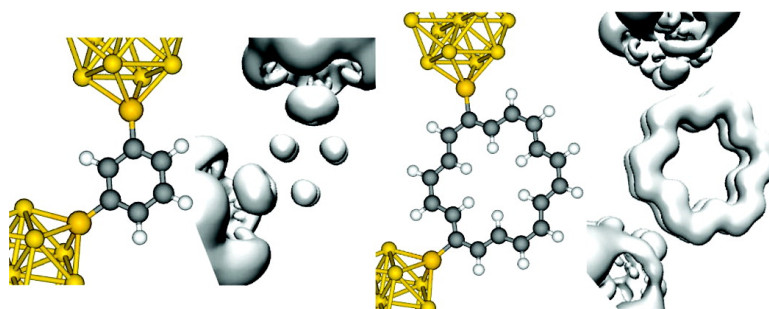


Quantum-Interference-Controlled Molecular Electronics

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Quantum-Interference-Controlled Molecular Electronics

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ABSTRACT

Quantum interference in coherent transport through single molecular rings may provide a mechanism to control the current in molecular electronics. We investigate its applicability, using a single-particle Green function method combined with ab initio electronic structure calculations. We find that the quantum interference effect (QIE) is strongly dependent on the interaction between molecular π -states and contact σ -states. It is masked by σ tunneling in small molecular rings with Au leads, such as benzene, due to strong π - σ hybridization, while it is preserved in large rings, such as [18]annulene, which then could be used to realize quantum interference effect (QIE) transistors.

The use of single molecules as functional devices is the ultimate end of the ongoing trend toward the miniaturization of electronic circuits.^{1–3} Despite significant progress that has been made in the past decade, several issues still challenge the realization of molecular electronics, notably, the sensitivity and control of molecule–lead contacts.^{4–6} Recently, Cardamone et al.^{7,8} proposed a novel mechanism to control electron transport through single molecular rings: the current is determined by the degree of destructive or constructive quantum interference between the two paths around a symmetric molecule. Such interference can be controlled by a third terminal providing elastic scattering or dephasing. Their use of a quantum interference effect (QIE) in the completely coherent quantum regime builds on previous work in semiconductor nanostructures^{9,10} and molecular nanostructures.^{11–16} Because the QIE stems essentially from the symmetry of a molecular device, it should not be affected significantly by the structure of the molecule–lead contact. We present the first study of this novel mechanism in realistic ab initio calculations.

QIE-controlled molecular electronics were proposed,^{7,8} using a model calculation for a benzene ring in which only the π molecular states were considered. The connection between the leads and the molecular states was treated phenomenologically, and the possibility of induced structural relaxation was ignored. Because these simplifications could have a big effect on the conductance, it is critical to investigate the validity of the QIE mechanism in realistic systems and to evaluate the factors that affect it.

In this paper, we investigate the QIE mechanism by performing quantum transport calculations for two molecular rings: one small (benzene) and one large ([18]annulene). We adopt a standard single-particle Green function method,^{17,18} combined with ab initio electronic structure calculations in which all the above-mentioned factors are fully taken into account. Two different electrodes (leads) are studied: gold, which has π - σ molecule–lead coupling, and a metallic (5,5) carbon nanotube (CNT), which has strong π - π coupling.

Our calculations show that the survival of the QIE mechanism is strongly dependent on the interaction between the molecular π -states and the contact σ -states. It is masked by σ tunneling in the small benzene–Au system, because of the strong π - σ hybridization, while it is preserved in the large [18]annulene/Au system, which then could be used to realize QIE transistors. With the CNT leads, we find that strong π - π molecule–lead coupling can significantly modify the QIE but does not destroy it.

Our method for calculating electron transport through molecular junctions has been described in detail previously;¹⁸ it combines a Landauer approach to transport with ab initio electronic structure methods.^{19–26} In particular, we use here density functional theory (DFT)²⁷ in the local density approximation (LDA), hybrid DFT in the B3LYP version,^{28,29} and Hartree–Fock (HF) theory. Several energy functionals are used to ensure that the conclusions are generally valid, because, to date, no functional is completely accurate for transport calculations. Usually, DFT-LDA and HF are the two extremes: the former overestimates the conductance and the latter underestimates the conductance.³⁰ The wave functions are expanded using a Gaussian 6-311G** basis

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set for the C, H, and S atoms, and a CRENBS basis set for Au atoms.³¹

Practically, the lead–molecule–lead system is divided into three parts: left lead, right lead, and device region. The latter contains the molecule plus parts of the leads to accommodate the molecule–lead interaction (see structures below). The self-consistent DFT or HF Hamiltonian of the device region plus the self-energies of the two semi-infinite leads, $\Sigma_{L,R}(E)$, are used to construct a single-particle Green function, $G_D(E)$, from which the transmission coefficient as a function of energy is calculated: $T(E) = \text{Tr}[\Gamma_L G_D \Gamma_R G_D^\dagger]$, where $\Gamma_{L,R}(E) = i[\Sigma_{L,R}(E) - \Sigma_{L,R}^\dagger(E)]$ is the coupling to the left or right lead. The conductance (G) then follows from a Landauer-type relationship.

For the benzene ring, we consider only gold leads. The self-energy due to the Au within the leads is treated in the wide band limit (WBL) approximation: $\Gamma(E) = -\gamma I$, with $\gamma = 3.0$ eV.³² But note that the key molecule–lead coupling is included explicitly in the Hamiltonian, because nine Au atoms are included in the central device region. Because the density of states of gold is quite flat around the Fermi energy, the use of the WBL for Au atoms is reasonable. For the large [18]annulene ring, we consider gold leads for benzene as well as (5,5) metallic carbon nanotube leads for which the self-energy is obtained via the ab initio calculation of atomic leads. For all systems, the atomic structure of the junction, including the molecule–lead separation, is optimized³³ by minimizing the atomic forces on atoms to be smaller than 0.02 eV/Å.

Let us start with the small system: the benzene ring in Figure 1a. All of the Au atoms included in the device region are shown; the WBL self-energy is applied to these atoms. The S atom is situated on a hollow site. Two structural configurations are considered: (1,4) and (1,3), in Figures 1a and 1b, respectively. The (1,4) configuration has constructive interference in the all- π model (the phase difference between the two paths around the ring is 0), whereas the (1,3) configuration has destructive interference (the phase difference is π).^{7,8} Still within the all- π model, the nonequilibrium many-body physics was subsequently studied in detail for these two configurations.³⁴

The transmission $T(E)$ found using several functionals is shown in Figures 1d and 1e. First, note that the transmission gap is dependent on the functional as expected: it increases in the order LDA, B3LYP, and HF. Also, the LDA equilibrium conductance for the (1,4) configuration is consistent with previous calculations ($\sim 0.1 G_0$).^{35–37} The key result here is the comparison between the (1,4) and (1,3) configurations. The all- π model predicts that the (1,3) configuration has a transmission node at the Fermi energy E_F that is due to total destructive interference.^{7,8} However, in our more-realistic calculation, this transmission node does not occur. For LDA and B3LYP, $G_{(1,3)}$ is smaller than $G_{(1,4)}$, by a factor of ~ 2 . For HF, the order is even reversed: $G_{(1,3)} > G_{(1,4)}$.

Several factors may destroy the perfect destructive interference present in the model described in refs 7 and 8: (i) lead-induced structural relaxation, which breaks the sym-

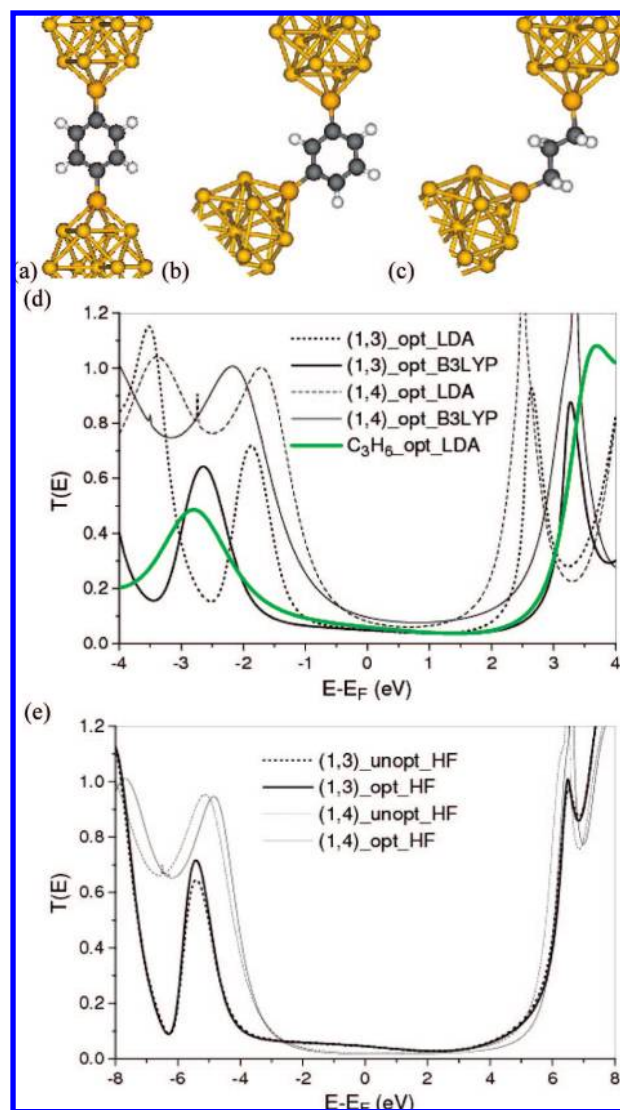


Figure 1. Optimized structures of the Au–S–benzene–S–Au system (device region only) with (a) the (1,4) constructive interference configuration and (b) the (1,3) destructive interference configuration. (c) The alkane configuration used for comparison. (d,e) Transmission functions obtained with different energy functionals. For the HF calculation, we consider cases both with and without the lead-induced molecular relaxation, as indicated. Note the absence of a clear difference between the (1,3) and (1,4) cases.

metry; (ii) the influence of the σ states; and (iii) beyond nearest-neighbor interactions, which cause other paths. Let us first examine the effect of structural relaxation using the HF calculation: results for relaxed and unrelaxed structures are compared in Figure 1e. The effect on $T(E)$ is clearly minor. Because of the symmetry of the additional paths, the effect of factor (iii) should also be small. Thus, we conclude that factors (i) and (iii) are not important.

The first hint of the strong effect of σ hybridization comes from the difference between the transport gap in Figure 1 and the HOMO–LUMO gap of an isolated benzene molecule. In LDA, for instance, the former is ~ 4.1 eV while the latter is 5.2 eV. This suggests that the HOMO and LUMO resonances may not be dominated by benzene π -states. To check this, in Figure 2, we plot the LDA local density of states (LDOS) both for the HOMO resonance (-2.5 eV to

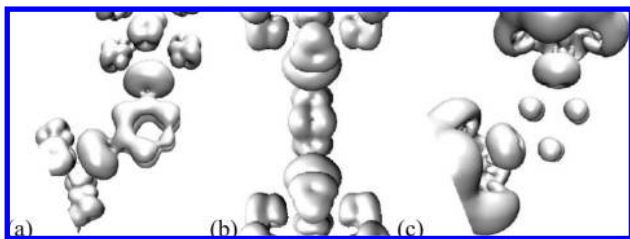


Figure 2. Local density of states (LDOS) for the (1,3) benzene/Au system using LDA. (a) Top view and (b) side view for the energy window $[-2.5, -1.0]$ eV (HOMO resonance) in Figure 1d. (c) Top view for the energy window $[-0.2, 0.2]$ eV. The influence of the σ bonds is clear in panels a and b.

-1.0 eV) and for near the Fermi energy (-0.2 to 0.2 eV). Figures 2a and 2b show that the HOMO resonance has large contributions from the contact Au–S states. Even in the benzene ring, the σ character is remarkable. Because of this strong π – σ hybridization, transport near the Fermi energy E_F consists largely of tunneling through the σ -states rather than through the π -ring, as clearly shown by the LDOS around E_F in Figure 2c. To further examine this conclusion, we replace the benzene ring with a σ -bonded C_7H_{14} molecule (see Figure 1c). $T(E)$ in Figure 1d (green line) shows that the conductance is very close to that of the (1,3) system, which suggests a similar transport mechanism. This shows directly that the conductance in the (1,3) configuration mainly comes from σ -tunneling, which masks the QIE effect.

Next, we turn to the larger [18]annulene ring, shown in Figure 3. We consider two configurations that yield destructive interference in the π -only model— $(1,7)$ and $(1,9)$ —and one constructive configuration— $(1,10)$. From the $T(E)$ given by LDA, B3LYP, and HF, one sees the same trend in the transport gap and in the equilibrium conductance: the smallest conductance is given by HF with the largest gap, which is ~ 1 order of magnitude smaller than the LDA result, which is consistent with a previous result for other long-chain molecules.³⁰ The key feature here is that the conductance for the $(1,7)$ and $(1,9)$ configurations is much smaller than that for the $(1,10)$ configuration, by ~ 2 orders of magnitude. *This indicates that, in contrast to benzene, the ideal destructive interference is largely preserved.*

To understand this, in Figure 4 we show the LDA LDOS near both the HOMO resonance (-1.0 eV to -0.2 eV) and the Fermi energy (-0.2 to 0.2 eV). One sees that the HOMO resonance is dominated by the [18]annulene π -states, and transport near the Fermi energy is basically through the π -ring. Because of the near-perfect destructive interference of the π -transmission,^{7,8} the residual conductance should come from σ -bond tunneling. To check this, we replace the [18]annulene ring with a σ -bonded C_7H_{14} chain (see Figure 3d). The $T(E)$ (the green line in Figure 3e) yields a conductance very close to that of the $(1,7)$ configuration, confirming our view.

How does one understand the difference in behavior between the small benzene ring and the large [18]annulene ring? The answer lies in the energies of the molecular levels. In LDA, for example, the energy of benzene π -states (HOMO) is -6.5 eV, which is in the energy window of the

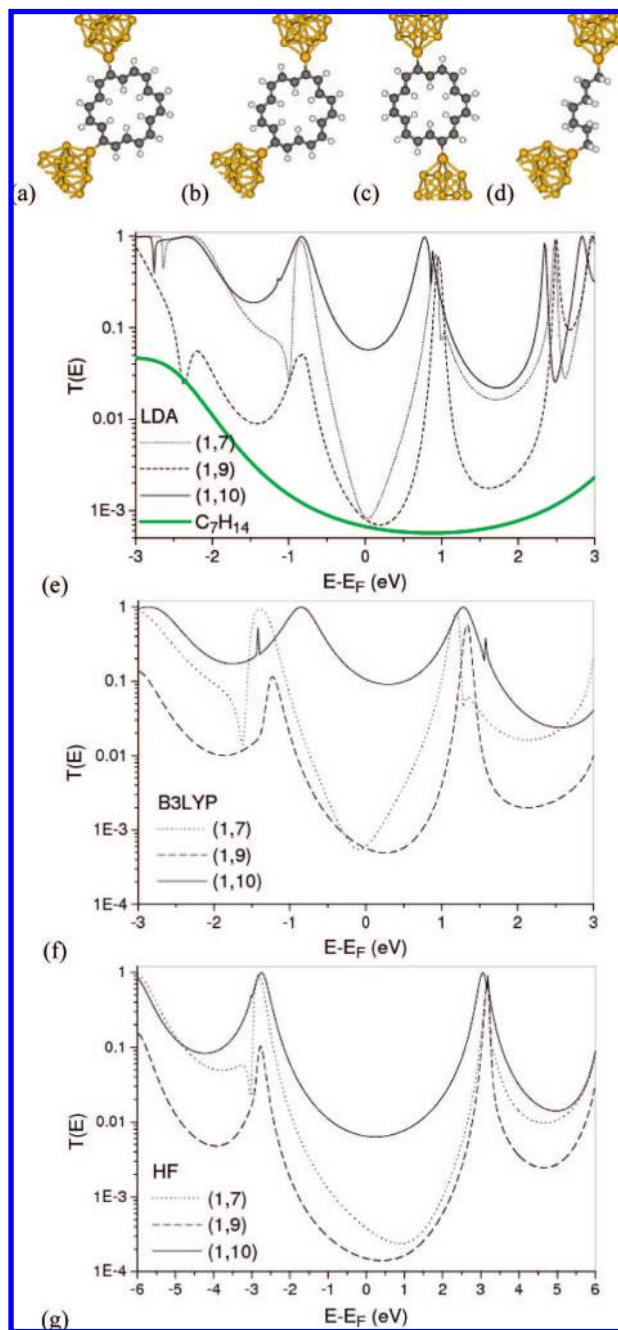


Figure 3. Optimized structures for Au–S–[18]annulene–S–Au (device region only) with (a) $(1,7)$, (b) $(1,9)$, and (c) $(1,10)$ lead configurations. (d) The alkane structure used for comparison. Transmission functions are given in (e) LDA, (f) B3LYP, and (g) HF. Note the clear difference between configurations with destructive and constructive interference.

Au–S bonding at the contact, from -7.0 to -5.7 eV. The larger size of [18]annulene means that its π -states (HOMO) are higher in energy, at -5.0 eV, which is well above the energy window of the Au–S bonding. Consequently, in [18]annulene, the π -orbital becomes the frontier orbital, which, therefore, dominates transport.

From this picture, one can see that the advantage of using larger conjugated molecules is 2-fold: First, the resulting π -dominated transport preserves the simple QIEs. Second,

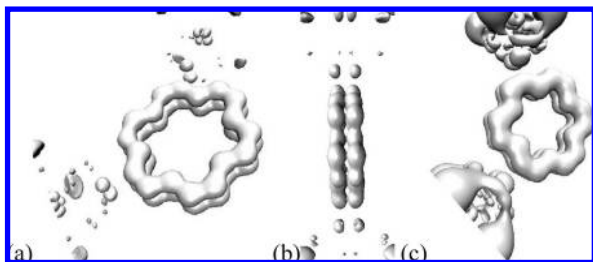


Figure 4. LDOS for the (1,7) [18]annulene/Au system from LDA: (a) top view and (b) side view for the energy window $[-1.0, -0.2]$ eV (HOMO resonance) in Figure 3e, and (c) top view for the energy window $[-0.2, 0.2]$ eV (Fermi energy). The π -orbital signature is clear.

the longer length suppresses σ -tunneling, which leads to a larger on/off ratio.

While Au electrodes have some advantages, they have a severe disadvantage as well: the contact transparency is poor (despite the strong chemical bond), which leads to a small equilibrium conductance, even in the case of constructive interference. For a more favorable case with strong coupling near the Fermi energy E_F , we use a metallic (5,5) carbon nanotube as a lead, connecting to the molecule through a five-membered ring.³⁸ The optimized structures are shown in Figure 5 for the (1,10) and (1,7) configurations; both have a coplanar structure, which provides overall conjugation and, thus, strong molecule–lead π – π coupling.

The strong molecule–lead coupling leads to a metal-induced gap state traveling into the molecule.³⁸ For short conjugated molecules, the two states originating from the two leads will meet in the molecule, causing a resonance peak in $T(E)$ around E_F . This is just what we see in Figure 5c for the constructive (1,10) configuration. [For $T(E)$ here, we do not use the WBL, but rather find the lead self-energy from an atomistic ab initio calculation.] The resonance peak decays as we artificially increase the molecule–lead separation (weaken the coupling), as shown in Figure 5c. For the destructive (1,7) configuration (see Figure 5d), an *antiresonance* peak appears at E_F , which indicates that the destructive interference applies in the strong coupling limit to the metal-induced gap state (although the antiresonance is rather narrow). For larger molecule–lead separation (weaker coupling), the antiresonance becomes wider and deeper; thus, the molecule–lead coupling significantly affects the quantum interference but does not destroy it. Note that, here, the metal-induced gap state leads to a much-larger constructive conductance and a larger on/off ratio, compared to that observed with the case of Au leads.

The effective destructive quantum interference can be used to control electric current through single molecular devices. To demonstrate this explicitly, we propose a model device structure, shown in Figure 6, using a Au–S–[18]annulene–S–Au (1,7) junction, where a local gate potential (due to an STM tip, for instance) is applied to a portion of the molecular ring, which will partially destroy the destructive interference, because of the additional scattering, depending on the gate voltage (V_g). The calculation is performed using the B3LYP functional. The computational techniques for transport in the

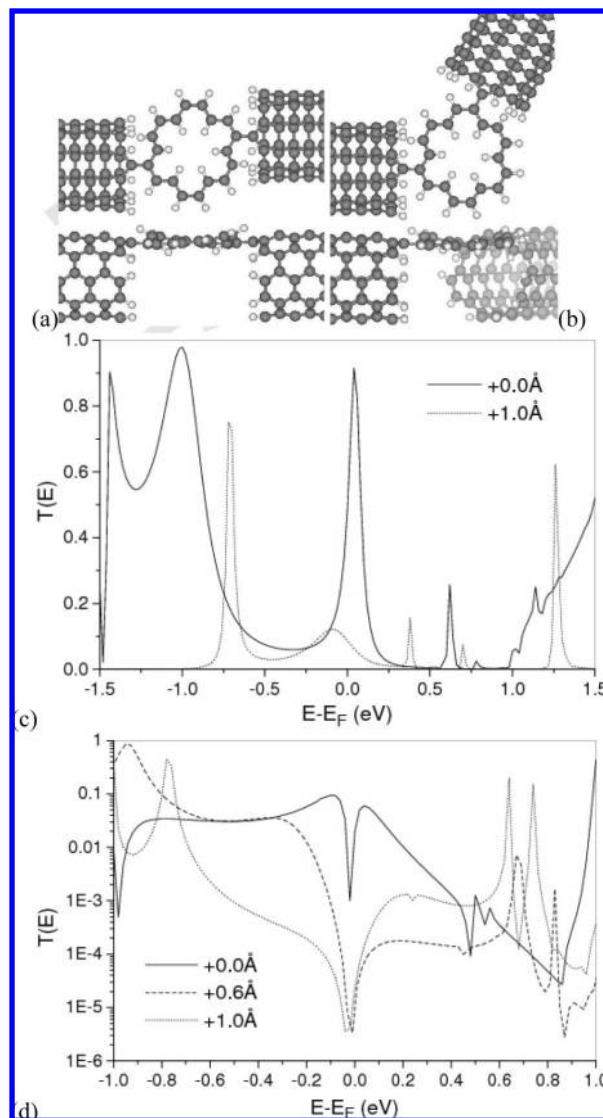


Figure 5. Optimized structures of the five-membered-ring-connected (5,5)CNT-[18]annulene-(5,5)CNT junctions with the lowest total energies: (a) constructive (1,10) and (b) destructive (1,7) configurations. Their transmission functions for different molecule–lead separations (indicated in the legend) are given in panels c and d, respectively. Note the resonance peak around the Fermi energy E_F in panel c and the antiresonance peak in panel d.

presence of a local gate potential shift has been described previously.³⁹ Figure 6b shows the transmission functions for different gate voltages. One can see that a small gate voltage can significantly modify the transmission function of the device, both shifting and greatly distorting the transmission valley. Most importantly, a small gate voltage can increase the equilibrium conductance by up to 3 orders of magnitude, which is a good behavior for field-effect QIE transistors.

We would like to finish this letter with a comment about the effect of molecular thermal vibration on QIE. For non-interference-related electron transport through single molecules that are not very long, molecular vibration should have a very small effect on the current–voltage (I – V) characteristics, because the transport is basically ballistic as long as extremely soft vibrational modes (which may lead to conformational changes) are absent. For QIE, the relevant

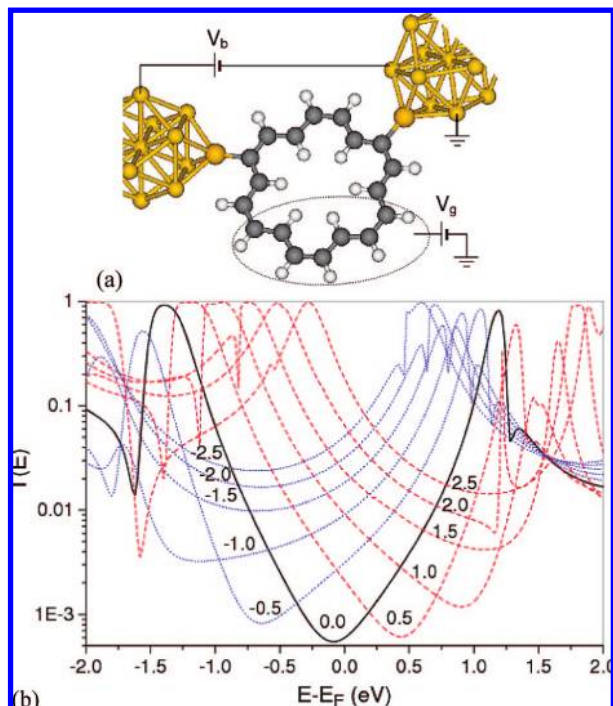


Figure 6. (a) Schematic drawing of an [18]annulene-based field-effect QIE transistor. The source–drain current is controlled by the gate voltage V_g , which causes elastic scattering in the gated region. The transmission functions for zero bias ($V_b = 0$) and different V_g are given in panel b.

vibrational modes are those that change the length difference between the two paths. Therefore, these modes involve changing the C–C bond length and have very high frequencies. As a result, the effect of molecular vibration on QIE for room temperature can be expected to be small.

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- (33) The structure optimization calculations are performed by using a numerical basis set of double- ζ plus polarization (DZP)⁴⁰ combined with the use of optimized Troullier–Martins pseudo-potentials.⁴¹ The generalized gradient approximation in the version of PBE⁴² is adopted for the exchange and correlation.
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