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Molecular Wire Junctions: Tuning the Conductance

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Junctions consisting of two electrodes and a single molecule acting as a wire can be investigated by scanning probe conductance measurements. The conductance for low temperature, short wire structures can be characterized by the elastic scattering of the electrons, as described by general Landauer formulas. Tuning the bridge energy levels either by field effect transistor (FET)-like behavior (charging) or by chemical bond formation can raise or lower the conductance by moving the poles of the molecular Green's function. For small molecular structures with particular HOMO/LUMO characteristics, functionalization might be a more effective means than Coulomb charging by external gates.

I. Introduction

The advent of directed assembly methods for their preparation, and of special molecular scale measurement methodologies (often based on scanning probe) for their observation, has made it possible to measure directly the conductance of molecular wire junctions.[1−10] In these structures, a single molecule or a small number of molecules provide pathways for electron motion between two external electrodes. A number of such measurements have been reported, and behaviors such as ballistic transport,[2−4] injection maxima,[5] energy level resonances,[11] quantized conductance,[12] negative differential resistance[5] and molecular rectification[13] have been observed.

Computationally, transport in junctions is complicated by the necessity for dealing both with the molecular wire itself and with the contact interfaces. In the low voltage regime at low temperatures, conductance is successfully discussed in terms of elastic scattering, following the Landauer picture developed for mesoscopic semiconductor structures. Several different formulations,[14−20] based on the Landauer formula itself or an equivalent Lippman−Schwinger scattering formalism, have been developed and utilized.

Recent results on single-nanotube transistors,[21a,d] crossed nanotube logic,[21b] and dynamic molecular gating[21c] have drawn renewed attention to molecular switching possibilities.

One obvious idea for modulating the current in molecular wire junctions follows from the chemical field effect transistor:[22] this involves localized Coulomb charging at a particular site on the molecular wire, and consequent modification of the energy levels and "gating" of the current. An alternative notion, apparently observed in recent measurements of conductance in molecular junctions containing charge-transfer pairs,[23] is modification of the transport by tuning the molecular wire pole structure by covalent or charge-transfer molecular interactions.

We examine these two modalities for tuning molecular wire conductance, by considering the simplest possible case: the conductance at low voltage, in the scattering limit, reducing the molecular wire to a single site structure. An analytical treatment can then be carried out, demonstrating that the conductance can be tuned quite sensitively either by charge modification or (more simply and more generally) by chemical bonding or charge-transfer interactions along the molecular wire. In particular, if the injection (Fermi) level is close to a molecular resonance, the latter route may be more efficacious.

II. Landauer Conductance at Small Bias

The first observations of modification of molecular conductances due to molecular interaction indicate[23] that, upon formation of the charge-transfer complex, the current through an adsorbed molecular layer increases and becomes more ohmic. We will model the low voltage part of this conductance, in the simplest model. Because the bridge is so short, thermal events are relatively small,[24,25] and we restrict ourselves to the low

voltage limit of the Landauer (coherent) conductance. Under these conditions, we will model the system as consisting of a molecule situated between two identical electrodes. The interaction between the molecule and the electrodes is arbitrary; for example, it could be taken from the Newns/Anderson description,[21,26] which represents the metal as a one-dimensional tight binding band. The Landauer conductance can then be written[14-21,27]

$$g = g_0 T$$

where

$$g_0 \equiv \frac{e^2}{\pi\hbar} = (12.8\Omega)^{-1} \tag{1}$$

is the quantum unit of conductance and where

$$g = \frac{e^2}{\pi\hbar} \mathrm{Tr}\{\Delta G^+ \Delta G\} \tag{2}$$

is the transmission probability. Here G is the molecular Green's function, and Δ is the imaginary part of the molecular self-energy due to interaction with the electrode. These are, in turn, defined by

$$G = (E - H_M - \Sigma)^{-1} \tag{3}$$

$$\Sigma = \Lambda - \mathrm{i}\Delta \tag{4}$$

In these definitions, E is the energy, H_M is the molecular Hamiltonian, and Σ is called the self-energy. Self-energy can be expressed in the atomic orbital representation on the molecule as

$$\Delta_{ij} = \delta_{ij}\Delta_{ii}(\delta_{i1} + \delta_{iN}) \tag{5}$$

where δ_{ij} is the Kronecker δ, that is unity for $i = j$ and vanishes for $i \neq j$, and it was assumed that the self-energy term occurs only[21] at the initial (site 1) and final (site N) ends of an extended molecule. More generally, the diagonal self-energy is defined by

$$\Delta_{ii}(E) = \pi\sum_{s}|V_{is}|^2\delta(E - E_s) \tag{6}$$

here E_s is the energy of the band state s in the electrode, and V_{is} is the matrix element between the ith atomic orbital on the molecule and the band state s. Evaluation of these self-energies is discussed extensively elsewhere.[14,21] Most molecular conductances are characterized by $T \ll 1$ in eq 1, except precisely at resonance.[16]

To gain analytic simplicity, and to demonstrate the modification of molecular circuit conductances by molecular structural modification, we discuss the two simplest possible cases: the reference system will be a structure represented by a single molecular orbital (one could imagine the HOMO of a molecule with a very large gap, or an atomic limit of the molecular situation). If the orbital energy of this single orbital is denoted ϵ_k, the Green's function is just

$$G = (E - \epsilon_k - \Sigma_{kk})^{-1} \tag{7}$$
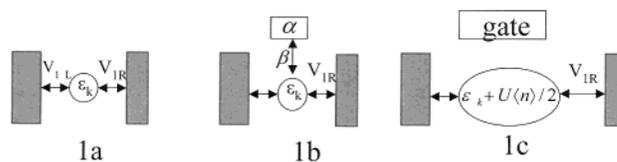
Figure 1. Schematic of a one-site bridge of energy ϵ_k coupled to left, right electrodes with coupling amplitudes V_{Rs}, V_{Ls}, respectively. In (a), the bridge is alone. In (b), it is bonded to a second site of energy α with coupling amplitude β. In (c), an electrostatic potential is applied by an external gate, and a charge shift of electrons occurs. In the Hartree−Fock treatment, the energy changes by $U\langle n\rangle/2$.

The conductance in turn follows as

$$g_s = g_0\frac{\Delta^2}{(E - \tilde{\epsilon}_k)^2 + \Delta^2} \tag{8}$$

where the g_s subscript denotes a single site, and we have defined the shifted orbital energy by

$$\tilde{\epsilon}_k = \epsilon_k - \Lambda_{kk} \tag{9}$$

generally, the Λ_{kk} (the real part of the self-energy) will be substantially smaller than ϵ_k.

For comparison with the simple case above (shown in Figure 1a) we will characterize two possible modifications. Figure 1b shows a situation in which the bridging molecular orbital has been modified by covalent interaction with another site, whose unperturbed energy is denoted by α. The mixing between the two has the strength β (the Huckel-like notation emphasizes the simple molecular orbital nature of this modification). The molecular Hamiltonian now becomes

$$H_M = \begin{pmatrix} \epsilon_k & \beta \\ \beta & \alpha \end{pmatrix} \tag{10}$$

$$G = \begin{pmatrix} E - \epsilon_k - \Sigma & -\beta \\ -\beta & E - \alpha \end{pmatrix}^{-1} \tag{11}$$

and simple inversion gives

$$G = \begin{pmatrix} \dfrac{(E - \alpha)w}{E - \epsilon_k - \Sigma} & \dfrac{\beta w}{E - \epsilon_k - \Sigma} \\ \dfrac{\beta w}{E - \epsilon_k - \Sigma} & w \end{pmatrix} \tag{12}$$

Here we have defined the normalizing factor w as

$$w = \frac{1}{E - \alpha - \dfrac{\beta^2}{E - \epsilon_k - \Sigma}} \tag{13}$$

Evaluation of the Green's function gives the relevant element as

$$G_{11} = \frac{E - \alpha}{(E - \tilde{\epsilon}_k)(E - \alpha) - \beta^2 - \mathrm{i}(E - \alpha)\Delta} \tag{14}$$

Of the four elements in the Green's function matrix for this situation, only the G_{11} is necessary, because the generalized Landauer formula of eq 1 in fact becomes

$$g_c = g_0\Delta_R\Delta_L|G_{11}|^2 \tag{15}$$

Here Δ_R and Δ_L are the self-energies arising from the interaction

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of the orbital of Figure 1a to its right and left linkages, respectively; the subscript on g_c refers to the covalent modification of Figure 1b.

We rewrite the real part of the denominator of eq 14 using

$$(E - \hat{E}_-)(E - \hat{E}_+) = (E - \tilde{\epsilon}_k)(E - \alpha) - \beta^2 \quad (16a)$$

where $\hat{E}_+$ and $\hat{E}_-$ are the roots of the polynomial, evaluated as

$$\hat{E}_\pm = \frac{1}{2}\{\alpha + \tilde{\epsilon}_k \pm \sqrt{(\alpha - \tilde{\epsilon}_k)^2 + 4\beta^2}\} \quad (16b)$$

For simplicity, we consider the limit

$$|\beta/(\alpha - \tilde{\epsilon}_k)| \ll 1 \quad (17)$$

this corresponds to the coupling between the reference level $\tilde{\epsilon}_k$ and the modifying level of energy α being substantially smaller than the energy difference between them. Under these conditions, the roots become

$$\hat{E}_\pm = \begin{bmatrix} \alpha + \dfrac{\beta^2}{\alpha - \tilde{\epsilon}_k} \\[2ex] \tilde{\epsilon}_k - \dfrac{\beta^2}{\alpha - \tilde{\epsilon}_k} \end{bmatrix} \quad (18)$$

For convenience, we set the origin of energy, E, to be the Fermi level of the metal comprising the two electrodes. The overall conductance can be written as

$$g_c(E) = g_o \Delta_R \Delta_L |G_{11}(E)|^2 \quad (19)$$

It is simplest to choose Δ_R and Δ_L equal to one another.

We now have derived the root structure of the modified bridge of Figure 1b. It remains to compute the conductance differences between the bare orbital of Figure 1a and the covalent modified one of Figure 1b.

III. Comparative Modifications: Covalency and Coulomb Gating

The simple single orbital molecular bridge of Figure 1a can be modified by a covalent interaction with the new molecular atomic site, as in Figure 1b. There has also been extensive interest[28] in building a molecular analogue to a field effect transistor (FET), in which an external gate is somehow applied to the bridging species, modifying its orbital energy and therefore its transmittance. Such an FET-like device is sketched in Figure 1c. One straightforward way to characterize this gating process would be to use an on-site Coulomb repulsion picture, which is the Hubbard limit of the Pariser−Parr−Pople model.[29] For such a situation, the molecular Hamiltonian can then be approximated (at the Hartree−Fock level) by

$$H_m^{(U)} = \epsilon_k + U\langle n \rangle/2 \quad (20)$$

Here U denotes the onsite electron repulsion term and n is the total number of electrons sitting on the site, which can be either integral or nonintegral. We have assumed that the numbers of up and down spin electrons on the site are the same and physically consider that the potential induced in the molecular bridge by the external gate causes a modification in the population. When the population of the electrons on the bridge increases, the local Coulomb energy also increases; therefore,

by applying positive or negative gate potentials, the population on the bridge will be modified, as will its single site energy.

We now compare the modification of the conductance through the circuit of Figure 1a by two different routes, the first of which is the covalent choice of Figure 1b, and the second the gating process described by eq 20 and denoted in Figure 1c. Denoting by $g_g^{(n)}$ the gated conductance of Figure 1c, the ratio of the conductance with and without an applied voltage on the gate can be written (using eq 8 and assuming resonant injection, so that $E = 0$)

$$\frac{g_g^{(n=0)}}{g_g^{(n=1)}} = \frac{\Delta^2 + [\tilde{\epsilon}_k + U/2]^2}{\Delta^2 + \tilde{\epsilon}_k^2} \quad (21)$$

This clearly shows that increasing the population decreases the conductance, if $U > 0$ (as is true in a simple Hubbard-type electron repulsion model) and if $E = 0$, so that injection is resonant. If $E \neq 0$, so that injection occurs in the gap between molecular levels, eq 22 becomes

$$\frac{g_g^{(n=0)}}{g_g^{(n=1)}} = \frac{\Delta^2 + (E - \tilde{\epsilon}_k - U/2)^2}{\Delta^2 + (E - \tilde{\epsilon}_k)^2} \quad (22)$$

In this circumstance, the conductance will decrease if

$$\tilde{\epsilon}_k + \frac{U}{4} > E$$

For comparison, the Green's function corresponding to the structure of Figure 1b is given (from eq 14) as

$$G_{11} = \frac{-\alpha}{\hat{E}_+ \hat{E}_- + i\alpha\Delta} \quad (23)$$

It follows that the conductance of this covalent two-site system, is

$$g_c = g_o \frac{\alpha^2 \Delta^2}{(\tilde{\epsilon}_k \alpha - \beta)^2 + \alpha^2 \Delta^2} \quad (24)$$

Then the ratio of g_s (the conductance in the single site circuit of Figure 1a) to the modified bridge of Figure 1b can be expressed as

$$\frac{g_s}{g_c} = 1 + \frac{\beta^2(\beta^2 - 2\alpha\tilde{\epsilon}_k)}{\alpha^2 \tilde{\epsilon}_k^2 + \alpha^2 \Delta^2} \quad (25)$$

In the limit $\beta^2 < 2\alpha\tilde{\epsilon}$ we observe that (assuming $\alpha > 0$)

$$\beta^2 < 2\alpha\tilde{\epsilon}_k \rightarrow g_s < g_c \quad (26)$$

so the covalent interaction between the bridging site and a second molecular entity, even if that second molecular entity does not directly couple to the electrodes, can increase the conductance. This is indeed seen in the charge-transfer structures calculated in ref 30.

For the simple models of Figure 1b,c, then, we have computed the conductances and shown that both modifications (the covalent one in Figure 1b and the Coulombic one of Figure 1c)

CONDUCTANCE RATIO
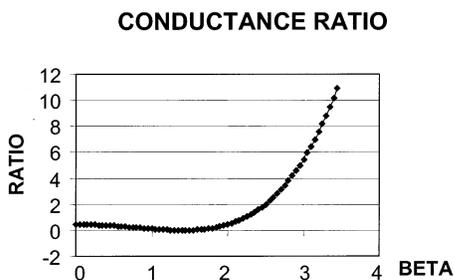
Figure 2. Ratio, $(g_s/g_c)/(g^{(n=0)}/g^{(n=1)})$, for the values $\alpha = 1$, $\tilde{\epsilon}_k = 2$, $n = 1/2$, $U = 40$ plotted as a function of $|\beta|$. The relative switching capability due to binding (Figure 1b) or gating (Figure 1c) clearly varies widely.

can modulate the transport. Consider now some vaguely realistic parameters such as

$$\tilde{\epsilon}_k = 2 \text{ eV}$$

$$U = 2 \text{ eV}$$

$$-\beta = 2 \text{ eV}$$

$$\alpha = 4 \text{ eV}$$

$$\Delta = 0.1 \text{ eV} \tag{27}$$

Under these conditions, a change in the population of the FET structure of Figure 1c from being fully unoccupied ($n = 0$) to being half occupied ($n = 1$) would give a conductance ratio of

$$\frac{g_g^{(n=1)}}{g_g^{(n=0)}} = \frac{4}{9} \tag{28}$$

By comparison, for this set of parameters, the change of the ratio of the transport through the single orbital species of Figure 1a to the two orbital species of Figure 1b is given by

$$\frac{g_s}{g_c} = \frac{1}{4} \tag{29}$$

The modulation ratios of the two situations compare as

$$\frac{g_s/g_c}{g_g^{(n=1)}/g_g^{(n=0)}} = \frac{1/4}{4/9} = \frac{9}{16} \tag{30a}$$

Under these conditions, the change using the Coulomb gate in Figure 1c is smaller than the covalent modification of Figure 1b. Upon decreasing the mixing with the adduct though, and going to $\beta = -1$, the ratio becomes

$$\frac{g_s/g_c}{g_g^{(n=1)}/g_g^{(n=0)}} = \frac{49/64}{4/9} \cong 1.70 \tag{30b}$$

Under these conditions, the FET type structure of Figure 1c leads to greater modification in the current than the covalent structure in Figure 1b.

More generally we find (from eqs 8, 14, 21, and 22)

$$\frac{g_s/g_c}{g_g^{(n=0)}/g_g^{(n)}} = \frac{(\alpha\tilde{\epsilon}_k - \beta^2) + \alpha^2\Delta^2}{\alpha^2\left(\tilde{\epsilon}_k + \frac{U}{2}\langle n \rangle\right)^2 + \alpha^2\Delta^2} \tag{31}$$

In Figure 2, we plot this as a function of $|\beta|$, for the reasonable values $\alpha = 1$, $\tilde{\epsilon}_k = 2$, $\langle n \rangle = 1/2$, $\Delta = 0.10$, and $U = 4$. Note that the relative abilities of gating and binding to modify current

can be varied smoothly from a ratio much less than unity to one that is much greater.

IV. Remarks

Characterization of current/voltage characteristics of molecular junctions remains in its infancy, both computationally and experimentally.[31-38] Still, some features have become clear. For large gaps and low temperatures, the transport in short molecular structures will be dominated by coherent, Landauer-type behavior (although at higher temperatures injection and thermalized transport should occur[24,25]). For large currents to exist, then, it is necessary to tune the energy levels so that the gaps can be reduced and the transport thereby increased.

Although the most obvious way to modify the energetics of the bridge is to use a gate electrode, the placement of such an electrode on top of a molecular scale wire is experimentally problematic. It is far easier to tune the levels by interaction with another chemical entity, for example, by charge-transfer interaction or covalent modification.

We demonstrate that, within a very simple single site picture, it is possible to show analytically that the currents can indeed be modified either by an external voltage gate or by chemical modification. The extent of such modification will vary depending on the energetics, the orbital mixings, the geometry of the new molecular species formed, and the voltage. Still, such modification is generally an applicable scheme for control of the current in molecular junctions.

References and Notes

(1) Dorogi, M.; Gomez, J.; Osifchin, R. G.; Andres, R. P.; Reifenberger, R.; *Phys. Rev.* **1995**, *B52*, 9071. Andres, R. P.; Bein, T.; Dorogi, M.; Feng, S.; Henderson, J. I.; Kubiak, C. P.; Mahoney, W.; Osifchin, R. G.; Reifenberger, R. *Science* **1996**, *272*, 1323. Hong, S.; Tian, W.; Henderson, J.; Datta, S.; Kubiak, C. P.; Reifenberger, R. *Superlat. Microstruct.* **2000**, *28*, 289.

(2) Hu, H.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435. Tans, S. J.; Devoret, M. H.; Dai, H.; Thess, A.; Smalley, R. E.; Geerligs, L. J.; Dekker, C. *Nature* **1997**, *474*, 474. Tans, S. J.; Verschueren, R. M.; Dekker, C. *Nature* **1998**, *393*, 49.

(3) Bockrath, M.; Cobden, D. H.; McEuen, P. L.; Chopra, N. G.; Zettl, A.; Thess, A.; Smalley, R. E. *Science* **1997**, *275*, 1922.

(4) Dai, H.; Wong, E. W.; Lieber, C. M. *Science* **1996**, *272*, 523.

(5) Lee, T.; Liu, J.; Dicke, J.; Andres, R. P.; Lauterbach, J.; Melloch, M. R.; McInturff, D.; Woodall, J. M.; Reifenberger, R. *Appl. Phys. Lett.* **1999**, *74*, 2869. Reed, M. A. *MRS Bull.* **2001**, *26*, 113. Chen, J.; Wang, W.; Reed, M. A.; Rawlett, A. M.; Price, D. W.; Tour, J. M. *Appl. Phys. Lett.* **2000**, *77*, 1224. Reichert, J.; Olds, R.; et al. *Phys. Rev. Lett.* **2002**, *176804*,.

(6) Cygan, M. T.; Dunbar, T. D.; Arnold, J. J.; Bumm, L. A.; Shedlock, N. F.; Burgin, T. P.; Jones, L., II; Allara, D. L.; Tour, J. M.; Weiss, P. S. *J. Am. Chem. Soc.* **1998**, *120*, 2721. Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. B.; Jones, L., II; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1323. Donhauser, Z. J.; et al. *Science* **2001**, *292*, 2303.

(7) Joachim, C.; Gimzewski, J. K.; Schlittler, R. R.; Chavy, C.; *Phys. Rev. Lett.* **1995**, *74*, 2102. Langlais, V. J.; Schlittler, R. R.; Tang, H.; Gourdon, A.; Joachim, C.; Gimzewski, J. K. *Phys. Rev. Lett.* **1999**, *83*, 2809. Kergueris, C.; et al. *Phys. Rev. B* **1999**, *59*, 12505.

(8) Leatherman, G.; et al. *J. Phys. Chem. B* **1999**, *103*, 4006. Cui, X. D.; Primak, A.; Zarate, X.; et al. *Science* **2001**, *294* 571–574.

(9) Clark, L.; Wybourne, M.; et al. *J. Vac. Sci. Technol.* **1997**, *B15*, 2925.

(10) Haag, R.; Rampi, M. A.; Holmlin, M. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 7895. Slowinski, K.; Chamberlain, R. V.; Mitler, C. J.; Majda, M. *J. Am. Chem. Soc.* **1997**, *119*, 11910.

(11) Mazur, U.; Hipps, K. W. *J. Phys. Chem.* **1995**, *99*, 6684.

(12) Schon, J. H.; Meng, H.; Bao, Z. N. *Science* **2001**, *294*, 2138–2140.

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(13) Metzger, R. M. *Acc. Chem. Res.* **1999**, *32*, 950. Zhou, C. W.; Kong, J.; Yenilmez, E.; Dai, H. *Science* **2000**, *290*, 1552.

(14) Datta, S. *Electronic Transport in Mesoscopic Systems*; Cambridge University Press: Cambridge, U.K., 1995. Samanta, M. P.; Tian, W.; Datta, S.; Henderson, J. I.; Kubiak, C. P. *Phys. Rev.* **1996**, *B53*, R7626. Datta, S. *Superlat. Microstruct.* **2000**, *28*, 253. Hong, S.; et al. *Superlat. Microstruct.* **2000**, *28*, 289.

(15) Sautet, P.; Joachim, C. *Chem. Phys. Lett.* **1988**, *153*, 511. Joachim, C.; Vinuesa, J. F. *Europhys. Lett.* **1996**, *33*, 635. Magoga, M.; Joachim, C.; *Phys. Rev. B* **1998**, *57*, 1820.

(16) Hall, L. E.; Reimers, J. R.; Hush, N. S.; Silverbrook, K. *J. Chem. Phys.* **2000**, *112*, 1510.

(17) Petrov, E. G.; Tolokh, I. S.; Demidenko, A. A.; Gorbach, V. V. *Chem. Phys.* **1995**, *193*, 237. Sumetskii, M. *Phys. Rev. B* **1993**, *48*, 4586; Sumetskii, M. *J. Phys. Condens. Matter* **1991**, *3*, 2651. Todorov, T. N.; Sutton, A. P. *Phys. Rev. Lett.* **1993**, *70*, 2138. Bratkovsky, A. M.; Sutton, A. P.; Todorov, T. N. *Phys. Rev. B* **1995**, *52*, 5036. Onipko, A.; Klymenko, Y.; Malysheva, L. *Phys. Rev.* **2000**, *B62*, 10480. Ness, H.; Shevlin, S. A.; Fisher, A. J. *Phys. Rev.* **2001**, *63*. Ness, H.; Fisher, A. J. *Phys. Rev. Lett.* **1999**, *83*, 452.

(18) Derosa, P. A.; Seminario, J. M. *J. Phys. Chem. B* **2001**, *105*, 471. Baer, R.; Gould, R. *J. Chem. Phys.* **2001**, *114*, 3385. Pantelides, S. T.; DiVentra, M.; Lang, N. D. *Physica* **2001**, *B296,* 72.

(19) Emberly, E. G.; Kirczenow, G. *Phys. Rev. B* **1998**, *58*, 10911; **2000**, *B62*, 10451.

(20) Mujica, V.; et al. *Adv. Chem. Phys.* **1999**, *107*, 403. Mujica, V.; Kemp, M.; Ratner, M. A. *J. Chem. Phys.* **1994**, *101*, 684. Mujica, V.; Kemp, M.; Ratner, M. A. *J. Chem. Phys.* **1994**, *101*, 6849. **1994**, *101*, 6856. Mujica, V.; Kemp, M.; Roitberg, A.; Ratner, M. *J. Chem. Phys.* **1996**, *104*, 7296. Yaliraki, S. N.; Kemp, M.; Ratner, M. A. *J. Am. Chem. Soc.* **1999**, *121*, 3428. Yaliraki, S. N.; Roitberg, A. E.; Gonzalez, C.; Mujica, V.; Ratner, M. A. *J. Chem. Phys.* **1999**, *111*, 50. Yaliraki, S. N.; Ratner, M. A. *Ann. N. Y. Acad. Sci.*, in press. Xue, Y.; Datta, S.; Ratner, M. A. *J. Chem. Phys.* **2001**, *115*, 4292.

(21) (a) Lieber, C. M. *Sci. Am.* **2001**, *285*, 58−64. Derycke, V.; Martel, R.; Appenzeller, J.; et al. *Nano Lett.* **2001**, *1*, 453−456. (b) Bachtold, A.; Hadley, P.; Nakanishi, T.; et al. *Science* **2001**, *294*, 1317−1320. Huang, Y.; Duan, X. F.; Cui, Y.; et al. *Science* **2001**, *294*, 1313−1317. (c) Collier, C. P.; Wong, E. W.; et al. *Science* **1999**, *285*, 391.

(22) Wu, D. G.; Ashkenasy, G.; et al. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 4496.

(23) Datta, S., submitted for publication.

(24) Segal, D.; Nitzan, A.; Davis, W. B.; Wasielewski, M. R.; Ratner, M. A. *J. Phys. Chem. B* **2000**, *104*, 3817−3829.

(25) For a comprehensive review of the theoretical models to date: see Nitzan, A. *Annu. Rev. Phys. Chem.* **2001**, *52*, 681.

(26) Newns, D. M. *Phys. Rev.* **1969**, *178*, 1123.

(27) Meir, Y.; Wingreen, N. S. *Phys. Rev. Lett.* **1992**, *68*, 2512.

(28) Ward, M. D. *J. Chem. Educ.* **2001**, *78*, 321; Mao, Y. Ph.D. Thesis, Northwestern University, 2000.

(29) Linderberg, J.; Öhrn, Y. *Propagators in Quantum Chemistry*; Academic: London, 1974). The Hubbard model on which this equation is based is the limit of the PPP model that holds when all Coulomb repulsions except on a single site are set to zero. It has been shown quite clearly that the Hubbard model, as used by the physical community, is inadequate for describing something as straightforward as the optical spectrum of benzene (which is described very well by the PPP model). In the particular case discussed in this manuscript, we actually deal only with a single site structure, so the difference between PPP and Hubbard vanishes. More generally, however, the Hubbard model is not quantitatively useful for molecular problems.

(30) Elicker, T. S.; Binette, J. S.; Evans, D. G. *J. Phys. Chem.* **2001**, *B105*, 370.

(31) Reed, M. A. *Proc. IEEE* **1999**, *87*, 652.

(32) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791.

(33) Ellenbogen, J. C.; Love, J. C. *Proc. IEEE* **2000**, *88*, 386.

(34) Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature* **2000**, *408*, 541.

(35) *Molecular Electronics: Science and Technology*; Aviram, A., Ratner, M. A., Eds.; Annals of the New York Academy of Science; New York Academy of Sciences: New York, 1998; Vol. 852. *Molecular Electronics*; Jortner, J.; Ratner, M. A.; Eds.; Blackwell: London, 1998. *Molecular Electronics*; Aviram, A., Mujica, V., Ratner, M. A., Eds.; Annals of the New York Academy of Science; in press. Petty, M. C.; Bryce, M. R.; Bloor, D. *Molecular Electronics*; Oxford University Press: Oxford, U.K., 1995.

(36) Andres, R. P.; Datta, S.; Janes, D. B.; Kubiak, C. P.; Reifenberger, R. In *The Handbook of Nanostructured Materials and Nanotechnology*, Nalwa, H. S., Ed.; Academic Press: New York, 1998.

(37) Ratner, M. A. *Mater. Today* 2002, Feb, 20.

(38) Kwok, K. S.; Ellenbogen, J. C. *Mater. Today* 2002, Feb, 28.