# Transport in State Space: Voltage-Dependent Conductance Calculations of Benzene-1,4-dithiol

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## ABSTRACT

We implement a method to study transport in a basis of many-body molecular states using the nonequilibrium Hubbard Green's function technique. A well-studied system, a junction consisting of benzene-dithiol on gold, is the focus of our consideration. Electronic structure calculations are carried out at the Hartree−Fock (HF), density functional theory (DFT), and coupled-cluster singles and doubles (CCSD) levels, and multiple molecular states are included in the transport calculation. The conductance calculation yields new information about the transport mechanism in BDT junctions.

Recent achievements in experimental techniques at the nanoscale have caused a surge in research on transport through molecular junctions. While the theoretical treatment of nonequilibrium systems at the level of simple models has become quite sophisticated, *ab initio* computations of realistic systems mostly rely on a mean-field treatment. In particular, within these schemes, the current is usually given by a Landauer-like[1] expression in terms of a matrix Green's function (GF) in a basis of (effective) orbitals that emerges from a density functional theory (DFT)[2] or semiempirical treatment.[3,4]

The orbital-based approach becomes inadequate, however, for resonant electron transport in molecular systems. Indeed, oxidation/reduction of a molecule leads to fundamental changes in its electronic structure.[5] Thus, the correct treatment of the system in the resonant regime requires a description in *molecular states* rather than effective single-particle orbitals. First-principles simulations, such as DFT-nonequilibrium GF (DFT-NEGF) treatments utilizing Kohn−Sham (KS) orbitals and Koopmans' theorem to define excitation and effective charging energies, naturally fail at higher biases where electronic excitations and charging occur.[6,7] There have been some attempts to improve the DFT-NEGF approach through a variety of methods including better exchange-correlation functionals (with proper derivative discontinuity)[8,9] and self-interaction correction.[10] While these methods can certainly improve the accuracy of the zero-bias conductance (which in molecular systems is usually off-resonant (note, here we discuss situations above the Kondo temperature)), different exchange-correlation potentials can still lead to drastically different conductance values in DFT treatments.[11] This is at least in part due to the fact that KS orbitals are relied upon, rather than the total energy (and electron density). Recent developments in *GW* techniques[12] are promising for improving the quality of orbital-based first-principles simulations.

An alternative approach to resonant and near-resonant transport, especially important in molecular junctions, relies on using molecular many-body states as the basis for the conductance calculations. In this way, all on-the-molecule correlations can be treated within sophisticated quantum chemistry methods and incorporated into the description of transport. The necessity for such a development has been realized in the community, and most schemes motivated in this way are based on either a scattering approach to transport[13−18] or quantum master equations (MEs).[19,20] The first neglect Fermi seas in the contacts and their influence on the system, while the latter neglect correlations between different many-body states and are generally applicable only in the limit of extremely weak molecule-contact coupling, when the characteristic relaxation time is much shorter than the time between electron transitions. Finally, a recently

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proposed NEGF approach based on many-body states[21] uses the Keldysh equation without justification.

Here, we present a different approach to computational molecular electronics. The consideration is based on the Hubbard GF method developed by Sandalov and co-workers for description of equilibrium mixed-valence compounds,[22] and applied later to elastic[23,24] and inelastic transport[25] within simple model calculations. This work is the first step toward the implementation of the method for realistic first-principles type calculations. The method utilizes $N$-electron many-body molecular states as the basis for transport calculations, with functional derivatives in auxiliary fields playing the role of perturbation expansion in the standard nonequilibrium diagrammatic technique (for a detailed description, see refs 23−25). These many-body states can be calculated at any desired level of electronic structure theory for the equilibrium isolated molecule, and electronic excited states and different charge states can be treated naturally. This provides us with the ability to systematically improve the treatment of molecular states and examine the effect on the calculated conductance. Additionally, correlations between different interstate transitions (induced by coupling to contacts) are included in the final result within a perturbative self-consistent procedure. The method is able to predict the impact of particular electronic transitions between many-body states on the transport. The generalized ME approach[20] is obtained as a limiting case, when both space and time correlations are disregarded.[25]

In the following, we focus on a classic transport system, benzene-1,4-dithiol (BDT) between gold electrodes, which was extensively studied experimentally with both mechanically controlled break-junctions (MCBJs)[26,27] and scanning tunneling microscope break junctions (STMBJs).[28,29] We perform electronic structure calculations at the Hartree−Fock (HF), DFT, and coupled-cluster singles and doubles (CCSD) levels. The calculation of self-energy terms is implemented with a Newns−Anderson tight-binding model.[30] Our results show that high-level electronic structure treatment is necessary to properly treat the internal structure of the molecular wire. We are able to reproduce the features that have been experimentally reported in finite-bias conductance measurements.

First, we briefly outline the state-based approach to electronic transport, which has been developed more fully elsewhere.[22−25] We begin with the usual Hamiltonian for a molecular junction,

$$\hat{H} = \sum_{k \in \{L,R\}} \varepsilon_k \hat{c}_k^\dagger \hat{c}_k + \hat{H}_M + \hat{H}_T \tag{1}$$

where $\hat{c}_k^\dagger / \hat{c}_k$ are the creation/annihilation operators for electrons in the contacts. The first term describes the left and right contacts, the second term is the isolated molecule Hamiltonian, and the last term allows transport via coupling between the contacts and molecule subsystems.

We use many-body states, $|N,i\rangle$ ($N$ represents the charge state of the molecule and $i$ the different electronic excitation

states in the charge block), as a basis and introduce the Hubbard $\hat{X}$ operators

$$\hat{X}_{(N,i;N',i')} = |N,i\rangle\langle N',i'| \tag{2}$$

to describe transitions between these states. In the basis of molecular states of the isolated molecule, the molecular Hamiltonian takes the form

$$\hat{H}_M = \sum_{|N,i\rangle} E_{N,i} \hat{X}_{(N,i;N,i)} \tag{3}$$

where $E_{N,i}$ are the molecule's energy eigenvalues. The transfer Hamiltonian can then be written

$$\hat{H}_T = \sum_{k \in \{L,R\}} \sum_{\mathscr{M}} V_{k\mathscr{M}} \hat{c}_k^\dagger \hat{X}_{\mathscr{M}} + h.c. \tag{4}$$

where $\mathscr{M} = (N,i;N+1,j)$ represents a transition from $|N+1,j\rangle \rightarrow |N,i\rangle$ (electron loss accompanied by change in electronic excitation index) and

$$V_{k\mathscr{M}} = \sum_{m \in M} V_{km} \langle N, i|\hat{d}_m|N+1,j\rangle \tag{5}$$

where the sum is over single electron basis $\hat{m}$, $d_m$ is the annihilation operator in the state, and $M$ indicates the molecular subspace of the system. Below, we utilize $m$ as an index for *atomic orbitals*. Equation 4 is the usual transfer Hamiltonian expressed in the molecular many-body basis. The coupling matrix element in eq 5 is a sum over the usual single-electron transitions weighted by the effective overlap between different many-body states.

The current through the junctions is given as usual[25] by the Meir−Wingreen expression.[31] The only difference is that in our case the trace goes over $\mathscr{M}$, the single-electron transitions between many-body states of the molecule. The steady-state current is

$$I_{L,R} = \frac{e}{\hbar} \int_{-\infty}^{\infty} \frac{dE}{2\pi} \mathrm{Tr}\big[\Sigma_{L,R}^<(E)\, G^>(E) - \Sigma_{L,R}^>(E)\, G^<(E)\big] \tag{6}$$

where the self-energies, $\Sigma$, are defined on the Keldysh contour as

$$[\Sigma_{L,R}(\tau,\tau')]_{\mathscr{M}\mathscr{M}'} = \sum_{k \in L,R} V_{k\mathscr{M}}^* g_k(\tau,\tau')\, V_{k\mathscr{M}'} \tag{7}$$

where $g_k$ is the GF for free carriers in the contacts.

The next step is calculation of the molecular GFs. The absence of Wick's theorem for the Hubbard operators makes the diagrammatic technique inapplicable. An alternative is the use of the functional derivatives in auxiliary fields approach,[32] which results in a hierarchy of approximations for the Hubbard GF in terms of the order of functional derivative taken. In what follows, we use the first loop approximation (for details, see, e.g., ref 25).

Having established the current expression and method for calculation of Hubbard GFs, we need the energy eigenstates and the self-energies. For the eigenstates, we focus on the energy levels in the isolated BDT molecule (no gold). To explore the impact of electronic structure theory accuracy on conduction results, we use a variety of methods. The neutral and anion charge states are chosen (other ionic states were significantly higher in energy), and the ground and first three excited states are included for each charge state. HF (restricted HF/unrestricted HF) calculations are carried out with the 6-31+G** basis set, and excited-state energies are obtained with configuration interaction singles (CIS). DFT (B3LYP, restricted KS/unrestricted KS) calculations are carried out with the 6-31+G** basis set, and time-dependent DFT (TDDFT) yields the excited-state energies. CCSD calculations are carried out with the aug-cc-pVDZ basis set and equation-of-motion method for excited states.[33] Recent work suggests[34] that, to accurately capture the electron affinities in benzene systems, fairly rigorous electronic structure theory and large basis sets are necessary, and so our choice of CCSD/aug-cc-pVDZ seems reasonable. Calculations were carried out with Q-Chem 3.1[35] (HF,DFT,CCSD) and Molpro 2006.1[36] (CCSD). The geometry optimized neutral structure of BDT (MP2, 6-31+G**) is used in all calculations. The energy levels are positioned relative to the contact Fermi level, and here we take $E_F = 0.4$ eV, which corresponds approximately to half of the gap between the neutral ground and anion ground (the closest molecular state). The temperature in the leads is 300 K, consistent with the room temperature measurements.[26,27]

The self-energies are defined in eqs 5 and 7. $V_{km}$ are the matrix elements representing electrode/molecule coupling, and these terms are calculated as usual by transforming from the atomic to molecular orbital basis. The matrix elements of the form $\langle N+1,j|d_m^\dagger|N,i\rangle$ are not in the usual NEGF treatment of transport and are a consequence of our state-based approach; they represent the overlap between electronic states with different electron occupation. For the sake of simplicity (to avoid having to code the matrix elements above within the coupled cluster equations), we use the same self-energy calculation for all energy eigenstate calculations (HF, DFT, CCSD). This approximation should be examined closely, and we will attempt higher-order treatment of these matrix elements in further work. For now, however, we use the KS orbitals from ground-state DFT calculations in order to calculate the quantities in eq 5 (i.e., the self-energies for neutral-anion transitions with different electronic excitation indices are assumed to be the same). For the $g_k$ term, we make use of the semielliptical Newns−Anderson result[30] for the self-energy of a one-dimensional tight-binding model. This model has been used in molecular conductance calculations before,[37,38] but we emphasize that higher level treatments of the electrode−molecule coupling could be carried out within this model. Therefore, we take benzene-1,4-dithiolate with one gold atom on each side (with Hay−Wadt effective core potential[39] for the gold atoms) and the S−Au bonds collinear. Since only MCBJ results[26,27] are available for the finite bias conductance of this system, we assume
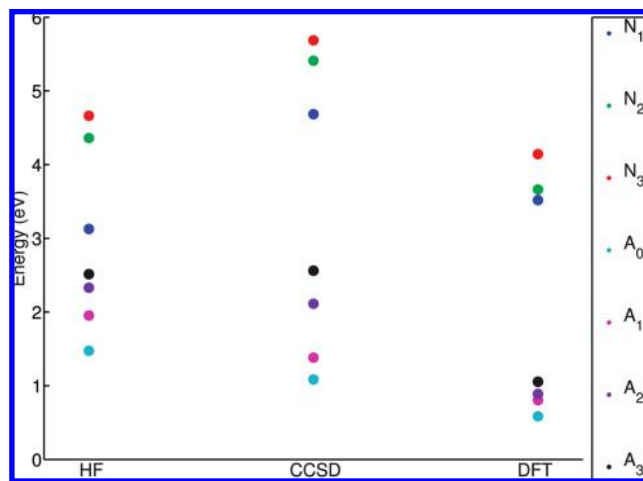


**Figure 1.** Electronic energies at different levels of theory relative to the neutral ground state ($N_0$). Three lowest-lying neutral excited states ($N_{1,2,3}$), the anion ground state ($A_0$), and the anion excited states ($A_{1,2,3}$) are shown. Details of the calculation are in the text.

the gold−sulfur bond lengths are asymmetric (3 and 6 Å).[40] Accordingly, we can assume the voltage drop is entirely across the more weakly coupled S−Au interface, and thus, we only need to calculate the electronic eigenstates at zero field. The symmetric results are available in the Supporting Information. The sums over $k,k'$ and $m,n$ are restricted to the atomic gold valence orbitals and the sulfur orbitals, consistent with the assumptions of the Newns−Anderson model.

We begin by presenting the electronic energy levels of the isolated BDT molecule at different levels of theory (Figure 1). The results show that considerable differences emerge as electronic structure treatments are improved. In particular, the DFT/TDDFT results underestimate both the neutral-anion energy gap as well as the excitation spectrum. This suggests that qualitatively different conductance spectra will emerge from these electronic structure treatments. In particular, the neutral-anion ground-state gap ($N_0 - A_0$) of BDT requires large basis sets: CCSD/cc-pVDZ yields an electron affinity (EA) that is off by 0.7 eV as compared to CCSD/aug-cc-pVDZ. Our CCSD result for the EA in BDT ($-1.09$ eV) is very close to the electron transmission spectroscopy measurement for benzene ($-1.12$ eV).[41]

Combining these electronic structure calculations with the self-energy terms yields the conductance (d$I$/d$V$) of the asymmetric gold−BDT−gold system at different levels of theory (ignoring the role of vibronic coupling). In Figure 2, we present these results and plot the conductance contributions from various electronic transitions. The doubly peaked structure seen by both Reed et al.[26] and Lörtscher et al.[27] is reproduced here in the CCSD calculations and is due to transitions between the neutral ground state ($N_0$) and the anion ground ($A_0$) and first excited state ($A_1$) for the first peak and between $N_0$ and $A_2$ for the second peak. The HF calculation also presents this double peak structure but originates from transitions between $N_0$ and $A_0$ (first peak) and $N_0$ and $A_1$ (second peak). The DFT calculation results
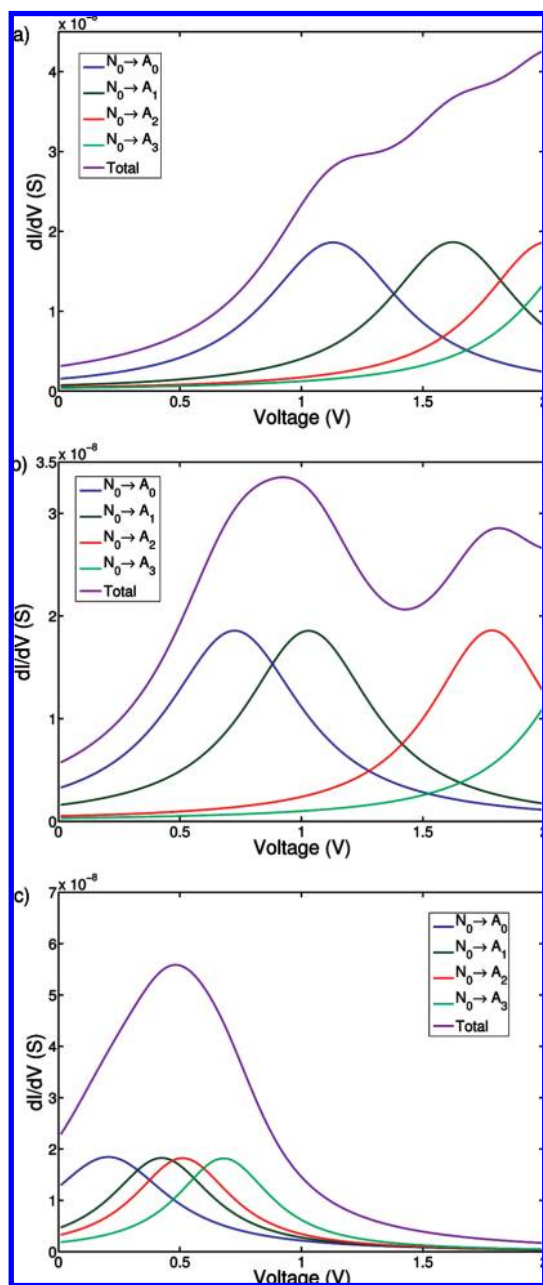
**Figure 2.** Conductance of the asymmetric BDT junction at various levels of theory. Total conductance as well as contributions from each state-to-state transition are shown. HF (a), CCSD (b), and DFT (c) results are shown. Other state transitions did not contribute significantly and are not shown.

in a single peak structure due to the underestimation of the anion excited-state energies in the TDDFT calculation.[42] For small, localized systems, such as BDT, it is not surprising that HF performs better than DFT methods due to large self-interaction error.[43] As expected, DFT overestimates the conductance due to the lower anion energies. This might be responsible for the overly large conductances found in traditional DFT-NEGF calculations of conjugated molecular wires.[44]

Given a reasonable set of parameters for the geometry of the junction (asymmetric Au–S bonds), we have been able to reproduce the qualitative features of the finite-bias conductance measurements in MCBJ experiments.[26,27] Other

computational treatments have been able to reproduce qualitatively the two peak structure of the BDT conductance spectrum. These have been based on Lippmann–Schwinger-based methods,[45] semiempirical Landauer treatments with *two* benzene molecules bridging the electrodes,[46] and equilibrium GF methods.[47] The state-based approach presented here, however, has the advantage of providing a hierarchy of improvements in the treatment of the molecule (electronic structure theory) and its coupling to the contacts (higher order functional derivatives), as well as the ability to indicate which transitions dominate the transport at each bias.

In future work, we intend to apply this method to study molecular junctions in which oxidation/reduction of the molecule leads to essential changes in its transport properties, such as negative differential resistance and hysteresis.[48]

**Supporting Information Available:** Electronic structure calculations and conductance results for the symmetric junction. This material is available free of charge via the Internet at http://pubs.acs.org.

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