

Do Aviram–Ratner Diodes Rectify?

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The donor–insulator–acceptor ($D\sigma A$) molecular diode proposed by Aviram and Ratner in 1974 is a classic component in molecular electronics.¹ The original idea was to illustrate the possibility of making molecular components with the same functionality as semiconductor devices, in this case a p–n junction diode. The p–n junctions are an integral part of semiconductor devices, and a molecular counterpart may play a similar important role in future molecular electronic components.

The $D\sigma A$ diode consists of two π -conjugated segments separated by one or several σ bonds. The σ bonds introduce an effective barrier for electron transfer between the wires. A π -donor group is attached to the D wire, while a π -acceptor group is attached to the A wire. Because of the lower oxidation potential of the D wire, its molecular levels will be higher in energy, see Figure 1B. Aviram and Ratner envisioned the charge transport as a three-step process, consisting of electron and hole injection into the A and D segments, and subsequent annihilation, and easy electron transfer will be in the A to D direction. In contrast, Ellenbogen and Lowe argue that electron transfer will be favorable in the opposite direction (from D to A), because at finite bias the HOMO of the D wire will become aligned with the LUMO of the A wire.²

In the past decade, $D\sigma A$ diodes have been synthesized, and rectifying behavior has been measured on molecular layers formed by Langmuir Blodgett (LB) techniques.^{3,4} To obtain a well-ordered LB monolayer, an aliphatic chain has to be attached to one end of the molecule.^{3,4} This chain will form a tunnel barrier and give rise to a strongly asymmetric coupling between the molecule and the two electrodes. It is known that such an asymmetric coupling in itself can lead to rectification,^{5–7} and on the basis of semiempirical modeling it has been proposed that the rectification observed in the experimental verification of $D\sigma A$ diodes is due to the aliphatic chain rather than the $D\sigma A$ bridge.⁸

Recently we have developed a new first principles method, Transiesta,⁹ for modeling molecular electronics devices under realistic operation conditions. The method is based on the density functional theory and gives a full self-consistent treatment of a molecular device coupled to electrodes with different electrochemical potentials. An important feature of the method is that it treats the entire system (molecule and electrodes) with chemical accuracy. The high accuracy of the method was recently illustrated for the IV spectra of atomic wires, in which case the modeling results could be compared with reliable experimental data.¹⁰ This opens the way for modeling artificial molecular structures and predicting their electrical properties prior to experimental verification. In this paper, we use the method to investigate the electrical properties of a $D\sigma A$ diode and obtain new insight into the operation principles of a rather complex molecular device.

We will consider a realization of the $D\sigma A$ diode proposed by Ellenbogen and Lowe.² Our computational setup is illustrated in Figure 1A. Two phenylene-ethynylene segments are connected via a dimethylene bridge and coupled to gold electrodes via thiolate bonds. An amino and a nitro side group are attached on the D and A part, respectively. The gold (111) surface is represented by a (3

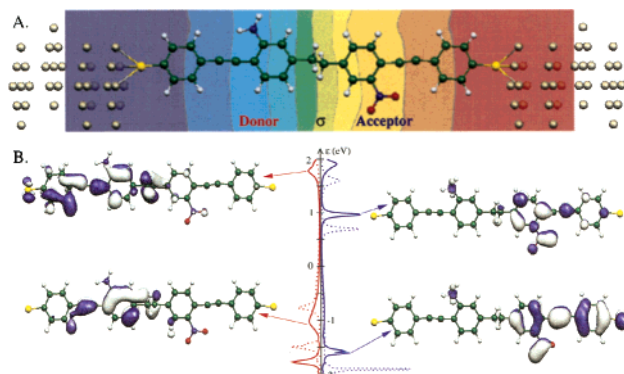


Figure 1. (A) The atomic structure of the $D\sigma A$ rectifier and the gold electrodes: H (white), C (green), O (red), N (blue), S (yellow), Au (gold). Contours show the voltage drop for a bias of 1 V. All atoms within the contour region are described self-consistently, and periodic boundary conditions are employed in the surface directions. (B) The PDOS of the D (solid red) and A (solid blue) molecular wires; dashed lines show the PDOS for a bias of 1 V. Next to the peaks in the projected density of states (PDOS) is shown the most relevant molecular states.

$\times 3$) cell with periodic boundary conditions. Initially the sulfur atom is positioned in the FCC-site geometry found by Grönbeck et al.,¹¹ and subsequently all molecular coordinates have been relaxed while keeping the gold atoms in fixed positions. The first two gold layers are included in the self-consistent cycle, while the remainder of the electrodes are described by bulk parameters. These are determined from a separate calculation of the bulk phase of gold employing the same model chemistry. Using a Greens function technique, we projected the electronic structure of the semi-infinite electrodes onto the third and fourth layer atoms.⁹

Figure 1B shows the density of states projected onto the orbitals of the D and A wires. Molecular states are localized either to the left or to the right of the σ barrier, and states in the D wire have ~ 0.7 eV higher energy than states in the A wire, in agreement with the picture of Aviram and Ratner.

The IV characteristics are shown in Figure 2A. This was obtained by changing the bias in steps of 0.1 V, performing a self-consistent calculation for each bias, and subsequently integrating the bias-dependent transmission coefficient (T) over the bias window to obtain the current.⁹ Although the IV curve is not symmetric, the current is of similar magnitude at both biases, and the molecule does not function as a rectifier. In the following, we will investigate the calculations in more detail to gain further insight into the complex IV characteristics.

Several insights can be gained from the transmission spectrum at zero bias, shown in Figure 2B. It has two low peaks at -1 and 1 eV ($T \approx 0.01$), and two high peaks at -1.7 and 1.9 eV ($T \approx 0.5$). To understand the origin of these peaks, we have diagonalized the molecular block of the self-consistent Hamiltonian, and the circles in Figure 2B show the eigenvalues of this molecular projected self-consistent Hamiltonian (MPSH). The eigenstates are localized in either the D (red circles) or the A wire (blue circles) and are illustrated in Figure 1B. The two low peaks can be related

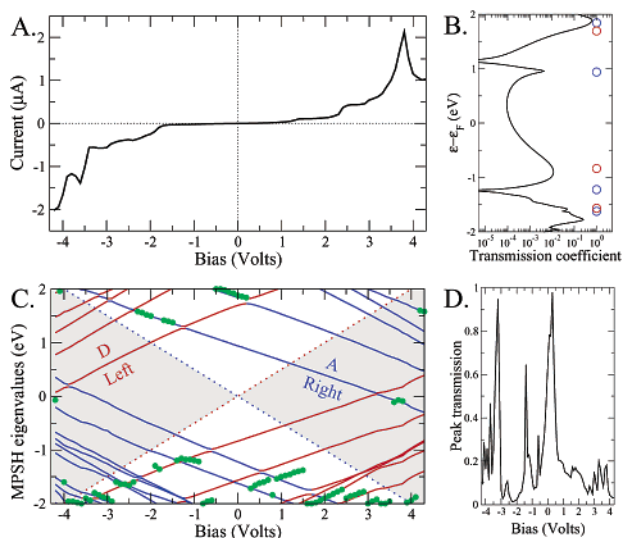


Figure 2. (A) First principles results for the IV characteristics, and (B) energy-dependent transmission coefficient (T) at zero bias. (C) The bias dependence of the eigenvalues of the MPSH localized in the left (solid red) and right (solid blue) molecular wire. Dotted lines show the chemical potential of the left (red) and right (blue) electrode, and the gray region between the lines is the bias window. The green dots show the energy at which the maximum transmission occurs, and in (D) is shown the corresponding value of T .

to transmission through the HOMO and LUMO states. The small misalignment between the transmission peaks and the MPSH states can be related to the coupling with the electrodes. The two next peaks (at -1.7 and 1.9 eV) are higher because a state localized in the D wire is close to alignment with a state localized in the A wire, and a tunneling electron can take advantage of both resonances. We also observe a dip in T at -1.2 and 1.2 eV due to destructive interference between the different transmission channels.

When a bias is applied, the molecular resonances will shift in energy, as illustrated by the projected density of states (PDOS) in Figure 1B. Because the resonances can be related to the eigenstates of the MPSH, the shifts will closely follow the eigenvalues of the bias-dependent MPSH. These are shown in Figure 2C, and we notice that the eigenvalues are either increasing or decreasing linearly with the bias. The slopes are in the ranges $[-0.40, -0.25]$ and $[0.25, 0.40]$ (eV/V), and the sign depends on whether the state is localized in the D or A wire. The slope of the curves can be understood from a dielectric model of the voltage drop through the molecule. The voltage drop at 1 V is illustrated in Figure 1A, and we note that it drops nearly linearly in the three different parts of the molecule, with a slope that is approximately twice as large in the σ part as compared to the π -conjugated wires, corresponding to a lower polarizability of this part. Because of a longer extent of the wires, the voltage drop is rather similar in the three different parts of the molecule. We expect states localized in the D (A) part to follow the average potential of this section and therefore have a slope around $1/3$ ($-1/3$), which is in fact the average slope of the red (blue) lines in Figure 2C.

The shaded region in Figure 2C illustrates the bias window. We see that the small steps in the IV characteristics appearing at -2.5 , -1.5 , 1 , and 2.5 V coincide with the biases where a molecular state is entering the bias window. These states are localized in either the D or the A part of the molecule and therefore have a small T . A much higher T can be obtained when a left and right localized molecular state align in energy, and if such an event takes place within the bias window a strong current can be expected. This is happening at -3.8 and 3.3 V and is the origin of the peaks in the current at -4 and 3.8 V. However, the absolute value of the current

is limited. For a completely delocalized state, we would expect $T = 1$, while the resonant states at -4 and 3.8 V have $T = 0.3$ and $T = 0.2$, respectively.

In Figure 2D, we show the maximum T within the energy window -2 , 2 eV as a function of the bias. For two biases (-3.2 , 0.4 V), we obtain $T \approx 1$, but in most cases $T < 0.2$. There is a tendency toward a decreasing maximum T with increasing bias. This can be related to the increasing field strength in the molecule, which tends to increase the localization within the π -conjugated regions. However, even for small biases the alignment of two molecular states does not necessarily give rise to a highly conductive transmission channel. For instance, the alignment of the two states at -1.2 eV for bias ~ -1 V gives rise to a $T \approx 0.2$.

In conclusion, we have investigated the bias-dependent electronic structure of a D σ A diode coupled to two metallic electrodes. We find that the electronic states are localized either in the D or in the A part of the molecule, except for particular biases where the voltage drop aligns two states, forming a resonant state delocalized over the entire molecule. If such an event takes place within the bias window, it can give rise to a sudden increase in the current, which can be exploited to obtain rectification. However, for this investigated implementation of a D σ A diode, we found no rectification. This was due to two effects: (1) a resonant state was formed at both bias polarities, that is, no asymmetry; and (2) the transmission coefficient (T) of the resonances was well below 1, due to electric field induced localization of the resonant levels. To obtain better diode characteristics, we propose to use other electroactive substituents to obtain a much smaller gap between the HOMO of the D part and the LUMO of the A part, so that resonant conditions can be obtained for a much smaller bias. Whether such a molecule will have favorable diode characteristics still depends on the size of the HOMO–LUMO transfer matrix element under resonant conditions. Thus, in principle, the Aviram–Ratner diode can be an effective rectifier; however, this work shows the advantage of evaluating possible candidates with advanced modeling tools prior to experimental verification.

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Supporting Information Available: Computational details and atomic geometries (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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