Electronic structure of the 
Au/benzene-1,4-dithiol/Au transport 
interface: Effects of chemical bonding

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Abstract

We present results of electronic structure calculations for well-relaxed Au/benzene-1,4-dithiol/Au molecular contacts, based on density functional theory and the generalized gradient approximation. Electronic states in the vicinity of the Fermi energy are mainly of Au 5d and S 3p symmetry, whereas contributions of C 2p states are very small. Hybridization between C 2p orbitals within the benzene substructure is strongly suppressed due to S-C bonding. In agreement with experimental findings, this corresponds to a significantly reduced conductance of the molecular contact.

Key words: molecular contact, electronic structure, electrical transport 
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1 Introduction

Molecular devices nowadays are becoming more and more important because of a rapidly increasing number of potential applications, spanning a wide range from new computer architectures to multifunctional chemical sensors and medical diagnostic tools. Exploring the use of specific molecules as active components in electronic circuits has been a field of special interest in recent years. Electrical properties of molecular devices are usually addressed by measuring the transport through a molecule sandwiched between metallic electrodes. The resulting transport characteristics, of course, reflects both the metal-molecule contact and the molecule itself. Because transport in general is restricted to a

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small number of valence orbitals, the features of a molecular device strongly depend on the local electronic structure at the different molecular sites. Details of the chemical bonding, such as hybridization or charge transfer, hence play a key role for understanding the device, and structural relaxation due to the metal-molecule contact has to be taken into consideration.

Experimentally, Au/benzene-1,4-dithiol/Au transport interfaces are prepared via the mechanically controllable break junction technique [1]. In a first step a thin gold wire, covered with a self-assembled benzene-1,4-dithiol monolayer, is stretched until breakage. The opposing gold contacts then are slowly moved together until the onset of conductance is reached. From the theoretical point of view, the prototypical Au/benzene-1,4-dithiol/Au interface likewise has attracted much attention. Band structure methods have succeeded in reproducing the shape of the experimental current-voltage characteristic of the contact when an external bias is applied. However, the absolute value of the conductance is overestimated by one or two orders of magnitude [2,3,4]. The current magnitude appears to be an extremely sensitive function of both the contact geometry and chemistry. But even if atomic details of the contact are taken into account, transport calculations fail to reproduce the experimental fact of a conductance gap at zero bias.

The benzene-1,4-dithiol molecule has π bonding and π* antibonding orbitals formed by the carbon and sulfur p orbitals perpendicular to the ring plane, as well as σ bonding and σ* antibonding orbitals due to in-plane orbital overlap. While both the σ and π orbitals are fully occupied, the antibonding orbitals stay empty. Because they mediate direct orbital overlap, σ states are subject to stronger bonding-antibonding splitting than π states, and therefore appear at lower energies. For a small bias, the conductance of the molecular contact shows Ohmic behaviour because of a smooth density of states near the Fermi energy. When the bias is increased, two conduction peaks are observed, which can be traced back to resonant tunneling through either π* or (at higher bias) π orbitals [2].

The erroneous prediction of metallic transport characteristics for experimentally insulating molecules has been associated with the continuous exchange-correlation approximation applied in standard density-functional schemes [5]. For the Au/benzene-1,4-dithiol/Au contact, it has been demonstrated that an atomic self-interaction correction is useful to compensate this shortcoming in an approximate way, opening a conduction gap in the current-voltage characteristic. However, in this letter we show that the modification of the chemical bonding in the benzene ring, resulting from the specific contact geometry, has serious effects on the local electronic structure and thus likewise explains the insulating state. We thus conclude that taking into account the very details of the crystal and electronic structure is mandatory in order to obtain adequate input for transport calculations.
2 Calculational Details

The electronic structure calculations presented in the following are based on density functional theory and the generalized gradient approximation. To be specific, we use the WIEN2k program package, a state-of-the-art full-potential code applying a mixed lapw and apw+lo basis [6]. In particular, the WIEN2k program allows for structural optimization of the interface geometry. Thus it is suitable to study effects of covalent bonding and hybridization in detail. A well-relaxed interface geometry is of great importance for reliable band structure results, as even small alterations of the orbital overlap, due to structural relaxation effects, may cause significant modifications of the electronic states [7,8,9,10,11].

In our calculations, the charge density is represented via 88491 plane waves, the \( \mathbf{k} \)-mesh for the Brillouin zone integrations comprises 72 \( \mathbf{k} \)-points, and the Perdew-Burke-Ernzerhof parametrization of the exchange-correlation potential is applied. While Au 5\( p \), S 3\( s \), and C 2\( s \) orbitals are treated as semi-core states, the valence states comprise Au 5\( d \), 6\( s \), 6\( p \), S 3\( p \), 4\( s \), C 2\( p \), 3\( s \) as well as H 1\( s \) orbitals. Corresponding atomic sphere radii amount to 2.6 \( a_B \) for the Au, 1.8 \( a_B \) for the S, 1.3 \( a_B \) for the C, and 0.7 \( a_B \) for the H spheres.

![Fig. 1. Schematic structure of the Au/benzene-1,4-dithiol/Au molecular contact.](image_url)

| Bond          | \( \text{Au-S} \) | \( \text{S-C1} \) | \( \text{C1-C2} \) | \( \text{C2-C2} \) | \( \text{C2-H} \) |
|---------------|-------------------|-----------------|-----------------|-----------------|-----------------|
| bond length   | 2.55 Å            | 1.76 Å          | 1.42 Å          | 1.38 Å          | 1.10 Å          |

Table 1

Bond lengths in the relaxed Au/benzene-1,4-dithiol/Au molecular contact.

Our calculation relies on the contact geometry shown in figure[1]. The benzene-1,4-dithiol molecule is sandwiched between two gold contacts in fcc \([001]\) ori-
3 Results and Discussion

Results of our LAPW calculation for the Au/benzene-1,4-dithiol/Au interface are shown in figures 2 and 3. We present partial densities of states (DOS) for...
Fig. 3. Au/benzene-1,4-dithiol/Au molecular contact: Partial C densities of states for carbon sites 1 and 2 (see figure 1). The DOS is normalized with respect to the number of contributing sites.

the contact Au sites (forming the top of the gold electrodes), the S sites, and the two carbon sites C1 and C2; compare the structure sketch in figure 1. For a quantitative analysis, the density of states is normalized with respect to the number of contributing sites in each case. In the energy range shown, almost all electronic states trace back to Au 5\textit{d}, S 3\textit{p}, and C 2\textit{p} orbitals, respectively. The partial DOS of the contact Au sites is dominated by a broad structure of Au 5\textit{d} states, which is centered at roughly −3.5 eV and extends far above the Fermi energy. The gross features of the DOS shape resemble the findings for fcc gold, reflecting metallic conductivity for these sites. Moreover, hardly any deviation from fcc gold is found for the electronic structure of Au sites in the third gold layer off the contact, which justifies the setup of our electrodes.

The S 3\textit{p} DOS is rather unstructured in a wide energy window reaching from about −5 eV to 4 eV. Especially, at the Fermi level a distinct DOS is present, with a magnitude similar to the Au 5\textit{d} DOS. This observation traces back to hybridization between gold and sulfur orbitals, as expected for Au-S bonding.

In the next step we turn to the C1 site, which is affected by S-C1 and C1-C2 bonding. As compared to the previous findings for gold and sulfur, we have a significantly reduced (but still finite) DOS in the vicinity of the Fermi energy.
Moreover, strong hybridization between C1 2p and S 3p orbitals is evident, as both densities of states have sharp peaks near −9 eV and −8 eV, and common structures around both −6 eV and −4 eV. Hence, remarkable S-C1 bonding is a typical feature of the benzene-1,4-dithiol molecule.

Sharp DOS peaks at −9 eV and −8 eV and a distinct structure reaching from about −7 eV to −5 eV likewise are present for the C2 site. These states belong to σ bonding orbitals of p symmetry, which is also true for the corresponding S and C1 states. Of course, σ bonding orbitals mediate the main part of the orbital overlap within the benzene ring and with adjacent sulfur atoms. They therefore are subject to strong hybridization. States at energies above −4 eV are expected to belong to π bonding and π* antibonding orbitals. In fact, the C2 2p DOS has characteristic peaks near −3 eV and 2.5 eV, which, however, are not found in the C1 2p DOS. Hybridization between π bonding orbitals at sites C1 and C2 hence is almost negligible. As a consequence, π-type coupling within the benzene ring is seriously reduced in case of the benzene-1,4-dithiol molecule, which we attribute to strong S-C1 bonding. Due to the latter, C1 π and π* states are subject to energetical shifts, yielding a rather unstructured DOS at energies above −4 eV. Since π bonding states are responsible for the electrical conductance of the benzene ring, reduced C1-C2 coupling leaves the whole ring insulating. In fact, the C2 2p DOS reveals hardly any states in the vicinity of the Fermi energy.

In conclusion, we have studied the electronic structure of the Au/benzene-1,4-dithiol/Au transport interface by means of band structure calculations within density functional theory. Taking into account the specific interface geometry, we have addressed the chemical bonding in the molecular contact. While coupling via σ bonding S 3p and C 2p orbitals is strong, hybridization between π bonding orbitals at neighbouring carbon sites is almost completely suppressed due to S-C bonding. As a consequence, the local DOS at carbon sites without sulfur bonding almost vanishes at the Fermi energy, which explains the experimental observation of an insulating state. A transport calculation neglecting the details of the chemical bonding in the benzene-1,4-dithiol molecule is expected to overestimate the conductance (at least at small bias), although the shape of the current-voltage characteristic may be predicted correctly [2,3,4].

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