

## Using local orbitals in DFT to examine oligothiophene conductance anomalies

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**Abstract.** At the heart of a quantitatively accurate metal-molecule-metal conductance calculation, the potential profile must reflect the surface physics between the metal and vacuum. In this work, we employ a local orbital basis and calculate the conductance over a suite of Hamiltonians to examine trends within a molecular system using a rapid, self-consistent scattering matrix method. As discussed above, this is justified as the tunneling barriers within the molecule largely determine the device's qualitative behavior. In this manner, the unexpectedly higher conductance experimentally measured on a four-membered oligothiophene, over its three-membered counterpart, is analyzed by calculating the conductance for a range of multi-atom displacements corresponding to a selected vibrational mode.

### 1. Introduction

The molecular conductance calculation typically involves two major steps. The energy spectrum calculation delivers a Hamiltonian to a transport kernel which describes the nonequilibrium electron dynamics through this system. The challenge in the first step involves the rendering of the physics of two very different systems. The isolated molecule, with its electrons bound in discrete orbitals, must be coupled to the metallic contact with its reservoir of electrons filling up a continuous band up to the Fermi level. The coupling hybridizes the molecular orbitals with the extended states in the contact defining a combined spectrum for the entire system. The delocalized metallic states can be best represented by a plane waves, a completely unbiased basis. In general, use of a local orbital basis is unable to reproduce the physically relevant surface potential of the metal. Using a plane wave basis in the density functional theory local density approximation (DFT-LDA), this potential can be realized. However, due to the large rank Hamiltonian produced in a plane wave basis, the transport calculation becomes intractable computationally. The inability to correctly reproduce this potential is a severe limitation on the ability to compute actual transport through molecules when the interfacial potential dominates the total potential. In many cases, however, tunneling through internal molecular barriers dominates the overall resistance of the structure. In this case, comparisons between molecules, or variations in molecular length, can be fruitfully studied with the local orbital basis.

The nature of the problem is shown, for the xylyldithiol molecular monolayer sandwiched between gold contacts, in Figure 1. Two potential plots are shown for planes away from and near the molecule. The workfunction corresponds well with experimentally measured values near 5 eV. However, the large number of plane waves needed to represent the metallic surface and the

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interconnecting molecule demands a large amount of computation in itself and furthermore, the rank of the Hamiltonian is often too large for the ensuing calculation of the conductance.

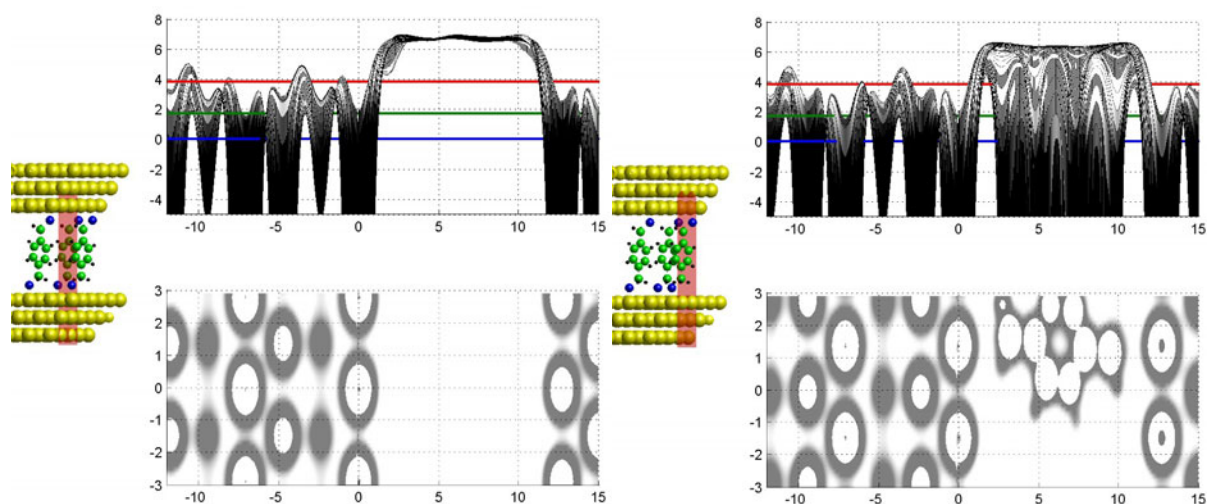


Fig. 1: Potential profiles for xylyldithiol molecule between gold leads as calculated using a plane wave basis. The left figures represent the situation in which no molecule is attached, so only the Au atoms appear on the left and right sides of the potential (top curves). The figure on the left indicates where the plot is taken (shaded region through the molecule, which is absent). The lower panel is a “top down” view of the atomic arrangement. The right figures have the molecule in place, and the modification due to the atoms of the molecule is evident. The green line is the Fermi level, the red line is the expected LUMO level, and the blue line is the HOMO level. The horizontal axes in the four plots is the position, in Angstrom, relative to the center of the last Au layer on the left.

This paper examines recent experimental phenomena observed with oligothiophenes. A local orbital basis was used because these systems are dominated by internal barriers. We show that, despite the inaccurate representation of the metallic surface that results from this approximation, the trends observed over a large suite of Hamiltonians do describe meaningful qualitative physical behavior for these systems.

## 2. Oligothiophenes

A group at AT&T, using a unique method of evaporating gold layers onto a quartz tip, produced current traces for three- and four-membered oligomers of a heterocyclic, organic system (hereafter referred to as T3 and T4) [1]. The interesting result was that, at low temperature, T4 showed a higher conductance than its shorter counterpart T3. Another group at Arizona State University, employing a completely different experimental setup involving a gold plated AFM tip repeatedly lowered into a monolayer on gold substrate, observed a similar trend at room temperature [2].

Our approach begins with calculations on the bandstructure of the two isomers of the infinite polymer. Both isomers can be characterized by the polyene backbone with periodic connecting sulphurs. The difference between the two lies in the number of double bonds within the heterocyclic ring. The benzenoid isomer structure is the stable configuration observed for the oligomers studied in this paper, but the quinoid isomer, with double bonds connecting the rings, showed a much lower bandgap, suggesting much improved conductance.

Diagonalization of the mass-weighted Hessian yields a set of eigenvalues corresponding to the frequency of vibration, and a set of eigenvectors describing the nuclear motions associated with the particular mode. Looking through the various atomic configurations, a specific mode was found which created a temporary quinoid configuration in the middle of T4, shown on the left in Figure 2. Using a treatment similar to that used in [3], Hamiltonians were calculated for twenty configuration

snapshots across the selected vibration for T3 and T4. The extrema for the T4 vibration are shown in Figure 2 where the quinoid (Q) and distorted benzenoid (B) ring characters are indicated. The T3 extrema have one internal quinoid ring for snapshot 1 and quinoids on the ends for snapshot 20. In both cases, snapshots 10 and 11 correspond to the (nearly) unperturbed benzenoid configuration.

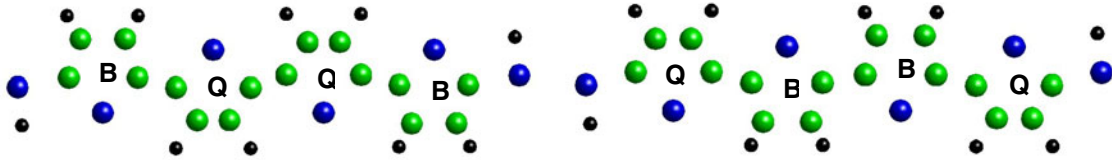


Fig. 2: Nuclear position extrema for T4 corresponding to snapshots 1 (left) and 20 (right) in future plots. Note inner ring quinoid cycle synchronization on left. The blue atoms are the sulphur atoms, while the green atoms are the carbon atoms. The black dots represent H atoms. The B and Q refer to benzenoid and quinoid configurations of double bonds.

The experimental setup used in [2], where molecules were isolated by raising the AFM tip until isolated molecular traces could be observed, suggests that the distortion of the molecule may influence its conductance. Our previous work, which investigated the conductance of distorted molecules, describes the procedure of using the Hellmann-Feynman forces to distort the molecule [4] although, in this study, the more accurate Hartree-Fock theory was used for this procedure. We observe a red shift for the selected mode after recalculating the vibrational spectrum with each stretching. The projected density of states (PDOS) on carbon and sulfur atoms are shown for the unstretched T3 and T4 molecules and for a stretch distance of  $0.8 \text{ \AA}$  in Figure 3. The T4 molecule shows the trend of increased PDOS, suggesting higher conductance, while the T3 molecule does not.

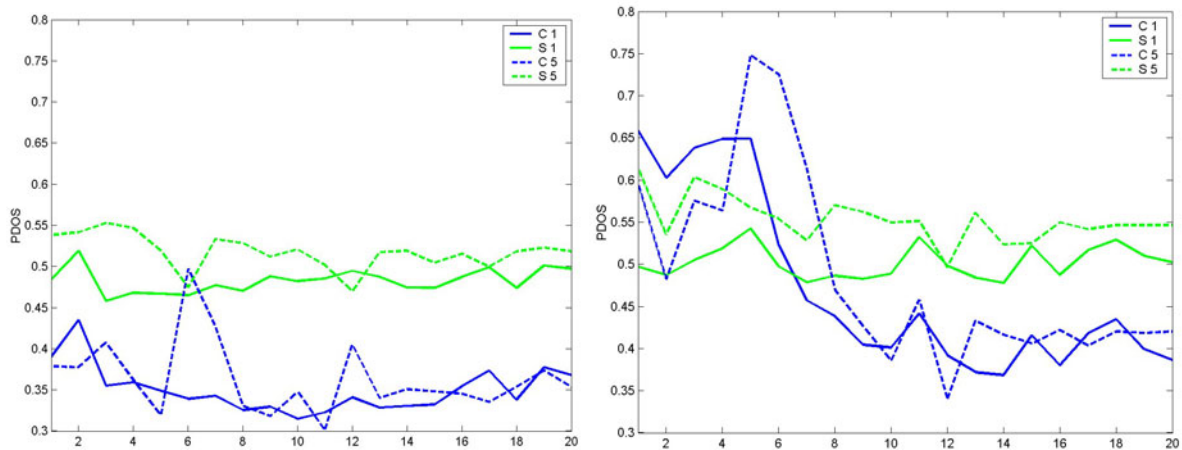


Fig. 3: PDOS of unstretched (label 1, solid curves) and stretched (label 5, dashed curves) for the T3 (left) and T4 (right) for carbon (C, green curves) and sulfur (S, blue curves) atoms at the Fermi energy for twenty snapshot configurations throughout the vibration. The 20 points refer to the positions of the atoms during a cycle of the atomic lattice vibration.

The transport calculation employs a rapid, self-consistent scattering matrix variant which propagates an incoming flux through the system, whence the transmission can be entered into the Landauer formula yielding the conductance [5]. The averaged conductance for the unstretched systems does not reveal a higher conductance for T4 over T3, but as the molecules are stretched, T4's conductance enhances and eventually reveals an order of magnitude enhancement over T3. Conductance over 20 snapshots for the stretched system is shown in Figure 4.

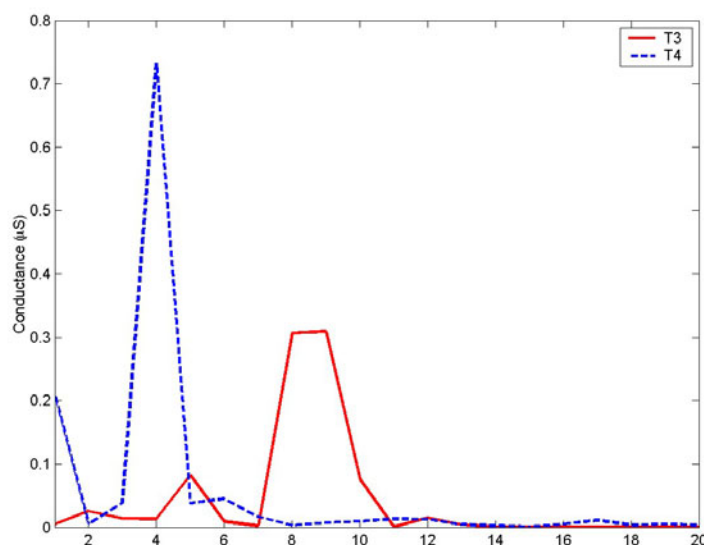


Fig.4: Conductance of three-membered (red) and four-membered (blue, dashed) oligothiophenes calculated over a suite of 20 nuclear displacement “snapshots” of a selected vibrational mode for a moderate stretching. Averaged, the four-membered oligothiophene (T4) has a higher conductance than the three-membered (T3), corresponding with experimental observations.

### 3. Conclusion

The inaccuracy of the local orbital basis in representing the metallic work function precludes any quantitative analysis of molecular conduction. However, the approach of examining a large suite of Hamiltonians and determining the trend gives results for the surprising conductance behaviour of T4. Stretching, combined with the nuclear positions within a specific vibrational mode, permit the interior rings of T4 to form a unique configuration, which lowers the tunnelling barrier for electrons. This configuration cannot be realized in T3. Future work will explore the implementation of plane wave basis codes on larger computer systems.

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