantum dots. In the meantime, simple rules were proposed to predict DQI in cross-conjugated molecules and PAHs. For example, Solomon et al. proposed that for a bipartite system, the electron transport will be dominated by DQI when a star is placed on every second atom and the leads bind to two atoms of the same type (either starred or unstarred) and a typical example for this rule is graphene molecules and graphene nanoribbons. Several other rules also lead to the conclusion that when the two leads are connected to two atoms in the same sublattice of a bipartite system, DQI will be observed. However, all these rules have been applied only to planar bipartite systems with an sp² hybridization network. It is well known that carbon nanotubes (CNTs) are also sp² hybridized bipartite systems and can be considered to be constructed by rolling up a graphene nanoribbon. However, the topology is totally different since it is a tube, not a plane. Although various quantum interferences such as Fabry–Perot interference and Sagnac interference as characterized by quantum conductance oscillation as a function of Fermi energy or gate voltage have been extensively studied, it is still unclear whether the rules above for predicting QI in planar carbon systems are applicable to CNTs and especially, whether DQI will always be observed when two leads are connected to the same sublattice, just like the planar bipartite system. Thus, in this work, based on a Hückel model, we study the transport properties of armchair CNTs with single site connections and weak coupling to the leads by varying the nanotube length and diameter. It is found that the transport properties as a function of the nanotube length present an oscillatory behavior with a period of 3, which is in clear contrast with graphene nanoribbons where no oscillatory behavior as a function of ribbon length is observed. For nanotube length as defined by the number of atomic planes \( n = 3p \) and \( 3p + 1 \) (with \( p \) an integer), a very sharp valley with the minimum as negligible as \( 10^{-12} \) in the transmission function is observed at the Fermi level when both leads are connected to the same sublattice, indicating the appearance of DQI, while for \( n = 3p + 2 \), no DQI but a resonant peak with height of 1.0 in the transmission function is observed at the Fermi level for the same connections. The appearance or disappearance of the resonant peak is well understood by considering the CNTs with finite length as circular periodic systems and making use of the band structure model of armchair graphene nanoribbons (AGNRs) which shows distinct three-family behaviors with varying ribbon width. In the meantime, the DQI in the \( n = 3p \) and \( 3p + 1 \) cases is explained in terms of the spatial distribution of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the CNTs.

II. Computation details

Fig. 1(a and b) show an example of a \((m, m)\) armchair CNT with the size \( m = 3 \) and the length \( n = 8 \) (atomic planes). Here the
atomic structure of a single-walled carbon nanotube is well described by its chiral indices \((m, k)\) that specify the perimeter of the carbon nanotube in terms of graphene by \(C = m\vec{a}_1 + k\vec{a}_2\), where \(\vec{a}_1\) and \(\vec{a}_2\) are two unit vectors of graphene with an angle of \(\pi/3\) between them. For an armchair CNT we have \(m = k\) and each atomic plane contains \(2m\) carbon atoms. These atomic planes can be divided into two alternating categories \(P\) (Fig. 1(c)) and \(Q\) (Fig. 1(d)), with a rotated angle of \(\pi/m\) between them. Two leads such as metallic atomic chains as labeled by \(E_1\) and \(E_2\) are connected to one atomic site in each of the terminating atomic layers. All the carbon atoms are numbered clockwise in each atomic plane and the indices between the atomic planes increase from left to right (see Fig. 1(a)), thus the atoms in one sublattice all have odd indices while those in the other sublattice all have even indices. The left terminating layer is taken as \(P\) (Fig. 1(c)), then with the increase of the atomic planes, the right terminating layer will be alternatively \(Q\) and \(P\) (Fig. 1(d and e)). For sake of convenience, the atoms in the right layer are renumbered with a prime starting from 1’ which keeps the same sovereignty as the original index without a prime. We employ a Hückel theory based tight-binding approximation to describe the system, with only the nearest neighbor interaction taken into account and the corresponding hopping parameter taken as \(t\).

When the metallic atomic chains serving as the leads are connected with atom \(r\) in the left terminating layer and atom \(s\) in the right terminating layer of the CNT, respectively, the equilibrium conductance is written as

\[
g_{rs} = \frac{2e^2}{h} T_{rs}(E_F), \tag{1}
\]

with the transmission function calculated by

\[
T_{rs}(E) = \text{Tr} \left( I^r (E) G^R(E) I^s (E) G^A(E) \right),
\tag{2}
\]

where the \(I^r\) and \(I^s\) matrices describe the couplings between the CNT and the leads that are connected by the sites \(r\) and \(s\), respectively. In this work, the wide band limit approximation is adopted, as done in other references such as ref. 61, thus the only nonzero matrix elements \(I_{r,s}^r\) and \(I_{r,s}^s\) in the \(I^r\) matrices are both taken as a constant \(\gamma\). \(e\) is the electron charge, \(\hbar\) Planck’s constant, \(E\) is the electron energy and \(E_F\) is the Fermi energy. \(G^{A,R}(E)\) is the advanced/retarded Green’s function of the CNT, as obtained by

\[
G^R(E) = \frac{1}{E - H - \Sigma^R}, \tag{3}
\]

with \(H\) being the Hamiltonian matrix of the isolated CNT and \(\Sigma^R = -\frac{i}{2}(\Gamma^r + \Gamma^s)\) the self-energy matrix from the leads. \(G^R\) is nearly proportional to the 0-th Green’s function \(G^0\) of the CNT, namely, that of the isolated molecule. In the weak coupling regime, \(G\) can be approximated as \(G^0\). Due to the single site connection to the leads, the transmission is proportional to \(|G_{rs}^0|^2\), thus the single matrix element \(G_{rs}^0\) determines the transport properties.

III. Results and discussion

First of all, the transmission functions of the \((3, 3)\) armchair CNT with length \(n = 6, 7\) and 8 under different connections were calculated as shown in Fig. 2. Without loss of generality, for the left terminating atomic plane, we chose connection sites 1 and 2 while the connection site in the right terminating atomic plane changes from 1’ to 6’ for the even–even case as shown in Fig. 2(e and f), the transmission curves are even all quite flat in a large energy range around the Fermi level, which is significantly different from other cases.

The reason why the transmission is connection dependent can be understood from the orbital analysis. As stated in the previous section, for single site connections to leads by atoms \(r\) and \(s\), the electron transport is solely determined by Green’s function matrix element \(G_{rs}^0\). In the weak coupling regime, the Green’s function can be approximated by the 0th Green’s function \(G^0\) of the CNT. It can be calculated either by the inversion of the Hamiltonian matrix as in eqn (3) by neglecting the \(\Sigma\) term, or by the contributions of all the molecular orbitals

\[
\begin{align*}
&\text{Fig. 2} \quad \text{Transmission functions for the (3, 3) armchair CNT with:} \quad (a\text{ and } b) \quad n = 6, (c\text{ and } d) \quad n = 7 \text{ and (e and f) } n = 8 \text{ atomic planes, calculated by setting } \tau = -1 \text{ and } \gamma = -0.2.
\end{align*}
\]
of the isolated CNT in the following form,

\[ G^{[n]}_{i,j}(E) = \sum_{\eta} \frac{C_{\eta \downarrow} C_{\eta \uparrow}}{E - E_{\eta} \pm i\eta} \]  

(4)

where \( C_{rn} \) is the wave function at site \( r \) in the state \( n \), \( E_{\eta} \) is the eigenvalue of state \( n \), and \( \eta \) is an infinitesimal positive number. Both \( C_{\eta \downarrow} \) and \( E_{\eta} \) are obtained by directly diagonalizing the Hamiltonian matrix \( H \) of the isolated CNT. As shown in eqn (4), both the energy differences \( E - E_{\eta} \) and the product of molecular orbital coefficients \( C^{*} \) determine the magnitude of Green’s function. From the frontier orbitals HOMO and LUMO play a major role in the transmission at the Fermi level. Therefore, when the sign of \( E - E_{\eta} \) it is seen that the front frontier orbitals HOMO and LUMO are opposite at the Fermi level. Therefore, when the sign of \( E - E_{\eta} \) is the same as that of \( C_{\eta \downarrow} C_{\eta \uparrow} \) the contributions from these two orbitals are cancelled. When their signs are different from each other, the contributions from these two orbitals are enhanced. Thus, the Green’s function can be approximated by the sum of the HOMO and LUMO, or the small number of orbitals around the Fermi level. The signs of \( E - E_{\eta} \) at \( E - E_{\eta} \) and \( E - E_{\eta} \) are opposite at the Fermi level. Therefore, when the sign of \( E - E_{\eta} \) as that of \( C_{\eta \downarrow} C_{\eta \uparrow} \) the contributions from these two orbitals are cancelled. When their signs are different from each other, the contributions from these two orbitals are enhanced. Thus, in the wave function distribution of the HOMO and LUMO in the following. According to eqn (4), we have to focus only on the wave function distributions at the sites of the left and right terminating layers.

The wave function at each site for the HOMO and LUMO for the odd sites and negative values at the even sites, while the ball size indicates the magnitude. The distributions at the left and right terminating layers are shown in the dashed line circles. It is seen that for the LUMO, the wave function has positive values at any sites in both terminating layers. In contrast, the HOMO has positive values at the odd sites and negative values at the even sites, which gives rise to different signs in \( C_{\eta \downarrow} C_{\eta \uparrow} \) and \( C_{\eta \downarrow} C_{\eta \uparrow} \) when the two connections are located at different sublattices. This will lead to CQI according to the above analysis. In contrast, when two connection sites are located at the same sublattice, both \( C_{\eta \downarrow} C_{\eta \uparrow} \) and \( C_{\eta \downarrow} C_{\eta \uparrow} \) will have the same sign, resulting in DQI. These are consistent with the transmission function as shown in Fig. 2(a and b). In contrast to the \( n = 6 \) case, in the \( n = 7 \) case, the HOMO is positive at any sites of both terminating layers, while the LUMO is positive at the odd sites and negative at the even values in both layers, as shown in Fig. 4, from which we see that it will also lead to the CQI and DQI as shown in Fig. 2(c and d).

As for \( n = 8 \), we need to consider 4 orbitals since there are two degenerate orbitals right at the Fermi level, as labelled by ‘F-1’ and ‘F-2’ and shown in Fig. 5(a and b). The orbital below/above the Fermi level is labeled as the HOMO and LUMO. It is interesting that in the two terminating atomic planes, the F-1 orbital is zero at odd sites and finite at even sites, while the F-2 is zero at even sites and finite at odd sites. It is well known that each molecular orbital will contribute a resonant transmission peak at the corresponding level. That is why we see a peak at the Fermi level. This peak will appear when both leads are connected to two sites of the same sublattice. For the even–even connection, the F-1 orbital mediates a resonant peak while for the odd–odd connection, the F-2 does. For odd–even or even–odd connection, the transmission contributed either by F-1 or by F-2 will be zero according to eqn (4), which leads to the disappearance of the resonant peak, consistent with transmission function in Fig. 2(e and f). At this time, the transmission is contributed mainly by the HOMO and LUMO. These two orbitals will enhance each other according to eqn (4) and the distribution of these two orbitals (see Fig. 5(e and f)).

To estimate how the variation in nanotube length affects the transport properties, we computed the transmission function with the length varying from \( n = 3 \) to 16 atomic planes for the (3, 3)CNT for the 1–1’, 2–2’, 2–1’ and 2–2’ connections, with the equilibrium conductance calculated by the CNT fermi level due to the F-1 orbital or F-2 orbital, and a minimum around \( 1 \times 10^{-11} \) at \( n = 3p + 2 \) which arises from the resonant peak at the Fermi level due to the F-1 orbital or F-2 orbital, and a minimum around \( 1 \times 10^{-11} \) at \( n = 3p + 2 \) which arises from the DQI of the HOMO and LUMO. For 1–2’ and 2–1’ connections, a maximum of
B₁/C₂₁₀/C₀₂ is observed at n = 3p and 3p + 1, although much less than that of the 1–1₀ and 2–2₀ cases obtained at n = 3p + 2, and a minimum around 1 × 10⁻² is observed at n = 3p + 2. From Fig. 6, it is seen that both the maximum and minimum in the n = 3p + 2 cases are much larger (by several order of magnitude) than those in the n = 3p and 3p + 1 cases correspondingly, from which it can be concluded that the n = 3p + 2 CNTs will conduct much better than the n = 3p and 3p + 1 families. For comparison, we have also calculated the transmission function of the 6-AGNR as a function of the nanoribbon length and the equilibrium conductances are shown in Fig. 6(a). For the AGNRs, we only calculated the nanoribbons with odd unit cells in length so that each carbon atom is included in a hexagon with no carbon atoms bonded only to one neighbor. All the odd numbers can still be classified into three families as n = 3p, 3p + 1 and 3p + 2. DQI is clearly observed under any nanoribbon length when the two connection sites are both located in the same sublattice but not observed otherwise. The presence of DQI in the graphene nanoribbons has been well explained by the real distribution of HOMO and LUMO in the references on the basis of eqn (4).⁵⁷ Obviously, we see that for AGNRs, with the increase of the ribbon length, there is no oscillation with a period of 3. This is in clear contrast to the case of carbon nanotubes.

Having discussed the variation effects of nanotube length, we next investigate how the diameter influences the transport properties. For an armchair (m, m)CNT, the diameter is determined by m. We have studied the armchair CNTs with the diameter varying from m = 3 to 8 and the length fixed at n = 6, 7, and 8, respectively. From the equilibrium conductance shown in Fig. 7, with the variation of m, it basically does not change. For n = 6 and 7, the maximum stays at ~ 1.0 × 10⁻² and the minimum stays at ~ 1.0 × 10⁻¹¹, suggesting CQI and DQI respectively from the HOMO and LUMO. For n = 8, the equilibrium conductance remains at a maximum ~ 1.0 for the odd–odd and even–even connections and a minimum ~ 1 × 10⁻⁴ for the odd–even and even–odd connections, with the former arising from the resonance at the Fermi level due to the F-1 or F-2 orbital and the latter from the CQI between the HOMO and LUMO.

Finally, we reveal the origin of the resonant peak at the Fermi level for the n = 3p + 2 cases, which is the most prominent feature of the transport properties of CNTs, compared with the graphene derivatives.⁴⁵–⁴⁸ Obviously, the peak arises from the resonance through a molecular orbital. As indicated above, actually, for n = 8, two molecular orbitals do appear at the Fermi level, but only one of them will contribute to the transmission for each connection type (1–1₀ or 2–2₀). Are there always two molecular orbitals located at the Fermi level for all the n = 3p + 2 cases, and if so, why? The 3-family periodic behaviors in Fig. 6 are reminiscent of the 3-family band gap behaviors of armchair graphene nanoribbons (AGNRs).⁵⁸ It is well known that in the tight-binding model, the AGNRs are metallic for n = 3p + 2...
and insulating otherwise, where the ribbon width \( n \) is the number of carbon dimer lines along the length direction. No matter how many \( k \)-points in the one-dimensional reciprocal space are chosen in the band structure calculations, two bands, namely the valence band and the conduction band, always cross exactly at the Fermi level at the \( G \) point, leading to two-fold degeneracy of the energy levels there. Zdetsis’s recent work reveals a new understanding of the 3-family behaviors of AGNRs in terms of aromaticity, topology and shell structure, etc. and specifically, the \( 3p + 2 \) AGNRs have mixed aromatic, electronic, and topological character, with vanishingly small bandgaps, while the \( 3p \) and \( 3p + 1 \) families are aromatic with large bandgaps. To understand the origin of the resonant peak in the \( n = 3p + 2 \) cases in our study, it is wise to start with the energy spectrum of the molecular orbitals. For a nanotube with finite length, the energy spectrum can be obtained in two ways. One is to deal with it as a molecule. We may write down the full tight-binding Hamiltonian directly with the matrix size as the total number of atoms (\( 2n^*m \)) and diagonalize it. The other is to deal with it as a periodic system, with the periodic direction turning around the tube axis. In this case, it is actually an AGNR, with a head-to-tail connection, and the \( k \)-dependent Hamiltonian matrix of a primitive cell with \( 2\pi \) atoms is diagonalized. When calculating the band structure for a periodic system, it seems that the \( k \)-point number can be chosen as any integer number and the larger the \( k \)-point number, the smoother the curve is. However, as a matter of fact, the number of \( k \) points has a definite physical meaning. When we study the general properties of a solid, conceptually it is dealt with as a periodic system with the first and the last primitive cells connected to each other, which is actually the Born-von Karman boundary condition. Thus it looks like a large circle. The larger the circle is, the more it behaves like an infinite solid. For this kind of periodic system with \( N \) primitive cells, a condition must be imposed that any wave function at any \( k \) should restore the original value after passing a whole circle. This requires that the \( k \) points can only take \( N \) discrete values, with \( k = \frac{2\pi h}{Na} \) \(( a \) the lattice constant) and \(-\frac{\pi}{a} < k \leq \frac{\pi}{a}\). Thus, the integer \( h \) has to satisfy \(-\frac{N}{2} < h \leq \frac{N}{2}\). For example, for \( N = 3 \), \( h = 0, \pm 1 \), while for \( N = 8 \), \( h = 0, \pm 1, \pm 2, \pm 3, 4 \). In return, when we calculate the band structure, the number of \( k \) points actually determines the number of primitive cells \( N \) that the solid contains. The \((m, m)\) CNTs are exactly elegant examples of periodic solids along the circumference, namely, AGNRs with \( N = m \). It is well known that for AGNRs with \( n = 3p + 2 \), at the \( \Gamma \) point, there will always be two energy levels at the Fermi level, no matter how the number of \( k \) points is chosen, or equivalently, no matter how large the diameter \( m \) (or \( N \)) is. Our calculations for the energy spectra of the finite nanotubes with the two methods are exactly the same (see Fig. 8 for examples with \( n = 6, 7, 8 \) and \( m = 3, 8 \)). Thus, for \( n = 3p + 2 \), we will always get a resonant peak at the Fermi level, consistent with what is obtained in Fig. 6 and 7(e, f). In contrast, for the \( n = 3p \) and \( 3p + 1 \) cases, there is an energy gap and the transmission at the Fermi level is contributed by the HOMO and LUMO, thus the maximum is much smaller (see Fig. 6 and 7(a–d)).

Fig. 7 The equilibrium conductance in the unit of \( G_0 = (2e^2/h) \) with \( m \) varying from 3 to 8 for the case with: (a) and (b) for \( n = 6 \); (c) and (d) for \( n = 7 \); (e) and (f) for \( n = 8 \).
IV. Summary

In conclusion, we have investigated the quantum transport properties of molecular junctions constructed by armchair CNTs with finite length and varying diameter, with single atomic site connections to two leads in the weakly coupling regime. Periodic transport behaviors as a function of the nanotube length are observed. Specifically, for \( n = 3p \) and \( 3p + 1 \) families, CQI and DQI are achieved with the change in the connection sites, just like graphene nanotubes and graphene molecules. In contrast, for the \( n = 3p + 2 \) family, no sharp DQI transmission valley is observed due to the resonant peak observed at the Fermi level. The DQI and CQI can be well explained by the real space distribution of the HOMO and LUMO. The resonant peak in the \( n = 3p + 2 \) cases is well understood by the energy spectrum of a periodic AGNR model in the tight-binding approximation. The study indicates that the simple rules previously proposed to predict DQI in planar bipartite systems cannot be applied to tubular bipartite systems entirely where exception may arise due to the difference in the structure topology and the subsequent energy spectrum.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We gratefully acknowledge financial support from the National Natural Science Foundation of China under Grant no. 11974355 and 12074230; the National Key R&D Program of China under Grants no. 2017YFA0304203, Fund for Shanxi “1331 Project”, and the Shanxi Province 100-Plan Talent Program. Calculations were performed in the Center for Computational Science of CASHIPS, the ScGrid of the Supercomputing Center and Computer Network Information Center of Chinese Academy of Sciences.

References

1. F. Evers, R. Korytář, S. Tewari and J. M. van Ruitenbeek, Rev. Mod. Phys., 2020, 92, 035001.