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Influence of external voltage on electronic transport properties of molecular junctions: the nonlinear transport behaviour*

Li Zong-Liang(李宗良)[a], Wang Chuan-Kui(王传奎)[a]†,
Luo Yi(罗 毅)[b], and Xue Qi-Kun(薛其坤)[c]

[a] *College of Physics and Electronics, Shandong Normal University, Jinan* 250014, *China*
[b] *Laboratory of Theoretical Chemistry, Royal Institute of Technology, SCFAB S-*10691 *Stockholm, Sweden*
[c] *State Key Laboratory for Surface Physics, Institute of Physics, Chinese Academy of Science, Beijing* 100080, *China*

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The influence of external voltage on the charge transport properties of benzene-1,4-dithiolate molecular junction has been investigated. Variations of the geometric and electronic structures for the molecule caused by the applied voltage are calculated at *ab initio* level. Based on the numerical results, we find that the energy shift and expansion coefficients in the end-site of the molecule for the frontier molecular orbitals show nearly linear dependence on voltage in the interested voltage interval. The charge transport properties of the molecular junction are then studied by employing the elastic scattering Green's function method. It is shown that the voltage has an obvious effect on the $I-V$ characteristic of the molecular junction, particularly the shape of the conductance curves. The $I-V$ curves are consistent with the experimental measurement quite well.

Keywords: electric field, current–voltage curves, molecular electronics
PACC: 7340G, 7115A, 3450D, 7200

1. Introduction

Recently rapid developments of the molecular electronics are witnessed. The available advanced nanometer technologies[1] make it possible to measure electronic transport properties of a single molecule.[2–5] In 1997, Reed *et al*[6] measured the conductance of a single molecular wire using benzene-1, 4-dithiolate at room temperature with a mechanically controllable break junction, and found that the conductance–voltage curve showed step-typed behaviour. Most recently, Xu *et al*[7] determined the conductance of a single molecule connected to two gold electrodes by repeatedly forming thousands of gold–molecule–gold junctions. Nazin *et al*[8] elucidated the precise atomic structure and local electronic properties of organic–metal interfaces in unprecedented detail. In addition, formal theories to describe charge transport properties of molecular devices have been developed by several groups.[9–14]

We applied the hybrid density functional theory in combination with the frontier orbital bonding concept to describe the chemical absorption and compute the coupling constant.[12,15–17] We have shown that good agreement between theory and experiment can be achieved for $I-V$ characteristics of molecular junction measured by Reed.[12,15] However, the calculations mentioned above are based on the approximation that the influence of the external voltage is neglected, namely, linear charge transport theory is formulated. It is well known that organic molecules have sensitive response to the applied field. Therefore, one can expect that external voltage may have an obvious influence on charge transfer characteristics of the molecular junction, especially, in the region of higher voltage. In the present work, we investigate the $I-V$ characteristic of the molecular junction with the influence of external voltage, which is taken as a development of the previous studies.[12–18]

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†Corresponding author. E-mail: ckwang@sdnu.edu.cn

2. Elastic scattering theory

The molecular junction is schematically shown in Fig.1. Electron transport through a molecule can normally be considered as a one-dimensional process. We assume that the molecule is aligned along the z-direction, which is also the direction of current transport. Energy states in the conduction band of the reservoir can be expressed as a summation, $E = E_{x,y} + E_z + E_c$, in the effective mass approximation, where E_c is the conduction band edge and is used as energy reference. The parabolic dispersion relation for the energy states in metal is assumed here. The electrons in the reservoir are assumed to be all in equilibrium at a temperature T and Fermi level E_{F}.

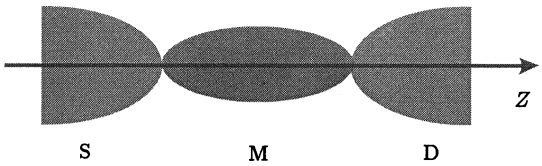


Fig.1. Molecular junction.

When an external voltage V is applied, the tunnelling current density from source (S) to drain (D) is

$$i_{\mathrm{SD}} = \frac{2\pi e}{\hbar} \sum_{E_{x,y}} \sum_{E_z^l, E_z^{l'}} f(E_{x,y} + E_z^l - eV)[1 - f(E_{x,y} + E_z^{l'})] \left|T_{l'l}(E_z^l, V)\right|^2 \delta(E_z^{l'} - E_z^l), \tag{1}$$

where $f(E)$ is the Fermi distribution function, $f(E) = \frac{1}{\mathrm{e}^{[(E-E_{\mathrm{F}})/k_{\mathrm{B}}T]} + 1}$. Here E_F is the Fermi energy, T working temperature, k_{B} Boltzmann constant and $T_{l'l}$ transition matrix element describing the scattering process from initial state $|l\rangle$ to final state $|l'\rangle$, which is a function of external bias and the injection energy along the z axis. The δ function represents the elastic scattering process. There is a corresponding term for reverse tunnelling for the case of high temperatures. The net current density from S to D can thus be written as[19,20]

$$i = \frac{2\pi e}{\hbar} \sum_{E_{x,y}} \sum_{E_z^l, E_z^{l'}} [f(E_{x,y} + E_z^l - eV) - f(E_{x,y} + E_z^{l'})] \left|T_{l'l}(E_z^l, V)\right|^2 \delta(E_z^{l'} - E_z^l). \tag{2}$$

If three-dimensional electron systems are taken as reservoirs, Eq.(2) can be evaluated by

$$i = \frac{2em^* k_{\mathrm{B}}T}{\hbar^3} \int_{eV}^{\infty} \ln\left\{\frac{1 + \exp[(E_{\mathrm{F}} + eV - E_z)/k_{\mathrm{B}}T]}{1 + \exp[(E_{\mathrm{F}} - E_z)/k_{\mathrm{B}}T]}\right\} |T(E_z, V)|^2 \, n_{1\mathrm{d}}^S(E_z) n_{1\mathrm{d}}^D(E_z) \mathrm{d}E_z, \tag{3}$$

where m^* is the electron effective mass.

For the three-dimensional system, the current is $I = Ai$, where A is the effective injection area, $A \approx \pi r_{3\mathrm{s}}^2$. Here $r_{3\mathrm{s}}$ is defined as $r_{3\mathrm{s}} = [3/(4\pi N_{3\mathrm{d}})]^{1/3}$, and the density of electrons is $N_{3\mathrm{d}} = (2m^* E_{\mathrm{F}})^{3/2}/(3\hbar^3\pi)$. The conductance G is obtained by

$$G = \frac{\partial I}{\partial V}. \tag{4}$$

Based on the elastic scattering Green's function theory, the transition matrix element can be expressed as[12,16,18]

$$T_{l'l}(E, V) = Y_{1l} Y_{l'N} \sum_{\eta} \frac{\langle 1|\eta\rangle\langle\eta|N\rangle}{z - \varepsilon_\eta}, \tag{5}$$

where

$$Y_{1l} = \sum_{\alpha} c_{l\alpha} d_{1\alpha}^*, \quad Y_{l'N} = \sum_{\beta} c_{\beta l'} d_{\beta N}, \tag{6}$$

represent the couplings between molecular end-sites and the reservoirs; $c_{i\alpha}(c_{\beta j})$ $(l \in i,\ l' \in j)$ is the interaction between orbital $\alpha(\beta)$ of the molecule and the outmost band $i(j)$ of the reservoirs, $\{d_{1\alpha}\}$ and $\{d_{\beta N}\}$ are expansion coefficients. $|\eta\rangle$ is the eigenstate of the Hamiltonian of a finite system that consists of the molecule sandwiched between two gold clusters: $H|\eta\rangle = \varepsilon_\eta|\eta\rangle$. The product of two overlap matrix elements $\langle 1|\ \eta\rangle\langle\eta|\ N\rangle$ describes the delocalization of orbital η. If we assume that metallic states interact with the molecular states in the same manner, i.e. $Y_{1l} = Y_{1S}$ for all l and $Y_{l'N} = Y_{DN}$ for all l', the transition matrix element becomes

$$T(E, V) = Y_{1S} Y_{DN} \sum_{\eta} \frac{\langle 1|\eta\rangle\langle\eta|N\rangle}{z - \varepsilon_\eta}, \tag{7}$$

where $z = E + \mathrm{i}\Gamma_\eta$, E is the energy at which the scat-

tering process is observed, and Γ_η is the level broadening of the energy state $|\eta\rangle$. The interference between different scattering channels in a short molecular wire is probably negligible, since energy spacing between molecular orbitals for a short molecule is considerably large. The transition intensity can then be written as

$$\begin{aligned}|T(E,V)|^2 =& \sum_\eta |T(E,V)|^2_\eta \\ =& \sum_\eta \frac{Y^2_{1S} Y^2_{DN} |\langle\eta|N\rangle|^2 |\langle 1|\eta\rangle|^2}{(\varepsilon_\eta - E)^2 + \Gamma^2_\eta}, \end{aligned} \quad (8)$$

Γ_η is the imaginary part of the self-energy,[20−22] which can be determined by

$$\begin{aligned}\Gamma_\eta(E) =& \Delta_S + \Delta_D \\ =& \pi Y^2_{1S} |\langle 1|\eta\rangle|^2 \sum_p \delta(E - E^S_p) \\ &+ \pi Y^2_{DN} |\langle\eta|N\rangle|^2 \sum_p \delta(E - E^D_p) \\ =& \pi Y^2_{1S} |\langle 1|\eta\rangle|^2 n^S(E) \\ &+ \pi Y^2_{DN} |\langle\eta|N\rangle|^2 n^D(E), \end{aligned} \quad (9)$$

where

$$n(E) = \rho_{1d} r_{is}. \quad (10)$$

For a symmetrical molecule with identical metal contacts, one has $Y_{1S} = Y_{DN}$ and $|\langle 1|\eta\rangle|^2 = |\langle\eta|N\rangle|^2$, and the level broadening becomes

$$\Gamma_\eta(E) = 2\pi Y^2_{1S} |\langle 1|\eta\rangle|^2 n(E). \quad (11)$$

3. Results and discussion

It is well known that organic molecules are systems easily influenced by external electric field. When a field is applied, the geometry of the molecule and then the electronic structure will be changed. Therefore, the transition intensity is field-dependent as described by Eq.(8), and the current through the molecular junction varies as a nonlinear function of the applied voltage.

3.1. Geometric structure of the molecular system

First, we perform the geometry optimization of the bare molecule benzene-1,4-dithiol ($C_6H_6S_2$) implemented by Gaussian 98.[23] Because the hydrogen of the two thiols will be desorbed when the bare molecule is adsorbed on a gold surface, we remove the hydrogen atoms of the two thiols while we sandwich the bare molecule between the two equilateral triangles of the gold clusters, then we keep the two equilateral triangles parallel and direct the faces to each other and optimize the extended molecule composed of three parts. The three gold atoms are used to simulate the interaction between the molecule and the gold (111) surface. The optimized structure is shown in Fig.2(a). Applying different strengths of the electric field to the system, we perform geometric optimizations again. Figure 2(b) is the structure of the molecular system when applying a voltage of 5V between the two gold clusters. In the figures, the bond lengths are shown in the corresponding positions. Comparing Fig.2(a) with 2(b), one can conclude that the effect of the field is very little on the structure of the benzene ring, but it is larger on the bonds of Au–S and S–C, especially on the bonds of Au–S at the anode side.

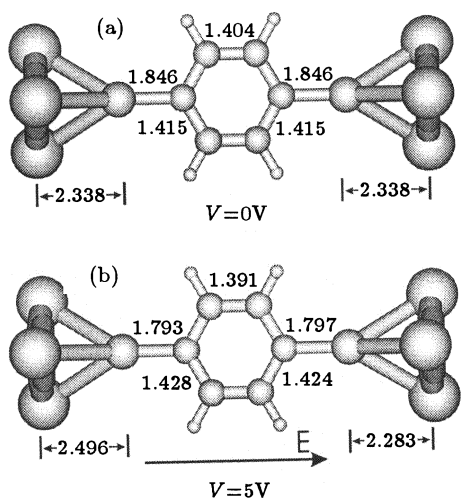


Fig.2. Geometric structure of the molecular system (unit: nm).

3.2. Electronic structures of the molecular system

It is noted that the conductance of a molecule is mainly determined by the molecular orbitals near the highest occupied molecular orbital (HOMO) and especially near the lowest unoccupied molecular orbital (LUMO) because the Fermi level lies in the gap of HOMO and LUMO. Therefore, we only describe the variation of eight energy levels near the HOMO and LUMO. At the same time, the variation of Fermi energy of the system is also described. The Fermi energy can be determined by

$$N(E_F) = \int_{-\infty}^{\infty} dE \frac{1}{e^{(E-E_F)/k_B T} + 1} \rho(E), \quad (12)$$

where

$$\rho(E) = \sum_i \frac{\Gamma}{2\pi[(E - E_i)^2 + (\Gamma/2)^2]} \quad (13)$$

is the energy density. Here Γ is a factor of energy broadening, which is about several $k_{\mathrm{B}}T$.

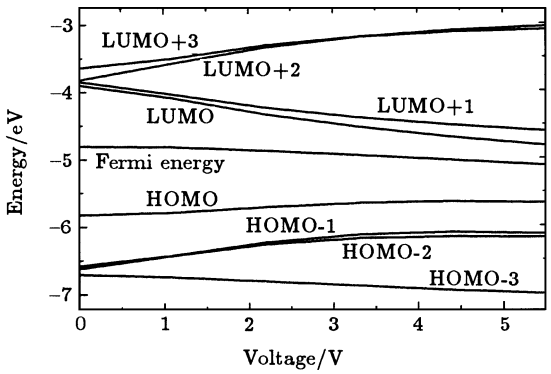


Fig.3. Variation of the energy level and Fermi energy of an extended molecule.

Figure 3 shows the trend of variation of energy levels of the extended molecule following the voltage applied. It can be seen that the general trends of the energy levels are not similar to each other with the increase of the applied bias. HOMO has a little ascending trend, while LUMO and LUMO+1 decline distinctly. Therefore, the width of energy gap between HOMO and LUMO decreases rapidly as the bias increases. LUMO+2, LUMO+3, HOMO-1 and HOMO-2 come up obviously. Fermi energy does not change much but only becomes a little lower. All these changes are important to the conductance property of the molecular system.

The energy density of the system for different voltages is displayed in Fig.4, from which one can see that the variation of the bias not only results in the change of peak values of energy density, but also causes the changes of peak positions.

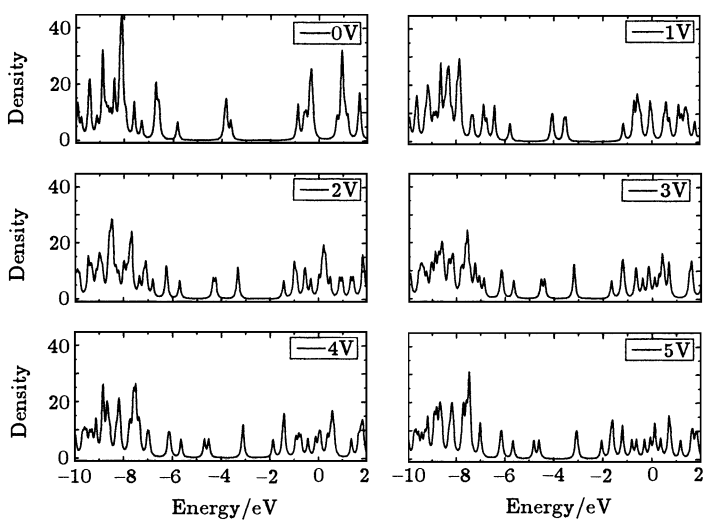


Fig.4. Variation of energy density of the system with different bias.

3.3. Nonlinear charge transfer properties of the molecular junction

It is noted that only the frontier molecular orbits will provide an efficient charge transfer channels at lower bias.[24] With the calculated results shown above, we give an approximate model for the energy shift and charge distribution of frontier molecular orbitals caused by the applied voltage. Namely, we assume that the energy levels of LUMO, LUMO+1,LUMO+2, LUMO+3 and Fermi energy take a linear shift versus the bias; and the expansion coefficients $\langle 1|\eta\rangle$ and $\langle \eta|N\rangle$ for a molecular orbital $|\eta\rangle$ are also linearly dependent on the bias. Then we can investigate the effect of applied bias on the charge transfer behaviour of the molecular junction.

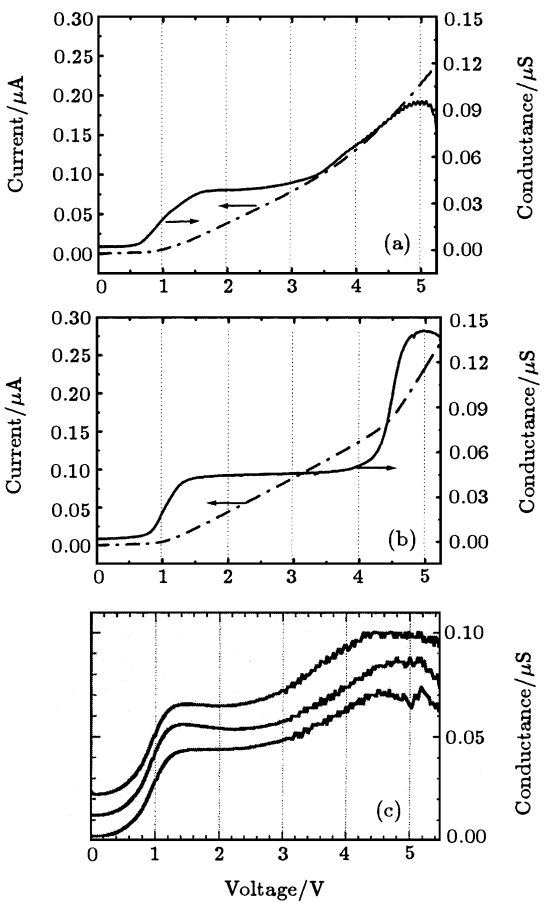


Fig.5. Current and conductance of the molecular junction. (a) with considering the influence of external voltage, (b) without considering the influence, and (c) the experimental data taken from Ref.(6).

The current and conductance properties of benzene-1,4-dithiol are shown in Fig.5. Comparing Fig.5(a) with Fig.5(b), one can observe the following effects on conductance of the molecular junction, caused by external voltage: (1) the slope of the transition is smoothed, (2) the plateau of conductance is narrowed, and (3) the value of conductance at high voltage is lowered. Furthermore, the bias in lower regime has little influence on the current and conductance of the molecular junction, which is reasonable and also supports the validity of linear charge transfer theory in lower voltage regime. When the influence of the voltage is included, the onset of the conductance is at a lower voltage because the energy of LUMO is pushed down with increasing voltage. It is noted that the curve of conductance given in Fig.5(a) agrees well with experimental measurements. This demonstrates the validity of our model for describing the influence of the voltage on current and conductance of the molecular junction.

4. Conclusion

We have shown that the external voltage has an obvious influence on the $I-V$ characteristic of a molecular junction, which results from the variation of geometric and electronic structures caused by the voltage. Taken benzene-1,4-dithiolate molecular junction as an example, it is observed that the influences on the conductance can be summarized as follows: (1) the slope of the transition between two steps is smoothed, (2) the plateau of conductance is narrowed, and (3) the value of conductance at high voltage is lowered. The $I-V$ curves are consistent with the experimental measurement quite well.

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