Effects of Electrode Distances on Geometric Structure and Electronic Transport Properties of Molecular 4,4’-Bipyridine Junction

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Abstract. Influences of electrode distances on geometric structure of molecule and on electronic transport properties of molecular junctions have been investigated by means of a generalized quantum chemical approach based on the elastic scattering Green’s function method. Numerical results show that, for organic molecule 4,4’-bipyridine, the geometric structure of the molecule especially the dihedral angle between the two pyridine rings is sensitive to the distances between the two electrodes. The currents of the molecular junction are taken nonlinearly increase with the increase of the bias. Shortening the distance of the metallic electrodes will result in stronger coupling and larger conductance.

1. Introduction

Because of the potential applications in the molecular electronics, recently there has been a lot of interest in single molecular device in the last decade. One found that a single molecular device has many interesting features such as negative differential resistance[1,2] and field-effect modulation. Based on these properties, some functional molecular devices, for instance, molecular transistors, molecular switch[3], and molecular rectifier have been designed. Detailed understanding of the electron transport through a molecule bridging a gap between two metal electrodes will be essential for the development of molecular electronics. Most of theoretical studies on electron transport in molecular electronic devices are based on the solid state physics approach[4,5]. While, the agreement between theory and experiment is generally poor, because that: the information about molecule-metal contacts in the experiments can’t be determined, and, in the calculation, some degrees of freedom of molecule are always frozen. However, the experiments were carried out at ambient conditions with mechanical break junctions, and the geometric and electronic structure of the molecule is very sensitive to the changing of the circumstances. Here, by applying the density functional theory and our developed elastic scattering Green’s function theory[6-10], we investigate the electronic transport properties of organic molecule 4,4’-bipyridine[11]. In the report, the influences of the distance between the two metallic electrodes on the molecule geometric structure and on the electronic transport properties are discussed in detail.
The molecular junction is schematically shown in figure 1, where M represents a molecule, S and D are electron reservoirs. Here the molecule that we will investigate is 4,4'-bipyridine.

![Figure 1. Scheme of molecular junction](image)

For a three-dimensional electrode, the net current density of the device from the source to the drain can be written as

\[
\mathbf{j} = \frac{4e mk_T}{\hbar} \int \left[ \ln \left( 1 + \exp \left( \frac{E_f - E_z + eV}{k_B T} \right) \right) - \ln \left( 1 + \exp \left( \frac{E_f - E_z - eV}{k_B T} \right) \right) \right] T(E_z) \left| n_{1D}^S(E_z) n_{1D}^D(E_z) \right| dE_z
\]

Then the total current from S to D is,

\[
I = A j = \left( \frac{9\pi e^2}{4} \right) \frac{9e k_B T}{2\hbar^2} \int \left[ \ln \left( 1 + \exp \left( \frac{E_f - E_z + eV}{k_B T} \right) \right) - \ln \left( 1 + \exp \left( \frac{E_f - E_z - eV}{k_B T} \right) \right) \right] T(E_z) \left| n_{1D}^S(E_z) n_{1D}^D(E_z) \right| dE_z
\]

where \( A \) is the inject area. Therefore the differential conductance can be written as,

\[
G = \partial I / \partial V
\]

In Eq.(1), the transition probability \( |T(E)|^2 \) can be determined by

\[
|T(E)|^2 = \left( \sum_{k'} \sum_n Y_{k'k} Y_{k'\alpha} \frac{|k'| n |n | k \rangle \langle n | (E - E_n) + \Gamma_{\alpha n, k k'}^2 \right) + \left( \sum_{kk'} \sum_n Y_{kk'} Y_{k\alpha} |k | n | \alpha \rangle \langle n | (E - E_n) + \Gamma_{\alpha n, k k'}^2 \right)^2}
\]

Where orbital \( |n \rangle \) is eigenstate of the Hamiltonian of the finite system that consists of the molecule sandwiched between two gold clusters, \( H_f | n \rangle = E_n | n \rangle \). The product of two overlap matrix elements \( \langle k' | n \rangle \langle n | k \rangle \) describe the delocalization of orbital \( |n \rangle \). \( E \) is the energy at which the scattering process is observed. \( Y_{k\alpha} \) and \( Y_{kk'} \) represent the couplings between the \( k \)-th atom of the molecule and the gold clusters,

\[
Y_{ks} = \langle k | U | S \rangle \sum_{n, \alpha, J} C_{\alpha n}^s \langle k_\alpha | U | S_\alpha \rangle C_{\alpha n}^s = \sum_{n, \alpha, J} C_{\alpha n}^s \langle k_\alpha | H | S_\alpha \rangle C_{\alpha n}^s
\]

\[
Y_{kk'} = \langle k | U | k' \rangle \sum_{n, \beta, J} C_{\beta n}^{k'} \langle k_\beta | U | k'_{\beta} \rangle C_{\beta n}^{k'} = \sum_{n, \beta, J} C_{\beta n}^{k'} \langle k_\beta | H | k'_{\beta} \rangle C_{\beta n}^{k'}
\]

where \( C_{\alpha n}^s \) is the expansion coefficient of the molecular orbital \( |n \rangle \) on the atomic orbital \( |\alpha \rangle \) of the atom \( k \) (\( k' \)) of the molecule, and \( C_{\beta n}^{k'} \) is on the atomic orbital \( |\beta \rangle \) (\( |\beta' \rangle \)) of the gold cluster \( S(D) \). The energy broadening \( \Gamma_{\alpha n, k k'} \) is determined by calculating the imaginary part of the self-energy[12,13].

The geometric optimization and the electronic structure calculations are performed at hybrid density-functional theory (DFT) B3LYP level with Lanl2DZ basis set in the Gaussian 98 package[14]. The electron transportation properties are obtained from the QCME program[10].
3. Results and discussion

The geometric optimization of the bare molecule 4,4'-bipyridine shows that there exists a dihedral angle of about 30 degrees between the two pyridine rings. Figure 2 shows the changing of the total energy of the bare molecule versus the dihedral. Then we sandwich the bare molecule between two gold clusters to compose extended molecules and perform optimizations again. The structure of the extended molecule is shown in figure 3. The numerical results show that the energetically favorable bonding site for the nitrogen atoms is on the top of a gold atom. In order to discuss the effect of the distance of electrodes, four different distances between the two gold clusters are considered.

![Figure 2](image2.png)

**Figure 2.** Energy of 4,4'-bipyridine molecule versus dihedral angle between two pyridine rings (take the minimum energy 13477.5303eV as the reference energy)

![Figure 3](image3.png)

**Figure 3.** Structure of the molecular junction

Table 1 shows some geometric data and the coupling constants for the molecular junction with the gold clusters in different distances. From the first three columns of the table one can find that the molecule will be compressed when shortening the distance between two gold clusters. The fourth column of the table shows the dihedral angles between the two pyridine rings. The numerical results show that shortening the distances between the electrodes will enlarge the dihedral. The last two columns of the table show the coupling constants between the nitrogen atoms and the nearer gold clusters. The coupling constants are also enlarged by shortening the distances. Because of the existence of the dihedral and the asymmetry of extended molecule, there exist some differences for the coupling constants in the two sides.

| Distance(nm) | Au1-Au2 | N1-N2 | C1-C2 | Dihedral (degree) | Coupling constant(eV) |
|--------------|---------|-------|-------|-------------------|----------------------|
|              |         |       |       |                   | left    | right   |
| 1.12         | 0.7094  | 0.1461|       | 24.30             | 0.669   | 0.665   |
| 1.10         | 0.6982  | 0.1446|       | 28.93             | 1.108   | 1.102   |
| 1.08         | 0.6860  | 0.1431|       | 33.26             | 1.550   | 1.543   |
| 1.06         | 0.6723  | 0.1418|       | 39.77             | 2.004   | 1.899   |

The calculated current and conductance curves for 4,4'-bipyridine molecular junction are shown in figure 4 as function of the distance between two gold clusters. It is seen from figure 4(a) that currents are taken nonlinearly increase with the increase of the bias. Furthermore, currents are also strongly dependent on the distance between the electrodes. In general, longer distance results in smaller current. Figure 4(b) shows the corresponding conductance of the molecular junctions. One can see that there exists conductance plateau around zero bias. When the distance between the gold clusters decreases, the value of the plateau is arisen and the plateau becomes slightly narrower. It can be
concluded that the changing of the distance can result in significant change of the molecule-metal interaction and therefore the electron transport properties of the device. The conductance curves all exist a steep increase at about 0.5V, which is of agreement with the experimental observation very well[11].

![Figure 4](image)

**Figure 4.** Current (a) and conductance (b) curves of the molecular junction. Distances of the two gold clusters are taken as d=1.06 nm(dot), 1.08nm(dash), 1.10nm(solid), 1.12nm(dash dot).

### 4. Summary

In summary, we have studied the current-voltage characteristics of organic molecular 4,4'-bipyridine electronic device by means of a generalized quantum chemical elastic scattering Green’s function approach. The influences of the distance between the electrodes on geometric structure of the molecule and on the electronic transport properties of the devices have been discussed in detail. It is found that the geometric structure of the molecule especially the dihedral angle between the two pyridine rings is sensitive to the distance between the two electrodes as well as the coupling constants. One can find that shorter the distance is, stronger the coupling, and consequently larger the conductance will be.

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