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Dynamic current suppression and gate voltage response in metal-molecule-metal junctions

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Abstract

We critically re-examine conductance in benzenedithiol(BDT)/gold junctions using real-time DFT simulations. Our results indicate a powerful influence of the BDT molecular charge on current, with negative charge suppressing electron transport. This effect occurs dynamically as the BDT charge and current oscillate on the femtosecond timescale, indicating that a steady state picture may not be appropriate for this single molecule conducting device. Further, we exploit this effect to show that a gate voltage can be used to indirectly control the device current by adjusting the molecular charge. Thus, it appears that transport in even this simple molecular junction involves a level of sophistication not heretofore recognized.
The conductance behavior of molecular devices subjected to an external potential has been the source of significant theoretical interest since the first experiments were performed some time ago\cite{1,2}. As one of the earliest and simplest single-molecule conductors to be studied, benzene dithiol (BDT) has become the de facto standard model system for both experimental\cite{1,3} and theoretical\cite{4–8} studies. In this work, we use a recently proposed real-time density functional theory (DFT) propagation technique\cite{9,10} to study several properties of electron transport through BDT at low bias.

When examining conductance through systems, such as organic molecules, in which electronic motion is hindered relative to metals, one must consider the Coulomb blockade (CB). First used to describe transport through quantum dots\cite{11}, CB refers to the resistance caused by the energetic cost of adding or removing an electron from an already charged molecule\cite{12,13}. As a result of this energy cost, conductance is especially sensitive to the charge on the molecular device in the CB regime\cite{4–6,14}.

Closely related to molecular charge and CB is the application of a gate potential. While the current is driven by a voltage applied within the metallic leads, a gate voltage is applied to the conducting device to alter its conductance properties. By shifting the energies of the molecule states, the gate voltage can induce charging of the molecule making gating a natural method to study CB effects. Single-molecule gate voltage experiments have been performed\cite{3,13,15}, however the difficulty in constructing three terminal devices using a molecule as small as BDT makes obtaining reliable results difficult. Theoretical studies of gating effects are not thus hindered\cite{16,17}, so that simulations have significant flexibility in studying CB physics.

The most popular theoretical method to examine molecular conductance is the nonequilibrium Green’s function (NEGF)\cite{7,18,19} method in which the Hamiltonian is used to generate Landauer-type conductance channels. Now, the NEGF method assumes a steady state conduction picture. Aside from being potentially inaccurate in the presence of molecular bound states\cite{21}, the steady state picture ignores the interior life of the junction: How and (how quickly) does the current build up? How many electrons are moving through the molecule at one time? In order to address these questions, one can instead use time-dependent density functional theory (TDDFT) to model dynamic transport in molecular junctions\cite{22}. Here, one applies a time-dependent potential to drive current in a fully nonlinear real-time propagation of a microcanonical system\cite{23}. We have previously applied this method to simple
1D conjugated carbon wires and have explored the conductance behaviors of both closed-shell and open-shell systems. Here we apply our real-time DFT propagation method to the gold-BDT-gold system (Fig. 1) in order to better understand the dynamics of transport in a real junction. We calculate the dynamic current-voltage response using several exchange-correlation functionals and observe a strong negative correlation between the instantaneous charge on BDT and the current through the junction - the dynamic equivalent of CB. Further, we find that our currents oscillate on the femtosecond timescale, calling into question the coherent steady-state picture invoked in the NEGF approach. Finally, we calculate currents under a gate voltage and observe that $V_g$ provides indirect control over the current by modifying the BDT charge. Taken together, our results suggest a much more intricate picture of transport through this junction - involving dynamic fluctuations between nonequilibrium states and strong electron-electron interactions - that has not previously been appreciated.

The system geometry under study is a BDT molecule covalently bonded to the 111 face between two Au$_{114}$ clusters in the fcc position. We construct the geometry by reflection symmetry on portions of a previously optimized geometry for phenylthiol chemisorbed to a gold surface. We replicate the gold layers in the 111 reciprocal direction to produce an elongated wire structure. The system geometry is included as supplementary data. We choose a structure elongated in the direction of electron transport ($Z$) to allow sufficient density of momentum states in the $Z$-direction and sufficient time before reflection at the wire ends manifests in the current. The electrons are described by the Hay-Wadt pseudopotential and minimal basis on the gold atoms and the Aldrichs VDZ basis augmented with heavy atom d functions on all other atoms. Calculations were performed using a development version of Q-Chem. We divide our system into an electron source, molecular device, and electron drain region as shown in Fig. 1a. We will use this system division to apply a voltage potential and to define the resulting time-dependent electron densities.

The real-time DFT propagation method used to calculate conductance properties have been described previously. Here we summarize the closed-shell method and its application in this work. We choose an unperturbed Hamiltonian and determine our initial state as the ground state of the entire system under that Hamiltonian. At time $t = 0$, we change the Hamiltonian and propagate the electron density, $\rho(t)$, according to the time-dependent Kohn-Sham (KS) method under the perturbed Hamiltonian. We construct the
FIG. 1: (a) Au$_{114}$-BDT-Au$_{114}$ system with source and lead regions labeled along with the effect of lead potential, $V$, and gate potential, $V_g$, on electronic energies in each region. Atoms depicted include H (gray), C (light blue), S (green), and Au (gold) (b) Time dependent density difference ($N_{tot}$) with linear fitting in the steady state region and (c) resulting current-voltage curve.

Using a voltage potential definition, we choose our initial Hamiltonian according to unbiased ground state DFT. We add an external potential at $t = 0$ to determine the adjusted Hamiltonian. The potential is defined using the population operators on the source ($\hat{n}_S$), molecular device ($\hat{n}_M$), and drain ($\hat{n}_D$). We follow our previous work and choose our population operators according to the Löwdin population definition. For a lead bias of $V$, the adjusted KS Hamiltonian is given by $\hat{H}_{KS}[\rho] + \frac{V}{2} \hat{n}_S - \frac{V}{2} \hat{n}_D$ where $\hat{H}_{KS}[\rho]$ is the unperturbed KS Hamiltonian. We include a gate voltage with the additional term $V_g \hat{n}_M$. The effect of
FIG. 2: TDDFT calculated current-voltage curve using B3LYP, LDA, and Hartree-Fock exchange-correlation functionals.

the lead and gate voltages on the electronic state energies in each region is shown in Fig 1a.

This method allows us to calculate the time dependent electron populations in the source, molecular device, and drain using the population operators defined above:

\[ N_R(t) = \int n_R(\mathbf{r}) \rho(t) d\mathbf{r} \quad R = S, M, D. \]

From these values, we define the current \( I = \frac{1}{2} \frac{d}{dt}(N_D - N_S) \) as the least-squares linear regression slope in \( \frac{1}{2}(N_D - N_S) \) over the time period of constant charge transport that begins shortly after application of the potential. In this work, the current is calculated over the time period of 0.24 to 1.57 fs. As an example, the regression fitting and resulting IV plot for the LDA functional are shown in Fig. 1b and c.

Using these methods, we have generated small bias IV curves with the LDA, B3LYP, and Hartree-Fock functionals. These results are shown in Fig. 2. We note that the calculated IV curves are mostly linear over the low-bias regime shown. For Hartree-Fock, the average conductance over the calculated range is 0, indicating that this voltage range lies within the HF predicted conductance gap for the system. On the other hand, both B3LYP and LDA predict no conductance gap at the plot resolution of Fig. 2. A decrease in the conductance gap with methods that do not include 100% exact exchange has been previously reported\(^{30,31}\).

The average conductances, calculated from the largest plotted voltage point are 16 \( \mu \)S with LDA, and 10 \( \mu \)S with B3LYP. For comparison, the conductance quantum is 77 \( \mu \)S and the contemporary experimental estimates of the conductance of BDT are approximately 1 \( \mu \)S.\(^3\) This order of magnitude overestimation of current over experiment is a common shortcoming.
of conduction calculations\textsuperscript{19,32}.

Although the difference in conductance between these methods has been associated with a decrease in the device HOMO-LUMO gap with the introduction of self-interaction error\textsuperscript{30,33,34}, we also notice a correlation with the density distribution in the equilibrium state. Using the Löwdin population definition, the total charge on the molecule is -1.38 with Hartree-Fock, -0.955 with B3LYP, and -0.851 with LDA. Thus, a more negative electronic charge on the molecular device correlates with a decrease in its conductance. This behavior resembles the Coulomb blockade described earlier in that the additional Coulombic energy cost from increased electronic density correlates with decreased conductance.

We can estimate the Coulomb energy associated with the charge differences if we simplify the molecular device to be a sphere of uniform charge density. In that case, the Coulombic repulsion energy is $E_C = \frac{3q^2}{20\varepsilon_0 R}$ where \( q \) is the total charge, and \( R \) is the radius. We choose the radius to be half the distance between the sulfur atoms in the BDT device, so \( R = 3.2 \) Å. The resulting energy difference between the LDA and HF calculated charges is 3.2eV. This energy is certainly sufficient to push the conduction states outside of the voltage window. Furthermore, it is likely that charging the device to -1 or below saturates the conduction bands. Thus it is reasonable that the difference in equilibrium molecular charge predicted by the various functionals accounts for some of the differences in conduction behavior.

We generate the IV curves from relatively short time dynamics \((t < 1.75 \text{ fs})\) in which the current is approximately steady, but we find significantly different behavior at longer times. In Fig. 3, we display real-time results for the junction over a larger time window under several external potentials. The dynamic data indicate that the electron density transport from the source to the drain does not occur at a constant rate. All three of the propagations include regions in which the time derivative of \( N_D - N_S \), and therefore the transient current, is 0 or even negative. The complex dynamics are a direct result of the non-equilibrium initial condition we have set up, and as such the precise oscillations will reflect the details of how the system is initialized\textsuperscript{23}. For example, if the Bias is turned on over the first 1 fs (as opposed to instantaneously at \( t=0 \)) the oscillations persist, although their magnitude and phase are somewhat altered. Further, we see similar current oscillations with B3LYP, but because these long-time dynamics are computationally intensive, we choose to focus on the LDA results with the expectation that the B3LYP results will be qualitatively similar. Qualitative similarities in the IV curve outside of the conductance gap with the various
FIG. 3: Time dependent density difference ($N_{\text{tot}}$) (a) and device charge (b) as calculated by LDA. The vertical lines are guides to the eye that indicate approximate times at which the first zero current regions begin for each potential.

functionals$^{30,31}$ suggests we may see similar results with HF as well.

In addition to the current oscillations, the long time simulations also demonstrate oscillations in the density on the molecule. These current and density oscillations demonstrate that the system does not evolve towards a steady state, but instead show oscillatory behavior consistent with the presence of a bound molecular state in the voltage gap$^{21}$. Although this suggests that the oscillations represent resonance with molecular states, energies associated with the large period oscillations are smaller than the HOMO-LUMO gap of the bare molecular device. Additionally, their periods are sensitive to the applied potential (cf. Fig. 3), so the states corresponding to these oscillations must have a significant component on the metallic leads.

The lead dependent nature of the oscillations initially suggests they are a finite system
effect and that the periods of zero current may be caused by either: 1) saturation of the finite leads or 2) reflection off the ends of the wire. We discount the first possibility, because the positive current always reappears and transports more electrons to the drain after the plateau. We examined the second possibility by performing test calculations using shorter gold wires and found that the oscillation frequencies do not show a systematic change with wire length. Thus, the oscillations would not seem to be a finite lead effect.

The dynamics in Fig. 3 indicate a correlation of a period of zero current with increased negative molecular device charge. The first period of zero current begins at 8.8 fs for the 0.544 V propagation, 4.0 fs for 1.09V, and 1.9 fs for 2.18V. At all of these points, the molecular charge profile indicates a region of increased negative charge. Although the 0.03 electron variation in charge is small, the uniform spherical charge approximation discussed above leads to a Coulombic energy variation of approximately 0.15 eV, which is significant relative to the voltages considered. Thus, we see a dynamic as well as static association between device charge and current, indicating a dynamic equivalent of Coulomb blockade. It is somewhat surprising that something similar to CB physics can be obtained from semilocal TDDFT, which is usually only able to describe mean-field-like evolution accurately. The key in this case is that while semilocal functionals neglect explicit electron correlation in space - so that static CB effects are absent - they recover correlation in time - so that the dynamic oscillations remain.

We note that the correlation observed between molecular charge and current is opposite to the previously reported tendency of a more negative charge to increase current. This calculation, unlike the others reported results, does not involve changes in lead-device separation which may impact current. Our results may implicate a LUMO-based transport pathway, which would cause current to decrease with a more negatively charged device.

The oscillatory current behavior shown in Fig. 3 is relevant to the NEGF formalism, because the NEGF formalism is based upon a steady state assumption. The long time calculations indicate that the system reaches an oscillatory, not steady, state. Our results indicate that some of the overestimation common to NEGF simulations may be due to this steady state assumption. To this point, we have computed net currents from the early (e.g. 1 fs) steady state period during which the density fits well into the NEGF picture. However, the average current over longer times (e.g. 10 fs) is clearly lower than the initial current because of the oscillations and one might argue that this is the more relevant timescale for
If the development of non-equilibrium oscillations is a general feature of molecular junctions, using the long-time current would thus systematically reduce the calculated conductance and improve the agreement of theory and experiment. The oscillations make precise calculations impossible, but the results in Fig. 3 suggest that the new definition would lead to a two- to three-fold improvement in calculated conductance for the BDT-gold junction. We believe this observation is significant and may play a role in bridging the gap between theory and experiment.

The association between charge and current suggests that we may be able to alter the current by inducing a change in the device charge. To that end, we introduce a gate voltage to the system under an external bias. Based upon the definition of gate voltage in Fig. 1a, we expect a positive potential to produce a less negative charge on the molecular device. We show in Fig. 4 the early time current with a fixed bias of 1.09 V as a function of gate voltage. As we did for external potentials, we focus on small gate voltages to avoid overwhelming the chosen basis. Examination of the charge dynamics (not shown) verifies that the linear fit time period for current calculation occurs after the molecular charge has equilibrated in response to the gate voltage. The results indicate that by increasing the gate voltage, and thereby making the device charge less negative, we increase the current. We calculate a low voltage response of current to gate voltage of 5.8 $\mu$A/V, or 36% of the response to external voltage.

This simulation suggests that we can control the current through BDT with the application of a gate voltage. As a positive gate voltage creates a less negative device charge, the
current increases. The device charge changes at a rate of 7.5 $q_e/V$ leading to a current to charge response of 0.77 $\mu A/q_e$. This is clearly much less than the response demonstrated in the dynamic results. However the impact of charge on current is significantly counteracted by the gate voltage required to generate the charge response.

In conclusion, our real-time simulations of the Au$_{114}$-BDT-Au$_{114}$ cluster suggest a picture where oscillations in charge drive transport, in contrast to the standard steady-state picture of electron transport. At a given instant, a reduction in current is associated with a more negative charge on BDT. This current suppression a dynamic effect similar to the Coulomb blockade, arising out of the temporal (rather than spatial) correlation between electrons. We further demonstrate that a gate voltage can be used to induce molecular charging, and thus impact the current by modulating the dynamic charge-current suppression. Moving forward, it should be noted that our results neglect relaxation of the nuclear framework. As these motions occur on the same timescale as the slowest oscillations shown in Fig. 3, the potential for vibronic interactions cannot be neglected and future work will examine the interplay between these slow oscillations and vibrational motion. Thus it would seem that time offers a new dimension for unravelling the rich mechanisms at work in molecular transport.

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31 J. S. Evans, O. Vydrov, and T. V. Voorhis, manuscript in preparation.


