

Momentum filtering effect in molecular wires

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We report a first-principles analysis of conduction properties of molecular junctions. We investigate the relationship between molecular orbitals in the scattering region of the junction and the band structure of the leads. By characterizing the nature of the orbitals and the Bloch states of the leads, we provide an understanding on why some Bloch states conduct better than others. In particular, we found that the molecule can behave as a momentum filter: only those Bloch bands having the same orbital character as the molecular states near the Fermi level conduct well. Adding a different end group to the molecule can help to couple different Bloch bands to the molecule.

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Charge transport through atomic-sized contacts has attracted intensive interests recently.^{1,2} In these nanoscale systems, charge conduction occurs via quantum channels raised from atomic or molecular orbitals.^{3–8} For example, Nielsen *et al.*³ attributed the different conduction behavior between Pt and Au atomic contacts to that Pt has an open *d* shell while Au has not. On the other hand, for a molecular device in the metal-molecule-metal configuration, where two metallic leads contact a molecule, the electronic states of the molecule and the leads are both important. The presence of leads as well as external fields also modify the electronic states of the molecule.⁹ From the Landauer picture of charge conduction,¹⁰ transport can be understood from the quantum scattering point of view: a metal lead provides incoming electrons on various Bloch bands which are scattered by the molecule and possibly transmitted to the second lead. There are many Bloch bands in a metallic lead, if all contribute well to conduction through the metal-molecule-metal junction, one would expect large conductance. However, of the many Bloch bands in a lead at an energy *E*, it has been found that only a few give substantial transmission through a given molecule^{11–14} under a bias voltage. It is an interesting and general question as why some Bloch states transmit efficiently through a molecule and others do not?

In this paper, we theoretically investigate the above mentioned question of molecular conduction for molecular wires where the metal leads are either Au or Al, and several molecules will be studied. By investigating the “band character” of the metal leads and the “scattering states character” on the molecule (see blow), the results strongly suggest that a molecule bridging the two metal leads can act as a momentum filter—only those incoming states with matched character to the molecule can conduct efficiently. We further found that adding a different end group to the molecule can couple different conducting bands to the molecule. Therefore it should be possible to design specific molecules which can choose or switch conducting channels between two electrodes.

Our calculations are based on a first principles technique¹⁵ which combines the Keldysh nonequilibrium Green’s functions (NEGF) with density functional theory (DFT). Very

briefly, our analysis uses a *s*, *p*, *d* real space linear combination of atomic orbital (LCAO) basis set^{15,16} and the atomic cores are defined by the standard nonlocal norm conserving pseudopotential.¹⁷ The density matrix of the device is constructed via NEGF and the external bias *V_b* provides the electrostatic boundary conditions for the Hartree potential which is solved on a three-dimensional real space grid. Once the density matrix is obtained, the Kohn-Sham effective potential *V_{eff}*(**r**; *V_b*), which includes contributions from Hartree, exchange, correlation and the atomic core, is calculated. This process is iterated until numerical convergence of the self-consistent density matrix is achieved. In this way, we obtain the bias dependent self-consistent effective potential *V_{eff}*(**r**; *V_b*), from which we calculate¹⁵ the transmission coefficient *T*(*E*, *V_b*) ≡ *T*(*E*, [*V_{eff}*(**r**; *V_b*)]), where *E* is the scattering electron energy and *T* is a function of bias *V_b* through its functional dependence on *V_{eff}*(**r**; *V_b*). The NEGF-DFT technique has several characteristics very useful for our purpose:^{15,18} (i) The formalism constructs charge density under external bias potential using NEGF, thereby treats open device structures within the full self-consistent atomistic model of DFT; (ii) it treats atoms in the device and the leads at equal footing so that realistic atomistic leads are used; (iii) it treats localized and scattering states at equal footing so that the charge density includes all of these contributions; (iv) it is numerically efficient so that rather large systems can be analyzed.

Figure 1 shows the calculated band structure along the lead direction of an Au (upper panel) and an Al (lower panel) lead,¹⁹ where **ka** is the Bloch number. We have shifted the Fermi level of the leads to *E_f*=0 for clarity. There are several Bloch bands for a given energy *E*, and we attempt to distinguish the *character* of each band by analyzing the corresponding Bloch eigenstates *Ψ*, as follows. Since we use a LCAO as basis in our DFT analysis,¹⁵ *Ψ* is expanded in terms of the atomic orbitals *ϕ_ν*,

$$\Psi = \sum_{\nu, I} c_{\nu, I}^I \phi_{\nu}(\mathbf{r} - \mathbf{R}_I), \quad (1)$$

where *I* is the index of atom situated at position **R_I**, and *ν* is the orbital index. For Au, *ν*=*s*, *p_x*, *p_y*, *p_z*,

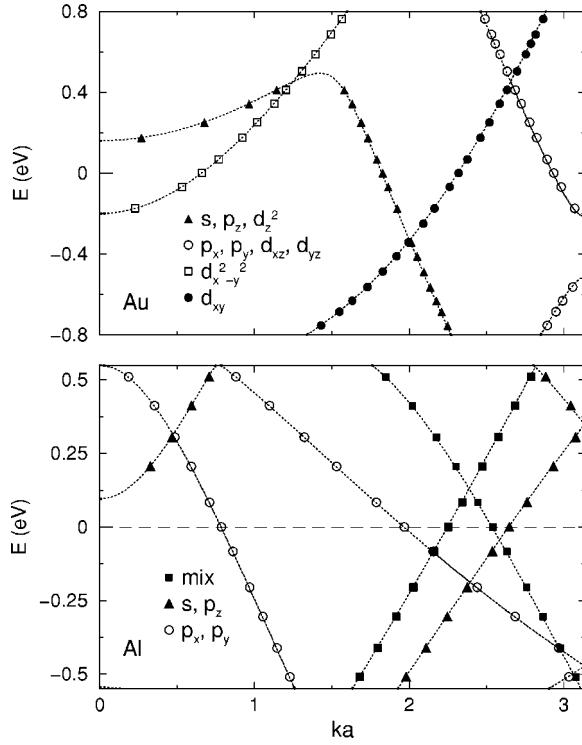


FIG. 1. Band structures of the Au (top) and the Al (bottom) lead, where ka is the Bloch number. The orbital character of each band is indicated by the symbols. Fermi level is at $E_f=0$.

$d_{z^2}, d_{xz}, d_{yz}, d_{x^2-y^2}, d_{xy}$; for Al, $\nu=s, p_x, p_y, p_z$. We then project the Bloch eigenstate to orbital ν of atom K :

$$P_{\nu,K} = \langle \phi_{\nu}(\mathbf{r} - \mathbf{R}_K) | \Psi \rangle \quad (2)$$

and sum this projection over all atoms inside the unit cell of a lead ($K=1-9$ for Au, $K=1-18$ for Al, see Ref. 19), hence the total projection to orbital ν is

$$P_{\nu} = \sum_K P_{\nu,K}. \quad (3)$$

For each orbital ν , we evaluate P_{ν} numerically using the NEGF-DFT *ab initio* technique. Typically we have found that for each incoming Bloch state, there are several P_{ν} 's which are at the order about 10^{-1} , and they are larger by at least a factor of 6 than the rest of the projections. We then call this Bloch state to have the “character” of orbital ν . Occasionally, there is a Bloch state for which all P_{ν} 's are very small ($<10^{-3}$) and no clear character can be assigned, we call this kind of Bloch state “mixed.” This way, the character of each Bloch band in the band structure of Fig. 1 was obtained as indicated by the symbols.

After defining the band character of the incoming states of the leads, we now investigate the main question of this work: for a given molecule bridging two leads, which of these Bloch bands will conduct? We use the molecular devices in Fig. 2 as examples, the molecules are biphenyl-dithiol and alkanedithiol ($C_6H_{12}S_2$). The molecule²⁰ is in contact with the hollow site of the two atomic scale Au (Al) leads¹⁹ whose band structures are shown in Fig. 1. The molecules are along the z direction and lie in the yz plane. The contact distance of the S-Au (from the sulfur atom to the surface of electrode) is 4.0 a.u. For Al device, the contact distance is fixed to be the same. The band structure of the Au and the Al lead are replotted in Fig. 2, but only those bands which conduct are now shown with symbols: in the following we refer these bands as “major conducting bands” because their contributions dominate the conductance of the entire device. Hence, by calculating contributions to conductance for each and every incoming Bloch state, we can find the major conduction bands. For the biphenyl-dithiol molecular device this band has p_x, p_y, d_{xz}, d_{yz} character for the Au lead [Fig. 2(a)], and p_x, p_y character for the Al lead [Fig. 2(c)].

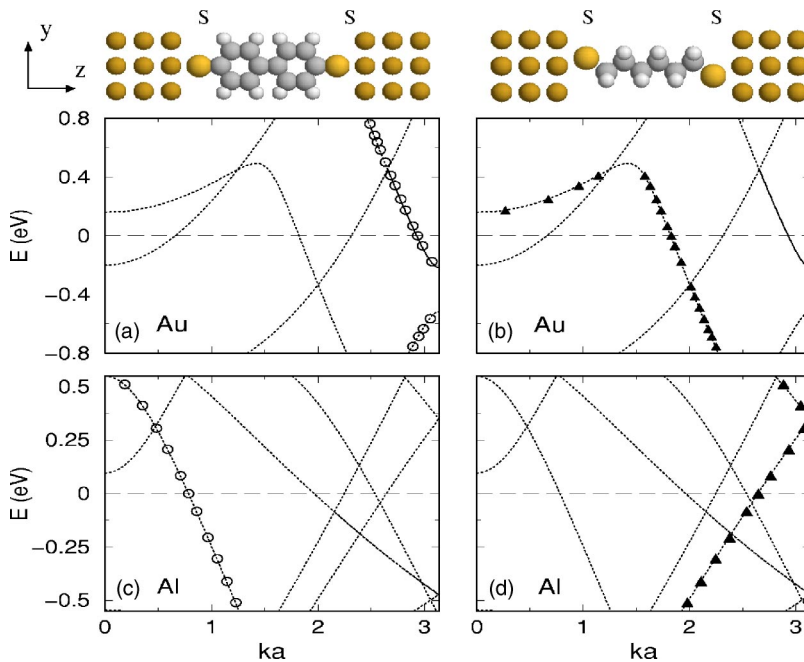


FIG. 2. Schematic illustration of the molecular device: biphenyl-dithiol and alkanedithiol ($C_6H_{12}S_2$). The molecule is along the z direction and lies in the yz plane. The band structure of the Au lead and the Al lead are shown. The major conducting band of the device is indicated by symbols. For biphenyl-dithiol, it is p_x character band as shown in (a) and (c). For alkanedithiol, it is s, p_z, d_{z^2} (Au) as shown in (b), or s, p_z band (Al) as shown in (d).

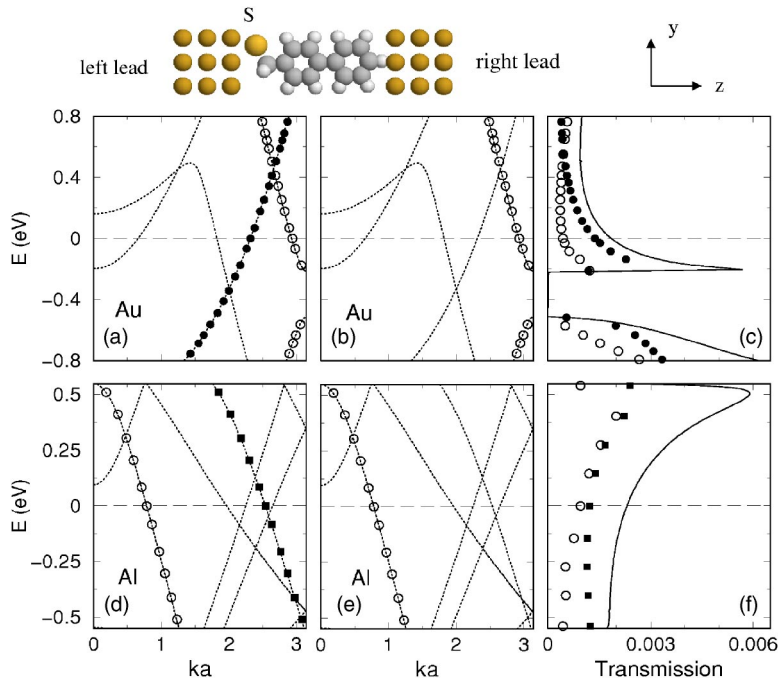


FIG. 3. Schematic illustration of a planar biphenyl methanethiol device. The molecule is along the z direction and lies in the yz plane. The band structures of the Au and Al lead are shown. The major conducting bands of the device are indicated by the symbols. For the left lead, they are the d_{xy} band and the p_x, p_y, d_{xz}, d_{yz} band (for Au), shown in (a); they are the “mix” band and the p_x, p_y band (for Al), shown in (d). For the right lead, it is the p_x character band as shown in (b) and (e). Transmission spectra are also shown in (c) for Au leads, and (f) for Al leads. The transmission coefficient of each conducting band of the left lead is indicated by symbols: they add up to give the total transmission (the solid line).

Next, we analyze electron scattering in the molecular part of the device.²¹ We do this by considering the molecular levels which mediate transport near the Fermi energy of the leads. These levels, of course, are not those of an *isolated* molecule because the molecule in the device is contacted by metallic leads and under a bias voltage. We determine them in the following fashion.⁹ After the NEGF-DFT iteration is completed to self-consistency, we diagonalize the sub-Hamiltonian matrix that corresponds to the molecule only. The eigenstates obtained this way can be viewed as the molecular orbitals under the device environment, and we refer to them as the renormalized molecular levels (RML).⁹ RML corresponds to the scattering states of the device: they mediate charge transport as shown before.^{9,21} We found, for the biphenyl-dithiol, the RML that carries current is dominated by π bond formed by the p_x orbital. In other words, the relevant RML wave function for this molecule has a dominant p_x character. Comparing with the major conducting band of the leads discussed in the last paragraph, we observe that both the incoming Bloch state and the molecular state which are important for transport, all have p_x character. Hence, there is a matching of orbital character. This is rather reasonable because matched states have the same spatial symmetry and therefore provide a better route for conduction.

We have further checked the above behavior of orbital character matching by investigating another device, the alkanedithiol device shown on the right-hand panel of Fig. 2. For this system the major conducting band was found to have s, p_z, d_{z^2} character for the Au lead [Fig. 2(b)], and s, p_z character for the Al lead [Fig. 2(d)]. Then, the RML analysis^{9,21} indicates that conduction through the alkanedithiol molecule is determined by a σ state, formed by s, p_y , and p_z orbitals. Therefore again, there is matching of states: the s, p_z orbitals appear in both the RML and the major conducting band. These two examples appear to sug-

gest that when a molecule bridges two leads, this molecule “chooses” the incoming band which has the same character as the molecule itself, to conduct. In this regard, the molecule acts as a momentum filter: only those Bloch states having the same orbital character of the molecule will conduct significantly.

This idea can be further confirmed from known results in literature. When a carbon atomic wire was contacted by Al leads, Ref. 11 showed that incoming Bloch states with the p_x, p_y character dominated conduction. From the above point of view, this is because a carbon wire has a pronounced π bond⁸ having the same character. Similarly, for an Au chain contacted by Au leads, Ref. 12 indicated that the Bloch states of the leads with s, p_z, d_{z^2} character conduct best. Again, from the above point of view, this is because conducting in the Au chain is dominated by s orbitals of the atoms.

The molecules studied so far are rather symmetrically coupled to the left and right leads. The top panel of Fig. 3 shows the structure of a third device we investigated, a planar biphenyl methanethiol junction²¹ which does not have the left-right symmetry.²² The molecule is along the z direction and lies in the yz plane. The contact distance of the S-Au (Al) is 4.0 a.u. and H-Au (Al) is 2.2 a.u.. The band structures of the Au and the Al lead are also shown. The major conducting bands of this device are indicated by the symbols in the band structure. Because this molecule is asymmetric toward the left and right leads, we found that there are two bands conducting for the left lead but only one band conducting for the right lead. For the right Au lead, as shown by the band structure of Fig. 3(b), the major conducting band is still the same as that in Fig. 2(a); this is because the contact to the right Au lead is topologically the same as that of the device in Fig. 2. Similarly, for the right Al lead, the major conducting band of Fig. 3(e) is the same as that of Fig. 2(c). On the other hand, for the left lead, there is an extra major conducting band, as shown in Figs. 3(a) and 3(d). This ob-

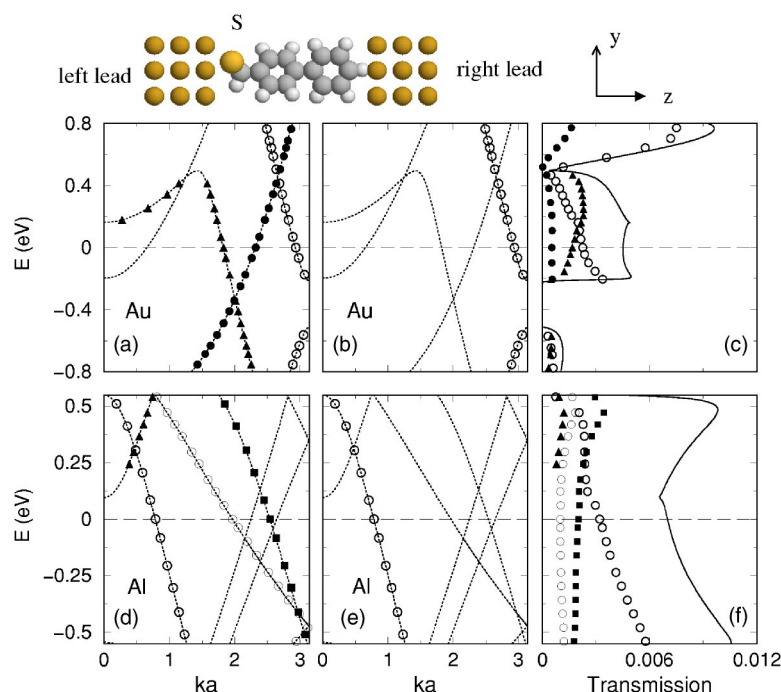


FIG. 4. Schematic illustration of a nonplanar biphenyl methanethiol device. The SCH_2 -group is vertically (orientated by the S-C bond) connected with a phenyl ring while the angle between two rings is 45 degrees. For the left Au lead, the major conducting bands of the device are the p_x, p_y, d_{xz}, d_{yz} band, the s, p_z, d_{z^2} band, and the d_{xy} band, as shown in (a). For the left Al lead, they are the p_x, p_y band, the “mix” band, a second p_x, p_y band, and the s, p_z band, as shown in (d). Their contributions to conductance are indicated by symbols in (c) and (f). For the right lead, it is p_x, p_y character band as shown in (b) and (e).

servation is rather interesting, the major conducting bands appear to be sensitive to the local structure of the molecule-lead contact, but less so to the parts of the molecule away from the contact.

Our analysis shows that for the left lead which is connected to the SCH_2 end of the molecule (Fig. 3), the two major conducting bands of Au lead are d_{xy} and p_x, p_y, d_{xz}, d_{yz} character band, while they are the “mix” and p_x, p_y band for the Al lead. For the right lead which is connected to a phenyl ring, the major conducting band has p_x character. The transmission spectra are shown in Figs. 3(c) and 3(f). The transmission coefficients of the two major conducting bands of the left lead are indicated by symbols: d_{xy} (solid circles) and p_x, p_y, d_{xz}, d_{yz} (empty circles) characters for the Au lead; “mix” (solid square) and p_x, p_y (empty circles) characters for the Al lead. The total transmission of these two eigenchannels of the left lead is equal to the transmission of the p_x character band of the right lead. For a device with Au lead, there is a transmission gap between -0.22 to -0.5 eV, due to the gap of the p_x, p_y, d_{xz}, d_{yz} band [see Figs. 3(a) and 3(b)]. These results indicate that, through the molecule, d_{xy} and p_x character band of the left lead can now couple to the p_x character band of the right lead. In other words, electrons coming from d_{xy} and p_x character bands of the left lead traverse the molecular orbitals through the SCH_2 -end group, then they transport to the p_x character band of the right lead. This way, by choosing the bridging molecule, the conducting channels of the two electrodes are switched.

When this molecular device is in a nonplanar conformation, more bands can conduct. As shown in the top panel of Fig. 4, the SCH_2 -group of the biphenyl methanethiol molecule is vertically (orientated by S-C bond) connected with a phenyl ring while the angle between two rings is 45

degrees.²² For the right lead, the major conducting band is still the p_x, p_y character band as shown in Figs. 4(b) and 4(e). For the left Au lead, shown in Fig. 4(a), the major conducting bands become the p_x, p_y, d_{xz}, d_{yz} band, the s, p_z, d_{z^2} band, and the d_{xy} band. Their contributions to conduction are indicated by symbols in Fig. 4(c). While the main filtering effect of the molecule is dominated by the two phenyl rings, the rotated SCH_2 -group makes the p_x, p_y, d_{xz}, d_{yz} band more conductive and further, interestingly, introduces a new s, p_z, d_{z^2} band to conduct. The ability of inducing more channels to conduct is important from device point of view. For the left Al lead, shown in Fig. 4(d), the major conducting bands become the p_x, p_y band, the “mix” band, a second p_x, p_y band, and finally the s, p_z band. Their contributions to conduction are shown by the symbols in Fig. 4(f). The rotated end group makes the p_x, p_y band couple better to the molecule than that of the “mix” band and introduces two new bands to conduct.

In summary, we found that molecules bridging two metallic leads give a momentum filtering effect so that only those bands having similar orbital character as the molecule itself will conduct significantly. By choosing different molecules to bridge, the incoming and outgoing bands with different character can be switched. Clearly, the filtering effect is only expected to play a role for molecules with reasonable length. For example, in a benzene methanethiol junction, which is short, all bands of the lead conduct.

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