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Contact configuration dependence of conductance of 1,4-phenylene diisocyanide molecular junction

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Abstract

The elastic scattering Green function theory in combination with density-functional theory is applied for studying electronic transport properties of single 1,4-phenylenediisocyanide molecules sandwiched between two gold electrodes at *ab initio* level. The special attention is paid to effect of contact configurations between molecule and electrodes on current and conductance characteristics of the molecular junction. Conductive features are shown to be strongly dependent on detailed contact structures. For the contacts formed in tetrahedron-typed configuration, good agreement in conductive features between theory and experiment can be achieved.

In recent years, preparation of molecular devices based on molecular electric features has become a major subject in nano-electronics [1]. Technologies of mechanically controllable break junction [2], scanning tunneling microscope [3], and sandwiched self-assembled monolayer [4], for instance, are used to measure current–voltage characteristics of a single molecule or molecular monolayer. At the same time, numerous theoretical works have also been conducted to understand electronic transport properties of molecular devices [5–14]. These theories can mainly be divided into two different categories, one is based on solid-state physics, the other is based on quantum chemistry which is more suitable for dealing with single molecular devices.

Molecular structure, contact configuration, and contact position between molecules and metal surface are regarded as dominative factors for determining current–voltage features of a molecular junction [15–19]. The good candidates of molecules to be used for fabrication of molecular devices are assumed to have delocalized charge inside. When molecular junctions are formed, the contact configuration between a molecule and electrodes takes ambient conditions, where it is difficult to know it from measurement. Theoretical results have demonstrated that contact configuration has obvious influence on charge transport properties of molecules [15,16]. The underlying mechanism can be understood that the interaction between molecules and electrodes is closely dependent on contact configurations, accordingly, molecular electronic structures and potential barrier at interface show a relation with contact structures.

Basing on elastic scatting Green function theory, we developed a quantum chemistry method to describe electron transport in molecular junctions, where interactions among all sites in the device are accurately taken into account, and it has been implemented in the QCME program [20]. With it, the calculated current–voltage characteristics of alkanemonothiol, bipyridine, and alkanedithiol molecular junctions are found to be in good agreement with experimental measurements [16,21]. It needs to say that our quantum chemical approach is particularly feasible for studying effect of contact configuration on electrical conduction of molecular junctions since in our model that allows to use any desirable contact geometry.

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In this Letter, we investigate electronic transport properties of organic molecular 1,4-phenylenediisocyanide devices with gold electrodes measured by Lee et al. [4]. The molecule has been reported to absorb on gold via the carbon lone pair electrons with a standing geometry to gold surface [22]. It was found that the end carbon atom of 1,4-phenylenediisocyanide prefers to locate on hollow position or top position of gold surface [23]. Three different contact geometries are thus considered: (i) a triangle structure with three gold atoms, (ii) a tetrahedron structure with four gold atoms, and (iii) a linear chain of three gold atoms (see Fig. 1). The bond length for Au–Au is fixed at 2.88 Å. The extended molecular systems are optimized at the hybrid density functional theory (DFT/B3LYP) with a LanL2DZ basis set in the GAUSSIAN 03 program [24], and their electronic structures are also attained. We have thus examined the variation of bonding distance between the end of molecule and the gold atoms closest to the molecule with different contact structures in detail. The effect of atomic configuration of gold electrodes on electrical conduction of the devices has carefully been studied. For a particular stable configuration, a good agreement in conductive features with conductance measurement can be achieved.

According to the method described in Ref. [25], the net current density of molecular system from one electron reservoir (S) to another reservoir (D) is expressed as

$$j=\frac{4emk_{\mathrm{B}}T_0}{\hbar^3}\int\left\{\ln\left[1+\exp\left(\frac{E_f-E_z+eV}{k_{\mathrm{B}}T_0}\right)\right]-\ln\left[1+\exp\left(\frac{E_f-E_z}{k_{\mathrm{B}}T_0}\right)\right]\right\}|T(E_z,V)|^2 n_{1D}^{S}(E_z)n_{1D}^{D}(E_z)\mathrm{d}E_z \tag{1}$$

Then the total current from S to D is

$$I=Aj=\pi r_{3s}^2 j=\left(\frac{9\pi}{4}\right)^{\frac{1}{3}}\frac{9ek_{\mathrm{B}}T_0}{2\hbar E_f^2}\int\left\{\ln\left[1+\exp\left(\frac{E_f-E_z+eV}{k_{\mathrm{B}}T_0}\right)\right]-\ln\left[1+\exp\left(\frac{E_f-E_z}{k_{\mathrm{B}}T_0}\right)\right]\right\}|T(E_z,V)|^2\frac{\mathrm{d}E_z}{E_z}. \tag{2}$$

Therefore, the differential conductance can be written as

$$G=\frac{\partial I}{\partial V}. \tag{3}$$

The choice of Fermi level is a major problem for the modelling of single molecular transport. In our calculations, the middle of HOMO and LUMO of the metal–molecule cluster is chosen as Fermi level, and non-equilibrium transport is considered by simply line-up Fermi energy of the extended molecule and the bulk metals.

In Eq. (1), the transition intensity $|T(E,V)|^2$ can be determined by

$$|T(E,V)|^2=\left(\sum_{kk'}\sum_{n}Y_{Dk'}(V)Y_{kS}(V)\frac{\langle k'|n\rangle\langle n|k\rangle}{(E-E_n(V))^2+\Gamma_{n,kk'}^2}(E-E_n(V))\right)^2+\left(\sum_{kk'}\sum_{n}Y_{Dk'}(V)Y_{kS}(V)\frac{\langle k'|n\rangle\langle n|k\rangle}{(E-E_n(V))^2+\Gamma_{n,kk_n}^2}\Gamma_{n,kk_n}\right)^2. \tag{4}$$

where $k(k')$ runs over all atomic sites, which are denoted as $1,2,\ldots J$, and sites 1 and J are two end sites of molecule that connect with two electron reservoirs, and orbital $|n\rangle$ is eigenstate of the Hamiltonian of the composite cluster-molecule-cluster system, $H_f|n\rangle=E_n|n\rangle$. The product of two overlap matrix elements $\langle k'|\ n\rangle\langle n|k\rangle$ describes delocalization of orbital $|n\rangle$. E is the energy at which the scattering process is observed. $Y_{kS}(V)$and $Y_{Dk'}(V)$ represent the couplings between $k(k')$ atom of the molecule and the gold clusters (noted by S and D) in the site representation,

$$\begin{aligned}Y_{kS}(V)&=\langle k|U|S\rangle=\sum_{n,\alpha,i}C_{n\alpha}^{k}\langle k_\alpha|U|S_i\rangle C_{ni}^{S}=\sum_{n,\alpha,i}C_{n\alpha}^{k}\langle k_\alpha|H|S_i\rangle C_{ni}^{S}\\ Y_{Dk'}(V)&=\langle D|U|k'\rangle=\sum_{n,\beta,j}C_{nj}^{D}\langle D_j|U|k'_\beta\rangle C_{n\beta}^{k'}=\sum_{n,\beta,j}C_{nj}^{D}\langle D_j|H|k'_\beta\rangle C_{n\beta}^{k'},\end{aligned} \tag{5}$$

where $C_{n\alpha}^{k}(C_{n\beta}^{k'})$ is the expansion coefficient of the orbital $|n\rangle$ on the atomic orbital $|\alpha\rangle$ ($|\beta\rangle$) of atom k (k') of the molecule, and $C_{ni}^{S}(C_{nj}^{D})$ is on the atomic orbital $|i\rangle$ ($|j\rangle$) of the gold atom cluster S (D). The energy broadening $\Gamma_{n,kk'}$ is determined by calculating the imaginary part of the self-energy [5,6],

$$\begin{aligned}\Gamma_{n,k'k}(E)&=\Delta_{kS}+\Delta_{Dk'}\\&=\pi Y_{kS}^2|\langle n|k\rangle|^2 n^{S}(E)+\pi Y_{Dk'}^2|\langle k'|n\rangle|^2 n^{D}(E),\end{aligned} \tag{6}$$

where $n^{\mathrm{S(D)}}$ is density of states of the source and drain.

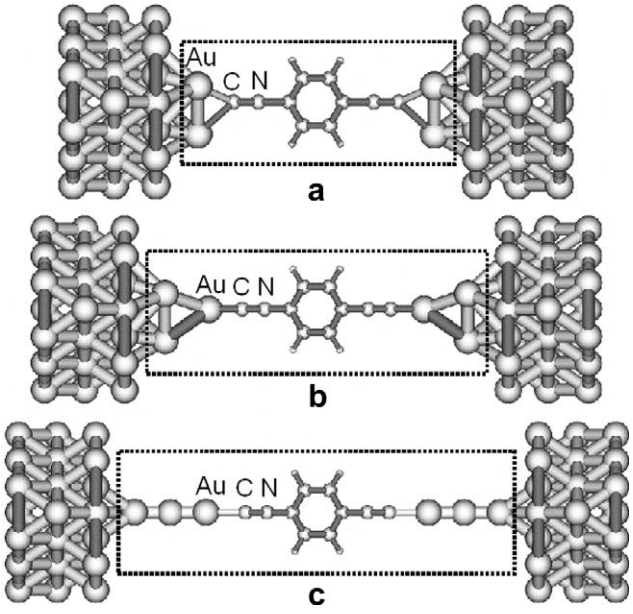

Fig. 1. Schematic structures of three kinds of gold-1,4-phenylenediisocyanide-gold junctions with local contact. (a) Triangle contact with three gold atoms at each side, (b) tetrahedron contact with four gold atoms at each side, and (c) chain contact with three gold atoms at each side. The dotted box indicates the extended molecule.