

Ab initio study of single molecular transistor modulated by gate-bias

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Abstract

We use a self-consistent method to study the current of the single molecular transistor modulated by the transverse gate-bias in the level of the first-principles calculations. The numerical results show that both the polyacene-dithiol molecules and the fused-ring oligothiophene molecules are the potential high-frequency molecular transistor controlled by the transverse field. The long molecules of the polyacene-dithiol or the fused-ring thiophene are in favor of realizing the gate-bias controlled molecular transistor. The theoretical results suggest the related experiments.

I. INTRODUCTION

Using organic molecules as functional units for electronic apparatus application is an interesting goal of nanoelectronic devices.^{1,2} The common and important function of these devices is that the current can be controlled effectively. In the last several years, many experimental and theoretical works were carried out to study the transport properties through a single molecule, or even to design the molecular electronic devices.^{3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28} At present, people have realized two major approaches to control molecular transport. One is through the conformational change in the molecule, the other is through the external transverse field to switch the molecule from an “on” to an “off” state. Many authors have focused their attention on the former one for a long time.^{20,21,22,23,24,25} Despite the conformational change in the molecule can be achieved by using the electric or light fields, its operational frequency is low. Now, the attention is transferred to the latter one due to its high operation frequency. Several experiments have identified their feasibility.^{26,27,28} Currently, the π -conjugated organic oligomers and polymers are the subject of considerable research interest in the organic semiconductors. The organic semiconductors can be employed as active layers in the field effect transistors (FET).²⁶ The gate-bias controlled molecular transistor is successfully achieved experimentally²⁸ from perylene tetracarboxylic diimide (PTCDI), a redox molecule. Recently, the current behavior of the single molecule has received increasing attention. Single organic oligomers such as pentathienoacene (PTA), pentacene, perylene and so on are all the key objects in the theoretical study. But at present, few theoretical work sheds light on the organic molecular transistor controlled by the transverse field. The rigorous treatment of the molecular device in theory calls for the combination of the theory of quantum transport with the first-principles calculations of the electronic structure in the self-consistent scheme. In this paper, we use the density functional theory (DFT) and non-equilibrium Green’s function to study the transverse field effect (TFE) on current transport of the single organic oligomer.

II. THEORY AND METHODS

The retarded Green's function of the molecule is expressed as follows

$$G_M^R = (E^+ S_M - F_M - \Sigma_1^R - \Sigma_2^R)^{-1}, \quad (1)$$

where S_M and F_M are the overlap matrix and Fock matrix of the molecule part, respectively. Σ_1^R (Σ_2^R) is the retarded self-energy of the left (right) electrode. It should be emphasized that the Fock matrix is obtained after the density matrix is obtained.

The density matrix of the open system is the essential function of the whole self-consistent scheme. It can be achieved by the Keldysh Green's function

$$\rho = \int_{-\infty}^{\infty} dE [-iG^<(E)/2\pi], \quad (2)$$

$$-iG^< = G_M^R (f_1 \Gamma_1 + f_2 \Gamma_2) G_M^A, \quad (3)$$

with the advanced Green's function $G^A = (G^R)^\dagger$, the broadening function of the left (right) lead Γ_1 (Γ_2). The Fermi distribution function of the left (right) lead f_1 (f_2) is expressed $f_i(E) = 1/(e^{(E-\mu_i)/kT} + 1)$ with $\mu_1 = E_f - \frac{1}{2}eV$, $\mu_2 = E_f + \frac{1}{2}eV$. E_f is Fermi level of the bulk Au. In our work, E_f is -5.1 eV which is an adjusted parameter around its work function (5.31 eV) for explaining experimental results.^{30,31}

If the transverse field is applied perpendicular to the transport direction, the corresponding potential energy term is included in the Fock operator

$$V_{E\perp}(\vec{r}) = e\vec{E}_\perp \cdot \vec{r}. \quad (4)$$

Our model is illustrated in Fig. 1 with the molecule attached by the gold electrodes from the both sides and the transverse electric field confined inside the molecule region. The potential zero point is set at the coordinate origin, the center of the line connecting two sulfur atoms and the whole molecule is not symmetric to the Au-S bond. Since the transverse field is localized in the molecule, its edge effect is very weak so that it almost has no effect on the electrodes. In the calculation, the applied longitudinal voltage points to the current direction shown in Fig. 1. The molecule is chemisorbed on the gold contacts by sulfur atoms. The sulfur atom sits on the hollow position of three nearest-neighbor surface gold atoms. The perpendicular distance between the sulfur atom and the gold FCC (111) surface plane is 2.0 Å, an usually acceptable distance. The temperature effect is not distinct for the short molecule, so we assume zero temperature in our calculation for simplicity.

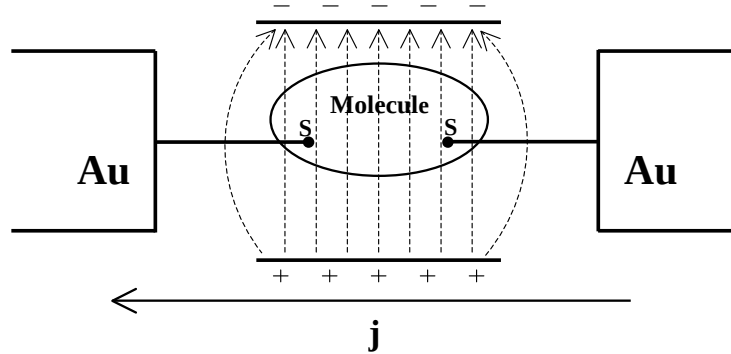


FIG. 1: Au lead-Molecule-Au lead open system. The molecule is chemisorbed to Au leads by sulfur atoms and is not symmetric to the Au-S bond. This transverse field is confined inside the molecule region without effect on Au leads.

The density matrix for the open system should be obtained self-consistently. In order to achieve this goal, we extended the inner loop in the standard quantum chemistry software GAUSSIAN03³¹ to the loop composed of the lead-molecule-lead open system under bias. At the beginning, the self-consistent procedure starts from a guess for the density matrix of the open system, which may be obtained from the converged density matrix of GAUSSIAN03 calculation for the isolated molecule. We feedback the density matrix to the GAUSSIAN's main program as a subroutine to obtain the new density matrix. The iterations continue until the density matrix converges to the acceptable accuracy (usually less than 10^{-5}). Then the density matrix is used to evaluate the transmission function (T), the terminal current, the electron number and the density of states (DOS) of the open system.^{29,30} In the calculations, we adopt DFT with B3PW91 exchange-correlation potential and LANL2DZ basis to evaluate the electronic structure and the Fock matrix. The basis set associates with the effective core potential (ECP), which are specially suited for the fifth-row (Cs-Au) elements including the Darwin relativistic effect.

III. RESULTS AND DISCUSSION

The sulfur atom in thiophene is sp^2 hybridized, and its p-orbital provides two electrons to the π system. The linearly condensed thiophene molecules possess the extended π conjugation and the high planarity. Of the cyclic single organic molecules, the thiophene-based compound is one of the promising class of organic materials. PTA is attractive, due to the stability of the thiophene ring and the good planarity.²⁶ Fig. 2 gives the DOS and T of PTA with the different transverse gate biases. The position of the broadened levels in equilibrium for the open system is determined by the singular points of the Green's function, obtained from equation $(F + \Sigma_1 + \Sigma_2)C = SC\lambda$. The molecular levels are modulated by the gate bias applied to the molecule with HOMO (LUMO) position at -6.47 (-3.93) eV for $V_g = -3.90$ V (a); -6.27 (-3.77) eV for $V_g = -1.95$ V (b); -6.09 (-3.60) eV for $V_g = 0$ V (c); -5.93 (-3.42) eV for $V_g = +1.95$ V (d), and -5.79 (-3.24) eV for $V_g = +3.90$ V (e). With decrease of the positive gate bias, the separation between HOMO and Fermi level increases, and the separation between LUMO and Fermi level decreases. For the positive gate bias $V_g \geq 0$, the Fermi level is close to HOMO, and PTA is the p-type or hole conduction molecule, while for the big negative bias PTA is the n-type or electron conduction molecule. For large positive bias $V_g = +3.90$ V, the HOMO, close to E_f , contributes to the initial rise of the current under the small applied voltage (1.0 V or so) in the longitudinal direction. Meanwhile LUMO is close to E_f in the case of large negative bias $V_g = -3.90$ V, it is responsible for the molecular conduction (Fig. 3). Fig. 2 illustrates that In Fig. 3 the gate bias successfully modulates the I-V characteristics of the PTA. At the voltage $V > -2.3$ V, due to the contribution from HOMO, the positive gate bias achieves the bigger molecular current and at the voltage $V < -2.3$ V, as LUMO enters the voltage window and contributes the molecular conduction, the inverse order of current appears. The inset illustrates the α electron number deviation from the equilibrium state as a function of bias. At applied voltage $V > -2.3$ V, for gate bias $V_g = -3.90$ V, the electron is responsible for the conduction ($N > N_0$) and electron number rises slowly, while for $V_g \geq -1.95$ V, the hole is responsible for the conduction ($N < N_0$), so electron number descends (the electron flows out of the molecule to the lead). At applied voltage $V < -2.3$ V, the molecule enters the electron- and hole- hybrid conduction region, accompanying the rapid rise of electron number, which means the electron contribution dominates the conduction.

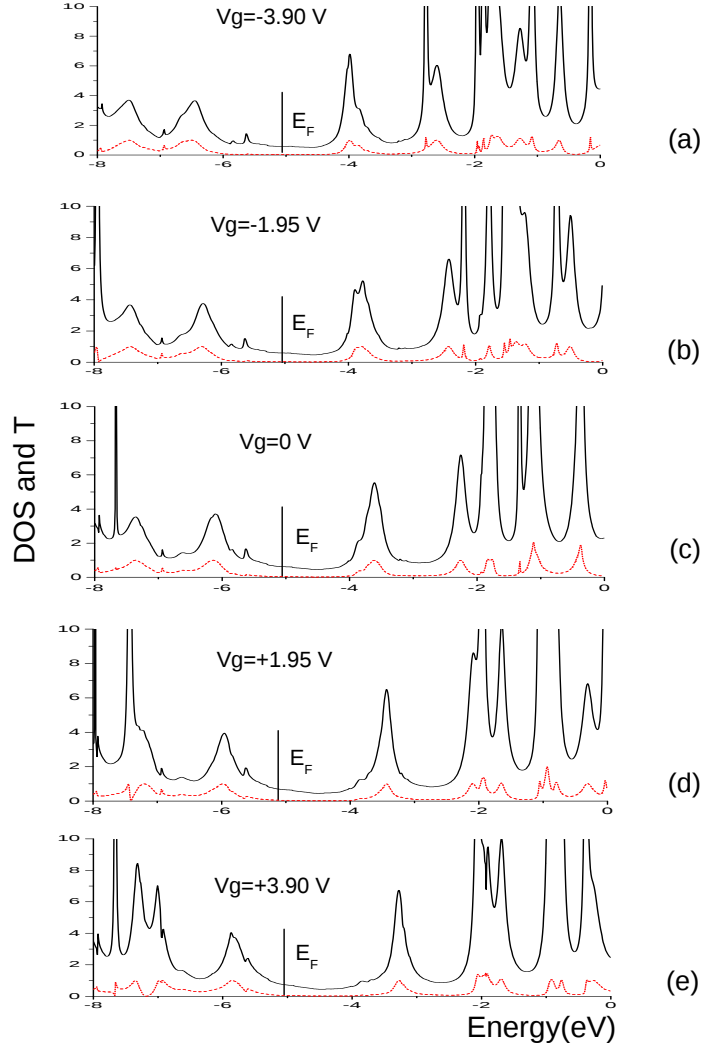


FIG. 2: DOS (solid) and T (dashed) as functions of energy for PTA with gold contacts connected, with the transverse gate bias: $V_g = -3.90$ V (a), -1.95 V (b), 0 V (c), $+1.95$ V (d), and $+3.90$ V (e). The vertical line denotes the position of Fermi level.

Similar to PTA, the good TFE is achieved by the other fused-ring thiophene molecules. Fig. 4(a) and (b) show the I-V curves of the 3-fused-ring thiophene and 7-fused-ring thiophene controlled by the gate bias. For example, at applied voltage $V = -1.0$ V, for the 3-fused-ring thiophene molecules, $(I_{V_g=+1.95V} - I_{V_g=0})/I_{V_g=0} \doteq 0.14$, $(I_{V_g=+3.90V} - I_{V_g=0})/I_{V_g=0} \doteq 0.30$; for the 7-fused-ring thiophene, $(I_{V_g=+1.95V} - I_{V_g=0})/I_{V_g=0} \doteq 0.58$, $(I_{V_g=+3.90V} - I_{V_g=0})/I_{V_g=0} \doteq 1.49$. Meanwhile at the same bias for PTA, $(I_{V_g=+1.95V} - I_{V_g=0})/I_{V_g=0} \doteq 0.29$, $(I_{V_g=+3.90V} - I_{V_g=0})/I_{V_g=0} \doteq 0.70$. The longer fused-ring thiophene molecules have better TFE property.

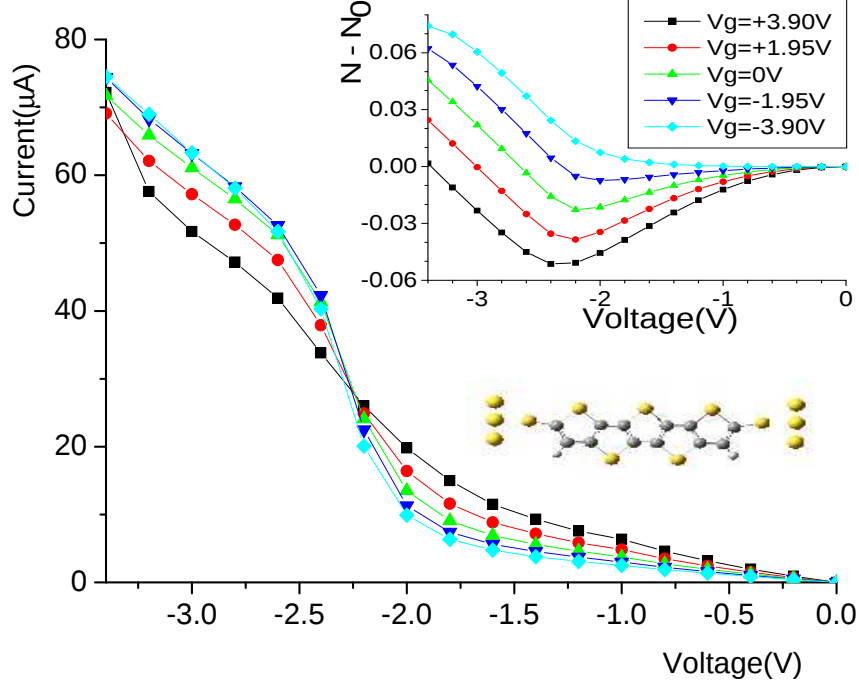


FIG. 3: Gate modulation of the I-V characteristics for PTA. The voltage -2.3 V is the crossover point for the current controlled by the gate bias. For voltage $V > -2.3$ V, either electron ($V_g = -3.90$ V) or hole ($V_g \geq -1.95$ V) is responsible for the current. For voltage -3.4 V $< V < -2.3$ V, the molecule enters the electron- and hole- hybrid conduction region, and the positive biased current is smaller than the negative ones.

Although the early experiment³² reported only weak gate effect on the molecular current observed for the single benzene-dithiol molecule. Our calculation found that the TFE can be improved by the longer polyacene-dithiol molecules, which present a good gate-bias controlled molecular transistor property. DOS and T of the single PDT, naphthalene-dithiol, and anthracene-dithiol in equilibrium without the longitudinal and transverse field are shown in Fig. 5, where both HOMO and LUMO are close to E_f with increase of the aromatic phenyl ring. The HOMO (LUMO) is -7.48 (-2.75) eV for the single PDT, -7.44 (-3.55) eV for the naphthalene-dithiol, and -6.98 (-3.86) eV for the anthracene-dithiol. The fact predicts that if the number of aromatic phenyl ring is increased to more than 3, HOMO and LUMO will be closer to E_f , and the TFE will be more apparent. For the pentacene, $|\text{HOMO} - \text{LUMO}| \doteq 2$ eV and E_f is almost in the middle of H-L gap, it has apparent TFE in the small bias.

The anthracene-dithiol is the n-type conduction molecule in the small voltage region, its

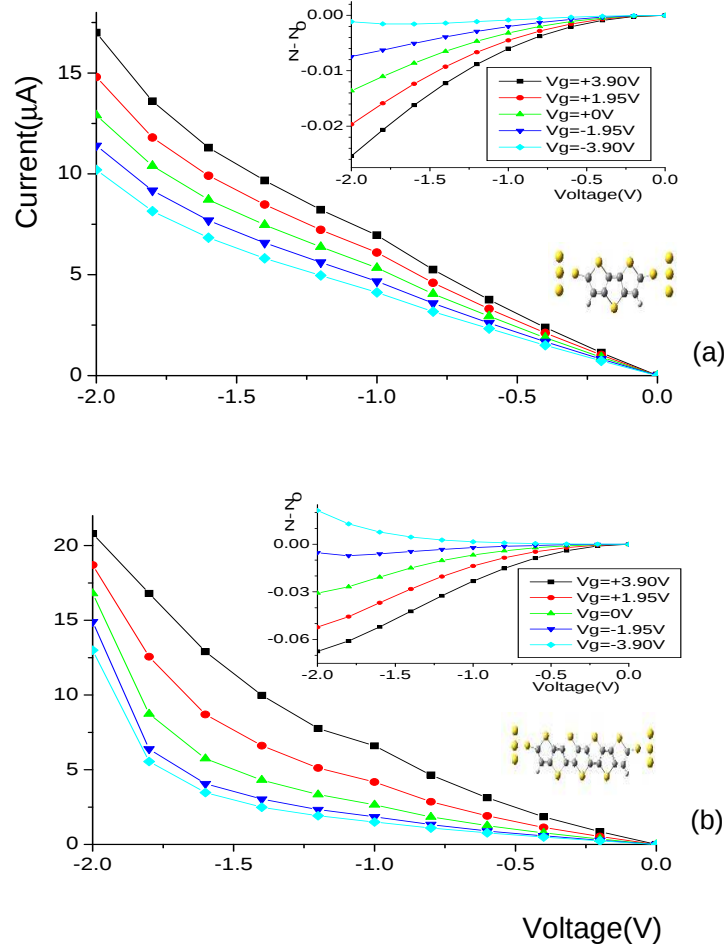


FIG. 4: I-V curves of two fused-ring thiophenes corresponding to the different transverse field: 3-fused-ring thiophene (a), 7-fused-ring thiophene (b). The inset shows the α electron number deviation from the equilibrium state with the modulation of bias.

LUMO is closer to E_f than HOMO [see Fig. 5(c)]. Its molecular levels can be modulated obviously by the gate-bias. With the gate-bias increased by increment 2.5 V from $V_g = -5.00$ V to $V_g = +5.00$ V, the HOMO of anthracene-dithiol leaves E_f by values -6.17 eV, -6.61 eV, -6.98 eV, -7.23 eV, -7.36 eV; and LUMO approaches to E_f by values -2.84 eV, -3.34 eV, -3.86 eV, -4.37 eV, and -4.83 eV, respectively.

With the gate bias $V_g = 5.00$ V, the separation between E_f and LUMO, $|E_f - \text{LUMO}| = 0.27$ eV, which leads the large current at small bias. The I-V curves of anthracene-dithiol controlled by the gate bias are shown in Fig. 6. The current magnitude of the anthracene-

dithiol is one order smaller than the one of the fused-ring thiophene molecules, which is in favor of the low-power device. The molecular transistor illustrates the effective current separation under control of the positive gate bias. For the applied voltage -1.0 V, $(I_{V_g=+2.50V} - I_{V_g=0V})/I_{V_g=0V} \doteq 0.61$, $(I_{V_g=+5.00V} - I_{V_g=0V})/I_{V_g=0V} \doteq 5.89$; while for -2.0 V applied voltage, $(I_{V_g=+2.50V} - I_{V_g=0V})/I_{V_g=0V} \doteq 3.05$, $(I_{V_g=+5.00V} - I_{V_g=0V})/I_{V_g=0V} \doteq 9.14$. We notice that in the voltage range from -1.0 V to -2.0 V, the current under the transverse field of $V_g = -5.00$ V is bigger than that at $V_g = 0$ V, which is not found for fused-ring oligothiophene molecules. The gate-controlled current separation for the negative bias is not effective, we have to use its positive-bias controlled function. For the anthracene-dithiol, the transverse field of $V_g = -5.00$ V makes HOMO close to -6.0 eV, accompanying the sudden rise of current around -2.0 V voltage, so its current is larger than the one for $V_g = 0$ where neither HOMO nor LUMO enters the voltage window. The inset of Fig. 6 illustrates the electron number deviation from equilibrium.

For the open system without the transverse bias, the α electron number has almost no variation below the applied voltage $V = 2.0$ V, since both HOMO and LUMO keep away from E_f in the voltage range. With increase of gate bias, LUMO is shifted to E_f gradually, and the electrons entering the molecule are more than that leaving the molecule, which makes the electron number increase. With decrease of bias, HOMO is close to E_f gradually, which makes the electron number decrease.

With increase in the number of aromatic phenyl ring, the TFE is improved. We found TFE of the naphthalene-dithiol is better than that of the single PDT, but not better than that of the anthracene-dithiol. For the single PDT, under bias -1.0 V, $(I_{V_g=+2.50V} - I_{V_g=0V})/I_{V_g=0V} \doteq 0.03$, $(I_{V_g=+5.00V} - I_{V_g=0V})/I_{V_g=0V} \doteq 0.11$, while under bias -2.0 V, $(I_{V_g=+2.50V} - I_{V_g=0V})/I_{V_g=0V} \doteq 0.04$, $(I_{V_g=+5.00V} - I_{V_g=0V})/I_{V_g=0V} \doteq 0.12$. The control of the molecular current by the gate bias is not discernible, which is consistent with the experiment.³¹ The I-V curves of the pentacene under the different gate bias are shown in Fig. 7. Under bias -1.0 V, the molecular device presents the obvious current modulation by the gate-bias: $(I_{V_g=+1.25V} - I_{V_g=0V})/I_{V_g=0V} \doteq 0.32$; $(I_{V_g=+1.875V} - I_{V_g=0V})/I_{V_g=0V} \doteq 1.31$; $(I_{V_g=+2.50V} - I_{V_g=0V})/I_{V_g=0V} \doteq 3.23$. The molecule illustrates the five times of the current modulation rate of the anthracene-dithiol under the same gate bias. Considering the stability of the structure, maybe the anthracene-dithiol is still a better candidate for the molecular transistor.

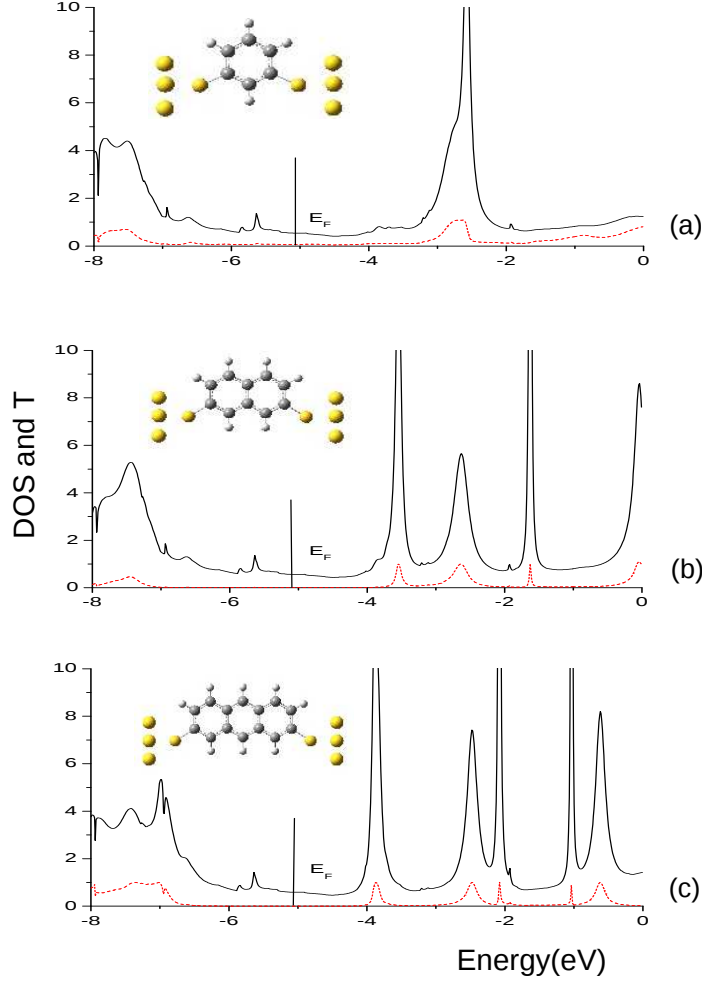


FIG. 5: DOS (solid) and T (dashed) as functions of energy corresponding to the different aromatic phenyl ring molecules with gold contacts for single PDT (a), naphthalene-dithiol (b), and anthracene-dithiol (c). The vertical line denotes the position of Fermi level.

The above TFE comes from the fact that with the increase in transverse field for the polyacene-dithiol, it will make energy levels lower and for the fused ring thiophene, with the increase in the transverse field, it will make energy levels higher. It should be noted that the energy level shift is determined by the choose of the potential zero point, which is set at the center of the line connected by two sulfur atoms in our model. If the potential zero point deviates from this point, the expression of chemical potential of left and right leads should be rectified: $\mu_1 = E_f - e(\frac{1}{2}V + \Delta V)$, and $\mu_2 = E_f + e(\frac{1}{2}V - \Delta V)$. ΔV is the electrical potential difference between the old zero point and the new one. However, the choose of

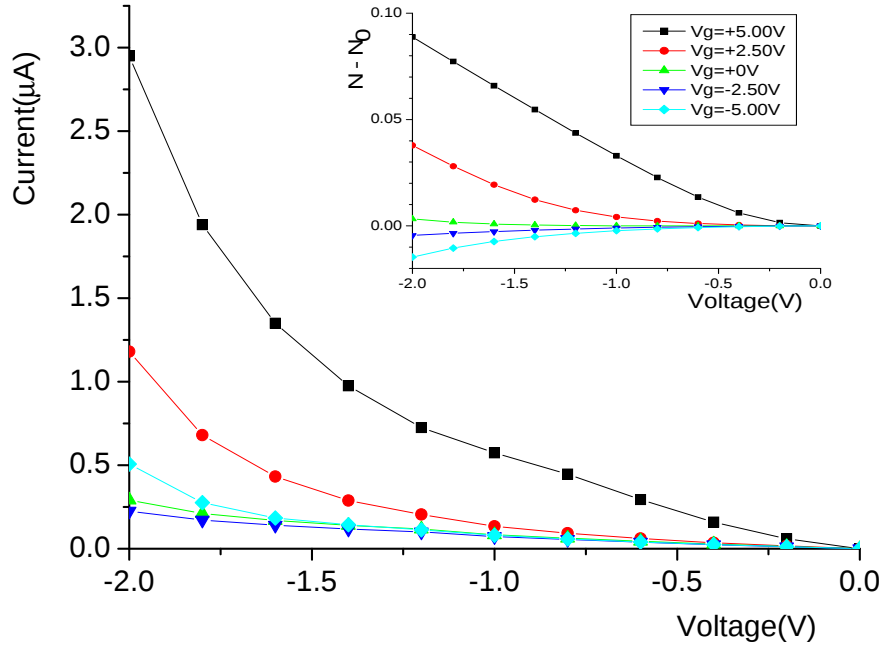


FIG. 6: I-V curves of pentacene corresponding to the different gate bias. The inset shows the variation of α electron number relative to that in equilibrium with the change of bias.

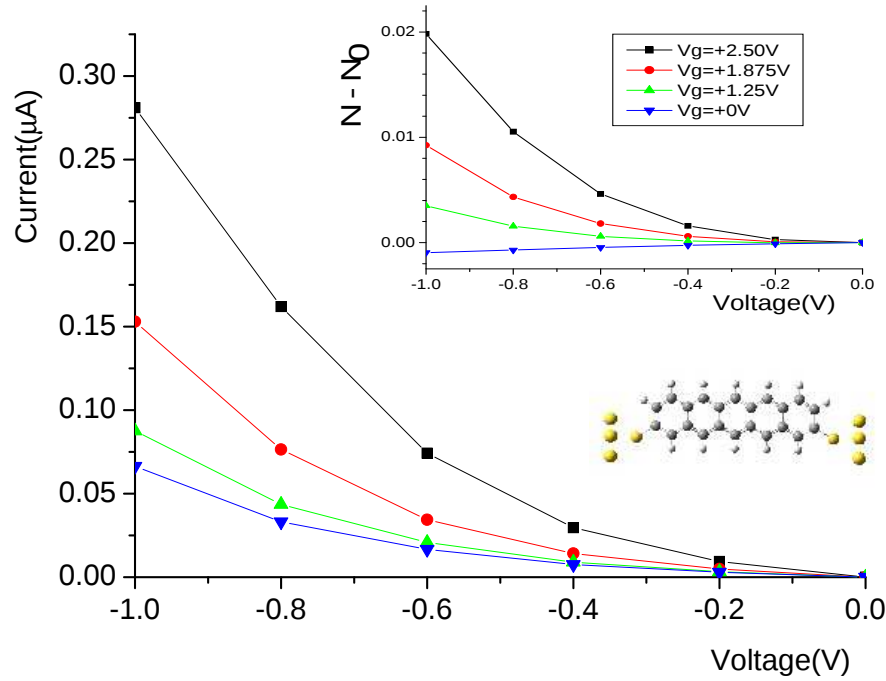


FIG. 7: I-V curves of anthracene-dithiol corresponding to the different gate bias. The inset shows the variation of α electron number relative to that in equilibrium with the change of bias.

zero point has no effect on the calculation results.

IV. SUMMARY

We use the self-consistent method based on the DFT and non-equilibrium Green's function to simulate molecular transport. In terms of Gaussian03, the electronic structures of the molecular device and the macroscopic leads are calculated on an equal footing. At the same time, the self-consistent iteration cycle is extended from the local molecule to the open system, by inserting the calculation of the density matrix of the open system as a subroutine. Our self-consistent results show that the long-length organic molecule can achieve better transport characteristics. Our investigation proves that both the polyacene-dithiol molecules and fused-ring oligothiophene molecules can be made as the high-frequency molecular transistors controlled by the transverse field. The theoretical results suggest the related experiments about the molecular devices.

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