Charge transport properties of Ru-complex molecules: the influence of humidity

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2 Theory

In this chapter we will first describe the basic concepts of the theory of molecular conductance, including the Landauer formalism. From there, we will give relevant examples of theoretical expressions and calculations for different molecular junction systems. More specifically, we discuss the possibility of observing diode-like behavior in molecular junctions.

2.1 Diffusive conductors

In every day usage of electronic conductors, such as metallic wires, we can note the heating of the wire when current passes through it. What happens microscopically is that charge carriers (in this case, electrons) scatter inelastically at dislocations, phonons, magnetic impurities or other charge carriers along their path in the conductor. This is due to the fact that the characteristic dimensions of the conductor are much larger than:

1) The electron mean free path l_e (the average distance the electron travels before encountering a scattering event),
2) The electron phase coherence length l_φ (the average distance the electron travels before its phase is randomized),
3) The Fermi wavelength λ_F (the de Broglie wavelength of the electron at the Fermi energy).

The loss in kinetic energy due to scattering is then transferred to lattice vibrations, resulting in the Joule heating of the conductor and hence, glowing of the bulk conductor at sufficiently high current levels. Indeed, this phenomenon is used in traditional incandescent light bulbs where current is passed through a tungsten filament, resulting in a bright glow due to temperatures reaching upwards of 3000 °C therein. This behavior is typical for diffusive electric conductors, see also Figure 2.1 a for a schematic overview.

In the diffusive case, it is apparent that the electrochemical potential μ will drop between any two points a and b along the conductive path as resistance arises due to the local scattering of charge carriers. Hence, the potential drop $V_{ab} = (\mu_a - \mu_b)/e$. With the current I, the four terminal resistance is written as $R_{4T} = V_{ab}/I$.

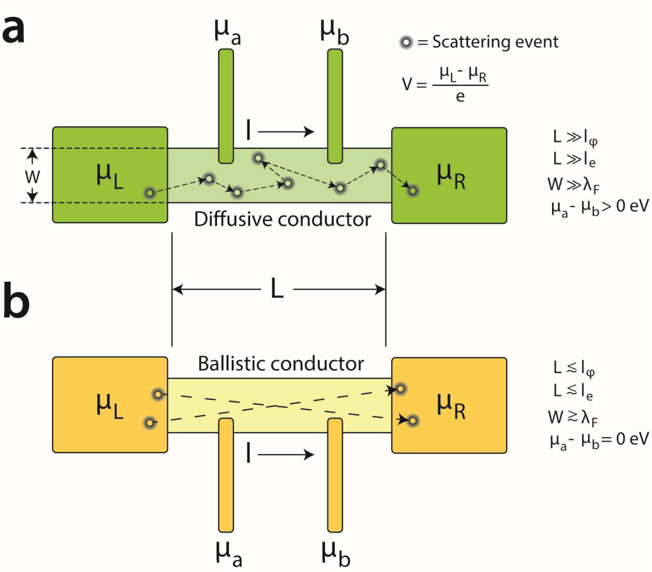

Figure 2.1: Schematic four-terminal configuration for a diffusive (green) and ballistic (yellow) conductor. The voltage probes a and b are positioned on the conducting path. The voltage V_0 is applied to the reservoirs with the electrochemical potentials μ_L and μ_{R+}.

2.2 Ballistic conductors

If we were to significantly reduce the size of the conductor such that parameter l_e becomes approximately the same or larger than the characteristic sample dimensions, we would have a situation where no scattering events occur and thus, no Joule heating arises along the conducting path. This is defined as a ballistic conductor.

Due to the absence of scattering, the difference between the chemical potentials between μ_a and μ_b would be 0 eV, and hence $R_{4T} = V_{ab}/I = 0$. The situation is completely different if we would measure the two terminal resistance $R_{2T} = V/I$, however. Due to the fact that the applied voltage V is non-zero (as is the current I), R_{2T} has a non-zero value, even though R_{4T} is zero(*53*). This seemingly contradictory result actually stems from the fact that the contacts add to the measured resistance in the two terminal case, which indicates that the voltage drop occurs at the contacts. For a ballistic conductor, the charge carriers can only move through quantized subbands N_S. Therefore, the number of subbands will determine the conduction:

$$G = \frac{2e^2}{h} \sum_{i=1}^{N_s} T_i \tag{1}$$

We can note that for each available channel (i.e., each subband), the conductance could increase with steps of $2e^2/h$ (which is called the conductance quantum, G_0). However, this is only valid if all electron modes pass through the conductor with perfect transmission probability equal to 1. In general, each channel i will have a transmission probability T_i which will be between 0 and 1. This expression (1) is called the Landauer formula.

2.3 Single-level model

Now that we have discussed the general description of ballistic conductance, we can move on to describing how electron transport through molecules occurs. Molecules, due to their nanometer-scale size, can also be described as ballistic conductors ($L < l_{\varphi}, l_e$ and $W \sim \lambda_F$). However, the transmission probability is very strongly energy dependent in accordance with the density of states of the molecular energy levels(*54*),(*55*). It is also for this very reason that molecular properties are sensitive to atomic changes in their structure or the environment, making them highly tunable. If we were to couple a molecule to a left (L) and right (R) electrode for the purpose of using it as a conducting bridge, we could describe its conductance by extending the Landauer formula as(*56-59*):

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} T(E)[f_R(E) - f_L(E)]dE \tag{2}$$

where the energy dependent transmission function T(E) is integrated over all energies. The Fermi-Dirac distribution is given by $f_{R,L}$:

$$f_{L,R}(E) = \left(e^{\frac{E - \mu_{L,R}}{k_B T}} + 1 \right)^{-1} \tag{3}$$

where k_B is the Bolzmann constant, T is the temperature, and the chemical potential of the left and right electrodes are given by:

$$\mu_{L,R} = E_F \mp \frac{1}{2} eV \tag{4}$$

One major factor determining the transmission as a function of energy, is the nature of molecular bonding to the metallic leads. Connecting the molecule to the metallic leads will hybridize the molecular orbitals with those of the metal. These effects will lead to a change in the energy dependency of the density of states (and hence, the transmission function during electron transport) of the molecule, as can be seen in Figure 2.2. Molecular energy levels are discrete if the molecule is not interacting with its environment in the gas phase. With increasing electronic interactions with the substrate, the electron transfer rates between the molecular levels and the electrodes will be proportional to $1/\tau_r$, with τ_r being the electron residence time on a molecular orbital. Due to Heisenberg's uncertainty principle, this will cause a broadening in the molecular orbital by $\Gamma = \hbar/\tau_r$. Also, image charges will play a significant role for increasing interaction with the substrate. This will cause a shift in molecular energy levels (in the case of Figure 2.2, the difference in energy between the LUMO and HOMO will get smaller). For more information on the effects of image charges, we refer to the articles by M. Perrin *et al.(60, 61)*.

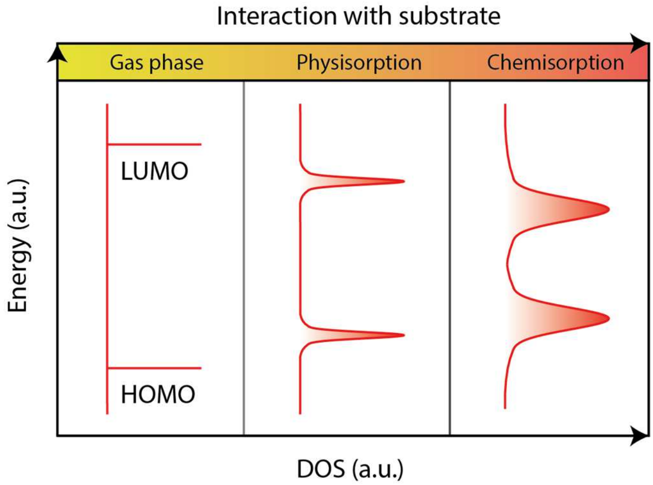

Figure 2.2: Molecular energy levels (in this case the HOMO and LUMO) shift and broaden due to increasing hybridization with the lead orbitals and image charges.

The situation where one molecular orbital dominantly contributes to the current is approximated with (and is also referred to as) a single-level system. Indeed, multiple levels that are lower or higher lying may contribute to the current given a sufficient bias voltage. For low bias voltages, however, a single molecular orbital will typically dominate the current. We give an example of such a single level system in Figure 2.3.

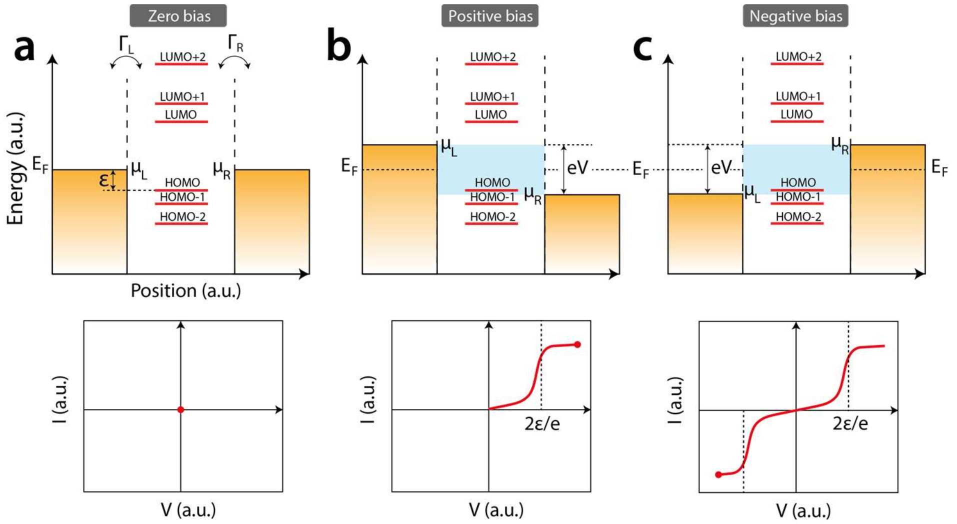

Figure 2.3: Schematic representation of a single-level system between left (L) and right (R) electrodes for zero bias (a), positive bias (b) and negative bias (c). The difference between the molecular energy level and the Fermi energy (E_F) is given by ε. By applying a bias, the chemical potential of the left (μ_L) and right (μ_R) electrode will shift as shown in (b) and (c), which will in turn create an energy window that allows for electron transfer between the electrodes. If the applied bias is sufficient, the energy window will pass through a molecular orbital, that will act as a conductive channel and hence will show a step-like increase (or decrease) in current in the current-voltage (I-V) diagram that is described by equation (6). The electron transfer rates from the left electrode to the molecular orbital and from the molecular orbital to the right electrode (which leads to level broadening) is represented by Γ_L and Γ_R, respectively.

The transmission function of each orbital will assume a Lorentzian curve with the peak transmission probability at the molecular energy level ε and broadening Γ (if we assume Γ_L and Γ_R being equal):

$$T(E) = \frac{(\Gamma^2/4)}{(E - \varepsilon)^2 + (\Gamma^2/4)} \tag{5}$$

Integrating this transmission function (while assuming T = 0 K and equal voltage drops at the contacts) as shown in equation (2) between μ_L and μ_R (equation (4)) can be done analytically and will give us the following expression for the current as a function of the applied bias for a single-level system:

$$I(V) = \frac{e\Gamma}{h}\left[\arctan\left(\frac{2}{\Gamma}\left(\frac{1}{2}eV - \varepsilon\right)\right) - \arctan\left(\frac{2}{\Gamma}\left(-\frac{1}{2}eV - \varepsilon\right)\right)\right] \tag{6}$$

With this general formula, we can explore the effects the individual parameters have on the current-voltage (I-V) characteristic, as later on in this thesis we will refer to these calculations for futher discussion.

For example, upon changing the level broadening Γ (Fig. 2.4a), we can note that I-V characteristic smoothens out for higher values of Γ while higher current values are achieved (Fig. 2.4b). The 'leveling out' of the I-V characteristic occurs when the voltage window includes the peak of the transmission function (i.e. resonant transport), effectively saturating the conductance channel (see Fig. 2.3b).

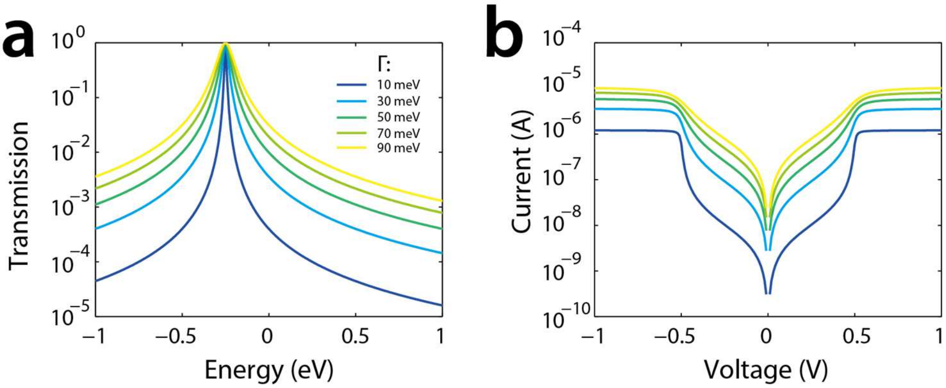

Figure 2.4: Calculated tranmission-energy. (a) and current-voltage (b) characteristics for a single-level system for varying values of Γ, while ε = -0.25 eV.

Changing the molecular energy level ε shifts the transmission peak (Fig. 2.5a) and therefore the bias voltage required to achieve resonant transport changes considerably (Fig. 2.5b). Keeping all other parameters constant, higher |ε| values translate to higher bias voltage levels before resonant transport is achieved.

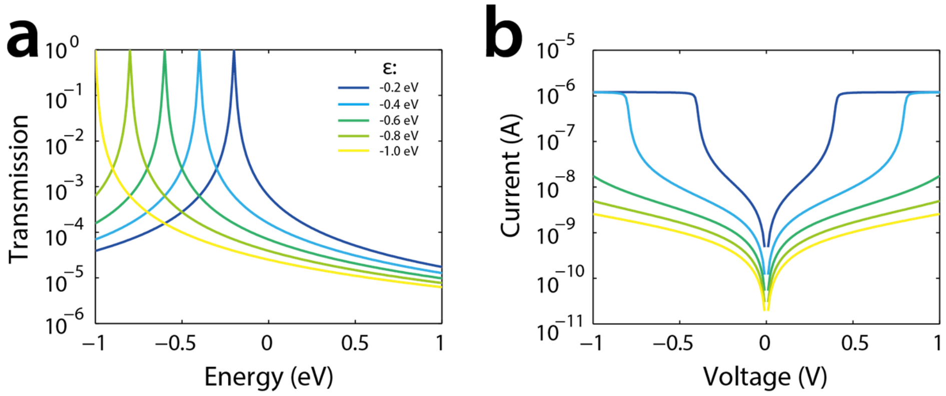

Figure 2.5: Calculated tranmission-energy (a) and current-voltage (b) characteristics for a single-level system for varying values of ε, while Γ = 10 meV.

If we observe the current-voltage relationship in the given examples, we can note that it is symmetric. This is also due to the fact that we have assumed a symmetric voltage drop at both the left and right contacts of the junction. Now, it is interesting to see how the current-voltage relationship will be affected if the voltage drop at the left and right hand side of the junction would be different. Would we able to produce a diode-like junction?

This asymmetric voltage drop could occur for example due to one electrode being a different metal than the other, or if an insulating layer exists at one electrode but not the other. By changing the ratio η of the voltage drop occurring at both contacts, the integration bounds will change with μ_L and μ_R given by:

$$\mu_L = E_F - (1 - \eta)eV \tag{7}$$

$$\mu_R = E_F + \eta eV \tag{8}$$

For example, a relatively large voltage drop at the right contact compared to the left contact (i.e. η > 0.5) will cause an asymmetric I-V characteristic, as can be seen in Figure 2.6.

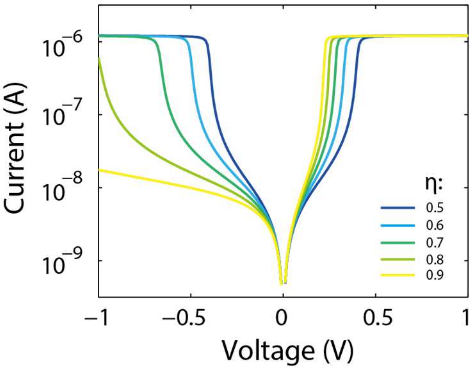

Figure 2.6: Calculated current-voltage characteristics for a single-level system for varying values of η, while Γ = 10 meV and ε = -0.25 eV.

A diode-like behavior for single level systems can thus be achieved with molecules by creating a voltage drop asymmetry at one of the contacts. This phenomenon is also called 'pinning' (due to molecular orbitals being relatively pinned to one of the electrode energy levels) and in literature, we can find literature reports of molecular diodes that are explained with a similar pinning model(*62, 63*).

2.4 Two-site model

Interestingly, there are more ways in which molecules can show diode-like characteristics even if a potential drop asymmetry is not present. An excellent example is the two-site model by Perrin *et al.*(*28*). This makes use of the difference in energies between two moieties in a molecule, where two misaligned localized molecular orbitals are sufficient to produce an asymmetric I-V characteristic, i.e. a two-site model.

A two-site system can occur in a molecule with two (conjugated) halves that are weakly coupled to each other. The two sites are at an average energy ε_0, and differ in energy, and this energy splitting increases slightly to Δ when a coupling constant τ is introduced.. The energies of these two LMOs shift as a function of the applied bias voltage, as can be seen in Figure 2.6.

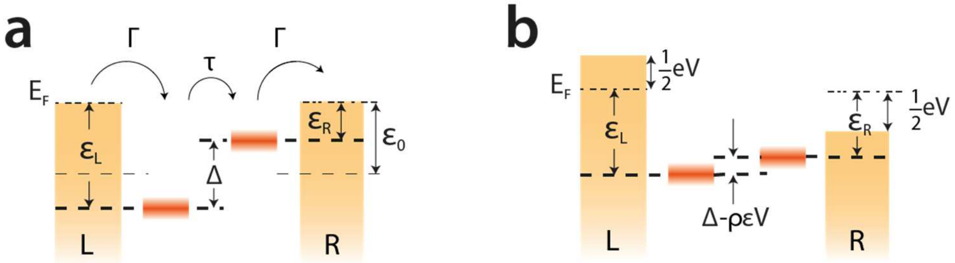

Figure 2.6: Schematic represention of a two-site model between left (L) and right (R) electrodes. The left and right sites have an average energy of ε_0. Due to the electronic coupling τ, the two sites will split further apart with the gap defined as Δ. The difference in chemical potential between the Fermi level and the left/right molecular orbital is then given by $\varepsilon_L/\varepsilon_R$ at zero bias. The electron transfer rates from the left electrode to the molecular orbital and from the molecular orbital to the right electrode (which leads to level broadening) is represented by Γ.

Furthermore, a voltage drop fraction ρ between the two sites allows both sites to shift in energy with respect to each other and the electrode Fermi levels. To further explore the effects of the individual parameters of our system, we would have to do calculations based on the non-equilibrium Green's function (NEGF) formalism, which is typically used to calculate I-V characteristics of molecules(*54, 56, 64, 65*). The current is calculated by integrating the transmission function over the chemical potential boundaries, dictated by the bias voltage (equation 4). The transmission is given by:

$$T(E) = \mathrm{Tr}\left(\mathbf{\Gamma}^L \mathbf{G}^R \mathbf{\Gamma}^R \mathbf{G}^A\right) \tag{9}$$

with Γ^L, Γ^R representing the electronic coupling to the left and right electrodes, respectively:

$$\mathbf{\Gamma}^L = \begin{pmatrix} \Gamma & 0 \\ 0 & 0 \end{pmatrix}; \mathbf{\Gamma}^R = \begin{pmatrix} 0 & 0 \\ 0 & \Gamma \end{pmatrix} \tag{10}$$

We assume equal coupling to both electrodes. The $\mathbf{G}^R$ and $\mathbf{G}^A$ represent the retarded and advanced Green's functions, respectively. Here, $\mathbf{G}^R$ and $\mathbf{G}^A$ are given by:

$$\mathbf{G}^R = \left[\varepsilon \mathbf{S} - \mathbf{H} - \mathbf{\Sigma}^L - \mathbf{\Sigma}^R\right]^{-1}; \mathbf{G}^A = \left[\mathbf{G}^R\right]^{\dagger} \tag{11}$$

with $\mathbf{S}$ the symmetric overlap matrix, $\mathbf{H}$ the Hamiltonian describing the molecule, $\mathbf{\Sigma}^{L,R}$ the complex self-energy matrix:

$$\mathbf{\Sigma}^{L,R} = \mathbf{\Lambda}^{L,R} + \frac{i\mathbf{\Gamma}^{L,R}}{2} \tag{12}$$

where we can neglect $\mathbf{\Lambda}^{L,R}$ in the wide band limit. The Hamiltonian is given by:

$$\mathbf{H} = \begin{pmatrix} \varepsilon_L + \frac{\rho eV}{2} & -\tau \\ -\tau & \varepsilon_R - \frac{\rho eV}{2} \end{pmatrix} \tag{13}$$

with the energy levels of the left and right sites given by:

$$\varepsilon_{L,R} = \varepsilon_0 \mp \frac{1}{2}\Delta \tag{14}$$

The difference in energy between the left and right sites is given by:

$$\Delta = \sqrt{(\rho eV)^2 + (2\tau)^2} \tag{15}$$

By taking these general equations, we can numerically calculate the I-V characteristics of a two site system using the Landauer formula, as can be seen in Figure 2.7a,b.

It can be seen in Figure 2.7b that without a voltage drop between the two sites (i.e. ρ=0), there would be effectively no asymmetry in the molecular junction given a symmetric voltage drop at the contacts.

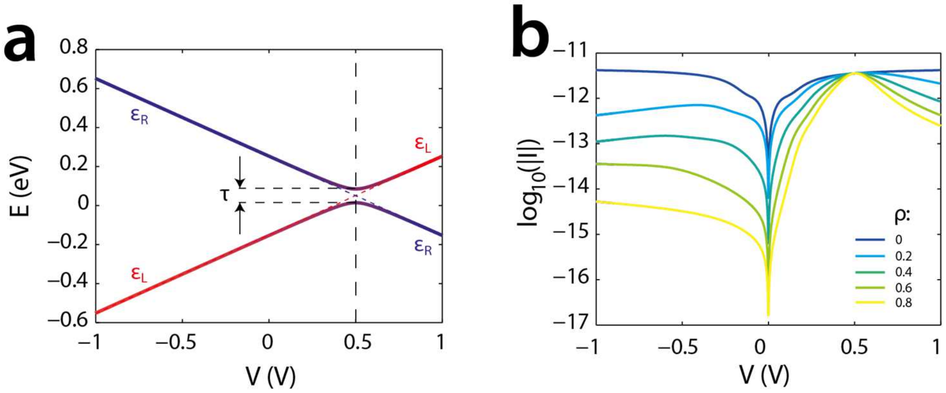

Figure 2.7: (a) Calculated chemical potentials of the left and right molecular orbitals (given respectively by ε_L and ε_R) as a function of bias voltage. The left and right molecular levels shift with respect to each other due to a voltage drop fraction ρ occuring between them. Due to electronic coupling between the two sites, the energy levels split with a constant τ. (b) The calculated I-V characteristic based on a two-site model with the parameters used is shown with varying values of the voltage drop fraction ρ between the two levels. In this case, our starting parameters for ε_L and ε_R are -0.15 eV and 0.25 eV, respectively. The value for τ = 50 meV, Γ = 100 meV, and in case of (a), ρ = 0.8.

Introducing a voltage drop between the two sites in combination with a misalignment at zero bias (as can be seen in Figs. 2.6 and 2.7a), will ensure that the levels align (in the given example at 0.5 V bias) at positive bias and further misalign at negative bias. If we would proceed to increase the bias, the levels would continue to shift and would start to misalign gradually (see Fig. 2.7a), after which the current would decrease and hence lead to negative differential resistance (NDR)(*28*).

Indeed, a two-site model without including contributions from lower or higher lying levels, would show NDR. However, molecules that can be modelled with a two-site system and yet have a large number of molecular orbitals near the Fermi level, may not show a pronounced NDR-effect due to contributions to the current from other molecular energy levels as the bias voltage is increased. More parameters can be varied to offer a more detailed understanding, but these remain outside the scope of this thesis. For this, we refer to a more detailed study(*66*).

2.5 Outlook

We will see in Chapters 4 and 5 how a two-site model is relevant for the discussion of selecting a suitable model to explain our experimental results, where we show diode-like I-V characteristics. It is usual for experimental results that show molecular diode behavior to be explained through a single level model with an asymmetric voltage drop occuring at the contacts. In this chapter, however, we also show that even without a voltage drop asymmetry occuring at the contacts, molecules can show diode-like I-V characteristics, provided their intrinsic electronic properties allow for it, as laid out in a two-site model.