

## Theory of Rectification in Tour Wires: The Role of Electrode Coupling

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We report first-principles studies of electronic transport and rectification in molecular wires attached to gold electrodes. Our *ab initio* calculation gives an accurate description of the voltage drop as well as the broadening and alignment of the molecular levels in the metal-molecule-metal complex. We find that the operation range and rectification in such strongly chemisorbed molecules is limited by the width of the transmission resonances and their proximity to the Fermi level.

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The study of electron transport through single molecules is a rapidly developing field, stimulated by many recent experiments [1–5] that show that single molecules can be made into useful functional elements of an electronic device. Rectifiers have played a key role in the development of molecular electronics both because they formed the basis for the first proposal of a unimolecular electronic device by Aviram and Ratner [6], and because they are one of the simplest functions to build into an electronic component [7]. The molecular rectifier proposed by Aviram and Ratner [6] and a related class studied by Metzger [3] have relatively complex structures, consisting of an organic molecule with donor-barrier-acceptor regions. In these devices, there is a built-in asymmetry in the structure of the molecule, which leads to asymmetric current-voltage characteristics. In this paper, we will concentrate on rectification in symmetric molecules. Some experiments on symmetric molecules have shown rectification [8–10], while others have found very little or no rectification [11,12]. Electronic transport experiments on such molecular monolayers are often performed by evaporating and chemisorbing the molecules to a substrate using an appropriate “alligator-clip” [13], which interacts strongly with the surface to selectively bind one part of the molecule to the substrate. A second probe [STM (e.g., [8]), evaporated metal electrode (e.g., [9]), or mechanical break junction (e.g., [11]) is then used to apply a bias and study the electronic transport properties, resulting in an asymmetry in the coupling strength of the electrodes used to draw the current, which is the origin of the current rectification.

The understanding is that the potential drop along the molecule changes the alignment of the molecular levels (the energies at which resonant tunneling occurs) with the electrochemical potential of the substrate and tip (the energy at which electrons or holes are injected). Asymmetric electrode coupling can result in an asymmetric potential profile along the length of the molecule [12]. If the potential profile is asymmetric, the molecular level can line up differently in positive and negative bias, resulting in rectification. While the potential drop plays a key role in aligning the molecular levels with the electro-

chemical potentials, the ultimate performance of such devices will also be influenced by the current reduction due to a weak coupling of the second electrode, and the width of the transmission resonance which carries the current, which can be significant for chemisorbed molecules that interact strongly with the surface [14].

In this paper, we will use state of the art first-principles electron transport calculations to study the relation between rectification and forward bias current for an organic molecule coupled to metallic electrodes. The organic molecule is a phenylene ethynylene oligomer [15], a so-called “Tour wire,” consisting of phenyl rings separated by tripled bonded carbon atoms, forming a long rigid molecule with  $\pi$ -conjugated delocalized frontier orbitals. Tour wires can be synthesized as long oligomers, and have become popular building blocks for molecular electronic components [15]. A thiol-gold bond is proposed to selectively couple the Tour wire to an Au(111) substrate. We will investigate the change in the current-voltage characteristics as the distance to a second Au(111) surface or tip is increased, thus weakening the molecule-tip coupling. We will compare our results with related experimental studies of rectification in symmetric single molecules [8–12].

The calculations have been carried out using a first-principles nonequilibrium Green’s function based electronic transport package, TRANSIESTA [16]. Recently, there have been several first-principles theoretical studies of electron transport in organic molecules under finite bias conditions [17,18] which differ mainly in their description of the semi-infinite electrodes and their interaction with the molecules in the contact region. Our method is based on density functional theory [19], treats the system self-consistently under finite bias conditions, and describes the electronic structure of the whole system (contact and electrodes) on equal footing. Since the coupling of the organic molecule to the electrode plays a central role in the present study, it is of particular importance to make an accurate model of the electrode itself and, most importantly, the molecule-electrode interface [20]. Therefore, for the purposes of this study, it is imperative to use a method that describes the electrodes

using the same model chemistry as the contact region [16,17], which is the only way to obtain a first-principles, parameter-free treatment of the broadening and alignment of the molecular levels.

The two systems we have investigated are shown in Figs. 1(a) and 1(b) [21]. They each consist of a 3-phenyl-ring Tour-molecule coupled to Au(111) electrodes [22], the first surface layer of which are shown here. Molecule *A*, depicted in Fig. 1(a) is symmetrically bonded to the Au electrodes with thiol end groups [23]. Molecule *B*, depicted in Fig. 1(b), is thiol-bonded to the left electrode while the other end is terminated by an H atom, not bonded to the right Au electrode. We will here consider the effect of increasing the vacuum distance  $d$  between the terminal H atom and the first atomic plane of the right Au(111) electrode.

In Figs. 1(a) and 1(b), we also show the induced density and potential for an applied bias potential of  $eV_b = \mu_L(V_b) - \mu_R(V_b) = -1$  eV, where  $\mu_L(V_b) = \mu_L(0) + eV_b/2$  and  $\mu_R(V_b) = \mu_R(0) - eV_b/2$  are the chemical potential of the left/right electrodes, respectively. For molecule *A*, the potential does not drop at the contacts but drops relatively uniformly along the length of the molecule. It is, however, clear that there is a difference in the screening properties in different parts of the molecule. The induced density consists mainly of anti-bonding  $\pi$  orbitals along the molecular axis, whereas the induced density and potential are screened out of the phenyl rings. The electric field sets up dipoles between the atoms along the molecular axis, which can be correlated to drops in the potential profile. When a bias is

applied to the system, the S atoms couple differently to the bands of the left and right Au(111) surfaces, resulting in induced charges of different orbital characters on the S atoms. In molecule *B*, the electric field increases near the right electrode and there is an additional drop at the right electrode due to the difference in dielectric constant of the molecule ( $\epsilon_M \sim 3.5\epsilon_0$ ) and the vacuum tunnel barrier. Again, the induced potential and density is screened out of the two leftmost phenyl rings of molecule *B* but the rightmost ring is influenced by the comparatively stronger field.

In Figs. 2(a) and 2(b), the calculated transmission spectra  $T(E, V_b)$  are plotted for different bias voltages  $-1.2$  V  $< V_b < +1.2$  V (each curve is vertically shifted for clarity, representing a difference of 0.1 V). The dashed lines represent the transmission spectrum at equilibrium. The current is obtained using the Landauer-Büttiker formula [24]:  $I = \int_{\mu_L}^{\mu_R} T(E, V_b) dE$ . The energy region which contributes to the current integral above, which we refer to as the *bias window*, is indicated by the thick black lines in Figs. 2(a) and 2(b). It is observed that the transmission is dominated by the highest occupied molecular orbital (HOMO), located  $\approx 1$  eV below the average electrochemical potential. The lowest unoccupied molecular orbital (LUMO) is further away from the bias window and thus does not significantly contribute to the current in this bias range. Molecule *A* has a high conductance of  $G \sim 10^{-2}G_0 (= \frac{2e^2}{h})$  with near perfect transmission resonance amplitudes ( $T \approx 1$ ) at the molecular levels. Such high conductivities have also been observed

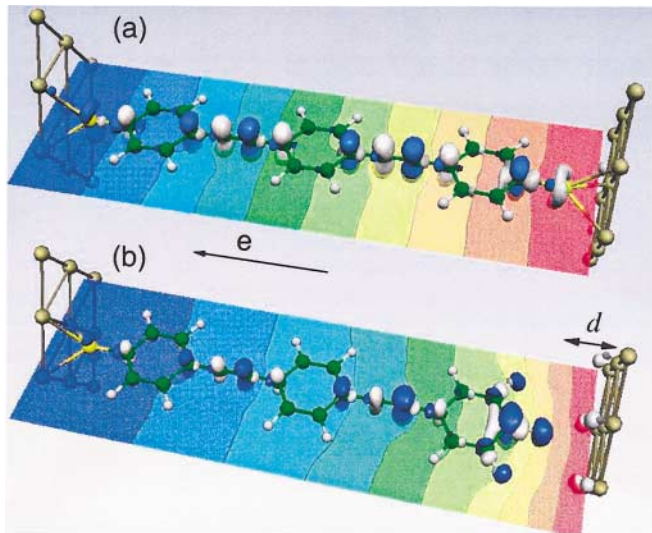


FIG. 1 (color). (a) Geometry of molecule *A* connected to two Au(111) surfaces. Isosurface of induced density and contour plot of induced potential at  $eV_b = \mu_L - \mu_R = -1$  eV. In the contour plot, red (blue) represents low (high) electrostatic potential and high (low) effective potential. For the isosurface, blue represents accumulation of positive charge (holes) and gray represents negative charge (electrons). (b) Similar to (a) but for molecule *B* at  $d = 2.7$  Å.

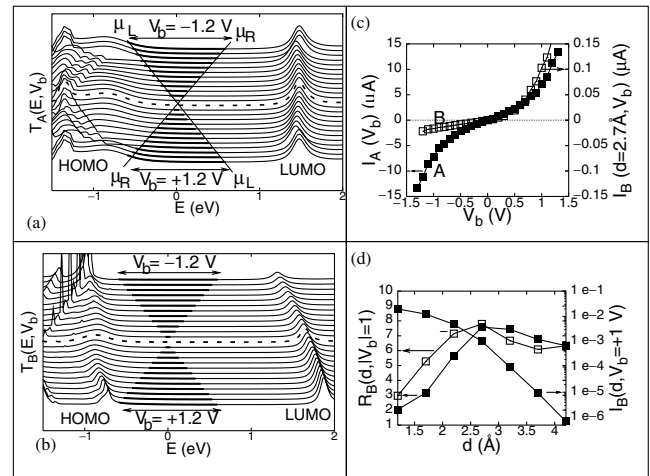


FIG. 2. (a) Transmission spectra,  $T(E, V_b)$ , (thin lines, shifted vertically for clarity), bias window (thick black lines), and equilibrium transmission (dashed line) for molecule *A*. Equilibrium conductance:  $G = 10^{-2}G_0$ . Transmission peaks correspond to  $T \approx 1$ . (b) Similar to (a) but for molecule *B* at  $d = 2.7$  Å. Equilibrium conductance:  $G = 10^{-4}G_0$ . Transmission peaks correspond to  $T \approx 10^{-2}$ . (c) Current-voltage characteristics of molecule *A* and molecule *B*. (d) Black squares: Rectification at  $V_b = \pm 1$  V and total current at  $V_b = 1$  V as a function of separation distance  $d$ . White squares: Rectification obtained from a simple model, introduced below.

in experiments using related molecules [1,5]. Molecule *B* has a significantly lower conductance,  $G \sim 10^{-4}G_0$ , and transmission resonance amplitudes ( $T \approx 10^{-2}$ ), due to the presence of a tunnel barrier between the molecule and the right electrode. In Fig. 2(c), we show the current in the molecules  $I_A(V_b)$  and  $I_B(d = 2.7 \text{ \AA}, V_b)$  as a function of applied bias  $V_b$ . Molecule *A* has a symmetric  $I$ - $V_b$  characteristic [ $R_A(|V_b|) \equiv I_A(+|V_b|)/I_A(-|V_b|) = 1$ ] a strong rectification effect is observed in molecule *B*:  $R_B(d = 2.7 \text{ \AA}, V_b = 1.0 \text{ V}) \equiv I_B(d = 2.7 \text{ \AA}, V_b = +1 \text{ V})/I_B(d = 2.7 \text{ \AA}, V_b = -1 \text{ V}) \sim 7$ , in good agreement with experimental measurements [8].

To explain this effect, we will consider the shift of the molecular levels under an external bias potential. The molecular levels follow the average effective potential within the molecule so we can write, to first order,  $E_M \approx \mu_L(V_b) - \delta E_M - \eta e V_b$ , where  $E_M$  is the energy of the molecular level,  $\delta E_M$  is the zero-bias displacement of the molecular level below  $\mu_L$ , and  $0 < \eta < 1$  refers to the fraction of the potential drop that occurs between the molecule and the left electrode [12]. The fraction  $\eta$  can be estimated from  $\epsilon_M$ , and the molecular length,  $L_M$ :  $\eta \approx \frac{1}{2} \frac{L_M}{\epsilon_M} / (\frac{L_M}{\epsilon_M} + \frac{d}{\epsilon_0})$ . In a symmetrically contacted molecule, such as molecule *A*,  $d = 0$ , and  $\eta = 1/2$ , and thus the molecular levels are unchanged by the bias potential. At higher voltages,  $E_M$  can approach either  $\mu_L$  or  $\mu_R$ , as illustrated in Fig. 2(a), where the HOMO is seen to approach  $\mu_R$  at positive voltages and  $\mu_L$  at negative voltages. In the case of molecule *B*, where  $d = 2.7 \text{ \AA}$ , there is an additional drop across the vacuum barrier and  $\eta \approx 0.4 < 1/2$  so that the energy levels begin to follow the substrate electrochemical potential,  $\mu_L$ . This is clearly seen in Fig. 2(b), where the HOMO and the LUMO follow  $\mu_L$  in both positive and negative bias polarities. From this, it is easy to understand why molecule *B* is a rectifier. At positive bias, the HOMO moves up in energy and  $\mu_R$  moves down, so that a larger fraction of the HOMO resonance peak enters the bias window while at negative bias, the resonance is pushed out of the bias window, resulting in a lower current.

Since the introduction of the vacuum gap leads to asymmetric current-voltage characteristics, it is natural to ask how much rectification this system can deliver as the vacuum gap is further increased. To investigate this, we have calculated the current at  $V_b = \pm 1 \text{ V}$  as a function of the molecule-tip separation distance  $d$ . The result is shown in Fig. 2(d). As the distance is increased, the forward current level decreases roughly exponentially. The potential drop fraction  $\eta$  decreases as the vacuum gap is increased and the HOMO becomes more closely tied to  $\mu_L$ , increasing  $R_B(d, |V_b| = 1 \text{ V})$ . It is important to note that one cannot obtain unlimited rectification by decreasing the molecule-electrode coupling:  $R_B(d, |V_b| = 1 \text{ V})$  saturates and even decreases slightly as the distance  $d$  is increased. A simple model introduced below, which takes into account only the width of the HOMO resonance, the zero-bias HOMO energy as a function of  $d$ , and

a subsequent shift by  $\pm \eta e V_b$ , agrees quite well with the *ab initio* results, as shown by the white squares in Fig. 2(d).

Similar explanations of rectification in symmetric molecules have previously been proposed in the literature, e.g., Refs. [10,12]. However, such studies did not consider the finite width of the molecular levels and their proximity to the Fermi level. We can, for the first time, directly extract this information from our *ab initio* calculations. From the data, it is clear that the resonances in such systems are generally quite broad and can significantly influence the rectification properties. Here, we introduce a simple model, illustrated in Fig. 3(a), which takes these factors into account to explain the rectification saturation in such systems. We will assume that the entire current is due to transmission through the HOMO level, that the width of the HOMO level is independent of the bias and its position follows the average potential within the molecule. We note that the transmission data in Fig. 2(b) can be approximated using a Lorentzian with width of  $\Delta \sim 0.2 \text{ eV}$  centered on the molecular level at  $\delta E_M$ . Integrating the Lorentzian transmission curve, one obtains the current as a function of bias voltage:  $I(V_b) = \tan^{-1}(\frac{\delta E_M + \eta e V_b}{\Delta}) - \tan^{-1}(\frac{\delta E_M + (\eta - 1)e V_b}{\Delta})$ . In Fig. 3(b), we show the rectification,  $R(|V_b|) \equiv \frac{I(+|V_b|)}{I(-|V_b|)}$ , as a function of the applied voltage  $V_b$  for  $\delta E_M = 5\Delta$  and different values of  $\eta$ . For finite  $\eta$ ,  $R(|V_b|)$  increases to a maximum around  $e V_b \approx 8\Delta$  and decreases at higher biases as the bias window becomes broad enough so that the transmission peak enters at both polarities. Thus, the proximity of the HOMO to  $\mu_L$ ,  $\delta E_M$ , limits the operation range of such a rectifier and, consequently, the total forward current. In Fig. 3(c), we plot the maximum rectification  $R_{\max}$  as a function of  $\delta E_M$  for different values of  $\eta$ . It is clear that  $R_{\max}$  is greatest at  $\eta = 0$  and decreases as  $\eta$  is

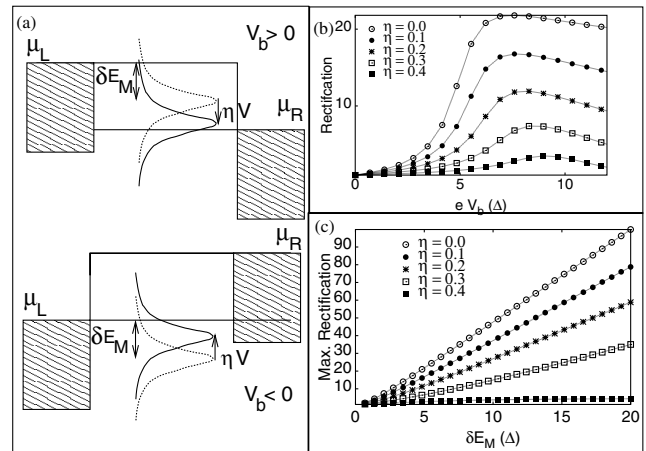


FIG. 3. (a) Simple model of rectification. The HOMO sits  $\delta E_M$  below  $\mu_L$  and is shifted by  $\pm \eta e V_b$  in positive/negative bias polarities. (b) Rectification as a function of applied voltage  $e V_b$  for  $\delta E_M = 5$  and for different values of  $\eta$ . (c) Maximum rectification as a function of  $\delta E_M$  for different values of  $\eta$ .

increased. Furthermore,  $R_{\max} \propto \delta E_M / \Delta$  and can thus be changed by either changing the alignment of the molecular levels,  $\delta E_M$ , or changing the width of the resonance  $\Delta$ .

We expect these broad resonances to be important in other strongly chemisorbed molecules on metallic substrates [8–12]. Using this model, one can estimate the maximum rectification one would expect from a given molecule. For the molecules studied in this paper, the width is of the order  $\Delta \sim 0.2$  eV, and the HOMO level sits around  $\delta E_M \sim 1.0$  eV. Using STM vacuum distances of  $d < 5$  Å, one estimates  $\eta \geq 0.25$  and  $R_{\max} < 10$ . Shorter one-phenyl ring molecules ( $L_M \approx 7$  Å), tend to decrease  $\eta$  (if  $d < 5$  Å,  $\eta \geq 0.15$ ) and one might thus expect stronger rectification. However, studies of these molecules [8,11,12] have found little or no evidence of rectification. We have studied the transmission properties of benzenethiol, coupled to Au(111) electrodes [25] and have found very broad transmission resonances of  $\Delta \sim 0.7$  eV and molecular levels at  $\delta E_M \sim 1.0$  eV, so that  $\delta E_M \sim 1.5\Delta$ . The increase in  $\Delta$  more than compensates for the decrease in  $\eta$  and we expect a  $R_{\max} < 4$  in this system. Such an estimate does not fully account for the lack of rectification in such experiments but serves to highlight that both the potential drop, described by  $\eta$  [12], and the width of the molecular resonances, described by  $\delta E_M / \Delta$ , must be taken into account. It is also interesting to compare our model to another experiment [9], in which a large rectification ratio of 500:1 was observed in a similar molecule. In our model, such a rectification effect would correspond to a level where  $\frac{\delta E_M}{\Delta} > 100$ . Assuming that  $|\delta E_M| < 2$  eV, a broadening of  $\Delta < 20$  meV  $\approx kT$  would be required. This is an order of magnitude smaller than the resonances we have calculated and suggests that the current in the above experiment is not mediated by any of the molecular levels that interact strongly with the surface.

In this paper, we have studied rectification in organic molecules with asymmetric electrode coupling. The results of our *ab initio* calculations were summarized by a simple model of general validity, which emphasizes the fact that both the potential profile and the width of the transmission resonances must be taken into account to understand such devices.

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 [23] The S atoms were placed 1.87 Å from the fcc position of Au(111). The precise absorption site of these molecules on Au(111) is not known. The broadening of the molecular level  $\Delta$  is weakly dependent on the coordination of the S atom and thus a different absorption site may slightly change the width of the transmission resonance.  
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