

Quantum interference comparison among benzene, naphthalene, and azulene single-molecule junctions

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ABSTRACT

The capability to build devices from single-molecular junctions depends on the fabrication of molecular structures. Here, we report important changes in the transmission coefficient for different connectivities of polycyclic aromatic hydrocarbons. In this study, we compared the density functional theory (DFT) with single-orbital tight binding (TB) to investigate the transmission coefficient of three different molecules, including benzene, naphthalene, and azulene, with various point connections with electrodes. In the case of benzene, the para connection led to constructive quantum interference (CQI) and the meta link to distractive quantum interference (DQI). Subsequently, azulene and naphthalene showed an equal number of atoms with five different connections. The results indicate that the even-even or odd-odd connection was DQI, and the even-odd connection was CQI. This finding is supported by the wave function molecular orbital plot. Finally, the TB calculations were in good agreement with those of DFT.

Introduction

The research on charge transport via single molecular junctions provides a basic understanding of the creation of functional circuits and single-molecule devices that rely on quantum effects[1-3]. New studies on quantum interference effects (QIEs) offer encouraging prospects for the control of charge transfer across single-molecule junctions[4-10]. Moreover, with crucial on/off ratios between conductive constructive quantum interference (CQI) and insulative destructive quantum interference (DQI) states, QIEs allow for powerful molecular switching, which suggests possible uses in molecular electronics in the future[11]. This introduction describes the core theoretical concepts and methods that form the foundation of the study of room-temperature single-molecule electronics. All waves, including gravitational, electromagnetic, water, and sound waves, are affected by interference.

This phenomenon occurs when two waves combine to form a single wave. Both waves have the potential to combine either constructively or destructively; the former results in a considerably high amplitude and the latter in a low one[12-18]. The corresponding important attributes include the adjustment of molecular junction electrical conductance through a multipath dependent on the molecular length, molecular conformation, alignment of the HOMO-LUMO gap to the metal electrodes' Fermi level, coordination geometry at the metal-molecule contacts, and the gap between molecular orbitals with the highest occupation and lowest unoccupied state. A prior study was conducted based on molecules similar to fluorene and various routes via a molecular wire[19-22]. Numerous investigations have demonstrated that conductance is higher when para (coupled) linkage via a basic unit is present than when isomeric meta (reduced coupled) linkage occurs. Such a phenomenon, which is explained by quantum interference (QI), is noted in PAH, such as benzene[23-26], naphthalene[20], pyrene[27], and anthanthrene[28], theoretically and experimentally. The motivation behind the current work

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is to investigate the combined effects of two important molecular variables on the single-molecule conductance of molecular wires for the first time: (i) heteroaromaticity in the wire's core and (ii) para versus meta pairing via the basic unit. Benzene, azulene, and naphthalene's electronic structures and their transport characteristics between gold electrodes were investigated in this paper using first-principle models. We examined how QI changes within those molecules and demonstrated that orbital rules, which are commonly utilized to calculate QI, are inapplicable to all molecules. Next, to comprehend QI in these molecules, we created a basic Hückel model. This study aimed to examine the correlation between the number of cyclic compounds with QI and aromaticity.

Methods

As described in the main text, these structures were constructed through simple tight-binding (TB) approximation models with one orbital per atom or obtained using the density functional theory (DFT). A self-consistent solution was found through calculation using the DFT method of each structure based on SIESTA[29]. By combining linear orbitals, SIESTA can construct an atomic orbital and account for core electrons through norm-conserving pseudopotentials. The generalized gradient approximation of the exchange and correlation functional was applied to a double- ζ polarized basis set and a real space grid defined with an equivalent energy cutoff of 250 Ry using the Perdew–Burke–Ernzerhof parameterization[30]. For all structures, the optimization of geometry was carried out for forces less than $40 \text{ meV}\text{\AA}^{-1}$. Transport Calculation: The nonequilibrium green function method was applied using the GOLLUM code[31]. The GOLLUM code, which was created and conserved at the universities of *Lancaster and Oviedo*, allows for the use of electronic transport computations[32]. Despite its most basic version, the TB method is an asset for the electronic structures of the studied molecules [33]. The process's benefit lies in its capability to simplify the electronic structure of complex systems into physically transparent

Hamiltonian matrices based on a minimal basis set of atomic orbitals, which provide a simple and natural comprehension. SIESTA enables the calculation of a large number of atoms. By contrast, in addition to the construction of a Hamiltonian for the system[34], the GOLLUM code's advantage lies in its capability to identify the electrodes and scattering area for Hamiltonians.

Results and Discussion

QI, which occurs when certain polycyclic aromatic hydrocarbons (PAHs) are incorporated into molecular wires, results in remarkable variations in conductance[35]. A relative phase shift possibly occurs between the two branches of benzene when electrons propagate through electrodes from left to right directions[36]. The combination of electronic wave functions along various pathways can lead to either constructive or destructive interference, which results in changes to the transmission probability[37]. Figure 1a shows the single-molecule chemical structure junction of benzene attached to gold electrodes through pyridine anchors. To study the probability of electric transmission through a benzene junction, we first minimized the geometry to the ground state for meta- and para-linked using the SIESTA code. Then, the Hamiltonian obtained from SIESTA combined with the GOLLUM code [38, 39] was used to calculate the transmission coefficient $T(E)$, which is the probability of electrons passing from the right electrode to the left as a function of energy. Figure 1b shows the point connection. Figure 1c displays the DFT $T(E)$ for benzene for para and meta connection to electrodes. We expected the DQI to appear for a single-molecule PAH when connected to the even-even or odd-odd point of the electrodes[40]. On the contrary, the even-odd connection was expected to be CQI. The $T(E)$ showed antiresonance for 3–5 point connections (DQI), and 1–4 points indicate a high $T(E)$, which led to CQI. This DFT result on $T(E)$ fully agrees with the finding obtained from the TB approximation (Figure 1d). Figure 1e shows the uniform distribution of charge on the whole backbone of the benzene

molecule. From the orbital rule, the HOMO orbital had a negative sign (red color) for position 1 and a positive sign for position 4 (blue color). Therefore, the product wave function became $\psi_1^H \psi_4^H < 0$, which is DQI at HOMO and $\psi_1^L \psi_4^L > 0$ for LUMO because all positive signs (blue colour) can lead to CQI. For meta connection, the wave function for HOMO and LUMO were subscript $\psi_3^L \psi_5^L < 0$ and $\psi_3^H \psi_5^H < 0$, respectively. Therefore, the $T(E)$ s were DQI (see Figure S1 more for details).

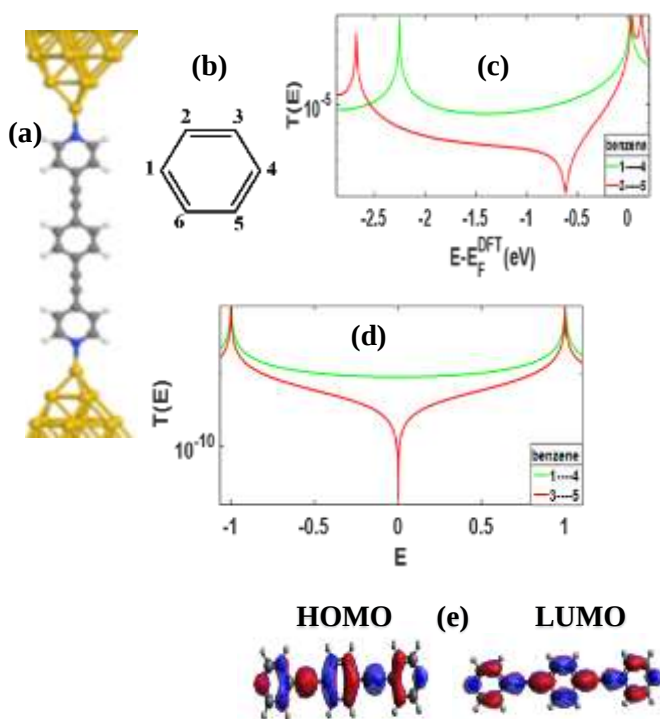


Figure 1. Quantum transport in benzene. a) A pyridine held the benzene core to the gold electrodes. b) Order of numbers in the molecular structure of benzene. c) DFT $T(E)$ for various connectivities of benzene. d) Basic TB model with a coupling $\gamma = -1$; all sites have zero on-site energies (ϵ). e) Benzene molecular orbital.

More calculations were performed to determine the attachment between the asymmetric structure and length. For this purpose, we selected the naphthalene and azulene single molecules, with both having 10 atoms. However, azulene is a nonalternant hydrocarbon consisting of five electron-rich and seven electron-poor rings. Figures 2c and 2d show the $T(E)$ for naphthalene under DFT and TB with different connectivities. Again, the odd-odd and even-even showed a connectivity with a

low $T(E)$, which implies DQI. On the other hand, even-odd had a high $T(E)$, which indicates CQI, and TB approximation fully agreed with the finding of the DFT methods (see Figures S2–S5 for more details). When the product rule of HOMO and LUMO was applied, the product $\psi_3^L \psi_8^L < 0$ and $\psi_3^H \psi_8^H > 0$. Therefore, we expected the transmission CQI as shown in Figure 2e.

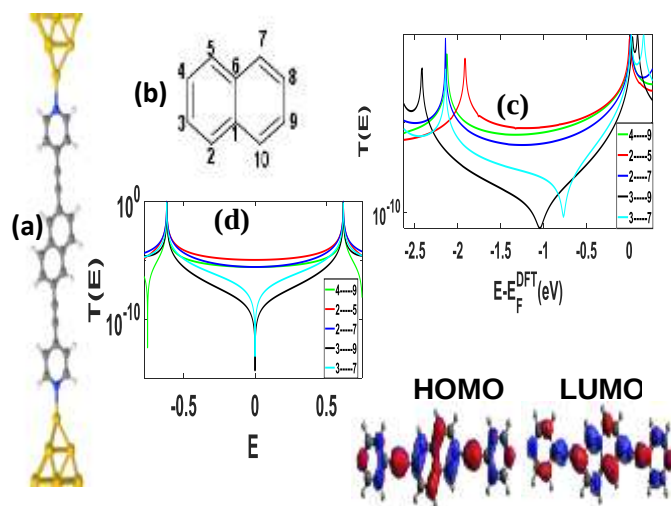


Figure 2. Quantum transport for naphthalene. a) A pyridine secures the core naphthalene to the gold electrodes. b) Order of numbers in the molecular structure of naphthalene. c) DFT transmission coefficient for various connectivities of naphthalene. d) A basic TB model with a coupling $\gamma = -1$ and all sites having zero on-site energies (ϵ). e) Naphthalene molecular orbital.

The transport characteristics of azulene between gold electrodes are investigated. Figure 3a shows the structure of azulene between two gold leads. Figure 3c displays the DFT $T(E)$ for azulene with different electrode connection points (Figure 3b). All structures LUMO dominated due to the pyridine anchor group, which means that the Fermi level ($E_F = 0$) is close to the HOMO position. The connectivities (2,6), (3,9), and (4,10) exhibited a lower value of $T(E)$, which is DQI, and the connectivities (4,9) and (3,8) displayed CQI as shown in Figure 3c (Figures S6–S9). TB approximation

was applied to compare the results obtained using the DFT approximation by selecting the local energies $\varepsilon = 0$, the coupling parameter $\gamma = -1$, simple TB approximation (Figure 3d) is in good agreement with the DFT method. HOMO and LUMO product rules are applied, and the product $\psi_2^L \psi_6^L < 0$ and $\psi_2^H \psi_6^H > 0$. Consequently, we anticipated the transmission of CQI depicted in Figure 3e.

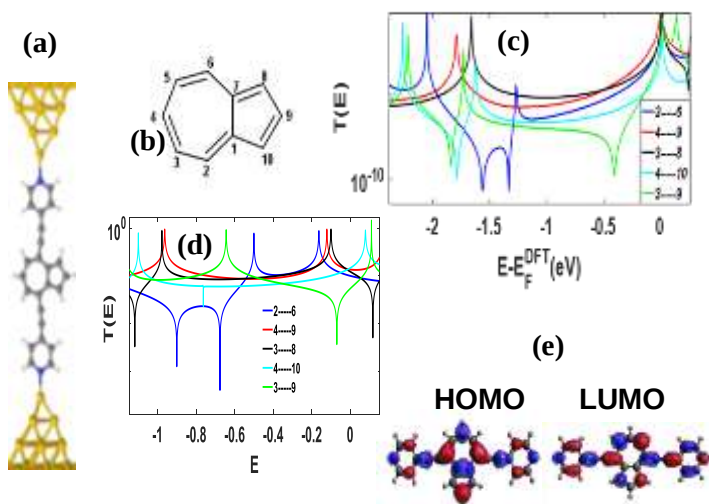


Figure 3. Quantum transport for azulene. a) A pyridine holds the core azulene to the gold electrodes. b) Order of numbers in the molecular structure of azulene. c) DFT $T(E)$ for various connectivities of azulene. d) A basic TB model with a coupling $\gamma = -1$; all sites have zero on-site energies (ε). e) Azulene molecular orbital.

Conclusion

This study proved that the finding of DFT method agrees with that of single-orbital TB approximation. We have shown that the $T(E)$ is highly dependent on the electron path in PAH molecules. When the connectivity point of electrodes was meta, as in benzene, the connecting point was odd-odd or even-even, and the transmission was low (DQI). Meanwhile, the connection was even-odd as in the para case in benzene (CQI) and so on for naphthalene and azulene. Moreover, the rule on QI depends on the shape of molecules in azulene and naphthalene. The wave function calculation enhances the idea of the QI rule in single-molecule.

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مقارنة التداخل الكمي بين البنزين والنفثالين والوصلة الجزيئية المفردة للأزولين

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الخلاصة:

تعتمد القدرة على بناء الأجهزة من ربط الجزيئات المفردة على تصنيع الهياكل الجزيئية. هنا نقدم تقريراً عن تغييرات كبيرة في معامل الانتقال للتوصيلات المختلفة للمركبات الهيدروكربونية العطرية متعددة الحلقات (PAHS). في هذه الدراسة، نستخدم نظرية الكثافة الوظيفية DFT مقارنةً مع أحادي الارتباط المداري المحكم TB للتحقيق في معامل الإرسال لثلاثة جزيئات مختلفة هي البنزين والنفثالين والأزولين مع ربط نقاط مختلفة مع الأقطاب الكهربائية. في حالة البنزين، يؤدي اتصال بارا إلى التداخل الكمي البناء CQI، والربط ميتا إلى تداخل كمي هدام DQI. بعد ذلك، يحتوي الأزولين والنفثالين على عدد متساوي من الذرات، وتظهر النتيجة أن الاتصال الزوجي-الزوجي أو الفردي-الفردي هو DQI. بينما الاتصال الزوجي-الزوجي هو CQI. ويدعم هذه النتيجة من قبل المخطط المداري الجزيئي للدالة الموجة. أخيراً، تتوافق حسابات الربط المحكم TB بشكل جيد مع نظرية كثافة الدالة DFT.

الكلمات المفتاحية: PAHS، DFT، التداخل الكمي، الربط المحكم، معامل النفاذية.