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Charge transfer and variation of potential distributions in the formation of 4, 4′-bipyridine molecular junction*

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In this paper the charge transfer and variation of potential distribution upon formation of 4, 4′-bipyridine molecular junction have been investigated by applying hybrid density-functional theory (B3LYP) at *ab initio* level. The numerical results show that there exist charge-accumulation and charge-depletion regions located at respective inside and outside of interfaces. The variation of potential distribution is obvious at interfaces. When distance between electrodes is changed, the charge transfer and variation of potential distribution clearly have distance-dependent performance. It is demonstrated that the contact structure between the molecule and electrodes is another key factor for dominating the properties of molecular junction. The qualitative explanation for experimental results is suggested.

Keywords: charge transfer, potential distribution, molecular junction
PACC: 7340C, 7360R, 7115A

1. Introduction

With the continuous minimization of electronic device, one developing trend is to construct functional electronic devices by using single molecules. Many theoretical[1−18] and experimental groups[19−32] have studied the electric properties of single molecules and have obtained exciting results in recent years. It has been noted that small conjugated molecules,[19−24] single- and multiple-wall carbon nanotubes[25] and macromolecules such as DNA[26−29] possess many useful device characteristics, for instance, molecular switch,[28−30] molecular memory,[26] negative differential resistance[27] and single-molecule transistors.[23] Currently, experimental techniques and theories in molecular electronics need to be developed, because not only do the theoretical results not give a good explanation for experimental measurement, but also the experimental results for the same molecule with different technique show great difference between each other.[19,20] Therefore, effort needs to be devoted in both experimental and theoretical areas for the application of single molecular devices.

When molecular devices are fabricated, how molecular junctions are formed is an open issue. It is known that the electronic structure of molecule is likely influenced by contact structure and external electric field[21,33,34], and the potential barrier at interface plays a key role for charge transfer in molecular junctions. However, detailed discussion for charge transfer and potential redistribution upon formation of molecular junction is not given. In this paper, based on first principles, we investigate charge and potential redistribution after the formation of molecular junction by considering several circumstances. Furthermore, a qualitative explanation for switching properties of the 4, 4′-bipyridine molecule[11−15] is suggested.

2. Computational details

Considering the local interaction between molecule and electrodes, we take two gold atom clusters and sandwich 4, 4′-bipyridine molecule between them in the calculation, where an extended molecule is formed. Based on our previous works,[34] the nitrogen atom of 4, 4′-bipyridine molecule can energetically sit on the top position of one gold atom.

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It is noted that the contact structure between the molecule and electrodes is difficult to be controlled and determined by experiment. Therefore, we choose two contact structures to discuss. The structure of gold-4, 4′-bipyridine-gold system with local contacts of an equilateral tetrahedron atom cluster (cont1) and a linear chain atom cluster (cont2) is schematically shown in Fig.1, where the x axis passes through the two nitrogen atoms.

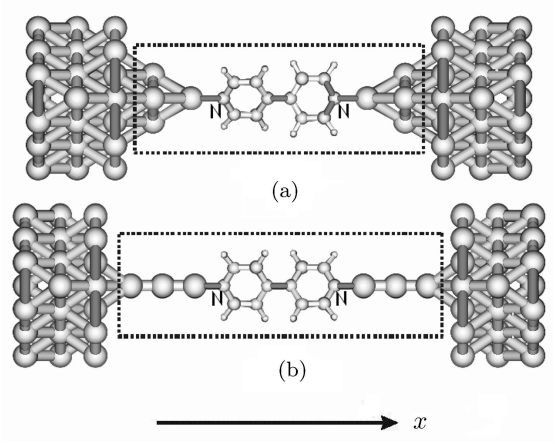


Fig.1. Schematic structures of 4, 4′-bipyridine molecular junction: (a) equilateral tetrahedron contact with four gold atoms at each side; (b) chain contact with three gold atoms at each side.

The interaction energy between the molecule and electrodes can be described by coupling parameters $Y_{kS}(V)$ and $Y_{Dk'}(V)$, which represent coupling between the atom $k(k')$ of the molecule and the gold clusters (denoted by S and D) in the site representation,[2,34]

$$\begin{aligned} Y_{kS} &= \langle k|U|S\rangle = \sum_{n,\alpha,i} C^k_{n\alpha}\langle k_\alpha|U|S_i\rangle C^S_{ni} \\ &= \sum_{n,\alpha,i} C^k_{n\alpha}\langle k_\alpha|H|S_i\rangle C^S_{ni}, \\ Y_{Dk'} &= \langle D|U|k'\rangle = \sum_{n,\beta,j} C^D_{nj}\langle D_j|U|k'_\beta\rangle C^{k'}_{n\beta} \\ &= \sum_{n,\beta,j} C^D_{nj}\langle D_j|H|k'_\beta\rangle C^{k'}_{n\beta}, \end{aligned} \tag{1}$$

where $C^k_{n\alpha}$ ($C^{k'}_{n\beta}$) is expansion coefficient of the extended molecular orbital $|n\rangle$ on the atomic orbital $|\alpha\rangle$ ($|\beta\rangle$) of the atom k (k') of the molecule, and $C^S_{ni}(C^D_{nj})$ is on the atomic orbital $|i\rangle$ ($|j\rangle$) of the gold atom cluster S (D). It is straightforward that the interaction energy between molecule and electrode can be obtained by summing up all the atoms in the molecule. Accordingly, the positive value of the coupling parameter between molecule and electrode increases the total energy of the whole system, while the negative value decreases it.

The geometric and electronic structures of molecules can be simultaneously changed by interaction between molecule and electrodes. In the calculation, distance between the two gold clusters is fixed, and geometric structure of the extended molecule is optimized at hybrid density-functional theory (DFT) B3LYP level with Lanl2DZ basis set implemented in Gaussian03 package.[35] The electronic density and potential distribution of the molecular junction are analysed. In order to view profiles of charge redistribution and potential variation upon formation of the molecular junction, we decompose the extended molecule into gold clusters and bare molecule, then the electronic densities and potential distribution of the individual parts are calculated. The charge transfer and potential variation are obtained by taking corresponding difference between the extended molecule and individual parts, i.e.

$$\begin{aligned} \Delta D &= D_{\rm EM} - (D_{\rm Au} + D_{\rm M} + D_{\rm Au}), \\ \Delta P &= P_{\rm EM} - (P_{\rm Au} + P_{\rm M} + P_{\rm Au}). \end{aligned} \tag{2}$$

3. Results and discussion

The influence of distance between the two electrodes on geometrical structures of a molecule is first investigated. We here just take the extended molecule with cont1 as an example. The optimized geometrical structures show that, when distance between the two electrodes is stretched, the molecule is firstly lengthened and then shortened (see Table 1). Moreover, when the distance is at 1.22 nm, the length of the molecule takes the largest value of 0.734 nm. The underlining mechanism is understandable by observing the coupling parameters between molecule and electrodes.

Variation of the coupling parameter between the molecule and left gold electrode with different distances between the two electrodes is shown in Fig.2. From Fig.2, one can see that, when the distance increases, the coupling parameter is firstly positive, and then goes to the negative region. The lowest value of the coupling parameter is reached at about 1.24 nm. As the distance is elongated from 1.24 nm, the coupling parameter tends toward zero. Accordingly, the molecular length is gradually returned to its natural length ($d_0 = 0.719$ nm). It is noted that, as the molecular structure is asymmetric, the coupling parameter

at left side is unequal to that at right side, but with little difference.

The dihedral between the two pyridine rings in molecule is also varied with variation of the distance between the two electrodes (see Fig.2). It seems that the dihedral and coupling parameters have the minimum absolute values simultaneously.

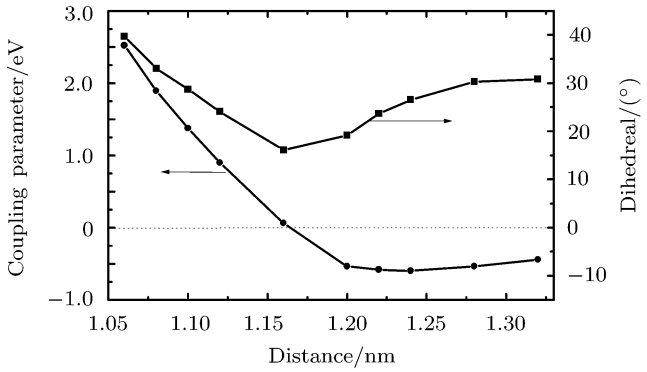


Fig.2. Coupling parameter between molecule and left gold cluster and dihedral between the two pyridine rings of the molecule with different distances between two electrodes. The molecular junction is shown in Fig.1(a).

The numerical simulation shown above seems to demonstrate that there exists optimized molecular junction with proper circumstance. However, the distance between two electrodes is strongly dependent on technical methods in forming molecular junctions. Thus the influence of two electrodes' distance on properties of molecular junctions needs to be discussed.[36]

Charge transfer and variation of potential distribution defined in Eq.(2) in the formation of the gold–molecule–gold junction with electrode distance at 1.08 nm for cont1 are presented in Fig.3. The spatial distribution of the transferred electrons is plotted as a function of position in the xy plane after integrating over the z axis, the cross-sectional view of potential variation is shown as a function of position in the xy plane. From Fig.3, one can see that charge density difference and potential difference have an obvious variation near interfaces between molecule and electrodes, while there is slight change in the interior of molecule. When the molecular junction is forming, the π electrons are transferred from central part of the molecule to its ends, and the charge is mainly accumulated at ends of the molecule because of presence of a potential barrier at the interfaces. At the same time, electrons are depleted on the extracting side of the potential barrier. The charge redistribution results in two resistivity dipoles with reversed direction at the metal–molecule interfaces, which will lead to a nonlinear transport effect for molecular devices.[7,37] The directions of the electric dipole moments are different from those caused by external fields.[34]

Table 1. Molecular length and net charge analysis for extended molecule with two kinds of contact structure under different distances of two electrodes.

	Distance/nm	Molecular length/nm	Molecule/e	Left Au cluster/e	Right Au cluster/e
Cont1	1.06	0.672	0.135	−0.059	−0.077
	1.08	0.686	0.124	−0.051	−0.073
	1.10	0.698	0.137	−0.054	−0.083
	1.12	0.709	0.139	−0.078	-0.061
	1.16	0.727	0.218	−0.090	−0.129
	1.20	0.732	0.346	−0.207	−0.139
	1.22	0.734	0.364	−0.168	−0.196
	1.24	0.733	0.382	−0.182	−0.200
	1.28	0.731	0.357	−0.177	−0.180
	1.32	0.728	0.296	−0.147	−0.148
Cont2	1.08	0.682	0.345	−0.164	−0.181

For greater clarity, charge transfer in the formation of the molecular junction with cont1 for electrodes in different distances is shown in Fig.4(a) by integrating over y and z axes. It can be seen that amounts of accumulated charge inside the interface and depleted charge outside the interface decrease as distance between the two electrodes increases. Moreover, in totality, the molecule contributes electrons to gold clusters as shown in Table 1. When the distance between the two electrode increases from 1.06 nm to 1.24 nm, the amount of charge transferred from molecule to gold clusters is enhanced. As the distance further increases, the amount of transferred charge decreases. Figure 4(b) shows the variation of potential distribu-

tion along x axis. One can see that the variation of potential at the interfaces becomes weaker as the distance increases. As a result, the height of the potential barrier located at the interface increases as the distance increases, which is disadvantageous for electron tunnelling through the molecular junction.

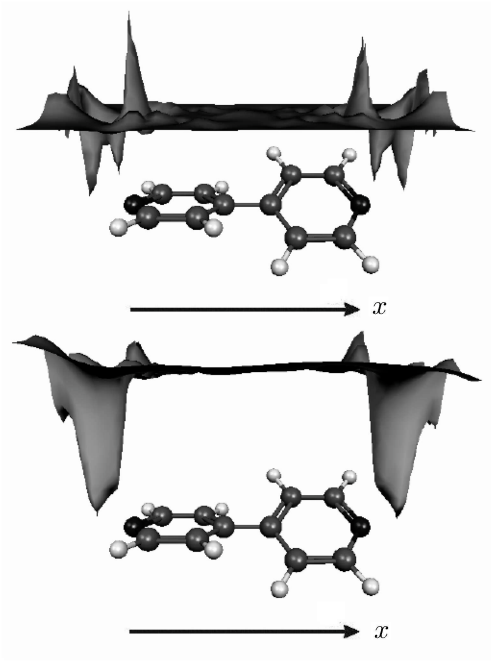


Fig.3. Spatial distribution of charge transfer (top) and variation of potential (bottom) in the formation of the molecular junction shows in Fig.1(a) with distance of 1.08 nm.

In order to investigate the effect of contact structure on the formation of molecular junction, we simulate the other contact structure (cont2 in Fig.1(b)), and display the charge transfer distribution and variation of the potential distribution (see Fig.5). The charge transfer and variation of the potential distributions show the similar behaviour as that for cont1. In detail, the peak amount of the accumulated charge of 0.066/a.u.^{2} for cont2 is smaller than that of 0.100/a.u.^{2} for cont1. While the maximum amount of the depleted charge of 0.086/a.u.^{2} for cont2 is almost equal to that of 0.084/a.u.^{2} for cont1. As a whole, the molecule contributes more charge to gold clusters with cont2 than that with cont1 (see Table 1). Furthermore, the bottom value of the potential variation at the interface is of −0.218 a.u. for cont2, which is deeper than −0.175 a.u. for cont1. This seems to demonstrate the lower potential barrier at the interface for the molecular junction with cont2. In addition, the coupling parameters for cont2 are 3.377 eV and 3.344 eV, which are also larger than 1.863 eV and 1.894 eV for cont1 respectively. With the above discussion, we may conclude that formation of molecular junction has a close relation with the contact structure, and the molecular junction with cont2 demonstrates a better electronic behaviour.

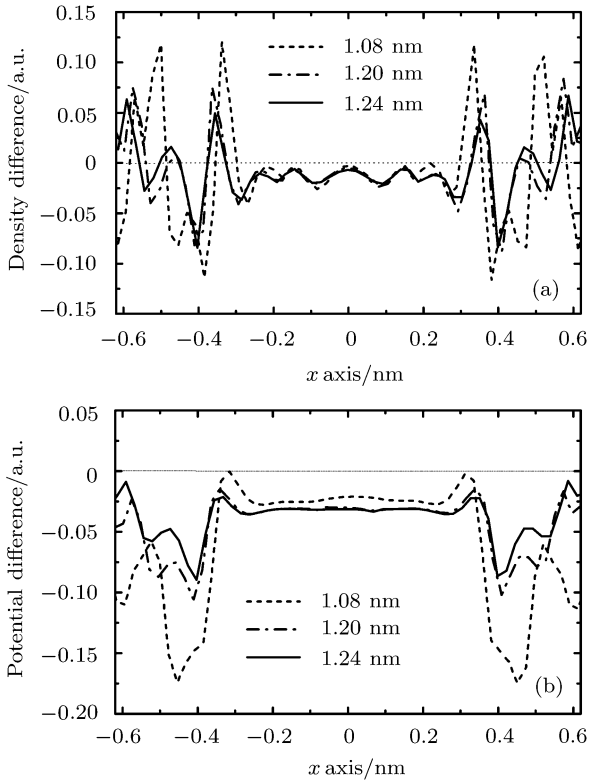


Fig.4. Spatial distribution of charge transfer (a) and variation of potential (b) along x axis in the formation of the molecular junction shown in Fig.1(a). Distances of the two electrodes are taken as 1.08, 1.20 and 1.24 nm.

When the molecular junction is formed, the paired electrons of nitrogen atom are used to form coordination bond between nitrogen and gold atoms. The π electrons in pyridine ring are thus attracted by nitrogen atoms to accumulate at the ends of the molecule, where nitrogen atoms possess negative net charges. As a result, mutual electrons of gold cluster will be pushed away from the inner gold atoms, and a depleted charge region is thus appeared there. With the above discussion, it is straightforward to give deduction that, if positive gate voltage is added to the 4, 4′-bipyridine molecule, the coordination bond intends to be broken down because the charge in molecule is prevented to shift towards gold atoms. Thereby, the molecular junction is hardly formed, and there is no measured current through the junction as demon-

strated in the experiment.[24]

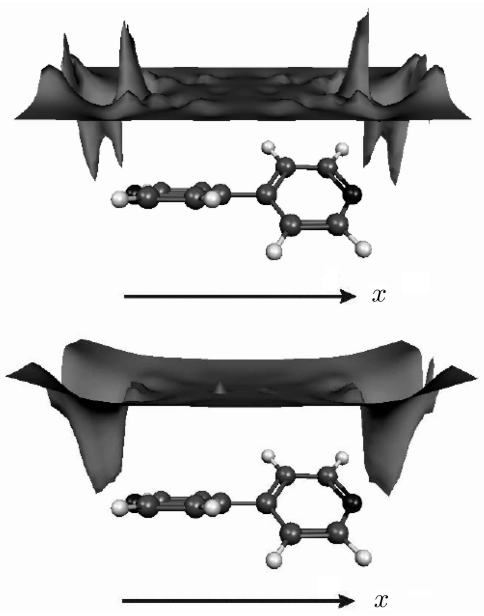


Fig.5. Spatial distribution of charge transfer (top) and variation of potential (bottom) in the formation of the molecular junction shows in Fig.1(b) with distance of 1.08 nm.

4. Conclusion

We have studied charge transfer and potential changes properties in the formation of the 4, 4′-bipyrindine molecular junction. The numerical results show that the coupling parameters have minimum value with the electrodes distance near 1.24 *nm*. Smaller absolute value of coupling parameter results in smaller dihedral angle between the two pyridine rings of 4, 4′-bipyridine molecule. The charge transfer and potential changes mainly take place near the interfaces between the molecule and electrodes. Moreover, charges are accumulated at inside of the interface and depleted at outside of the interface. Additional electric dipole moments are thus produced near the interfaces between the molecule and electrodes in the formation of the molecular junction. The charge transfer and variation of potential distribution are highly dependent on the distance of electrodes. The contact structure between molecule and electrodes has a great effect on the properties of molecular junction.

References

[1] Mujica V, Kemp M and Ratner M A 1994 *J. Chem. Phys.* **101** 6849

[2] Wang C K, Fu Y and Luo Y 2001 *Phys. Chem. Chem. Phys.* **3** 5017

[3] Luo Y, Wang C K and Fu Y 2002 *J. Chem. Phys.* **117** 10283

[4] Wang C K and Luo Y 2003 *J. Chem. Phys.* **119** 4923

[5] Luo Y, Wang C K and Fu Y 2003 *Chem. Phys. Lett.* **369** 299

[6] Xue Y Q and Ratner M A 2004 *Phys. Rev.* B **70** 081404

[7] Xue Y Q and Ratner M A 2003 *Phys. Rev.* B **68** 115406

[8] Jiang J, Lu W and Luo Y 2004 *Chem. Phys. Lett.* **400** 336

[9] Paulsson M, Frederiksen T and Brandbyge M 2006 *Nano Lett.* **6** 258

[10] Taylor J, Brandbyge M and Stokbro K 2003 *Phys. Rev.* B **68** 121101

[11] Wu X J, Li Q X, Huang J and Yang J L 2005 *J. Chem. Phys.* **123** 184712

[12] Li Q X, Wu X J, Huang J and Yang J L 2005 *Ultramicroscopy* **105** 293

[13] Ángel J and Pérez-Jiménez 2005 *J. Phys. Chem.* B **109** 10052

[14] Hu Y B, Zhu Y, Gao H J and Guo H 2005 *Phys. Rev. Lett.* **95** 156803

[15] Hou S M, Zhang J X, Li R, Ning J, Han R S, Shen Z Y, Zhao X Y, Xue Z Q and Wu Q D 2005 *Nanotechnology* **16** 239

[16] Wu Z J, Zhu K D, Yuan X Z and Zhen H 2005 *Acta Phys. Sin.* **54** 3346 (in Chinese)

[17] Li Z L, Wang C K, Luo Y and Xue Q K 2005 *Chin. Phys.* **14** 1036

[18] Liu X L, Xu H, Ma S S, Deng C S and Guo A M 2006 *Acta Phys. Sin.* **55** 5562 (in Chinese)

[19] Reed M A, Zhou C, Muller C J, Burgin T P and Tour J M 1997 *Science* **278** 252

[20] Xiao X Y, Xu B Q and Tao N J 2004 *Nano Lett.* **5** 267

[21] Cui X D, Primak A, Zarate X, Tomfohr J, Sankey O F, Moore A L, Moore T A, Gust D, Harris G and Lindsay S M 2001 *Science* **294** 571

[22] Dadosh T, Gordin Y, Krahne R, Khivrich I, Mahalu D, Frydman V, Sperling J, Yacoby A and Israel B J 2005 *Nature* **436** 677

[23] Albrecht T, Guckian A, Ulstrup J and Vos J G 2005 *Nano Lett.* **5** 1451

[24] Xu B Q and Tao N J 2003 *Science* **301** 1221

[25] Frank S, Poncharal P, Wang Z L and de Heer W A 1998 *Science* **280** 1744

[26] Liu Z M, Yasseri A A, Lindsey J S and Bocian D F 2003 *Science* **302** 1543

[27] Chen J, Reed M A, Rawlett A M and Tour J M 1999 *Science* **286** 1550

[28] Yasutomi S, Morita T, Imanishi Y and Kimura S 2004 *Science* **304** 1944

[29] Xu B Q, Li X L, Xiao X Y, Sakaguchi H and Tao N J 2005 *Nano Lett.* **5** 1491

[30] Terabe K, Hasegawa T, Nakayama T and Aono M 2005 *Nature* **433** 47

[31] Csonka Sz, Halbritter A, Mihály G, Shklyarevskii O I, Speller S and van Kempen H 2004 *Phys. Rev. Lett.* **93** 016802

[32] Fang J H, Liu L W, Kong W J, Cai J Z and Lü L 2006 *Chin. Phys.* **15** 1071

[33] Nitzan A and Ratner M A 2003 *Science* **300** 1384
[34] Li Z L, Zou B, Wang C K and Luo Y 2006 *Phys. Rev.* B **73** 075326
[35] Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Montgomery J A, Vreven T, Kudin K N, Burant J C, Millam J M, Iyengar S S, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson G A, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox J E, Hratchian H P, Cross J B, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Ayala P Y, Morokuma K, Voth G A, Salvador P, Dannenberg J J, Zakrzewski V G, Dapprich S, Daniels A D, Strain M C, Farkas O, Malick D K, Rabuck A D, Raghavachari K, Foresman J B, Ortiz J V, Cui Q, Baboul A G, Clifford S, Cioslowski J, Stefanov B B, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin R L, Fox D J, Keith T, Al-Laham M A, Peng C Y, Nanayakkara A, Challacombe M, Gill P M W, Johnson B, Chen W, Wong M W, Gonzalez C and Pople J A 2003 GAUSSIAN 03 (Pittsburgh PA: Gaussian Inc)
[36] Zou B, Li Z L, Wang C K and Xue Q K 2005 *Acta Phys. Sin.* **54** 1341 (in Chinese)
[37] Landauer R 1957 *IBM J. Res. Dev.* **1** 223
Landauer R 1988 *IBM J. Res. Dev.* **32** 306