Insights into molecular conduction from I-V asymmetry

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We investigate the origin of asymmetry in the measured current-voltage (I-V) characteristics of molecules with no inherent spatial asymmetry. We establish that such molecules can exhibit asymmetric I-V characteristics due to unequal coupling with the contacts. In contrast with spatially asymmetric molecules, conduction takes place through essentially the same level in both bias directions. The asymmetry arises from a subtle difference in the charging effects, which can only be captured in a self-consistent model for molecular conduction. For HOMO-based conduction, the current is smaller for positive voltage on the stronger contact, while for LUMO conduction, the sense of asymmetry is switched.

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Future electronic devices are quite likely to incorporate molecular components, motivated by their size, mechanical flexibility and chemical tunability. This vision is nearing reality with the capacity to self-assemble, functionalize, and reproducibly measure the current-voltage (I-V) characteristics of small groups of molecules. Molecular I-Vs have revealed a wide range of conductance properties, from metallic conduction in carbon nanotubes [1] and quantum point contacts [2], to semiconducting behavior in DNA [3] and conjugated aromatic thiols [4], and insulating behavior in alkyl thiol chains [5]. Interesting device characteristics such as rectification [6], switching [7] and transistor action [8] have also been reported.

The classic paradigm for asymmetry in molecular I-V measurements is the Aviram-Ratner diode, consisting of a semi-insulating molecular species bridging an electron donor-acceptor pair [9]. A positive bias on the contact at the donor end brings the energy levels on the donor and acceptor sites into resonance, while the opposite bias moves the system away from resonance, leading to a strongly asymmetric I-V characteristic [10]. Spatial asymmetry in the molecule is essential in generating the I-V asymmetry, causing the energy levels, the electrostatic potential and electron wavefunctions to be quite different for positive and negative voltages [11].

In this paper, we address an I-V asymmetry experimentally observed for spatially symmetric molecules [12,13] that is qualitatively different from and weaker than the rectification in spatially asymmetric molecules. The molecular I-V curves seen for these systems start off being symmetric, but pick up a weak, reversible asymmetry as the contacts are manipulated (Fig. 1). In contrast to spatially asymmetric molecules, conduction in these molecules at opposite voltages occur through essentially the same molecular levels with very similar wave functions. We show that the origin of the observed asymmetry is nontrivial, involving self-consistent shifts in the energy levels due to charging effects. Asymmetry in charging arises due to unequal coupling with the contacts, and can be present in conduction measurements performed with a break junction [12], an STM tip [14] or an evaporated gold contact [10]. Remarkably, the sense of the asymmetry depends crucially on whether the conducting level is HOMO or LUMO. We establish that for a spatially symmetric molecule the current is lower for positive bias on the stronger contact if conduction is through a HOMO level, and higher if conduction is through a LUMO level.

![Figure 1](image-url)
all these models predict similar symmetric I-Vs, the sense of the I-V asymmetry for asymmetric contacts pins down the nature of the conducting orbital rather restrictively; for instance, the I-V asymmetry measured for PDT with an STM tip indicates HOMO-based conduction, as we show later.

![Diagram](image)

FIG. 2. Schematic description of resonant current conduction through discrete molecular levels broadened by interaction with the contacts. Onset of current corresponds to crossing a molecular level by a contact chemical potential under bias. For a molecule strongly coupled to a substrate, and with a large gap DOS (a), the chemical potential of the other (weaker) contact crosses the HOMO and LUMO levels at opposite bias. In a typical molecular conductor (b) on the other hand, the same level is crossed both ways.

Non self-consistent description of molecular conduction. An isolated molecule has discrete molecular levels, that are broadened upon coupling with contacts into a continuous density of states (DOS) due to hybridization with the metal wave functions. For molecules like PDT the broadening is weak enough that the DOS shows a clear HOMO-LUMO gap (HLG). The difference in the work functions between the metal and the molecule leads to charge transfer between them, and the molecular levels adjust due to Coulomb charging until the heterostructure is in equilibrium. Under bias the contact chemical potentials split by the applied voltage \( \mu_2 - \mu_1 = eV \). As long as both potentials lie in the HLG, all HOMO levels are occupied and LUMO levels unoccupied, and there is essentially zero current. Once the bias is large enough that a contact chemical potential crosses a molecular level, that level is filled by one contact and emptied by the other, and starts conducting current. Thus the specific levels contributing to conduction for either bias direction depend on the way \( \mu_1 \) and \( \mu_2 \) are disposed relative to the molecular levels under bias.

One can get an asymmetric I-V with a symmetric molecule provided the latter is coupled strongly enough to the substrate to be in equilibrium with it, resulting in \( \mu_1 = E_F \). The potential of the other contact (say, an STM tip) moves freely under bias, \( \mu_2 = E_F + eV \) (Fig. 2a). If furthermore there is a large density of metal-induced gap states (MIGS) in the gap, then the electrostatic potential and the molecular levels stay pinned to \( \mu_1 \) and don’t vary with \( V \). For positive and negative substrate bias, \( \mu_2 \) crosses the LUMO and HOMO levels respectively, yielding a strongly asymmetric I-V, since the LUMO and HOMO transmissions are quite different in general. The conductance gap is then given by the HLG, a property intrinsic to the molecule itself.

In practice, however, spatially symmetric molecular species typically exhibit symmetric I-Vs [4], with a conductance gap that varies from experiment to experiment [22]. The MIGS are usually not appreciable causing the electrostatic and chemical potentials to separate. The average electrostatic potential across the molecule is \( V/2 \), which shifts the levels along with the applied bias. Relative to the molecular levels therefore, the contact potentials move in opposite directions symmetrically, \( \mu_{1,2} = E_F \mp eV/2 \) (Fig. 2b). The same molecular level (HOMO in the figure) is crossed for either bias by the contact chemical potentials, leading to a symmetric I-V, with a conductance gap given by \( 4(E_F - E_{\text{HOMO}}) \) [23]. The gap is no longer the HLG, but depends on both the molecular chemistry and the contact microstructure.

The above non self-consistent description of molecular conduction can be put on a quantitative footing by using an appropriate molecular Fock matrix \( F \) (ab-initio or semi-empirical), followed by a non-equilibrium Green’s function (NEGF) formulation of transport [24]. For a given Fock matrix \( F \), overlap matrix \( S \), and contact self-energies \( \Sigma_{1,2} \) with corresponding broadenings \( \Gamma_{1,2} = i \left( \Sigma_{1,2} - \Sigma_{1,2}^\dagger \right) \), the energy levels are given by the poles of the nonequilibrium Green’s function \( G \), while their occupations are obtained from the corresponding density matrix \( \rho \) and the contact Fermi functions \( f_{1,2} \):

\[
G(E) = (ES - F - \Sigma_1 - \Sigma_2)^{-1}
\]

\[
\rho = (1/2\pi) \int_{-\infty}^{\infty} dE \left( f_1 G_1 G_1^\dagger + f_2 G_2 G_2^\dagger \right)
\]

\[
f_{1,2}(E) = \left[ 1 + \exp \left( (E - \mu_{1,2})/k_B T \right) \right]^{-1}.
\]
The number of electrons $N$ and the steady-state current $I$ are then given by:

$$N = 2 \text{ (for spin)} \times \text{trace}(\rho S)$$

$$I = \frac{2e}{\hbar} \int_{-\infty}^{\infty} dE \, \text{trace}(\Gamma_1 G \Gamma_2 G^\dagger) \left[ f_1(E) - f_2(E) \right]. \quad (2)$$

The important point to notice is that since the same molecular level is being crossed both ways, the current is symmetric in the coupling constants $\Gamma_{1,2}$ and one is stuck with a symmetric I-V for a symmetric molecule, no matter how asymmetric the contacts are.

Let us suppose that the contacts are strongly asymmetric ($\Gamma_1 \gg \Gamma_2$). For negative bias on the strong contact (a), the latter is trying to fill the nearest (HOMO) level, while the weaker contact is trying to empty it, with the net result that the HOMO level stays filled, with current onset set by the voltage where $\mu_2$ first crosses the (neutral) molecular level. For positive bias (b), however, the HOMO level is emptied out, which charges up the molecule positively. This adds a self-consistent charging energy that lowers all the energy levels, postponing thereby the point where the HOMO is crossed by $\mu_1$. In effect, this stretches out the voltage axis, leading thus to a smaller conductance for positive bias on the stronger contact, as mentioned earlier. For LUMO-based conduction the argument is reversed, since filling the LUMO level charges up the molecule negatively.

![Fig. 3. Origin of asymmetry in charging: one side (say a substrate) is strongly contacted while the other is weak. Although the same level is crossed by the contact potentials for opposite bias, for positive substrate voltage (b) the HOMO level is emptied by the stronger contact, which positively charges the molecule and shifts the energy levels down.](image)

The asymmetric I-V cannot simply be explained by suggesting that the average electrostatic potential across the molecule is $\eta V$, $\eta$ decreasing from 0.5 as a contact is drawn out. Such a theory yields an asymmetry only in the onset voltages for conduction, rather than a dragged out I-V as in Fig. 1 (the latter actually corresponds to different conductance peak values in the two bias directions). One will then need to invoke a voltage-dependent $\eta$ to explain Fig.1, which formally amounts to our self-consistent charging description below.

**Self-consistent description (Charging induced asymmetry)** The above description of molecular conduction does not include the effects of charging and electronic Stark shift back on the levels. For a small molecule with a large ($\sim 1$ eV) capacitive charging energy, charging effects need to be taken into account self-consistently. In the following, we show that such effects can lead to contact-induced asymmetries of the sort observed in Fig. 1.

The effect of differential charging on the I-V asymmetry is explained schematically in Fig. 3 for a single level.

![Fig. 4. Extended Hückel-based I-V characteristics for Phenyl Dithiol (PDT), including self-consistent charging effects. The central graph (symmetric) is for symmetric weak couplings ($\Gamma$s decreased symmetrically by a factor of 10 relative to their chemisorbed values) of the PDT molecule with Au(111) contacts. The lower graph corresponds to decreasing $\Gamma_2$ five times relative to $\Gamma_1$, which stretches out the voltage axis in the direction of the stronger contact, i.e., along positive bias on contact 1. Reversing the couplings yields the upper graph. This graph can also be obtained without reversing the couplings, by simply raising $E_f$ so that the conduction occurs through the LUMO level instead.](image)

We illustrate self-consistent charging effects in a PDT molecule modeled by a extended Hückel description of the Fock matrix $F$, coupled to the NEGF equations described earlier. The self-energies are calculated for Au(111) contacts using a recursive technique. Charging effects are incorporated in $F$ by adding a term $U_{SC}$ describing the deviation from the equilibrium electron count $N_0$ within the local density approximation:

$$U_{SC} = U_0 (N - N_0), \quad (3)$$

and solving for $F$ self-consistently with equations and.
The constant charging energy $U_0$ ($\sim 0.7$ eV per electron) corresponds to a flat electrostatic potential profile in the molecule, and serves to shift all the energy levels rigidly by a constant.

Fig. 4 shows the I-V characteristic for PDT with weak symmetric contacts (central graph), with contact self-energies 0.1 times their chemisorbed values, assuming HOMO conduction ($E_f = 10$ eV). Weakening the coupling with the right contact ($\Gamma_2 = 0.2 \Gamma_1$) stretches the voltage axis along contact 1 (lower figure). The I-V asymmetry can be switched (upper figure) either by switching the contact couplings, or by raising $E_f$ enough to generate LUMO-based conduction.

The calculated trend in the I-V characteristics agrees qualitatively with the experiments on symmetric molecules with asymmetric contacts. In break-junction experiments in general, the molecules are likely to adsorb separately onto the two contacts symmetrically, leading to symmetric I-Vs even for asymmetric contacts. In carefully controlled break-junction experiments, however, a single molecule is expected to couple simultaneously with both contacts. This allows one to induce asymmetry easily by manipulating the contacts, changing the I-V from symmetric to asymmetric and back, as well as flipping the sense of the asymmetry by interchanging contact couplings. Weak I-V asymmetries are also seen in STM measurements of symmetric molecules such as PDT, where the conductance is lower for positive substrate bias. Since the coupling of the molecule with the STM contact is evidently weaker than with the substrate, the above asymmetry implies that conduction in PDT is HOMO-based.

In summary, we have established that even for spatially symmetric molecules, contact asymmetry can induce an asymmetric I-V through differential charging, the sense of the asymmetry depending on whether conduction is through a HOMO or a LUMO level.

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