

# **From Molecular Structure: Controlling the Quantum Interference in Single Molecule Junction**

Xiangyang Wei

Supervisor: Prof. Dr. R.C. (Ryan) Chiechi

## **Content**

**Abstract**

**1. Introduction**

**2. Theoretical Background**

**2.1 Electron Transport in Molecular Junction**

**2.2 Calculation of Transmission Coefficients**

**2.3 Tight-binding approach & Density Functional Theory**

**2.3.1 Basics of Tight-binding approach**

**2.3.2 DFT in Molecular Junction**

**2.4 Source of Quantum Interference**

**2.4.1 Transmission Plot**

**2.4.2 Mach-Zehnder Resonance and Cyclic-Conjugated System**

**2.4.3 Fano Resonance and Cross-Conjugated System**

**3. Controlling the Interference Feature**

**3.1 Adding Substituent**

**3.2 Replication of Component**

**3.3 Different Anchoring Position**

**3.4 Heteroatom-Substituted**

**4. Conclusion**

**Reference**

## Abstract

Quantum interference is an important feature in single molecular junction. And it from the Mach-Zehnder resonance and Fano resonance. The interference feature can be calculated by tight-binding approach and density functional theory. From the transmission plot, we can easily judge if a single molecular junction has the interference feature. By comparing the transmission plots of the molecules with similar structures, the key influencing factors of the quantum interference in molecule structure can be figured out.

## 1. Introduction

Moore put forward his prediction that the density of components per integrated circuit would be doubled every year on 1965 [1]. The performance of dense integrated circuit is strongly connected with its density of components. People are eager to develop smaller and smaller electronic component. The single molecule looked like an excellent choice for electronics industry due to its nanometer size. Aviram and Ratner published their famous paper *Molecular rectifiers* on 1974 [2]. This is the first time a single molecule is proposed to be used as an electronic component, which can be considered as the beginning of molecular electronics.

The molecular electronics is defined as the field of science that investigates the electronic and thermal transport properties of circuits in which individual molecules (or an assembly of them) are used as basic building blocks [3]. It has become an interdisciplinary field containing many traditional disciplines like electrical engineering, mesoscopic physics, quantum chemistry, organic chemistry. The single molecule junction is the core of research of molecular electronics. It contains two leads (electrodes) and an extended molecule, showed in Fig 1 [4]. The drive of developing molecular electronics device advances the measurement capabilities and the fundamental understanding on single molecule level and it is beyond where it started, the electronic transport characterization, illustrated in Fig 2 [5]. But the movement of electrons in a single-molecular junction is still the central field of molecular electronics.

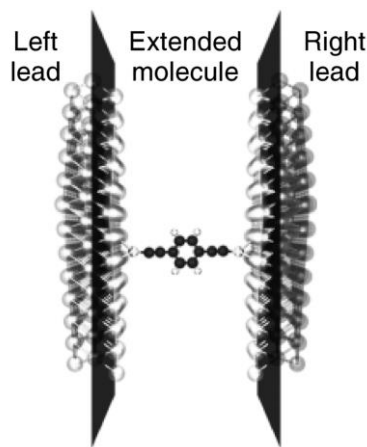


Fig 1 The structure of single molecule junction [4]

Except the extended molecule itself, the environment also can strongly impact the electronic transport characterization of a single-molecular junction. For example, the alkali metal ions in solution may have influence on a kind of crown-ether-based molecular junction [6]. According to the calculation, when an ion enters the cavity of crown-ether structure, the conductance of the junction will be improved. And the molecule junction can discriminate different kind of alkali metal ions. Fig 3 illustrates some factors in junction that may influence the transport properties [4]. The quantum interference, especially the destructive quantum interference, is the most interesting influence on transport properties from the extended molecule itself. Because the destructive quantum interference can help the device achieve “off” state. This is the key to make the molecular electronics devices have the potential to be functional such as switches, gate dielectrics instead of just “molecular wires”.

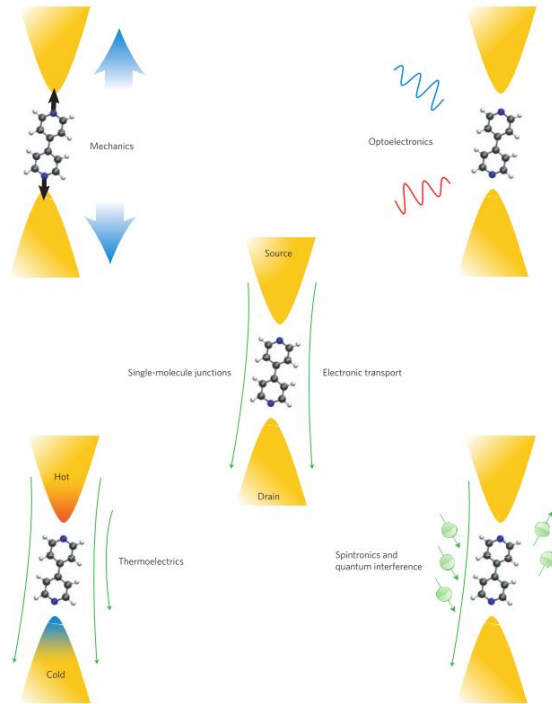


Fig 2 Probing multiple properties of single-molecule junctions. [5]

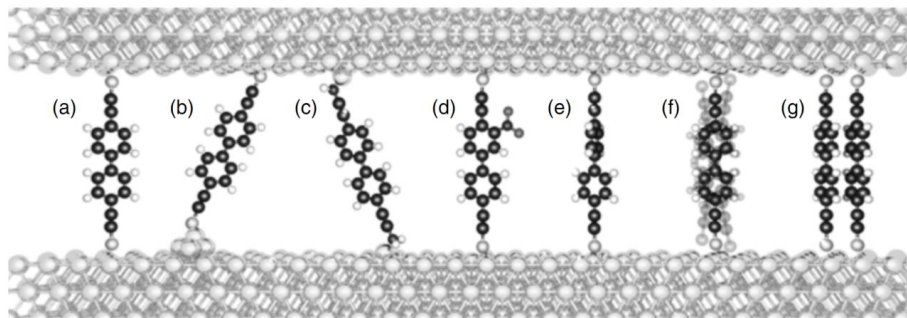


Fig 3 Some of the details of a junction that may impact transport properties: (a) the binding site, (b) binding orientation and electrode structure, (c) binding groups, (d) substituent effects, (e) conformational flexibility, (f) thermal fluctuations, and (g) intermolecular interactions [4].

## 2. Theoretical Background

### 2.1 Electron Transport in Molecular Junction

When the electrons transport through a conductor, the situation will be different due to the scale of the sample. There are many impurities in the normal scale conductor. The collisions happen during the transport of electrons which is called diffusive regime. But when the scale becomes much smaller, the electrons can pass without collision and only be limited by scattering with the boundaries of the sample. This is ballistic regime. The Landauer approach, put forward by Rolf Landauer in the late 1950's [26], is used to describe the coherent transport in molecular junction. And the central idea of this approach is that if one can ignore inelastic interactions, a transport problem can always be viewed as a scattering problem, which means that the transport properties like the electrical conductance are related to the transmission probability for an electron to cross the system [3]. In the classical physics, the matter with the energy lower than the barrier cannot through the barrier. But in the quantum mechanism, all matter can exhibit wave-like behavior, which is proposed by Louis de Broglie.

So when the electron wave meets an potential barrier, it has the possibility to be reflected and also has the possibility to be transmitted (Show in Fig 4). The transmission possibility is  $T=|t|^2$ , and the reflection possibility is  $R=|r|^2$ . The transmission in a molecular junction is showed in Fig 5,  $R(E)+T(E)=1$ . The relation between current and transmission

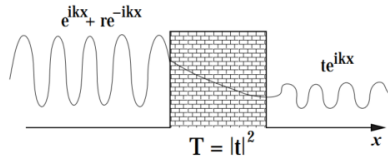


Fig 4 The electron wave transport through a potential barrier [3]

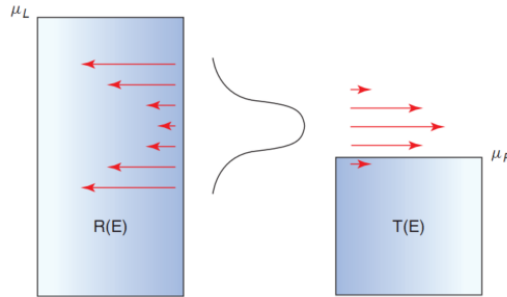


Fig 5 Transmission in a molecular junction [27]

is expressed as the Landauer formula

$$I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} dE (f_L(E, V) - f_R(E, R)) T(E, V)$$

$f_L(E)$  and  $f_R(E)$  are the Fermi distribution of the left and right metal lead. The bias  $V$  will make the Fermi level of right and left leads shifted to  $E_f + eV/2$  or  $E_f - eV/2$ .

## 2.2 Calculation of Transmission Coefficients

As a molecule is bonded to metal electrodes, the energy levels of the molecule become different. There will be a charge transfer between electrodes and a molecule due to the dissimilarity of their electronic structures, which leads to the Molecular Orbital energy level shifts ( $\Delta$ ). And the molecular states are coupled to the continuum states of the electrodes, and it results in a finite broadening ( $\Gamma$ ) of molecular energy level [28].

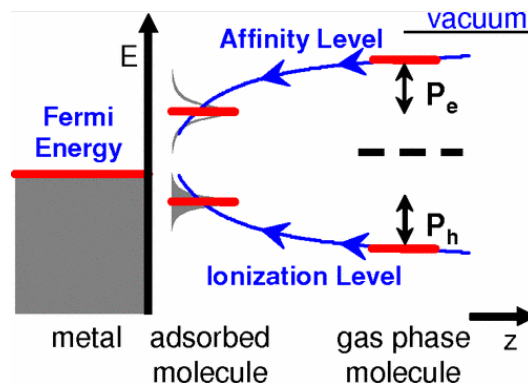


Fig 6 Schematic energy level diagram indicating polarization shifts in the frontier energy levels (ionization and affinity) of a molecule upon adsorption on a metal surface. [29]

To describe the molecular junction, the Hamiltonian of the whole system can be divided into the extended molecule, the left and right leads and the interaction between the molecule and leads:

$$H = H_M + H_L + H_R + V_{int}$$

The extended molecule is a finite system and the leads are semi-infinite system. The surface part of the lead is included into the extended molecule, so the rest part of the lead can be treated as a bulk system. And using self-energy to treat the semi-infinite properties of the leads, the effective Hamiltonian can be given by:

$$H_{eff} = H_M + \Sigma_L + \Sigma_R$$

The self-energy terms can be used to calculate the energy level shift  $\Delta$  and the energy level broadening  $\Gamma$ .

The Hamiltonian and overlap matrices can be write as

$$H = \begin{bmatrix} H_L & H_{LM} & 0 \\ H_{ML} & H_M & H_{MR} \\ 0 & H_{RM} & H_R \end{bmatrix}$$

$$S = \begin{bmatrix} S_L & S_{LM} & 0 \\ S_{ML} & S_M & S_{MR} \\ 0 & S_{RM} & S_R \end{bmatrix}$$

From the matrices above, the green function matrices can be calculated. Then according to the Landauer–Büttiker formula, we can get the transmission coefficients  $T(E)$

$$T(E) = \text{Tr}[\Gamma_L(E)G^a(E)\Gamma_R(E)G^r(E)]$$

$\Gamma$  is the broadening of molecular energy level.  $G^a$  is the advanced Green's function and  $G^r$  is the retarded Green's function.

Therefore, once the corresponding Hamiltonian is known, the transport properties of molecular junction can be computed. There are two electronic structure methods have the largest impact in the field of molecular electronics, tight-binding approach and the density functional theory (DFT). The DFT is more accurate because it includes the interaction between electrons, which TB neglect. And compared to the TB, the DFT also provides more information about the electron structure than TB.

## 2.3 Tight-binding approach & Density Functional Theory

### 2.3.1 Basics of Tight-binding approach [3]

The tight-binding model describe a single-particle Hamiltonian written in a local basis. The key of this approach is linear combination of atomic orbitals, and its form of Hamiltonian is

$$H = \sum_{ij,\alpha,\beta} H_{ij,\alpha,\beta} |i\alpha\rangle\langle\beta j|$$

Where  $|i\alpha\rangle$  denotes the state of a localized orbital  $\alpha$  centered around atom position  $R_i$ . This form means many-body interactions such as the electron-electron interaction are neglected. There are two cases can be solved by tight-binding approach, small finite system and infinite periodic system. The molecule belongs to the small finite system. In this case, the Hamiltonian can be diagonalized by writing the wave function as a combination of the localized orbitals:

$$\Phi(r) = \sum_{j\beta} c_{i\alpha,j\beta} \phi_{j\beta}(r)$$

This leads to the following set of equations for the coefficients

$$\sum_{j\beta} [H_{i\alpha,j\beta} - ES_{i\alpha,j\beta}] c_{i\alpha,j\beta} = 0$$

Where E is the energy and

$$S_{i\alpha,j\beta} = \int dr \phi_{\alpha}^*(r - R_i) \phi_{\beta}(r - R_j),$$

is the overlap between the states  $|i\alpha\rangle$  and  $|j\beta\rangle$ . These equations have non-trivial solutions if  $\det(\mathbf{H} - \mathbf{E}\mathbf{S}) = 0$ . The roots of this secular

equation yield the eigenenergies or energy levels of the finite system and the eigenfunctions are the corresponding waves functions of this system.

The extended Hückel method is a tight-binding model written as the Hamiltonian operating on adjacent atomic orbitals,  $i$  and  $j$ .  $\langle i|H|j\rangle$  describes the hopping energy,  $t$ .  $\langle i|H|i\rangle$  describes the on-site energy,  $\epsilon_i$ .

$$\langle i|H|j\rangle = KS_{ij} \frac{(\epsilon_i + \epsilon_j)}{2}$$

### 2.3.2 DFT in Molecular Junction [28]

The probability to find an electron in the volume element  $dx_1dy_1dz_1$  around the point  $(x_1,y_1,z_1)$  is given by:

$$\rho(x_1, y_1, z_1) dx_1 dy_1 dz_1 = n dx_1 dy_1 dz_1 \int \Psi^* \Psi ds_1 dx_2 \dots dx_n$$

The density functional theory focus on the electron density instead of the wave function. In DFT, there are only three space variables, while the  $N$ -electron wave function needs to study  $3N$  variables. The observables of a molecular system like energy can be unambiguously defined by the electron density of the system. And the potential for the ground state of a finite system is directly defined by the electron density.

In molecular junction, the retarded Green's function matrix is related to the electron density by following two equation:

$$\rho(r) = \sum_{\alpha\beta} D_{\alpha\beta} \phi_{\alpha}(r) \phi_{\beta}(r)$$

and

$$D = -\frac{1}{\pi} \text{Im} \int [G^r(E) f(E - \mu)] dE$$

where  $\phi_{\alpha}(r)$  is a localized atomic basis orbital and  $D_{\alpha\beta} = \sum_{i=1}^{\text{occ}} f_i c_{\alpha i}^* c_{\beta i}$  is the density matrix element where  $f_i$  is the occupation number of the  $i$ -th state and  $c_{\alpha i}$  is the expansion coefficient of the  $\phi_{\alpha}(r)$  for the  $i$ -th state. The retarded Green's function  $G^r$  based on the effective Hamiltonian gives the electron density, but the Hamiltonian itself is a functional of the electron density. Therefore, the final electron density should be calculated in a self-consistent manner as shown in Fig 7.

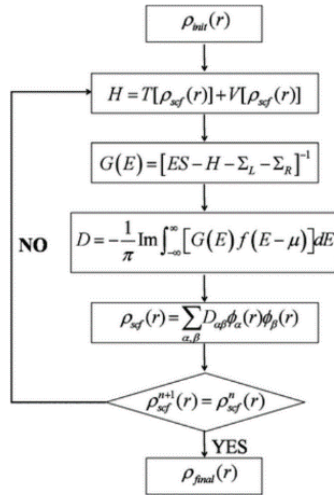


Fig 7 Self-consistent loop of the NEGF + DFT method

## 2.4 Source of Destructive Quantum Interference

### 2.4.1 Transmission Plot

Using the calculation results from tight binding approach or DFT, we can draw a plot to describe the relation between the transmission coefficient and the energy level. This is transmission plot. Fig 8 is an example of transmission plot. And the transmission plot is also drawn as showed in Fig 9.

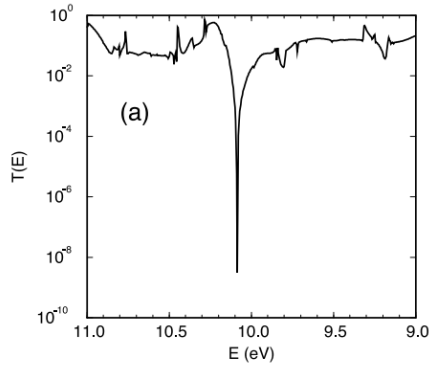


Fig 8 An example of transmission plot [30]

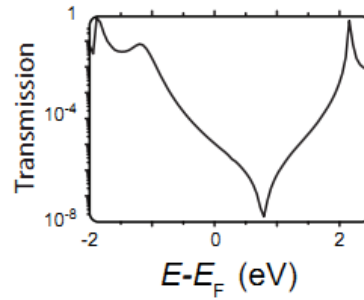


Fig 9 Example of transmission plot[31]

Except they shows different molecular junction, the difference between Fig 8 and Fig 9 is the horizontal axis. Taking the Fermi level of zero bias leads as zero point is easy to calculate the molecular conductance. The bias will make the Fermi level of right and left leads shifted to  $E_r+eV/2$  or  $E_r-eV/2$ . By averaging  $T(E)$  over an energy widow of width  $eV$  centred on the Fermi energy, the conductance  $G=I/V$  is obtained. Under the limit of zero voltage and zero temperature

$$G = G_0 T(E_f)$$

$G_0$  is the quantum conductance [4, 7].

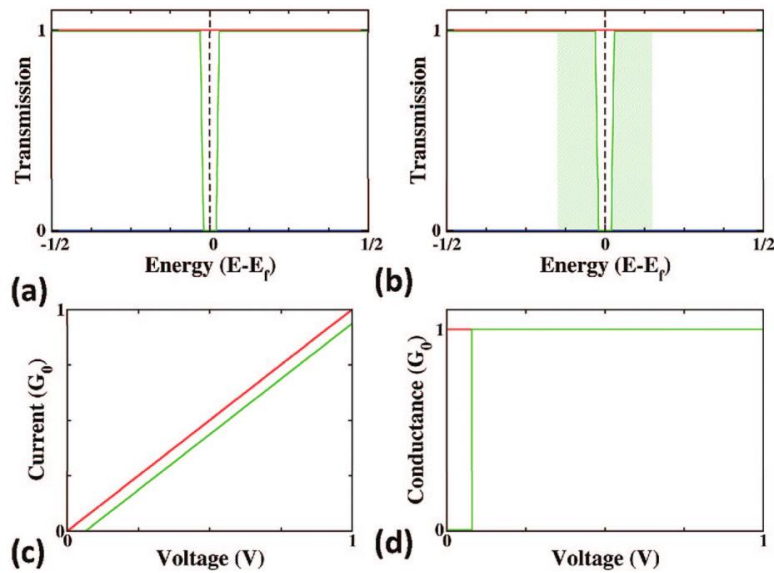


Fig 10 Transmission and current/voltage behavior of a voltage switch [12]

Fig 10 shows the relation between transmission plot, current/voltage plot and conductance/voltage plot. Red line represents the Au wire and the green line represents an ideal molecular switch. To calculate the current and conductance of (a), the transmission plot (assuming invariance to applied voltage) is integrated between the chemical potentials of the leads, shown as the shaded region in (b). Then we get the current/voltage plot and conductance/voltage plot through transmission plot.

The basic idea of quantum interference is that the different electron wave enhances or cancels each other. When the electron wave enhances each other, there will be constructive quantum interference, whereas will be destructive quantum interference. So the constructive quantum interference in the transmission plot will be showed as a peak, and the destructive quantum interference will be showed as a dip.

#### 2.4.2 Mach-Zehnder Resonance and Cyclic-Conjugated System

Mach-Zehnder resonance occurs when partial de Broglie waves of Energy  $E$  traveling different paths. They will be constructive or destructive [7]. This resonance can be seen in cyclic-conjugate system, which contains multiple-paths. The simplest system in this case is benzene ring. There are three different cases, para coupling, ortho coupling and meta coupling. After calculation, the meta case shows destructive quantum interference due to multipath zeroes [8]. This rule can be simply extended to a group of molecules which taken benzene as center. Like oligo(3)-phenylenevinylene (OPV3) derivatives, the constructive interference and destructive interference occur in para-OPV3 and meta-OPV3 respectively [11].

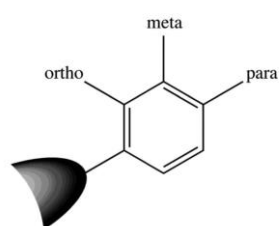


Fig 11 Three different ways to attach electrodes to benzene [8]

#### 2.4.3 Fano Resonance and Cross-Conjugated System

Fano resonance occurs when  $E$  coincides with the energy of a bound state located on a pendant group, which couples to a backbone state [7]. The model showed in Fig 12 can be used to explain the physics of Fano resonances.  $\epsilon_0$  is the backbone state and it couples to the leads.  $\epsilon$  represents the state on the side group, and it couples to  $\epsilon_0$  instead of the leads. At  $E = \epsilon$ , the transmission vanishes. This destructive quantum interference is between the direct path crossing the backbone and the path contains the side group. The instance is polyene.

The Fano resonance is insensitive to connectivity and Mach Zehnder resonance is connectivity dependent. When the system becomes bigger, the influence from two mechanisms will be difficult to be distinguished [8]. Like in the molecular wire containing anthraquinone units and pendant carbonyl groups, the Fano resonance and Mach-Zehnder resonance coexist [9].

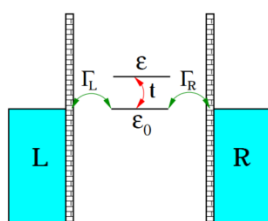


Fig 12 Schematic representation of a simple that illustrates the physics of Fano resonances [3]

### 3. Controlling the Interference Feature

The anchoring group can influence the single molecular conductance [10]. It may also influence the position of destructive quantum interference slightly, but the variation in anchoring group can't construct or destroy the destructive quantum interference of the single



molecule. Therefore, in this part, the controlling is mainly around tuning the central structure of molecule.

### 3.1 Adding Substituent

In generally, there are only two kinds of substituent. The electron-withdrawing group acts as acceptor and the electron-donating group acts as donor. If we only consider the influence from the substituent as electron acceptor or donor. The HOMO and LUMO will shift to higher energy due to donor, so the position of destructive quantum interference features in the transmission will be higher and vice versa. This prediction works on the cross-conjugated system like the system shown in Fig 13 (The one exception is the phenyl-substituted group shown in blue Fig 13 (a), where the increased electron delocalization provided by the aryl ring narrows the HOMO- LUMO gap.) [12].

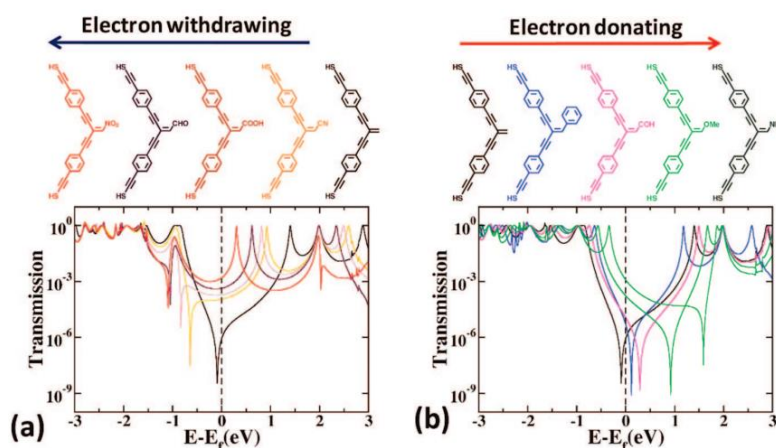


Fig. 13 Effect of (a) electron-withdrawing and (b) electron-donating groups attached to the cross-conjugated unit. [12]

But the story of aromatic hydrocarbon is much more complicated. As shown in Fig. 14, For a 1,3-linked benzene, an electron acceptor in position 2 is shown to have the same effect on the antiresonance energy as an electron donor in position 4 and vice versa. Substituents in position 5 have no effect on the antiresonance energy. The effects appear to be additive, such that a donor in position 2 will counteract a donor in position 4, leading to cancellation of the substituent effect [13]. This exist in all aromatic hydrocarbons. And counter- and nonactive substituent positions can be predicted by the diagrammatic approach in Ref [13].

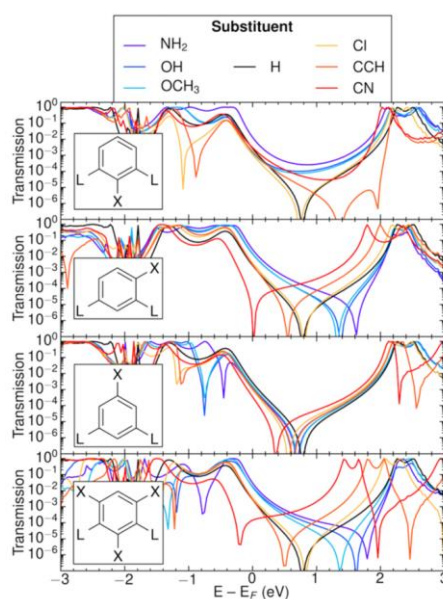


Fig. 14 Transmission of 1,3-linked benzene calculated with DFT [13]

### 3.2 Replication of Component

When we take a small molecule as a starting point and make partial or entire molecule repeated, the quantum interference of new molecule can be enhanced. The repeat can be divided into three types: 1) Repeat the linear part, which also means increasing the length; 2) Repeat the functional part; 3) Repeat entire molecule.

The cross-conjugated system can be a good example to explain the first and the second kind repeat. In cross-conjugated system, the pendant structure is the functional part. As described in Fig 15, two new groups of molecules still both keep the destructive quantum interference feature in transmission spectrum. But the interference minimums of them become incomparable from start. The HOMO-LUMO gap becomes smaller due to the increased conjugation length in Fig.15(a), and the transmission minimum decreases slowly. The HOMO-LUMO gap changes a little in Fig. 15(b), but the transmission minimum decreases quickly. It may be because the growth of the number of side group enhance leads to stronger Fano resonance.

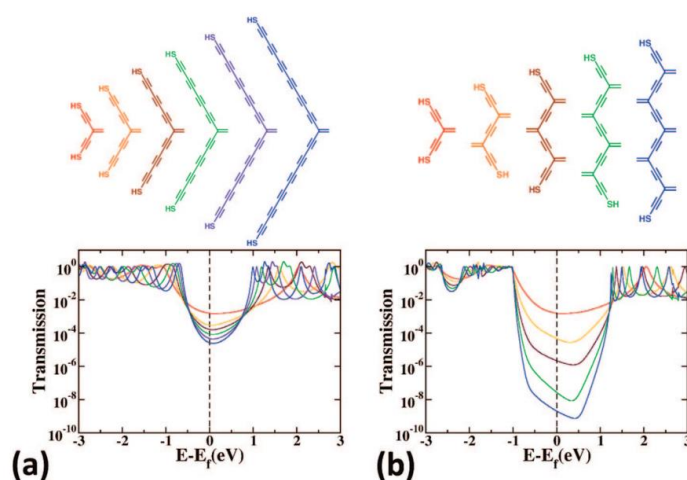


Fig. 15 The interference minimum with increasing molecular length. [12]

The para-connected benzene is considered to have constructive quantum interference. In Fig. 16, the entire unit is repeated and two para-connected benzene structures are connected between the same anchoring atoms. In this structure, the constructive quantum interference is confirmed to be enhanced [14].

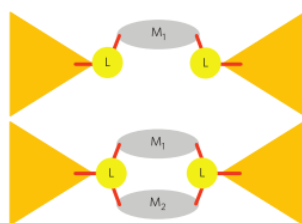


Fig. 16 Schematic representation of circuits with one (top) and two (bottom) molecular backbones (M) connected in parallel through common links. [14]

### 3.3 Different Anchoring Position

Back to the Fig 11, which shows different anchoring position choice on benzene, the theoretical work has already shown the destructive quantum interference will appear in the meta-connected benzene, but para-connected and ortho-connected will show constructive quantum interference [15-16]. And there are some other similar situations in Fig 17. Not only the single rings in Fig 17 but also multiple rings

structure[17-19] and the cross-conjugated structures [15, 20] show different quantum interference under different anchoring position. In molecular orbital view, they still hold the same molecular orbitals despite of different anchoring position. So the HOMO-LUMO view can help us interpret some quantum interference feature change, but it can't predict the destructive quantum interference in single molecule.

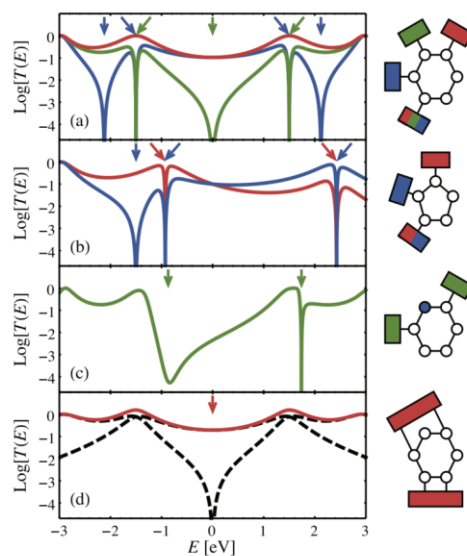


Fig 17 Transmission functions (left) and schematics (right). The arrows near the top of each transmission plot signify interferences predicted; in all cases, the theory in Ref [16] accurately identifies interference features. (a) Transport through a benzene molecule connected to the electrodes in the ortho (blue), meta (green), and para (red) configurations. (b) Transport through a five-membered ring connected in the 1,2 (blue) and 1,3 (red) positions. (c) Transport through a pyridine-like molecule connected at the 2 and 6 positions. (d) Transport through a benzene molecule that couples to each electrode at two sites (red) The dashed black lines show the independent transmission through the channels [16].

Instead of computation, there is a simple strategy developed by Markussen to judge if the molecule in can perform destructive quantum interference. The rule is that if, after removing all atoms in the shortest path between the electrodes, the atoms that remain cannot be grouped into neighboring pairs we predict interference [21]. The example application and the calculation confirmation are shown in Fig 18. However,

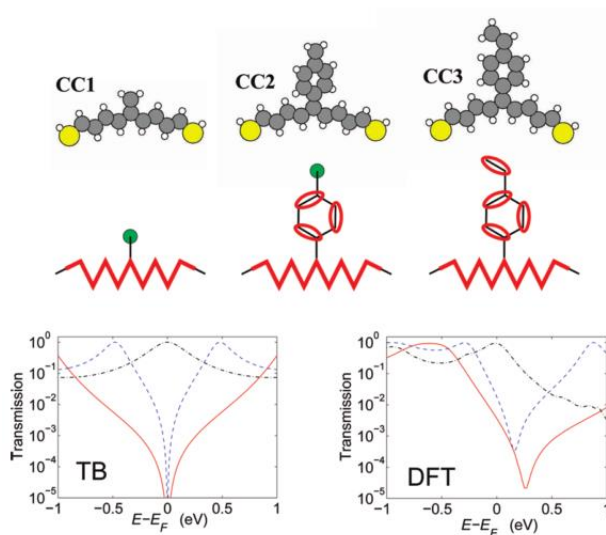


Fig 18. Molecular structures (top), application of the graphical QI scheme (middle), and transmission functions from TB models (bottom left) and DFT (bottom right) for three cross-conjugated molecules. The transmission function color code is as follows: CC1 (solid red), CC2 (dashed blue), CC3 (dashed-dotted black).

absolutely trusting this strategy is also dangerous. Fig 19 shows two examples that don't obey the rules put forward by Markussen. The molecule LC2 doesn't have ungrouped atom, but it shows destructive quantum interference. And the molecule CC2 have ungrouped atom, but it shows constructive quantum interference. This unnormal behavior is due to this two kind conjugated molecules containing closed loops. And a closed-loop molecule can be identified as having disconnected ring fragments when drawing a single path that connects the leads [22].

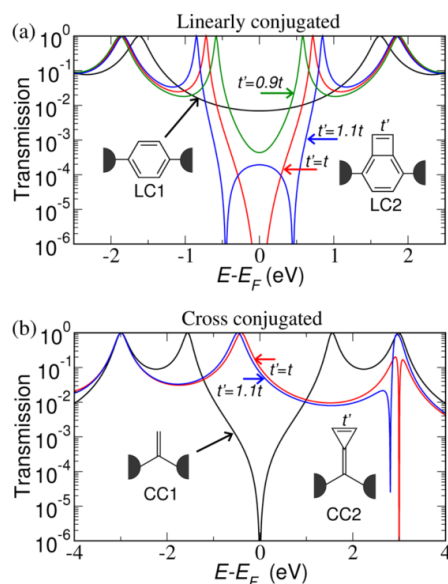


Figure 19. Transmission for a Hückel model with hopping  $t = -3\text{eV}$  between nearest-neighbor atoms for pairs of (a) linearly conjugated and (b) cross-conjugated molecules. The effect of bond length alternation is included by a modified hopping element  $t'$  for the bonds indicated in the insets [22]

### 3.4 Heteroatom-Substituted

When the heteroatom was introduced into aromatic hydrocarbon, the symmetry of system is broken and the molecular orbitals changed. Fig 20 shows the molecular orbitals of benzene and pyridine. The replacement of carbon makes the LUMO and HOMO nondegenerate. And the number of different kinds connection to leads increases.

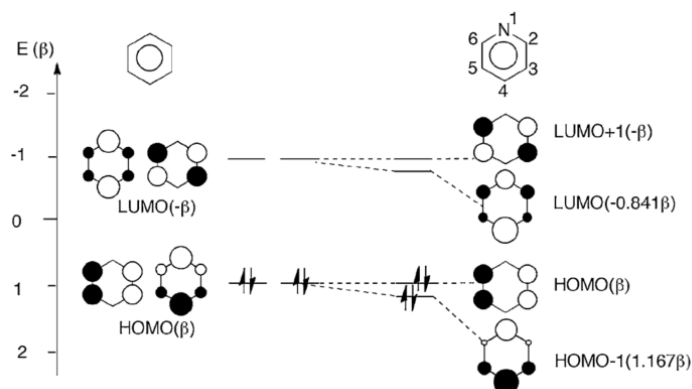


Fig. 20 Molecular orbitals diagram near the Fermi level of benzene and pyridine [23]

The heterocyclic aromatic hydrocarbon can be divided into two group, polyaromatic hydrocarbon (PAH) substituted structure and

linear conjugated hydrocarbon substituted structure.

In polyaromatic hydrocarbon substituted One of the carbon atoms within the “parent” PAH core is replaced by a heteroatom to yield a ‘daughter’ molecule. Take atoms  $i$  and  $j$  as anchoring position to the electrodes. The effect of heteroatom substitution onto an odd-numbered site is summarized by the following qualitative rules:

- (a) When  $i$  and  $j$  are odd, both parent and daughter have low conductances
- (b) When  $i$  is odd and  $j$  is even, or vice versa both parent and daughter have high conductances
- (c) When  $i, j$  are both even, the parent has a low conductance and the daughter a high conductance [24].

The example of naphthalene and quinolone can be used to verify this rule.

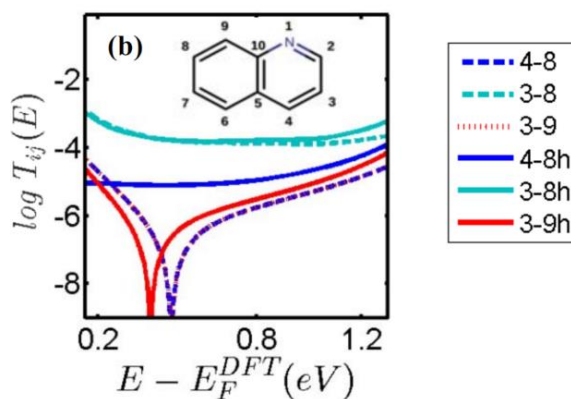


Fig. 21 DFT results for the corresponding the transmission coefficients  $T_{ij}(E)$  of the molecules connected to gold electrodes naphthalene parents (dashed lines) and quinolone daughters (solid lines) [24].

The linear conjugated hydrocarbon substituted structure is showed in Fig 22. In these kind single molecular junctions, the destructive quantum interference can be alleviated by the substitution, but the constructive quantum interference won't be effected. [25]

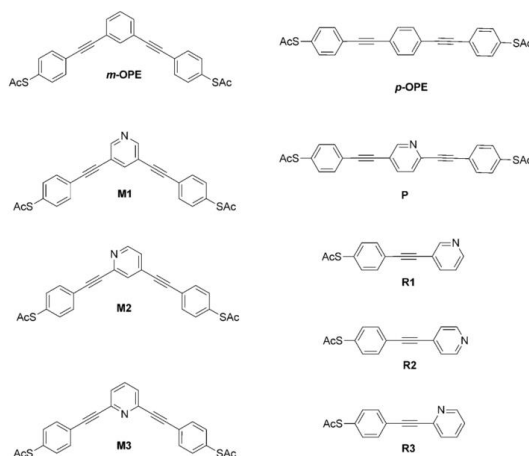


Fig 22. The linear conjugated hydrocarbon substituted structure [25]

#### 4. Conclusion

The electrons transport through the molecule by tunneling or hopping between different energy states of the molecule. **And The** molecule structure determines the energy states of the molecule. When we change the molecule structure, the performance of the molecule in molecular junction also becomes different. The empirical rule gives us a general direction to control the interference feature in the

molecular junction. Combined with the confirmation by calculation, we can design molecules with interference feature for potential application by those empirical rules. In the real environment, there will be a lot of molecules around the single molecular device. And the reactivity of single molecule is higher than in a group. The substitutes which almost **don't** have influence on the interference feature can be added on the single molecule structure to protect it by steric hindrance. Or replacing the carbon atom on some position by the heteroatom to improve the reactivity greatly with some specific ions/molecules, the behavior of single molecular device will be totally different after the reaction. This can be used to make sensors.

**There are many other potential functions can be achieved** by modifying the molecule structure. At the same time the biggest limitation of this approach is that the adjustment is based on the known structures. There are still many other unknown influencing factors and for big molecules, these small changes may be useless.

#### **Reference:**

- [1] Moore G. B Cramming more components onto integrated circuits,[Electronics, vol. 38[J]. Apr, 1965, 19: 114-117.
- [2] Aviram A, Ratner M A. Molecular rectifiers[J]. Chemical Physics Letters, 1974, 29(2): 277-283.
- [3] Scheer E. Molecular electronics: an introduction to theory and experiment[M]. World Scientific, 2010.
- [4] Cross Conjugation: Modern Dendralene, Radialene and Fulvene Chemistry[M]. John Wiley & Sons, 2016.
- [5] Aradhya S V, Venkataraman L. Single-molecule junctions beyond electronic transport[J]. Nature nanotechnology, 2013, 8(6): 399-410.
- [6] Ismael A K, Al-Jobory A, Grace I, et al. Discriminating single-molecule sensing by crown-ether-based molecular junctions[J]. The Journal of Chemical Physics, 2017, 146(6): 064704.
- [7] Lambert C J. Basic concepts of quantum interference and electron transport in single-molecule electronics[J]. Chemical Society Reviews, 2015, 44(4): 875-888.
- [8] Hansen T, Solomon G C, Andrews D Q, et al. Interfering pathways in benzene: An analytical treatment[J]. The Journal of chemical physics, 2009, 131(19): 194704.
- [9] Ismael A K, Grace I, Lambert C J. Connectivity dependence of Fano resonances in single molecules[J]. Physical Chemistry Chemical Physics, 2017, 19(9): 6416-6421.
- [10] Hong W, Manrique D Z, Moreno-Garcia P, et al. Single molecular conductance of tolans: experimental and theoretical study on the junction evolution dependent on the anchoring group[J]. Journal of the American Chemical Society, 2012, 134(4): 2292-2304.
- [11] Arroyo C R, Frisenda R, Moth-Poulsen K, et al. Quantum interference effects at room temperature in OPV-based single-molecule junctions[J]. Nanoscale research letters, 2013, 8(1): 234.
- [12] Andrews D Q, Solomon G C, Van Duyne R P, et al. Single molecule electronics: increasing dynamic range and switching speed using cross-conjugated species[J]. J. the American Chemical Society, 2008, 130(51): 17309-17319.
- [13] Garner M H, Solomon G C, Strange M. Tuning Conductance in Aromatic Molecules: Constructive and Counteractive Substituent Effects[J]. The Journal of Physical Chemistry C, 2016, 120(17): 9097-9103.
- [14] Vazquez H, Skouta R, Schneebeli S, et al. Probing the conductance superposition law in single-molecule circuits with parallel paths[J]. Nature Nanotechnology, 2012, 7(10): 663-667.
- [15] Sam-ang P, Reuter M G. Characterizing Destructive Quantum Interference in Electron Transport[J]. arXiv preprint arXiv:1702.01341, 2017.
- [16] Reuter M G, Hansen T. Communication: Finding destructive interference features in molecular transport junctions[J]. 2014.
- [17] Xia J, Capozzi B, Wei S, et al. Breakdown of interference rules in azulene, a nonalternant hydrocarbon[J]. Nano letters, 2014, 14(5): 2941-2945.
- [18] Taniguchi M, Tsutsui M, Mogi R, et al. Dependence of single-molecule conductance on molecule junction symmetry[J]. Journal of the American Chemical Society, 2011, 133(30): 11426-11429.
- [19] Mayor M, Weber H B, Reichert J, et al. Electric current through a molecular rod—relevance of the position of the anchor groups[J]. Angewandte Chemie International Edition, 2003, 42(47): 5834-5838.

- [20] Andrews D Q, Solomon G C, Goldsmith R H, et al. Quantum interference: The structural dependence of electron transmission through model systems and cross-conjugated molecules[J]. *The Journal of Physical Chemistry C*, 2008, 112(43): 16991-16998.
- [21] Markussen T, Stadler R, Thygesen K S. The relation between structure and quantum interference in single molecule junctions[J]. *Nano letters*, 2010, 10(10): 4260-4265.
- [22] Pedersen K G L, Borges A, Hedegård P, et al. Illusory connection between cross-conjugation and quantum interference[J]. *The Journal of Physical Chemistry C*, 2015, 119(48): 26919-26924.
- [23] Li X, Staykov A, Yoshizawa K. Orbital views of the electron transport through heterocyclic aromatic hydrocarbons[J]. *Theoretical Chemistry Accounts*, 2011, 130(4-6): 765-774.
- [24] Sangtarash S, Sadeghi H, Lambert C J. Exploring quantum interference in heteroatom-substituted graphene-like molecules[J]. *Nanoscale*, 2016, 8(27): 13199-13205.
- [25] Liu X, Sangtarash S, Reber D, et al. Gating of Quantum Interference in Molecular Junctions by Heteroatom Substitution[J]. *Angewandte Chemie International Edition*, 2017, 56(1): 173-176.
- [26] Landauer R. Spatial variation of currents and fields due to localized scatterers in metallic conduction[J]. *IBM Journal of Research and Development*, 1957, 1(3): 223-231.
- [27] Reimers J R. Computational Methods for Large Systems[J]. *Electronic Structure Approaches for Biotechnology and Nanotechnology*, 2011.
- [28] Kim W Y, Choi Y C, Min S K, et al. Application of quantum chemistry to nanotechnology: electron and spin transport in molecular devices[J]. *Chemical Society Reviews*, 2009, 38(8): 2319-2333.
- [29] Neaton J B, Hybertsen M S, Louie S G. Renormalization of molecular electronic levels at metal-molecule interfaces[J]. *Physical review letters*, 2006, 97(21): 216405.
- [30] Emberly E, Kirczenow G. Electrical conductance of molecular wires[J]. *Nanotechnology*, 1999, 10(3): 285.
- [31] Guédon C M. Molecular charge transport: relating orbital structures to the conductance properties[M]. Leiden Institute of Physics (LION), Faculty of Science, Leiden University, 2012.
- [32] Cuniberti G, Fagas G, Richter K. *Introducing Molecular Electronics*[M]. New York: Springer, 2010.