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Theoretical study of electron transport properties of an organic molecule

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Electron transport properties of benzene-(1,4)-dithiolate sandwiched between two gold electrodes were investigated using first-principles calculations. It was found that the peak energies and the peak widths in the transmission spectra are strongly dependent on the contact structures. Furthermore, the contributions of MOs to the transmission coefficients also depend on the contact structures. Especially, only the channel related to HOMO-3, HOMO, and LUMO+1 contributes to the conductance at zero bias. These results suggest that the determination of the contact structure is essential for estimating the properties of molecular devices.

Key words: *electron transmission; first principles calculations; organic molecule; benzenedithiolate*

1. Introduction

Recently, transport properties of single-organic molecules have attracted much attention. One of the most prominent systems in this field is the dithiolate molecule between gold surfaces. Since the conductance of a benzene-(1,4)-dithiolate (BDT) sandwiched between two gold electrodes was measured experimentally [1], it has been intensively investigated theoretically. However, it is still unclear how the conductance depends on the atomic configurations around the contact. Knowing how the contact geometry influences the conductance through the metal–molecule–metal sand-

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wich structure requires both, a precise determination of the molecule–metallic-electrode interface structure, and an evaluation of the conductance for different geometries with fair accuracy. The transmission properties of the BDT molecule sandwiched between two gold electrodes by means of *ab initio* method were investigated, and the effect of the contact structures was examined. The transmission coefficients were evaluated with the Lippmann–Schwinger equation. It was found that the peak energies and the peak widths in the transmission spectra are sensitively dependent on the contact structures. Furthermore, the contributions of molecular orbitals (MOs) of the BDT molecule to the transmission coefficients also depend on the contact structures. Especially, only some of MOs contribute to the conductance at zero bias. These results suggest that the determination of the contact structure is essential to estimate the transport properties of molecular devices.

2. Calculation method

The transmission coefficients are evaluated by using the Lippmann–Schwinger equation. The details are described in Refs. [2–4]. The wave function is expressed with the two dimensional plane waves parallel to the surface and the real-space mesh along the surface normal. The electrodes are replaced by bi-jellium which corresponds to the metallic gold (r_s ~3) and the organic molecule is inserted between the bi-jellium. This method uses the non-local pseudopotentials, which allow organic materials to be studied. The electronic states were decomposed into eigenchannels [5]. The conductance is evaluated within the Landauer formula [6], in which the conductance unit is $G_0 = 2e^2/h$.

3. Results

The electron transport properties of the BDT molecule sandwiched between two gold electrodes have been studied so far, and it was found that the transmission coefficients and the projected density of states (pDOS) are sensitively dependent on the contact structures [4, 7]. Here, the results for two typical structures are shown. Figure 1 shows the atomic configurations of the two. In Figure 1a, one Au atom is inserted between the molecule and the jellium electrode at each side, rendering a model of adsorption at the on-top site. In this geometry, the benzene ring is upright to the electrode surface and the C, S and Au atoms form a straight line. In Figure 1b, three Au atoms are inserted at each side to simulate the hollow site structures [8]. In this case, the benzene ring is slightly tilted from the surface normal by about 20 degrees.

Figure 2 shows (a) the eigenchannel transmission and (b) the pDOS as a function of the incident electron energy for the structure shown in Fig. 1a. The Fermi level is set to be 0.

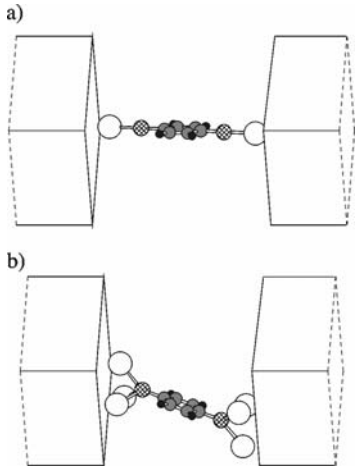

Fig. 1. Metal–molecule–metal junction structures: a) one Au atom is inserted between the molecule and the jellium electrode to each side to simulate the ontop adsorption structure and (b) three Au atoms are inserted to simulate the follow site adsorption structure

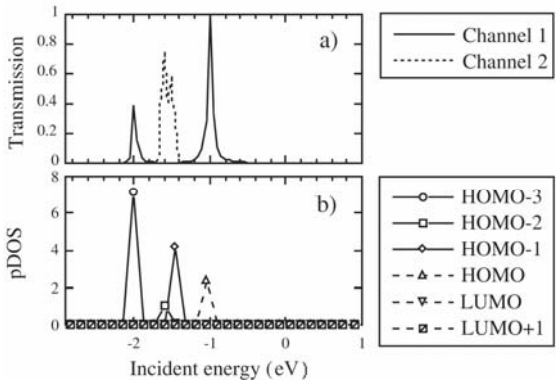

Fig. 2. Transmission spectrum (a) and pDOS as a function of the incident electron energy (b) for the structure in Fig. 1(a)

In Figure2a, two transmission channels with non-vanishing magnitudes are plotted. The first one has two peaks, located at –2.0 eV and –1.0 eV. These two peaks have the same symmetry. The second channel has one peak at –1.5 eV, with a different symmetry. The magnitudes of other channels are too small to be visible. Figure 2b shows the pDOS with respect to the MOs of an isolated BDT molecule, in order to clarify which MOs contribute to the transmission properties. The MOs from HOMO-3 to LUMO+1 were considered here, neglecting other MOs with only marginal or vanishing contribution. HOMO-3, HOMO, LUMO, and LUMO+1 are related to π orbitals, whereas HOMO-2 and HOMO-1 are related to σ orbitals. It is noteworthy that HOMO-3, HOMO and LUMO+1 bear one kind of symmetry when projected to the plane normal to the transmission direction, and HOMO-2 and HOMO-1 bear another [4]. These symmetries are important to analyse the transmission spectra and the con-

ductance. HOMO-3 has a peak at –2.0 eV matching well to the peak at the –2.0 eV in the transmission spectrum (Fig. 1a). Similarly, HOMO-2, HOMO-1, and HOMO have peaks corresponding to the transmission resonance. In Figure 2a, the two peaks related to HOMO-3 and HOMO form the first channel, as the two have the same symmetry. Similarly, HOMO-2 and HOMO-1 form the second channel, as they have a different symmetry.

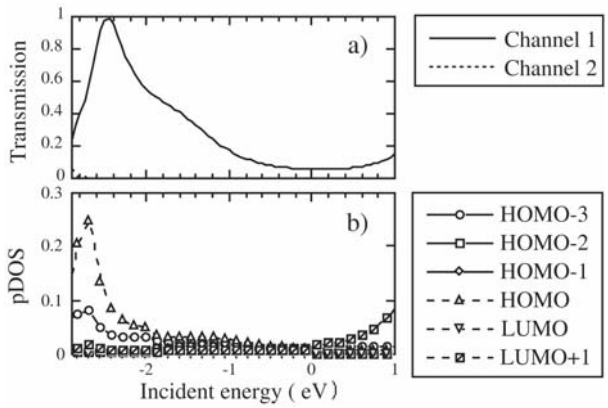

Fig. 3. Transmission spectrum (a) and pDOS as a function of the incident electron energy (b) for the structure in Fig. 1b

Figure 3 shows (a) the eigenchannel transmission and the (b) pDOS as a function of the incident electron energy for the structure shown in Fig. 1b.The position and width of the conductance peaks are very different from those in Fig. 2. Only one channel is visible in Fig. 3a, with one resonance taking place at –2.5 eV. The peak width is much larger than that in Fig. 2. This may be readily understood by the fact that the S–Au interaction is greatly strengthened as a direct result of the increased coordination number. In the same way as in Fig. 2, the peaks of the transmission spectra can be attributed to the MOs. For the structures shown in Fig. 1b, there is only one channel bearing remarkable transmission, and no contribution from other MOs than HOMO-3 and HOMO to the transmission coefficient. Thus these first principles calculation results demonstrate that the contributions of MOs to the transmission properties can vary strongly with the contact configurations.

The conductance at zero bias corresponds to the sum of the eigenchannel transmissions at the Fermi level. For both structures, only the first channel contributes to the conductance, suggesting that among all MOs, only HOMO-3, HOMO and LUMO+1 contribute to the conductance at zero bias, while HOMO-2, HOMO-1, LUMO and other MOs do not. Although the reason for this difference among the MOs' contribution is unclear at this point, it must be concerned with the MOs symmetry. The conductances are calculated to be $0.003G_0$ and $0.058G_0$ for the structures shown in Figs. 1a and b, respectively. The conductance of the former is very small compared to the latter.

These results are extremely different from the previous experimental results [1], which shows a very small conductance (~$10^{-5}G_0$). Although some theoretical groups, including us, have tried to overcome the discrepancy between the experimental and the theoretical results, it remains a problem. This may mean that the models adopted here are inappropriate to explain the experiments. One of the reasons for this discrepancy is the lack of the information about the atomic configurations in the experiment. Recently, a new experimental report [9] shows a greatly higher conductance ($0.01G_0$) for the Au–BDS–Au system. This new experimental result is very welcome to theorists because it shows the same order of conductance. However, the comparison between experimental and theoretical works must be done carefully. There is a remarkable experimental report about the measurement of the conductance through a single organic molecule sandwiched between two gold electrodes [10]. It showed that the conductance measured at low temperature is very different from that at room temperature. Further examinations into both measurements and simulations are still necessary to clarify the transport properties of a single organic molecule.

4. Conclusion

Electron transport properties of a benzene-(1,4)-dithiolate molecule sandwiched between two gold electrodes were studied by using first-principles transmission calculations. It was found that the transmission spectra and the contributions of the molecular orbitals (MOs) to the transmission coefficients are strongly dependent on the contact structures, and furthermore, not all MOs contribute to the conductance.

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References

[1] REED M.A., CHOU C., MULLER C.J., BURGIN T.P., TOUR J.M., Science, 278 (1997), 252.
[2] LANG N.D., Phys. Rev. B, 52 (1995), 5335 and references therein.
[3] KOBAYASHI N., AONO M., TSUKADA M., Phys. Rev. B, 64 (2001), 121402.
[4] NARA J., GENG W.T., KINO H., KOBAYASHI N., OHNO T., J. Chem. Phys., 121 (2004), 6485.
[5] BRANDBYGE M., SORENSEN M.R., JACOBSEN K.W., Phys. Rev. B, 56 (1997), 14956.
[6] BUETTIKER M., IMRY Y., LANDAUER R., PINHAS S., Phys. Rev. B, 31 (1985), 6207.
[7] NARA J., KINO H., KOBAYASHI N., TSUKADA M., OHNO T., Thin Solid Films, 438-439 (2003), 221.
[8] NARA J., HIGAI S., Y.MORIKAWA, T.OHNO, J. Chem. Phys., 120 (2004), 6705.
[9] XIAO X., XU B.,.TAO N.J, Nano Lett., 4 (2004), 267.
[10] REICHERT J., WEBER H.B., MAYOR M., VON LÖNEYSEN H., Appl. Phys. Lett., 82 (2003), 4137.

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