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Symmetry, delocalization, and molecular conductance

P. Delaney, M. Nolan, and J. C. Greer
 NMRC, University College Cork, Cork, Ireland

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Molecules bonded between two metal contacts form the simplest possible molecular devices. Coupled by the molecule, the left and right contact-based states form symmetric and antisymmetric pairs near the Fermi level. We relate the size of the resulting energy splitting ΔE to the symmetry and degree of delocalization of the coupling molecular orbital. Qualitative trends in molecular conductances are then estimated from the variations in ΔE . We examine benzenedithiol and other molecules of interest in transport. © 2005 American Institute of Physics.
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I. INTRODUCTION

The prototypical structure for the study of single molecule charge transport has been formed by bonding *p*-benzenedithiol (BDT) between two gold contacts.¹ This system has been considered in the break junction study of Ref. 1 and in many theoretical studies.^{2–10} For the growing field of molecular electronics, it is important to understand the bonding and electronic structure within this and other contact-molecule-contact structures. Previously, we have studied the interactions between thiol molecules and gold, focusing particularly on the influence of molecular geometry and chemical substitution on the junction electronic structure.^{2,11} The present work aims to develop a simple model of this electronic structure so as to predict qualitative trends in molecular conductance.

Figure 1 shows the representative contact-molecule-contact junctions we study here. Figure 1(a), Au₁₃-BDT-Au₁₃, is the prototypical metal-molecule-metal junction. We validate our model by examining our density functional theory (DFT) results for this structure, and then use the model to explain trends we see in other phenyl derived molecules as we increase the molecular length [Figs. 1(a) to 1(c) and 1(d)] or interrupt the conjugation¹² [Figs. 1(b) and 1(e)]. We will compare our predictions with experimentally known results.

II. METHODS

It is necessary to include the metal contact in any study of a molecular device, and in the present work we choose a 13 atom gold nanocluster, Au₁₃.^{2,11} The molecular junctions so constructed are shown in Fig. 1. Full geometry optimization of these structures in *C*_{2h} symmetry for Figs. 1(a), 1(c), and 1(d), *C*₂ symmetry for Fig. 1(b), and *C*_s symmetry for Fig. 1(e) is carried out within DFT, using the TURBOMOLE package.¹³ The B3-LYP¹⁴ exchange-correlation functional and a double zeta quality polarized split valence basis set¹⁵ are applied, along with a medium integration grid. Electric fields are applied using a linearly varying potential as standard.

III. RESULTS

A. The Au₁₃-benzenedithiol-Au₁₃ junction

First we examine the electronic structure of the Au₁₃-benzenedithiol-Au₁₃ junction of Fig. 1(a). In Fig. 2(a) we show the DFT eigenvalues of the junction near the Fermi level. At -6.50 eV we find that the highest occupied molecular orbital (HOMO) of BDT has coupled with the metallic orbitals to give HOMO-4 of the junction. Now turning to the cluster of states around the Fermi level, 0.90 eV above the molecular derived orbital, we see *pairs* of states: two outlying states separated from a nearly doubly degenerate central pair. In the present work we will work in the low-field regime, so these four are the relevant states for electronic transport.

B. Two-level model

As we have two large contacts coupled weakly by a molecule, the pairs of energy levels should be treatable using 2×2 matrix models, just as for diatomic molecules. This involves one parameter, the off-diagonal coupling β . This validity of this model can be deduced from the Schrödinger equation and been used to study electron transfer in donor-bridge-acceptor molecules.¹⁶ Here, the symmetry of the junction is *C*_{2h} with the mirror plane containing the in-page horizontal and the page normal; we will classify states as *parallel* (even) or *perpendicular* (odd) under this symmetry.

In the absence of the molecule, the left contact has *C*_{3v} symmetry and has two degenerate states from the doubly degenerate “*e*” irrep $|L_{\text{perp}}\rangle$, $|L_{\text{par}}\rangle$ of energy E_0 near the Fermi level. Introducing the molecule gives matrix elements $\langle L|V_{\text{molecule}}|m_{2pz}\rangle$ and $\langle m_{2pz}|V_{\text{molecule}}|R\rangle$ which indirectly couple the contact states. As the molecule preserves the mirror plane, the parallel and perpendicular states remain decoupled and we get two separate two-state models of the DFT calculation. Looking at the DFT orbital plots in Fig. 3, we indeed see that the central pair are a symmetric (*a_u* irrep of *C*_{2h}) and antisymmetric (*b_g*) combination of two perpendicular left and right gold contact states $|L_{\text{perp}}\rangle$, $|R_{\text{perp}}\rangle$, which are odd under the mirror symmetry, with a small energy splitting of 1 meV. Similarly, the outer pair are a sym-

FIG. 1. Molecular structure of representative contact-molecule-contact junctions, where the molecule is bonded between two Au_{13} nanoclusters. The molecules bond to gold clusters via sulfur atoms. (a) Benzenedithiol; (b) *trans* dimercaptoacetoamidobenzene, DMAAB; (c) two phenyl rings linked by an acetylenic (C-C) group; (d) three phenyl rings linked by acetylenic groups; (e) same as (d) but with the central phenyl ring rotated by 90° .

metric (a_g) and antisymmetric (b_u) combination of two parallel states $|L_{\text{par}}\rangle$, $|R_{\text{par}}\rangle$, even under the mirror symmetry, with a larger energy splitting of 79 meV. We extract an effective coupling term $\beta = \langle L | V_{\text{molecule}} | R \rangle$, with $\beta_{\text{par}} = 79/2$ meV and $\beta_{\text{perp}} = 1/2$ meV. These are the off-diagonal terms in our two 2×2 matrix models whose eigenvalues are $E_0 \pm \beta$ and have an energy splitting of $\Delta E = 2\beta$. We shall now investigate the difference in the magnitude of the coupling between the two cases and propose two tests for good conductance.

We first note that in Fig. 4(a) the molecular orbital of BDT is delocalized over the (short) length of the molecule, and therefore can have appreciable matrix elements with the left and right contact states; this is our first test for strong coupling between the contacts and consequently good current-carrying abilities.

Analyzing now the two perpendicular states, even though the coupling molecular orbital passes the primary test of being *delocalized* over the whole molecule, *symmetry* comes into play as a secondary criterion. Near the Fermi level the relevant orbitals are the sulphur $3p$ and carbon $2p_z$ -derived orbitals. The overlap of the two determines the coupling β between the contacts. The coupling is caused by the molecular HOMO $|m\rangle$ —the LUMO is further from the Fermi level and localized on the carbons, away from the

FIG. 2. (a) The high-lying occupied eigenenergies of Au_{13} -BDT- Au_{13} . (b) A comparison of the DFT and two-state model eigenvalues for the parallel (outer plots) and perpendicular (inner plots) states. The electric field strength is given as a multiple of 0.051 V/nm, which is 10^{-4} a.u.

sulphurs. The HOMO is even under the mirror plane, so the matrix elements $\langle L_{\text{perp}} | V_{\text{molecule}} | m \rangle$ and $\langle m | V_{\text{molecule}} | R_{\text{perp}} \rangle$ must be zero, showing the cause for the small 1 meV splitting. Pictorially, in $|L_{\text{perp}}\rangle$ the $3p$ orbital points in the plane of the page and is perpendicular to the carbon $2p_z$ orbitals (hence the name). It cannot interact with them, resulting in an essentially nonbonded interaction across the molecule. For the $|L_{\text{par}}\rangle$ contact state, on the other hand, the sulfur p orbitals are parallel to the carbon p orbitals giving a larger matrix element. Real contacts probably have no symmetry, but the picture developed here still applies; the magnitude of the conductance will vary if the angle between the sulphur $3p$ and the carbon $2p_z$ orbitals changes. Symmetry effects between gold $6s$ and sulphur $3p$ orbitals have also been seen in Ref. 4. Here we consider the sulfur atoms as being part of the contacts, as from the DFT orbital plots there can be appreciable charge on the sulfur orbitals, even when the benzene contribution proper is not visible.

To include the effect of the electric field, we simply shift the energies of the left and right localized states to $E_0 \pm eV/2$, where V is the voltage across the junction. In the

FIG. 3. MO plots and energy eigenvalues of the four highest occupied junction orbitals of $\text{Au}_{13}\text{-BDT-Au}_{13}$. The different orientations of the p orbital of the sulfur atom in these states are highlighted by a ring. The irrep of each orbital is also given.

spirit of the model, we calculate V from the simple formula $V = Fd$, the product of the applied electric field F and the distance $d = 14 \text{ \AA}$ between the central gold atoms of each cluster. For example, a field strength of 0.051 V/nm (10^{-4} a.u.) gives an applied voltage of 0.070 V and therefore energy shifts of $\pm eV/2 = \pm 0.035 \text{ eV}$.

Summarizing, we find that the Schrödinger equation $H\Psi = E\Psi$ in the $|L\rangle$, $|R\rangle$ basis is given by the 2×2 matrix eigenvalue problem

$$\begin{pmatrix} E_0 + eV/2 & \beta \\ \beta & E_0 - eV/2 \end{pmatrix} \begin{pmatrix} \varphi_L \\ \varphi_R \end{pmatrix} = E \begin{pmatrix} \varphi_L \\ \varphi_R \end{pmatrix}. \quad (1)$$

In Fig. 2(b) we compare the DFT and the model energy eigenvalues as a function of applied electric field for the parallel and perpendicular orbitals: the simple model agrees well with the *ab initio* DFT results. We propose that the electronic structure of the junction in the bias field involves a competition between the molecular coupling β causing delocalization of the junction orbitals over the two contacts and the electric field shift $eV/2$ which tends to polarize the orbit-

FIG. 4. Highest occupied MOs of the isolated molecules which make up junctions Figs. 1(a)–1(e). It is noted that the HOMOs of molecules 4(b) and 4(e) are not as delocalized over the whole molecule.

als, localizing them on one of the contacts. For example, this explains why the parallel orbitals polarize significantly slower than the perpendicular orbitals.

Having captured the electronic structure of the junction, to complete the analysis we wish to estimate whether the molecule will conduct well or poorly. As well as the information stored in β , we must include the coupling of the finite gold clusters to the body of the gold wires. Due to this interaction $|L\rangle$ and $|R\rangle$ are no longer stationary states, but dissipate over time into the bulk states of the wire, so we need a second energy scale Γ which gives the lifetime of a contact state. An explicit formula for the transmission factor $T(E)$ through a two-state system coupled to a continuum is¹⁷

$$T(E) = \frac{4\Gamma^2\beta^2}{[(E - E_S)^2 + \Gamma^2][(E - E_A)^2 + \Gamma^2]}, \quad (2)$$

where $E_{S,A} = E_0 \pm \beta$ are the energies of the symmetric and antisymmetric junction orbitals. The parameter Γ is given by the formula $\Gamma = \pi t^2 \text{LDOS}(E)$, where t is a gold-gold hopping matrix element and $\text{LDOS}(E)$ is the gold local density of states. As our model is simple we shall set $\Gamma = 0.5 \text{ eV}$ and neglect its energy dependence. This is a somewhat arbitrary choice and the absolute magnitudes of the currents flowing depend sensitively on the value of Γ taken; however, relative trends between molecules should be stable.

From the numerator of Eq. (2) we find the qualitative conclusion that larger energy splitting $\Delta E = 2\beta$ gives larger

FIG. 5. Transmission vs incident energy curve for Au_{13} -BDT- Au_{13} . The upper plot is for the parallel orbitals, while the lower plot is for the perpendicular orbitals. The transmission is plotted on a logarithmic scale.

molecular conductances. Explicitly, we see how the orthogonality between the sulfur and carbon p orbitals closes one of the gold contact conductance channels, as β_{perp} is much smaller than β_{par} and from the Landauer formula $\sigma = T(E_F) G_0$, where G_0 is the quantum of conductance. In Fig. 5 we plot on a logarithmic scale the transmission coefficient $T(E)$ versus energy for the parallel and perpendicular states; one can see the difference in scale of the curves. The peak height is given approximately by $4\beta^2/\Gamma^2$ so the factor of 79 change in β makes the peak value of $T(E)$ change by a factor of $79^2 \approx 6200$.

C. Application to phenyl derived molecules

We now consider the other molecules of Fig. 1 and demonstrate the usefulness of our two-state model for quickly predicting effects found in our *ab initio* DFT calculations.

1. The effect of localization on the molecule: DMAAB

The junction formed by the interaction of Au_{13} and the *trans* conformation of the dimercaptoacetoamidobenzene (DMAAB) molecule is shown in Fig. 1(b). Here the sulfur atoms are separated from the phenyl ring by the presence of the CH_2 groups. This group localizes the HOMO $|m\rangle$ and so we expect the matrix elements between the contact orbitals $|L\rangle$, $|R\rangle$ and the molecular orbital $|m\rangle$ and the energy splitting ΔE to be small. Indeed, the DFT computations show that the four highest occupied molecular orbital (MOs) of the junction come in two doubly degenerate pairs. In an electric field we also expect the potential difference across the junction to quickly overpower the splitting ΔE , and this is also the case with DFT. Therefore this molecule will have a low conductance value, and as the junction orbitals polarize quickly, we might expect comparatively strong nonlinear conductance behavior.

FIG. 6. The four highest occupied energy eigenvalues of three-phenyl molecule Fig. 1(d) as the central phenyl ring is rotated from 0° to 90° about the molecular axis. The full lines are the parallel states (filled diamonds and triangles) and the perpendicular orbitals are represented by the unconnected points (X and unfilled square shapes). The two perpendicular eigenvalues are almost degenerate, and hence appear superimposed.

2. Longer molecules: planar phenylene ethynylene junctions

In addition to the benzenedithiol molecule of Fig. 1(a) we now consider the phenylene ethynylene molecules presented in Figs. 1(c) and 1(d), which allow us to study the effect of increased molecular length. From the DFT calculations we find this reduces the parallel energy splitting; for BDT ΔE_{par} is 79 meV, 50 meV for Fig. 1(c), while for Fig. 1(d), the energy splitting is 36 meV, less than half that of BDT. We note that the splitting between the perpendicular orbitals remains tiny for all these molecules; current flow occurs by tunneling through the parallel orbitals, with the magnitude of the low-bias current decreasing as the length of the bridging molecule is increased, as a Landauer formula theory¹⁸ and two experimental studies^{19,20} have shown. Our model also correctly predicts that the parallel orbitals polarize more quickly as the molecular length is increased, due to the smaller ΔE value.

3. Breaking symmetry: rotating the central phenyl ring

We have already seen that symmetry plays an important role in determining the overlap $\langle L|V_{\text{molecule}}|m_{2pz}\rangle$ between (say) a left-contact sulfur p orbital and the phenyl C $2p_z$ -derived HOMO $|m_{2pz}\rangle$ and hence the conductance of phenyl derived molecules. Now we rotate the central phenyl ring shown in Fig. 1(d) about the molecular axis to see if a similar effect can be observed, though this time we are varying the effective interaction between *two phenyl rings*.

In Fig. 6, we plot the eigenenergies of the four highest occupied junction states as a function of the rotation angle θ

of the central phenyl ring. To help understand the origin of the energy changes, Figs. 1(e) and 4(e) show the molecule rotated by 90° and the HOMO at this angle. The HOMO shown in Fig. 4(e) is no longer delocalized over the length of the molecule: conjugation is interrupted by the rotation of the phenyl ring.

Analyzing this more complicated molecule will show the essential ideas of our model. Transport through the benzenedithiol junction was determined by the conductance of the *weakest link* of the system: the matrix elements $\langle L | V_{\text{molecule}} | m_{2p_z} \rangle$ and $\langle m_{2p_z} | V_{\text{molecule}} | R \rangle$ which are much smaller than the internal matrix elements between neighboring gold $6s$ orbitals or between neighboring carbon $2p_z$ orbitals. Due to the strong internal coupling, when benzene interacts with the gold contacts each contact state changes little: the relative coefficients of the atomic orbitals stay nearly the same. Thus, the electronic structure of the junction can be modeled by postulating two rigid blocks, one on the left and one on the right, with an effective interaction parameter β .

Here, for the rotated three-phenyl molecule, we have *three* weak links. First we model the two weak links between each contact and its adjacent outer phenyl ring. As before, this gives us parallel and perpendicular orbitals on the left and right *contact-phenyl block*. This coupling, β_{par} and β_{perp} , is weaker than any other matrix element in the contact + outer-phenyl unit, justifying the analysis. The perpendicular orbitals have negligible weight on the outer phenyls and so cannot subsequently couple across the central phenyl, resulting in the two lowest doubly degenerate and essentially constant eigenenergies of Fig. 6.

Having eliminated the perpendicular states, we now consider the left and right parallel states $|L_{\text{par}}\rangle$, $|R_{\text{par}}\rangle$, which couple through the third weak link, the central phenyl ring, with an effective coupling matrix element $\beta(\theta)$. This coupling $\beta(\theta)$ will be even weaker than the contact to edge-phenyl matrix element β_{par} , and so again we can treat the contact-outer-phenyl states $|L_{\text{par}}\rangle$, $|R_{\text{par}}\rangle$ as two blocks with fixed internal structure. Symmetric and antisymmetric combinations result from the coupling $\beta(\theta)$ and we see in Fig. 6 that the DFT energy splitting $\Delta E(\theta)$ changes with angle as expected from the varying overlap of the blocks. Therefore for the rotated structure shown in Fig. 1(e) we would expect a reduced current magnitude compared to Fig. 1(d). Indeed, Anariba and McCreery have shown that the current magnitude through a twisted terphenyl structure is lower than through the planar structure,²¹ again validating our idea that qualitative trends in molecular conductances can be predicted using this simple model and the ideas of delocalization and symmetry breaking.

We consider how to extend the two-state model to those properties for which it is not valid. For example, in Fig. 6 we see that the energy of one of the parallel states is altered much more than the other by rotating the central phenyl ring. The two-state model would predict that both levels would shift equally, one shifting up and one shifting down by the same amount. To devise a model which gets this physics correct, we can use a model based on the three states $|L_{\text{par}}\rangle$,

$|m\rangle$ and $|R_{\text{par}}\rangle$, where $|m\rangle$ is the coupling state on the central phenyl. The Schrödinger equation is now given by

$$\begin{pmatrix} E_0 & t & 0 \\ t & E_m & t \\ 0 & t & E_0 \end{pmatrix} \begin{pmatrix} \varphi_L \\ \varphi_m \\ \varphi_R \end{pmatrix} = E \begin{pmatrix} \varphi_L \\ \varphi_m \\ \varphi_R \end{pmatrix}, \quad (3)$$

where E_0 is the energy of the two contact states $|L_{\text{par}}\rangle$ and $|R_{\text{par}}\rangle$, E_m is the energy of the coupling molecule state and $t(\theta) = \langle L_{\text{par}} | V_{\text{molecule}} | m \rangle = \langle m | V_{\text{molecule}} | R_{\text{par}} \rangle$ is the hopping matrix element. By parity symmetry, one eigenstate of this Hamiltonian is $\Phi(1, 0, -1)$, and by calculating $H\Phi$ one sees this has eigenvalue E_0 , independent of the value of $t(\theta)$; the other contact-derived state does depend on $t(\theta)$. This is the reason why one state in Fig. 6 varies much more with the rotation angle than the other.

IV. CONCLUSION

In this paper, we have examined the qualitative influences of symmetry breaking and delocalization on the conductance of a molecular junction, capturing more involved DFT calculations with a simple two-level model involving a single parameter β , which we then use to estimate the junction conductance. We find two conditions for large β and good conductance. The first is that the coupling molecular orbital be delocalized over the molecule. The second is favorable symmetry: the overlap between (say) the left contact state and the coupling molecular orbital can depend strongly on the relative orientation of two p orbitals. We plan to use this model in future work to investigate molecular devices.

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