The Quantum Mechanical Study of Electronic Properties of Ethane-Dithiol ($C_2H_4S_2$) Nano-Molecular Wire, by Using the Density Functional Theory& Green Function

Ahmadi R.,[1*] Darvish Ganji M.[2]

[1] *Department of Chemistry, Shahre-Rey Branch, Azad Universit, Iran*
[2] *Department of Chemistry, Ghaemshahr Branch, Azad University, Iran*
[*] *Corresponding author, e-mail: Roya_Ahmadi_Chem@yahoo.com*

Abstract

We report a first-principles study of electrical transport in a single molecular conductor consisting of ethane-dithiol ($C_2H_4S_2$) sandwiched between two Au (100) electrodes. We show that the current was increase with increasing the external voltage biases. The projected density of states (PDOS) and transmission coefficients under some external voltage biases are analyzed, and it suggests that the variation of the coupling between the molecule and the electrodes with external bias leads to the increase of the current. Therefore, we propose that the most origin of electron transport mechanism in molecular devices is caused by the characteristics of the molecule and the electrodes as well as their cooperation. Furthermore, the transport properties of the buthane-dithiol ($C_4H_6S_2$) molecular wire are also investigated. The results show that the buthane-dithiol molecular wire has a lower conductivity than the ethane-dithiol ones at a given external biases thus; it is a better insulator device for the molecular electronics technology.

Introduction

One of the most important goals in the engineering of electronic devices is the miniaturization. The present technologies of micro structuring semiconductor material, especially silicon, are expected to reach their limits in the next decade. The smallest transistors are of about 100 nanometers wide, and tens of millions of them may be integrated on a single chip. Below this size the controlled doping becomes more and more difficult. The next important step in the miniaturization might be done by reducing the electronic devices to the scale of molecules. This new field of physics and chemistry is called molecular electronics. Recently several researchers have measured charge transport in single or small groups of organic molecules connected to metal contacts (Reed *et al*. 1997, Chen *et al*. 1999, Tian *et al*. 1998, Collier *et al*. 1999, Cui *et al*. 2001, Reichert *et al*. 2002). The experiments have shown that these novel molecular wire systems have a variety of interesting transport properties such as rectification (Reed *et al*. 1997), negative differential resistance(Chen *et al*. 1999), and switching behavior (Collier *et al*. 2000) to name just a few. In parallel, there have been theoretical attempts at understanding molecular conduction, both at the semi empirical (Tian *et al*. 1998, Emberly *et al*. 1998) and first-principles (Damle *et al*. 2001, Brandbyge *et al*. 2002, Derosa & Seminario 2001, Di Ventra *et al*. 2000, Palacios *et al*. 2001, Palacios *et al*. 2002) levels. Understanding molecular conduc-tion is challenging, since it involves not just the intrinsic chemistry of the molecule, but extrinsic factors as well, such as the metal-molecule bonding geometry, contact surface microstructure and the electrostatics of the environment. Aviram and Rather (Aviram & Rather 1974) were the first to propose sophisticated molecule-based systems analogous to diodes and triodes.

Since their proposals, such systems have indeed been synthesized, and some techniques to connect them to external electrodes have been developed. Electronic transport through single, or at most a few, molecules adsorbed on an Au surface was observed with scanning tunneling microscope (STM), where the tip served as a counter electrode (Datta *et al*. 1997, Joachim *et al*. 1995). STM can be used not only in the tunneling regime to image adsorbates but also in the contact regime to build few-atom nanoscopic contacts (Porath *et al*. 1997, Hou *et al*.

1999, Agraït *et al.* 1993, Pascua *et al.* 1993). In addition to the STM, mechanically controllable break junctions have also provided powerful tools to study the electronic transport in metallic nanobridges or individual molecules (Pascua *et al.* 1993, Muller *et al.* 1992, Krans *et al.* 1995, Yanson *et al.* 1997, Scheer *et al.* 1998, Reed *et al.* 1997, Park *et al.* 2000).

A break junction is made by spanning two metallic contacts by a metallic nanowire, which is then stretched and broken using piezos. This yields two atomically sharp metallic nanocontacts. In the experiments (Reed *et al.* 1997, Reichert *et al.* 2002) the break junction was exposed to a solution of the organic molecule of interest. The molecules, which were functionalized at both ends with a chemical group that binds with the metal, self-assembled onto both of the metallic tips. The solution was then evaporated, leaving behind two metal tips coated with organic molecules. The tips were then brought together, a bias voltage was applied between them and the resulting electric current that flowed from tip to tip through the self-assembled monolayer's (SAM) was measured.

Connecting a few molecules, or even a single molecule, to conducting electrodes forms the basis of a lively research activity in this field. Examples of nanowires include those constructed from aromatic dithiols (Reed *et al.* 1997), carbon spheres (Joachim 1995), carbon nanotubes (Tans *et al.* 1998), and alkene thiols (Anders *et al.* 1997). Molecular wires studied in recent years can be broadly divided into two categories; those based on n-alkane chains which have a large (6 eV or greater) band gap separating their highest occupied molecular orbital (HOMO) and their lowest unoccupied molecular orbital (LUMO), and those based on conjugated molecules that have a band gap of, 2–4 eV. Alkanethiol (CH$_3$-(CH$_2$)n-1SH) is one of the molecular systems that has been studied extensively due to its ability to form a robust SAM on gold surfaces and is useful for synthesizing insulating layers.3,35 Recently tunneling has been identified as the main conduction mechanism for alkanemonothiol SAMs formed in a nanometer scale junction.36 However, the corresponding physical mechanisms governing the electron transport phenomenon in most of this experimental work are seldom mentioned. Thus we present a full atomistic ab initio description of the electron transport through the molecular wire especially alkanethiol system.

The most common way of connecting conjugated molecules to an electron source/drain is by making a TTsubstituted molecule, i. e., a TT molecule in which a hydrogen atom in its end group has been replaced by an S atom, and attaching this to an Au electrode via sulfur-gold "S-Au" binding. In computational modeling of molecular nanowires, the main task has been to provide insight into how the molecule-to-metal electronic coupling and the geometry of the metal contacts affect the flow of current through the wire.

In this paper, we report on first-principles calculation of the I-V characteristic curves of a ethane-dithiol (C$_2$H$_4$S$_2$) molecular nanowire, as shown schematically in Figure 1.
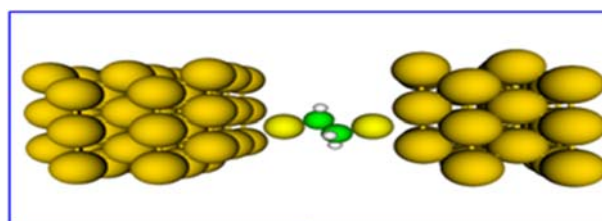

Figure 1. A conjugated ethane-dithiol molecule is chemisorbed onto the gold electrodes via the thiolate terminal groups.

Furthermore, we have also computed the projection of the density of states (PDOS) of the combined system onto all the C$_2$H$_4$S$_2$ basis orbitals and the transmission function of the nanowire and the electrodes, and have investigated the effect of the coupling between the molecular and electrodes states.

The organization of the papers is as follows. We start with a brief description of the Density Functional based Non-Equilibrium Green's Function method Section II, and in Section III, we present calculations of the (*I-V*) spectrum of a C$_2$H$_4$S$_2$ and a C$_4$H$_8$S$_2$ molecular junctions, together with an analysis of the molecular levels are important for electron transmission. In Section IV the results are summarized.

Computational Details
The quantum mechanical calculations have been performed using a recently developed first-principles package SMEAGOL (Rocha *et al.* 2005), which is based on the combination of DFT (as implemented in the well tested SIESTA method (Soler *et al.* 2002 & SIESTA) with the NEGF

approach(Jauho *et al.* 1994 & Haug *et al.* 1996). SMEAGOL is capable of fully self-consistently modeling the electrical properties of nano-scale devices that consist of an atomic scale system coupling with two semi-infinite electrodes. Such nano-scale devices are referred to as two-probe systems and they are divided into three parts for theoretical calculations: left and right electrodes, and a central scattering region. The scattering region actually includes a portion of the semi-infinite electrodes. The simulation procedure of such two-probe systems can be described briefly as follows.

Firstly the electronic structure of two electrodes is calculated only once by SMEAGOL to get a self-consistent potential. This potential will be shifted rigidly relative to each other by the external potential bias and provides natural real space boundary conditions for the Kohn-Sham (K-S) effective potential of the central scattering region. Then from the Green's function of the central scattering region, it can obtain the density matrix and thereby the electron density. Once the electron density is known, the DFT Hamiltonian matrix, which is used to evaluate the Green's function, can be computed using the above boundary conditions by means of standard methods.

$$\hat{G} = \lim_{\delta \to 0} \left[(E + i\delta)\hat{S} - \hat{H}_{S[\rho]} - \hat{\Sigma}_L - \hat{\Sigma}_R \right]^{-1}$$

Where $\hat{H}_{S[\rho]}$ is DFT Hamiltonian $\hat{\Sigma}_L$ and $\hat{\Sigma}_R$ self-energies, respectively for the left and right lead. E is energy and δ is imaginary part of partial energy. This procedure is iterated by cycling until self-consistency field (SCF) is achieved. Moreover, the current through the atomic scale system can be calculated from the corresponding Green's function and self energies using Landauer-Buttiker formula (BÄuttiker *et al.* 1985).

$$I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} dE \left[f_l(E - \mu_L) - f_r(E - \mu_R) \right] T(E,V)$$

Where μ_L and μ_R are the electrochemical potentials of the left and right electrodes, respectively,

$$\mu_L - \mu_R = eV_b$$

and f_l, f_r are the corresponding electron distribution of the two electrodes. $T(E,V)$ is the transmission coefficient at energy E and bias voltage V, which is given by:

$$T(E,V) = Tr\left[\text{Im} \Sigma_l(E) G^R(E) \text{Im} \Sigma_r(E) G^A(E) \right]$$

Where $G^R(E)$ and $G^A(E)$ are the retarded and advanced Green's function of the central region. Based on the eigen channel decomposition of the conductance, this total transmission $T(E)$ can be decomposed into nonmixing eigen channels $T_n(E)$ (Brandyge *et al.* 1997) as

$$T(E) = \sum_n T_n(E)$$

In our DFT calculation, the local-density approximation (LDA) to the exchange-correlation potential[45] is used. Only valence electrons are considered in the calculation, and the wave functions are expanded by localized numerical (pseudo)atom orbitals (PAO's) (Artacho *et al.* 1999). The atomic cores are described by norm-conserving pseudo potentials (Troullier & Martins 1991).

The structural model for our theoretical analysis is illustrated in Fig. 1. In this two-probe system, $C_2H_4S_2$ molecule couples with two atomic scale Au (100) electrodes which extend to reservoirs at $\pm\infty$ where the current is collected. Three Au atomic layers have been chosen for the electrode cell in the z-direction. In the central scattering region the $C_2H_4S_2$ molecule couples with two atomic layers to both the left and right electrode. These atomic layers in the central scattering region are large enough (Roland *et al.* 2002) so that the perturbation effect from the scattering region is screened and they are denoted as surface-atomic layers In the entire electrode, the gold atoms have been arranged in an ideal fcc (100) configuration with the lattice parameter of bulk gold. It has been assumed that the S's of the $C_2H_4S_2$ each placed above the hollow sites of the electrodes. An SCF calculation by Sellers (Sellers *et al.* 1993) has shown this to be energetically favorable for an alkanethiol. Thus the $C_4H_8S_2$ molecule in Figure 1. is positioned symmetrically above the hollow sites of the two Au surfaces. Since there is no direct experimental information regarding the geometry of the molecule and its attachment to the leads, thus we place the molecule between the electrodes assuming the Au-S distance of 2.39 Å (Brandbyge *et al.* 2003).

Results and discussion

Figure 2. Shows the I-V curve of the system. We will show that the increase in the current can be understood by studying the changes of coupling between the molecular orbitals in the $C_2H_4S_2$ and incident states in the electrodes under various external biases Figure 3. Shows the zero bias transmission spectra of the system.
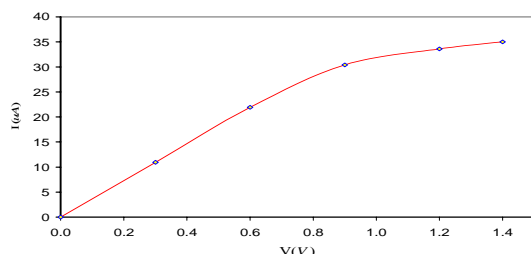

Figure 2. Current-Voltage (I-V) curves of the tow-probe system shown in Figure 1.
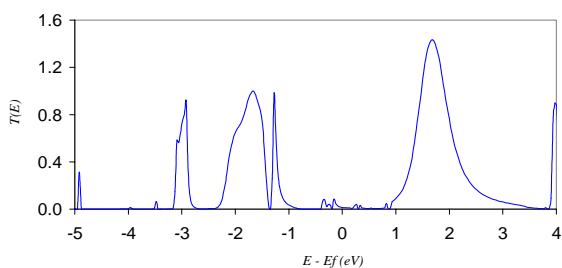

Figure 3. a) Transmission function under zero bias as function of the injection energy of electron of the $C_2H_4S_2$ molecule coupled to Au (100) electrodes.

It has a region of weak transmission below the Fermi energy, and a peak of stronger strength above, where electrons incident from one of the electrodes can transmit across the molecule to the other electrode significantly. To understand why incident states in these two energy regions can transmit across the molecule significantly, we calculated the projection of the density of states (PDOS) of the combined system onto all the $C_2H_4S_2$ basis orbitals. The PDOS will give us information on how much the basis orbitals in the molecule contribute to the eigenstate of the whole open system and how strongly the molecule couples with the electrodes at a certain energy E. The PDOS is shown in Figure 4.

We note that, corresponding to the T-E curve, there is also an energy region where the PDOS takes a comparatively large value. A strong coupling makes incident electrons at certain energy easily transmit across the molecule, and this will give rise to a large transmission coefficient at this energy. This is clearly shown by comparison of the transmission spectra and PDOS spectra shown in Figure 3 and Figure 4. As a consequence, a large

transmission coefficient indicates a strong coupling between the electrodes and the molecule, and the evolution of transmission curves with external biases can help us understand how the changes of the coupling between the electrodes and molecule determines the I-V characteristics in the system.

Therefore, the voltage dependence of the transmission function will be studied next. Now we divide the whole energy region into two kinds of regions according to whether T(E, Vb) = 0 or not in them. In the regions where T(E, Vb) is not zero the incident electrons can transmit across the molecule, and we call them Transmission regions. In the other regions where T (E, Vb) is zero the incident electrons cannot transmit across the molecule, and we call them transmission intervals. The current in the system is calculated by the Landauer-Buttiker formula, which are transmission spectra dependent. We will now show the changes of the transmission function under various biases Figure 5. We see that the transmission interval near the Fermi energy under zero bias is broadened and splitted at increasing biases. It can be explained by the relative shift of the energy regions of the left and right electrodes.
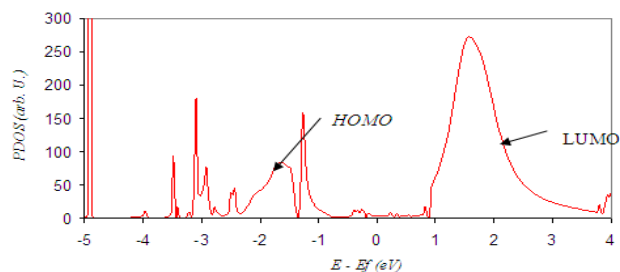

Figure 4. The projection of the density of states (PDOS) of the combined system onto all the $C_2H_4S_2$ basis orbitals. All energy is relative to the Fermi energy of the open system.
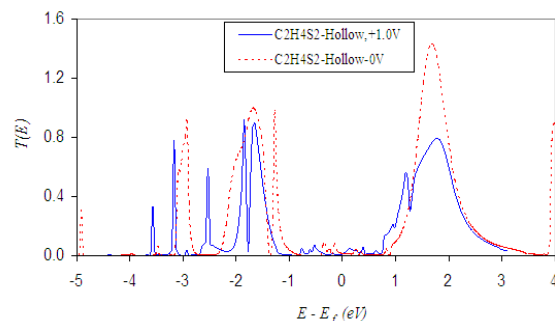

Figure 5. Transmission coefficients under various bias voltages (solid lines indicate V = 1.0 V and dashed lines indicate V = 0.0 V) as a function of energy. Energy is relative to the Fermi energy of the open system.

Now let us see why the current was increased with increasing the bias voltage. As mentioned above the current, I is obtained from:

$$I(V) = \frac{2e}{h} \int_{-\infty}^{+\infty} dE \, [\, f_l(E - \mu_l) - f_r(E - \mu_r)\,] T(E,V)$$

Where μ_L and μ_R are the electrochemical potentials of the left/right electrodes. The region between μ_L and μ_R is called the bias window or integral window, as shown in Figure 5. with strong peaks above the the Fermi energy. Thus, the current is determined by $T(E,V_b)$ in the bias window and is further only determined by the transmission regions in the bias window because $T(E,V_b)$ is zero in the transmission interval and has no contribution to the current. It can be seen further only determined by the transmission regions in the bias window because $T(E,V_b)$ is zero in the transmission interval and has no contribution to the current. It can be seen from Fig.5 that with the external bias increasing from 0.0V to, for instance, +1.0 V, the new transmission region broadens and splits rapidly since the electrons in the higher energy regions of the left electrode can transmit across the molecule to the lower energy regions of the right electrode in an increasingly wider energy region. As a result, the larger transmission coefficient indicates a strong coupling between the molecular orbitals in the $C_2H_4S_2$ and the incident states from the electrodes, thus the current increases quickly under increasing the bias voltage.

To further investigate the transport properties of the alkanes nano molecular wires we will calculate the current intensity of the larger alkanes, for instance, the buthane-dithiol ($C_4H_8S_2$) then, compare its *I-V* characteristics with the ethane-dithiol ones. Figure 6 shows the schematics of the buthane-dithiol molecular wire sandwiched between two Au (100) electrodes.

Similar calculations have been carried out for the structural relaxation and then *I-V* characteristics of the buthane-dithiol molecular junction. The result is depicted in Figure 7. It can be seen that the ethane-dithiol which has a shorter length than the buthane-dithiol shows a higher current intensity at various external voltage biases. Thus wherever we need to a higher current intensity in the molecular electronics devices then, the shorter alkanes will be convenient to implement and vice versa.
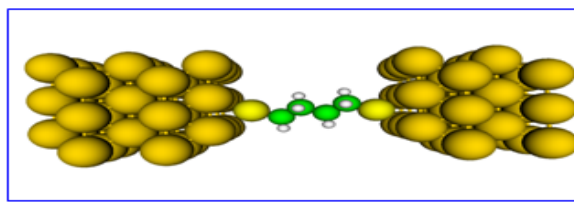

Figure 6. A conjugated buthane-dithiol molecule is chemisorbed onto the gold electrodes via the thiolate terminal groups.
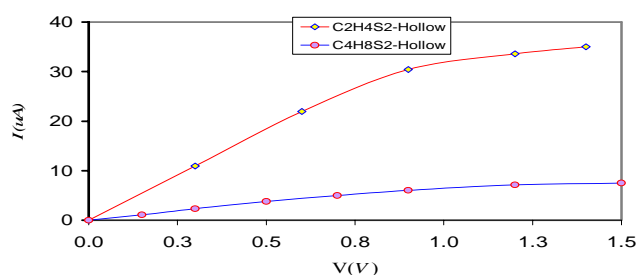

Figure 7. Current-Voltage (*I-V*) curves of the tow-probe systems of the ethane-dithiol and the buthane-dithiol attached between two Au (100) electrodes.

Conclusions

In conclusion, we have studied the *I-V* characteristics in ethane-dithiol coupled to Au (100) electrodes via the S end groups. Our study showed that the increasing in the current in this device is determined by displacement of the energy regions under various external biases. The energy regions describe the coupling of the incident states in the electrodes and the molecular orbitals in the functional molecule and are determined by features of both the molecule and the electrodes. Thus, a molecule may display different transport behaviors in different situations, for instance, with a different selection of electrodes. All these remind us that in the design of molecular devices the information of the electrodes must also be taken into consideration very seriously. We have also investigated the length dependence of the current intensity of the alkane molecular wires. The results showed that the shorter alkanes have higher current intensity than the others. Thus when we need to the high conductor wires then we must implement the shorter alkanes such as ethane-dithiol but, in the case we need to an insulator device thus, it is better to implement a larger alkane such as buthane-dithiol.

References

Agraït N., Rodrigo J.C., Vieira S. 1993: Conductance steps and quantization in atomic-size contacts. *Phys. Rev. B.* **47:** 12345–12348.

Anders R. P., Bielefeld J. D., Henderson J.I., Janes D.B., Kolagunta V.R., Kubiak C.P., Mahoney W.J., Osifchin R.G. 1997: Self-assembly of a two-dimensional super lattice of molecularly linked metal clusters .*Science* **273:** 1690–1693.

Artacho E., Suanchez-Portal D., Ordejon P., Garcia A., Soler J. M. 1999: Linear-Scaling ab-initio Calculations for Large and Complex Systems. *Phys. Status Solidi B.* **215:** 809–817.

Aviram A., Ratner M., Chem A. 1974: *Phys. Lett.* **29:** 277–283.

BÄuttiker M., Imry Y., Landauer R., Pinhas S.1985: Generalized many-channel conductance formula with application to small rings. *Phys. Rev. B.* **31:** 6207–6215.

Brandbyge M., Mozos J.-L., Ordejon P., Taylor J., and Stokbro K.,2002: Density-functional method for no equilibrium electron transport. *Phys. Rev. B* **65:** 165401–165418.

Brandbyge M., Mozos J.L., Ordejon P., Taylor J., Stokbro K. 2003: Theoretical study of the nonlinear conductance of Dithiol benzene coupled to Au(1 1 1) surfaces via thiol and thiolate bonds. *Comp. Mat. Sci.* **27:** 151–160.

Brandyge M., Srensen M.R., Jacobsen K.W. 1997: Conductance eigenchannels in nanocontacts. *Phys. Rev. B.* **56:** 14956–14956.

Chen J, Reed M.A., Rawlett A.M., Tour J.M., 1999: Large On-Off Ratios and Negative Differential Resistance in a Molecular Electronic Device. *Science* **286:** 1550–1552.

Collier C.P., Mattersteig G., Wong E.W., Luo Y., Beverl K.y., Sampaio J., Raymo F.M., Stoddart J.F., Heath, J.R. 2000: Catenane-Based Solid State Electronically Reconfigurable Switch. *Science* **289:** 1172–1175.

Collier C.P., Wong E.W., Belohradsky M., Raymo F.M., Stoddart J.F., Kuekes P.J., Williams R.S., Heath J.R. , 1999: Electronically Configurable Molecular-Based Logic Gates. *Science.* **285:** 391–394.

Cui X.D., Primak A., Zarate X., Tomfohr J., Sankey O.F., Moore A.L., Moore T.A., Gust D., Harris G., Lindsay S.M. 2001: Reproducible Measurement of Single-Molecule Conductivity. *Science.* **294:** 571–574.

Cuniberti G., Fagas G., and Richter K. 2002: Fingerprints of mesoscopic leads in the conductance of a molecular wire. *Chem. Phys.* **281:** 465–476.

Damle P.S., Ghosh A.W., and Datta S. 2001: Molecular Conduction: Paradigms and Possibilities. *Phys. Rev. B* Rapid Comms. **64:** 515–525.

Datta S., Tian W., Hong S., Reifenberger R., Henderson J. I., Kubiak C. P. 1997: Current-Voltage Characteristics of Self-Assembled Monolayer by Scanning Tunneling Microscopy. *Phys. Rev. Lett.* **79:** 2530–2533.

Derosa P.A., Seminario J.M. 2001: Electron transport through single molecules: Scattering treatment using density functional and green . *J. Phys. Chem. B* **105:** 471–481.

Di Ventra M., Pantelides S.T., and Lang N.D. 2000: First-Principles Calculation of Transport Properties of a Molecular Device. *Phys. Rev. Lett.* **84:** 979–982.

Emberly E.G., Kirczenow G., 1998: Theoretical study of electrical conduction through a molecule connected to metallic nanocontacts. *Phys. Rev. B.* **58:** 10911–10920.

Hall L.E., Reimers J.R., Hush N.S., Silverbrook K. J.2000: From molecules to metallic wires Unified description of molecular conduction. *Chem. Phys.* **112:** 1510.

Haug H., Jauho A.P. 1996: Quantum Kinetics in Transport and Optics of Semiconductors, Springer-Verlag, Berlin, Heidelberg.

Hou J.G., Yangl J., Wang H., Li Q., Zeng C., Lin H., Bing W., Chen D.M., Zhu Q. 1999: Identifying Molecular Orientation of Individual C_{60} on a Si(111)-(7×7) Surface. *Phys. Rev. Lett.* **83:** 3001–3004.

Jauho A.P., Wingreen N.S., Meir Y. 1994: Time-dependent transport in interacting and noninteracting resonant-tunneling systems *Phys. Rev. B* **50:** 5528–5544.

Joachim C., Gimzewski J.K., Schlittler R.R., Chav C.Y. 1995: Electronic Transparence of a Single C_{60} Molecule. *Phys. Rev. Lett.* **74:** 2102–2105.

Krans J.M., van Ruitenbeek J.M., Fisun V.V., Yanson I.K., de Jongh L.J. 1995: Episodic ejection of relativistic jets by the X-ray transient GRO J1655 − 40. *Nature* (London). **375:** 464–468.

Lee T., Wang W., Reed M. A. 2005: Intrinsic Electronic Transport through Alkane dithiol Self-Assembled Monolayer. *Jpn. J. Appl. Phys.* **44:** 523–529.

Muller C.J., Ruitenbeek J.M., Jong L. J. 1992: Conductance and super current discontinuities in atomic-scale metallic constrictions of variable width. *Phys. Rev. Lett.* **69:** 140–143.

Palacios J.J., P´erez-Jim´enez A.J., Louis E., and Verg´es J.A. 2001: An *ab initio* approach to electrical transport in molecular devices. *Nanotechnology* **13:**378–381.

Palacios J.J., P´erez-Jim´enez A.J., Louis E., SanFabi´an E., andVerg´es J.A. 2002: First-principles approach to electrical transport in atomic-scale nanostructures. *Phys. Rev. B* **66:** 035322–35334.

Park H., Park J., Lim A.K.L., Anderson E.H., Alivisatos A.P., McEuen P.L. 2000: *Nature* (London) 407: 57 Joachim C. 1995: Electronic Transparence of a Single C_ {60} Molecule. *Phys. Rev. Lett.* **74:** 2102–2105.

Pascual J.I., Méndez J., Gómez Herrero J., Baró A. M., García N., Binh V. T. 1993: Quantum contact in gold nanostructures by scanning tunneling microscopy. *Phys. Rev. Lett.* **71:** 1852–1855.

Paulsson M. and Stafstr¨om S. 2001: Self-consistent-field study of conduction through conjugated molecules. *Phys. Rev. B* **64:** 35416–35426.

Perdew J.P., Zunger A. 1986: Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys .Rev .B*. **33:** 8822– 8824.

Porath D., Levi Y., Tarabiah M., Millo O. 1997: Tunneling spectroscopy of isolated C_{60} molecules in the presence of charging effects. *Phys. Rev. B* **56:** 9829–9833.

Reed M.A., Zhou C., Muller C.J., Burgin T.P., Tour J.M. 1997: Conductance of a Molecular Junction. *Science.* **278:** 252–254.

Reichert J., Ochs R., Beckmann D., Weber H.B., Mayor M., and Lohneysen H.v. 2002: Driving Current through Single Organic Molecules. *Phys. Rev. Lett*. **88:** 391–395.

Rocha A.R., Garc´ıa-Su´arez V.M., Bailey S.W., Lamber C.J.T., Ferrer J., Sanvito S. 2006: *SMEAGOL* (Spin and Molecular Electronics in an Atomically-Generated Orbital Landscape. www.smeagol.tcd.ie).

Rocha A.R., Garc´ıa-Su´arez V.M., Bailey S.W., Lambert C.J. , Ferrer J., Sanvito S. 2005: Towards molecular spintronics *Nature Materials.* **4:**332−335.

Roland C., Meunier V., Larade B., Guo H. 2002: Charge transport through small silicon clusters *Phys. Rev. B*. **66:** 35332–35339.

Samanta M. 1999: Master's Thesis, Purdue University.

Scheer E., Agrait N., Cuevas J.C., Yeyati A. L., Ludoph B., Martin-Rodero A., Bollinger G.R., van   Ruitenbeek J.M., Urbina C. 1998: The signature of chemical valence in the electrical conduction through a single-atom contact. *Nature* (London). **394:** 154–157.

Sellers H., Ulman A., Schnidman Y., Eilers J.E. 1993: Structure and binding of alkanethiolates on gold and silver surfaces: implications for self-assembled monolayers. *J. Am. Chem. Soc.* **115:** 9389–9401.

Siesta replaces core electrons by pseudo potentials and describes valence electrons by an atomic-like basis set.

Soler J.M., Artacho E., Gale J.D., Garc´ıa A., Junquera J., Ordej´on P., anchez-Portal D.S. 2002: The SIESTA method for ab initio order-*N* materials simulation . *J. Phys. Condens. Matter.* **14:** 2745–2779.

Tans S.C., Verschueren R.M., Dekker C. 1998: Room-temperature transistor based on a single carbon nano tube. *Nature* (London). **393:** 49–52.

Tian W., Datta S., Hong S., Reifenberger R., Henderson J.I., Kubiak C.P. 1998: Conductance spectra of molecular wires . *J. Chem. Phys*. **109:** 2874–2882.

Troullier N., Martins J.L. 1991: Finite-difference-pseudo potential method: Electronic structure calculations without a basis. *Phys. Rev. B*. **72:** 1240–1243.

Wang W., Lee T., Reed M. A. 2003: Mechanism of electron conduction in self-assembled alkanethiol monolayer device. *Phys. Rev. B*, **68:**35416–35423.

We use a double-ζ + polarization basis set for the organic and a single-ζ polarized basis set for the gold *s, p and d* channels. The exchange and correlation potential is calculated using the local density approximation (LDA).

Yanson A.I., Ruitenbeek J.M. 1997: Do Histograms Constitute a Proof for Conductance Quantization?. *Phys. Rev. Lett*. **79:** 2157–2157.