Design of Molecular Rectifiers

Shriram Shivaraman, ECE
✉ss626@cornell.edu

Introduction

Molecular electronics involves using molecules as replacements for conventional devices and interconnects. Conventionally, electronics has scaled as per Moore's law viz. there has been a doubling of devices per chip every 18-24 months. However, there are potential roadblocks in the near future arising from both monetary and physical constraints. A current fabrication line costs $2.5 billion to construct, and the cost is projected to rise above $100 billion by year 2015 – a main reason why many semiconductor firms are preferring to go "fabless". The physical constraints facing the silicon-based semiconductor industry are excessive leakage currents and statistical variations in doping profiles in small dimensions. Thus, it is widely accepted that alternatives have to be sought out in order to ensure continued scaling.

Molecular electronics

Molecular electronics proposes a bottom-up construction methodology that uses the self-assembly property of molecules to build computational circuitry. This gives rise to the prospect of manufacturing circuits in a rapid cost-efficient flow-through process. Also, the density of devices envisioned for molecular electronic circuitry is ~ 10^{13} transistors per cm^2. Also, molecules are small and identical units, so the variation from one device to the other does not occur in terms of physical properties. Also, the discrete energy levels of molecules provide a handle for fine tuning of transport properties to the shrewd chemist and physicist. Also, molecules are amenable to other applications which exploit their abilities to be printed easily on low cost substrates, as sensors etc.

However, some outstanding issues remain before molecular electronics becomes a computing reality. There are no well-defined production and fabrication methods for molecular electronic circuits. Interfacing from the molecular scale to the microscale is another challenge. Also, the inherent disorder present in self-assembled structures requires defect-tolerant architectures. Besides that, the performance of molecular devices is questionable in terms of speed, stability, reproducibility and reliability.

Molecular rectifier

This work looks at molecular rectifiers which ideally have a two-terminal I-V characteristic as shown in Fig. 1.

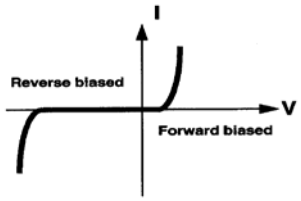


Figure 1: Ideal I-V characteristic of a molecular diode

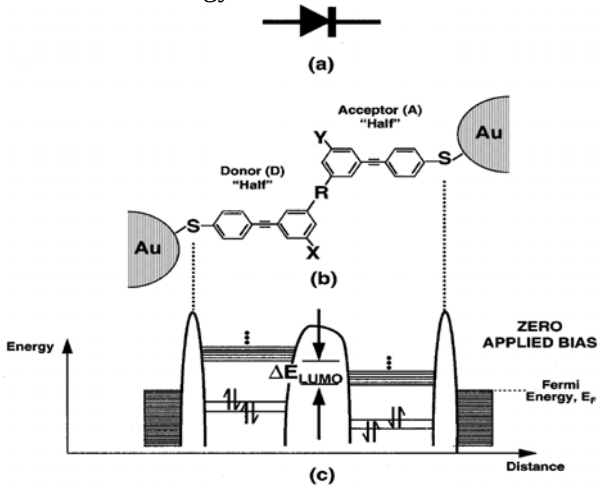
A molecular rectifying diode consists of a donor-spacer-acceptor combination and was first proposed by Aviram and Ratner in 1974 [1]. Here, we consider the donor and acceptor species to be substituted phenylenes and the spacer to be an aliphatic group [2]. The donor part has an electron donating group –X, e.g., $–CH_3$, $-NH_2$ or –OH and the acceptor has an electron withdrawing group –Y, e.g., –CN, -CHO or $–NO_2$. The substituents can be thought of as intramolecular dopants : -X acting as an n-type

dopant and –Y acting as a p-type dopant. The fact of these dopant being intramolecular automatically takes care of the statistical dopant fluctuation problem, since each molecule is an identical unit.

Working of the molecular rectifier

The electron donating group X tends to place more electron density on the phenyl ring, which increases the mutual electronic repulsion on the ring. This pushes up the energy levels of the molecular orbitals on the donor side of the rectifier molecule. The acceptor side of the molecule works the opposite way: the electron withdrawing group Y tends to reduce the electron density on the ring, leading to reduced electronic repulsion on the acceptor side of the molecule, which in turn causes the energy levels on this side to be lowered. This causes an energy difference, ΔE_{LUMO}, between the lowest unoccupied molecular orbital (LUMO) localized on the donor side and the LUMO localized on the acceptor side, as schematically shown in Fig. 2. The aliphatic spacer group ensures that the electron density on either side of the rectifier molecule does not equilibrate by establishing a tunnel barrier. There are also barriers on either side of the molecule at the contacts, which serve to maintain a degree of electrical isolation, while still allowing current flow under bias. These barriers are not considered in the results presented in this work. Only the isolated rectifier molecule is considered.

The working of a molecular rectifier under bias is discussed next. Application of a positive voltage on the donor side and a negative voltage on the acceptor side leads to forward bias and a current flow. As shown in Fig. 3(a), this causes the energy levels on



$$\Delta E_{LUMO} = E_{LUMO}(Donor) - E_{LUMO}(Acceptor)$$

Figure 2: Equilibrium state of the molecular rectifier

the donor side to be shifted down and the energy levels on the acceptor side to be shifted up. This causes a decrease in ΔE_{LUMO}. As soon as the Fermi level of the right-side contact exceeds the LUMO level on the acceptor side and ΔE_{LUMO} drops to zero, the rectifier starts to conduct by resonant electron tunneling through the aliphatic barrier. In the reverse bias situation (see Fig. 3(b)), the acceptor side energy levels are shifted down and the donor side energy levels are shifted further up, leading to an increase in ΔE_{LUMO}. Also, the Fermi level on the donor side needs to be raised up by a large energy in order to reach the LUMO on the donor side. This effectively blocks conduction in the reverse bias till large voltage biases. The capacitive couplings between the contacts and the molecule need to be engineered in order for conduction to take place at appropriate voltages. This issue is not addressed in the present work. Also, it may be noted that the height of the spacer barrier plays an important role in determining the breakdown voltage.

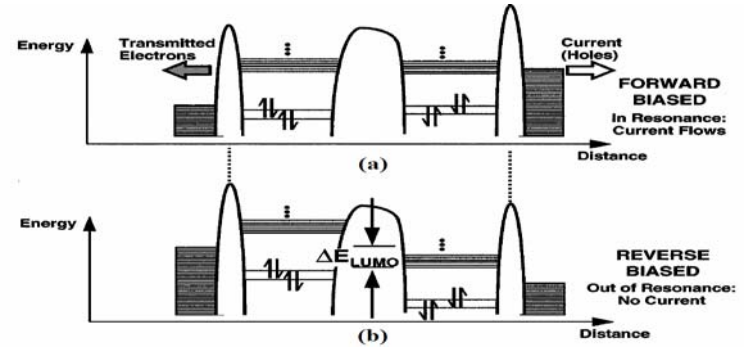


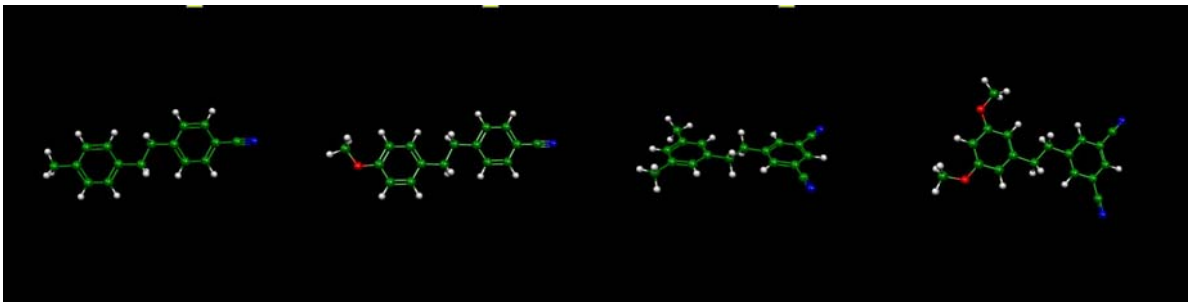
Figure 3: Rectifier operation under (a) Forward bias (b) Reverse bias

Design of the rectifier

An important parameter determining the turn-on voltage is ΔE_{LUMO}. Higher the turn-on voltage, better is the charge localization on the two sides of the molecule and better is the discrimination between forward and reverse biases. The objective of this calculation would be to calculate this energy gap for different substituents on the donor and acceptor sides of the molecule as performed in [2]. The choice of the aliphatic group is an important one for the rectifier. As mentioned before, though it does play a role in determining the breakdown voltage, here, the only properties expected of the spacer group is effective localization and possible parallel orientation of the donor and the acceptor sides. The parallel orientation is desired so as to increase π-orbital coupling of the donor and acceptor sides and enhance current under forward bias. Also, a very large spacer group is not desirable, as it incorporates lots of degrees of freedom and also limits current during forward bias by providing a thicker barrier for direct tunneling. So, a dimethylene $–CH_2CH_2-$ group is chosen for –R-, which is the smallest group that allows a coplanar arrangement of the donor and acceptor halves of the molecule. It is assumed that the optimal geometries will have parallel rings and that this will be enforced by the medium in which the molecules are embedded.

Method

The software Gaussian 03 [3] is used to calculate the molecular orbitals (MOs) using a STO 3-21G basis set in a Hartree-Fock formulation. The geometries of the candidate molecules, shown in Fig. 4, are optimized by starting from a near-parallel configuration for both the in-plane and out-of-plane cases. Molecules (a) and (b) are mono-substituted with $–CH_3$ and $-OCH_3$ respectively on the donor side and –CN on the acceptor side, while molecules (c) and (d) are their di-substituted counterparts. The HOMO and LUMO levels are calculated using Koopmans' theorem. The MOs were plotted using Molekel [4], [5] to visualize their localization.

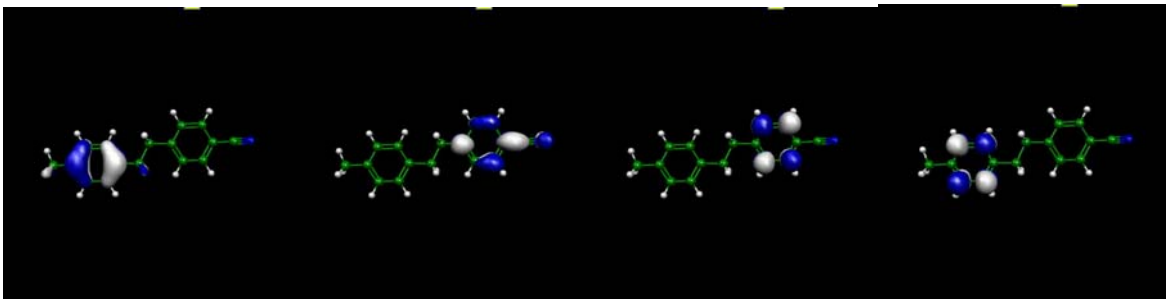


(a) **(b)** **(c)** **(d)**

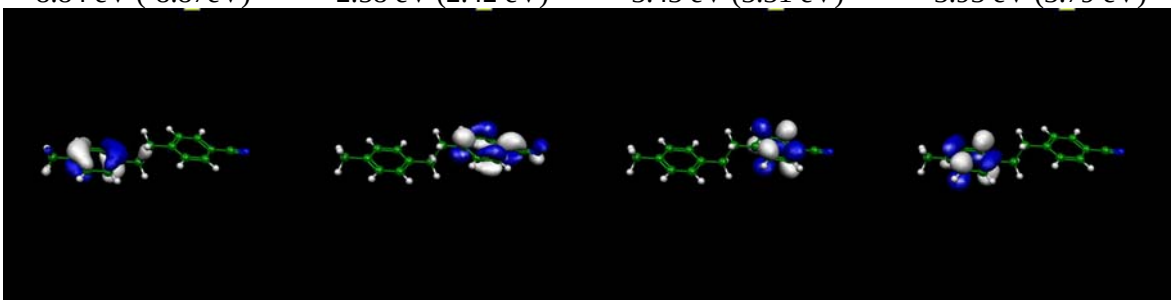
Figure 4: Candidate rectifier molecules

Results and discussion

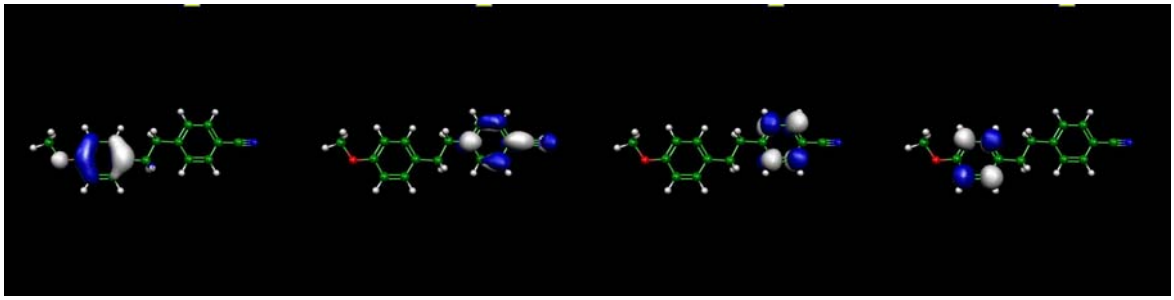
The HOMO and LUMO levels obtained for the different molecules are shown in the figures below, while Table 1 summarizes the obtained ΔE_{LUMO} values. Comparisons are made with the values obtained in [2]. As expected, the molecules show localization of the HOMO on the donor side, while the first two LUMOs are localized on the acceptor side. ΔE_{LUMO} is calculated as the difference between the lowest LUMO on the acceptor side and the lowest LUMO on the donor side.



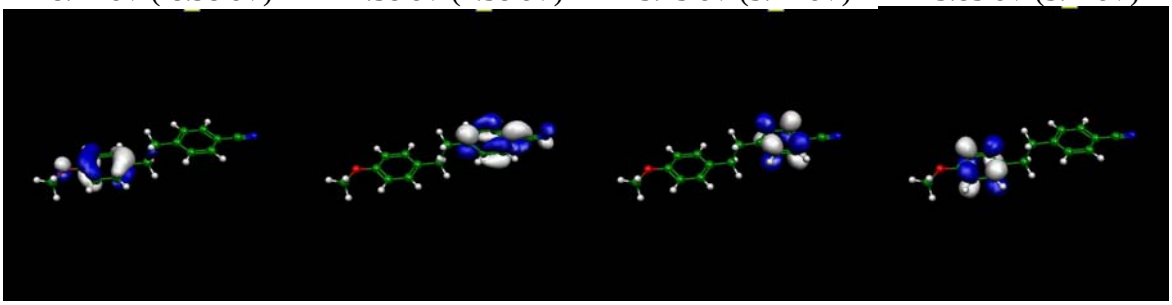
-8.84 eV (-8.87eV) 2.58 eV (2.42 eV) 3.43 eV (3.31 eV) 3.93 eV (3.79 eV)



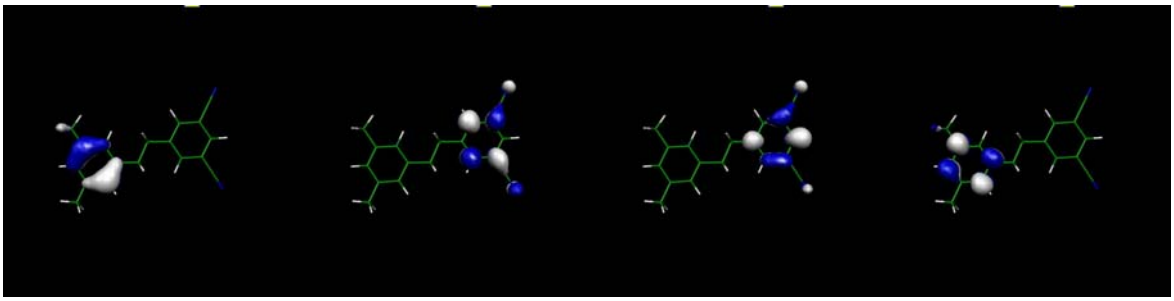
-8.79 eV 2.55 eV 3.43 eV 3.86 eV



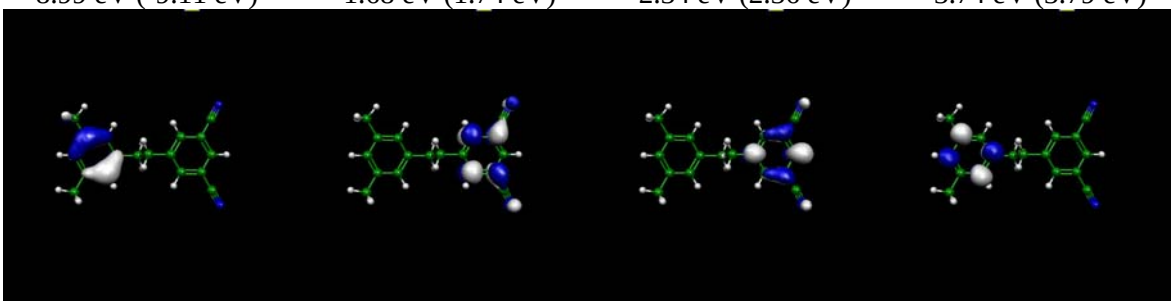
-8.47 eV (-8.98 eV) 2.58 eV (2.38 eV) 3.43 eV (3.24 eV) 3.83 eV (3.71eV)



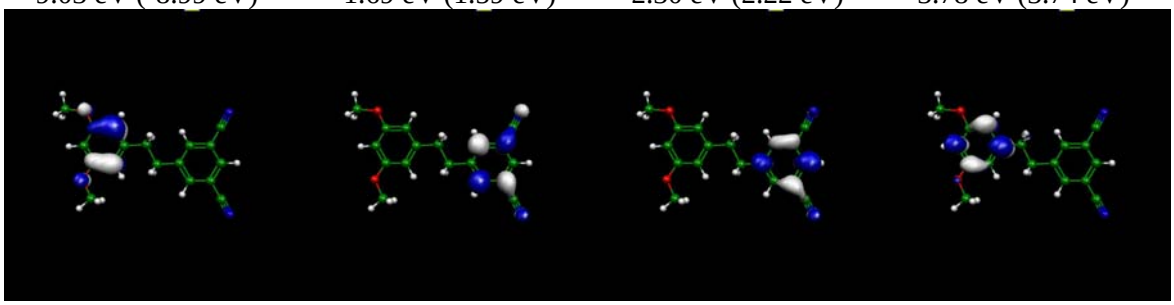
-8.44 eV 2.56 eV 3.43 eV 3.79 eV



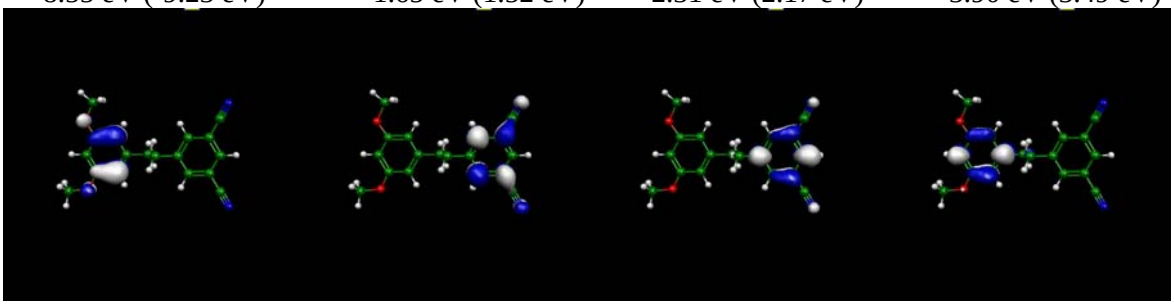
-8.99 eV (-9.11 eV) 1.68 eV (1.74 eV) 2.34 eV (2.36 eV) 3.74 eV (3.79 eV)



-9.03 eV (-8.99 eV) 1.69 eV (1.59 eV) 2.30 eV (2.22 eV) 3.78 eV (3.74 eV)



-8.55 eV (-9.23 eV) 1.65 eV (1.52 eV) 2.31 eV (2.17 eV) 3.90 eV (3.49 eV)



-8.58 eV (-9.24 eV) 1.67 eV (1.50 eV) 2.28 eV (2.12 eV) 3.88 eV (3.74 eV)

Figure 5: HOMO and LUMO orbitals of molecules shown in Fig. 4 for both in-plane followed by out-of-plane configurations. Values in brackets indicate those reported in [2].

Table 1: ΔE_{LUMO} for molecules in Fig. 4

Molecule	Calculated ΔE_{LUMO}	ΔE_{LUMO} [2]
Fig. 4(a) – In plane	1.35 eV	1.37 eV
Fig. 4(a) – Out-of-plane	1.31 eV	-
Fig. 4(b) – In-plane	1.25 eV	1.33 eV
Fig. 4(b) – Out-of-plane	1.23 eV	-
Fig. 4(c) – In plane	2.06 eV	2.05 eV
Fig. 4(c) – Out-of-plane	2.09 eV	2.15 eV
Fig. 4(d) – In-plane	2.25 eV	1.97 eV
Fig. 4(d) – Out-of-plane	2.21 eV	1.99 eV

Also, as expected, the mono-substituted rectifiers have lower built-in voltages as compared to their di-substituted counterparts. Also, the molecules seem to be robust to out-of-plane rotations, as long as the planes are parallel. There are some discrepancies between the values reported in [2] and our calculations, the reason for which is not apparent. According to our calculations, we conclude that the disubstituted methoxycyano molecule has the highest built-in voltage in the in-plane configuration.

Conclusions

The disubstituted molecules have a significant intrinsic potential drop of 2V, which is good for practical applications. However, the results from the abinitio Hartree-Fock (HF) calculations performed in this report must be treated cautiously, as Koopmans' theorem does not take into account relaxation energies. Besides, the HF method neglects electron-electron correlations. Density functional methods and semiempirical methods like Outer Valence Green Function OVGF(AM1) may give better results, but they also are not fool-proof. Though theory can give us an order of magnitude estimate, the best possible way to know surely would be to synthesize the molecule and measure HOMO and LUMO by photoelectron spectroscopy experiments.

References:

1. A. Aviram and M. A. Ratner, "Molecular rectifiers," *Chem. Phys. Lett.*, Vol. 29, pp. 277–283, 1974.

2. James C. Ellenbogen and J. Christopher Love, "Architectures for molecular electronic computers. I. Logicstructures and an adder designed from molecular electronic diodes*", Proc. IEEE*, Vol. 88, 3, March 2000.

3. Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

4. MOLEKEL 4.3, P. Flükiger, H.P. Lüthi, S. Portmann, J. Weber, Swiss Center for Scientific Computing, Manno (Switzerland), 2000-2002.

5. Stefan Portmann & Hans Peter Lüthi, "MOLEKEL: An Interactive Molecular Graphics Tool", CHIMIA (2000) 54 766-770.