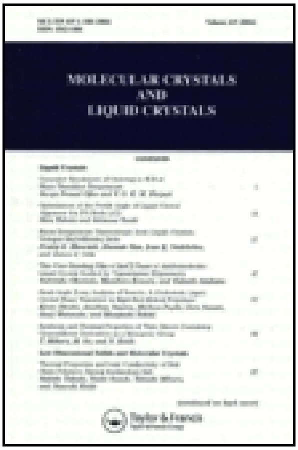

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Tunneling Through Localized States of a Single Molecule

E. G. Petrov [a]

[a] Bogolyubov Institute for Theoretical Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine

Version of record first published: 31 Aug 2006

To cite this article: E. G. Petrov (2005): Tunneling Through Localized States of a Single Molecule, Molecular Crystals and Liquid Crystals, 426:1, 49-58

To link to this article: http://dx.doi.org/10.1080/15421400590890714

Mol. Cryst. Liq. Cryst., Vol. 426, pp. 49–58, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590890714

Tunneling Through Localized States of a Single Molecule

E. G. Petrov
Bogolyubov Institute for Theoretical Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine

A mechanism of formation of an interelectrode current based on a resonant tunneling through localized electronic levels of a single molecule is proposed. It is shown that an external electric field applied to a molecule brings to the transformation of extended molecular orbitals into localized molecular orbitals. It results in the essential modification of nonlinear current-voltage characteristics of the molecule. Local voltage division factors reflecting the partial voltage biases within a molecule are specified, and an analytic expression for the $I-V$ characteristics of a two-site molecule is derived.

Keywords: electron transfer; localized levels; single molecule

1. INTRODUCTION

Recent experimental results on conductivity of single molecules and molecular wires [1–4] indicate a strong deviation of the current–voltage ($I-V$) characteristics from the Ohmic regime typical of metallic wires. Some experiments have also shown rectification properties of a single molecule [5–8]. To explain the experiments, different modifications of the Landauer–Buttiker approach are employed along with the molecular orbital theory (cf., e.g., [2,9–14]). In such an approach, the molecule is identified with an electronic device which is connected to electronic reservoirs, i.e. electrodes (substrate and tip, source and drain). Typically, electron transfer through the molecule is studied as a scattering process while the energy characteristics of the molecule are associated with the extended lowest unfilled and highest occupied

This work was supported in part by the NASU program on Fundamental Researches as well as VW Stiftung (priority area *Intra- and Intermolecular Electron Transfer*).

Address correspondence to E. G. Petrov, Bogolyuber Institute for Theoretical Physics, National Academy of Science of UK, Metrologichna Str., 14-B Kiev, 03143, Ukraine. Tel.: 380-44-266-9141, Fax: 380-44-266-5998, E-mail: epetrov@bitp.kiev.ua

molecular orbitals (LUMOs and HOMOs). The basic expression for the current reads as

$$I = \frac{2e}{h}\int_{-\infty}^{\infty} dET(E,V)[f(E-\mu_L) - f(E-\mu_R)] \approx \frac{2e}{h}\int_{\mu_L}^{\mu_R} dET(E,V) \quad (1)$$

where e is the electron charge $(e < 0)$, $f(x)$ is the Fermi function, $\mu_{L(R)}$ is the electrochemical potential of the left (right) electrode, and

$$T(E,V) = Tr\big(\hat{\Gamma}^{(L)}(E,V)\hat{G}(E,V)\hat{\Gamma}^{(R)}(E,V)\hat{G}^{+}(E,V)\big) \quad (2)$$

is the transmission function. It is determined through the matrices $\hat{\Gamma}^{(L)}(E,V)$ and $\hat{\Gamma}^{(R)}(E,V)$ defined in terms of the self-energies and through the single-particle Green function of a molecule $\hat{G}(E,V)$ $(\hat{G}^{+}(E,V)$ is its adjoint). In the case of a symmetric molecule having strongly delocalized MOs, the molecular levels are shifted under an external bias voltage V in such a way that one can introduce the voltage division factor η identical for all levels . In supposition of negligible dependence of $T(E,V)$ on V, Eq. (1) can be represented in a simpler form [4,5]

$$I = -\frac{2e}{h}\int_{E_F+eV\eta}^{E_F+eV(1-\eta)} T(E)dE \quad (3)$$

so that a molecular conductance $g(V) = dI/dV$ reads

$$g(V) \approx g_0[\eta T(E_F + eV\eta) + (1-\eta)T(E_F + eV(1-\eta))], \quad (4)$$

where $g_0 = e^2/\pi\hbar = \left(12.8\Omega^{-1}\right)$ is the quantum unit of conductance.

For a symmetric molecule which, in turn, is symmetrically contacted to the electrodes, one has to substitute $\eta = 1/2$. In the other cases, the fraction η differs from 1/2 [8,15].

If a molecule has strongly localized levels, one cannot introduce a unique fraction η valid for all MOs. This means that the reduction of the basic form (1) to a simplified one, Eq. (3), becomes impossible. The goal of the present communication is to derive the form of an interelectrode current in a case where the applied voltage is able to transform the localized MOs into the delocalized MOs and vice versa.

II. MODEL AND BASIC EQUATIONS

To demonstrate the modification of an interelectrode current mediated by a single molecule, we restrict ourself by the case of a linear molecule which has N sites of electron localization divided by the bridging groups (bonds) (cf. Fig. 1). LUMO and HOMO energies of these groups

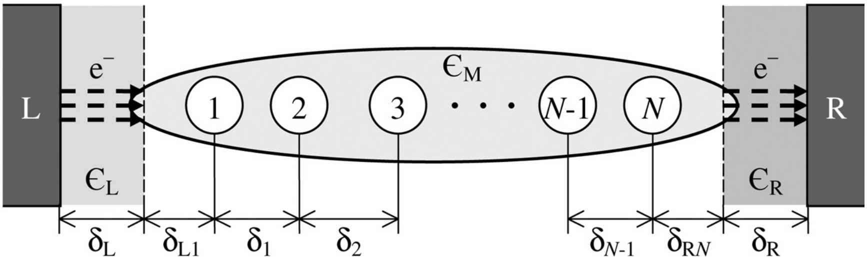

FIGURE 1 Position of the N-site molecule between the electrodes. Quantities δ_L denote the characteristic distances in the device, $\in_L$ ($\in_R$) and $\in_M$ are the permittivities of the medium near the left (right) electrode and within the molecule, respectively.

(bonds) are assumed to be positioned far from the Fermi energy E_F and thus participate in the electron transfer (ET) process as virtual levels forming superexchange couplings between localized MOs. Owing to such a superexchange coupling, the localized MOs $|m\lambda_m\rangle$ ($m = 1, 2, \ldots, N$ is the position of a site, λ_m is one of the localized MOs belonging to the site m) are transformed to the extended MOs of the whole molecule, $|\mu\rangle = \sum_{m\lambda_m} u_\mu(m\lambda_m)|m\lambda_m\rangle$. In the framework of the model under consideration, just these extended MOs (with energies $\tilde{\varepsilon}_\mu$) give the main contribution to the conductance. Such a model has been already utilized to describe the formation of an inelastic current through a molecular wire [7–19]. Here, we consider the elastic tunneling through a molecule noting that, due to the interaction with electrodes, the energies $\tilde{\varepsilon}_\mu$ have imaginary parts so that $\tilde{\varepsilon}_\mu = \varepsilon_\mu - i\gamma_\mu$. To evaluate the transmission function, Eq. (2), we rewrite it in the matrix form as

$$T(E, V) = \sum_{\mu_1\mu_2}\sum_{\mu_1'\mu_2'} \Gamma^{(R)}_{\mu_1\mu_2} G_{\mu_2\mu_2'} \Gamma^{(L)}_{\mu_2'\mu_1'} G^{+}_{\mu_1'\mu_1}, \tag{5}$$

where the imaginary part of the self-energy,

$$\Gamma^{(s)}_{\mu\mu'} = 2\pi \sum_{\mathbf{k}} V^{*}_{s\mathbf{k}\mu} V_{s\mathbf{k}\mu'} \delta(E - E_{s\mathbf{k}}), \tag{6}$$

is defined by molecule-electrode couplings $V_{s\mathbf{k}\mu}$ as well as conduction band energies $E_{s\mathbf{k}}$ ($s = L, R$; $\mathbf{k}$ is the wave vector). The further simplification is possible when a molecular Hamiltonian H_M that specifies a Green function $G(E, V) = (E - H_M)^{-1}$ is represented in the basis of the extended states $|\mu\rangle$. This yields $G_{\mu\mu'} = \delta_{\mu\mu'}\left(E - \tilde{\varepsilon}_\mu\right)^{-1}$ and thus

$$T(E,V) = \sum_{\mu\mu'} \Gamma^{(R)}_{\mu\mu'} \frac{1}{E - \tilde{\varepsilon}_{\mu'}} \Gamma^{(L)}_{\mu'\mu} \frac{1}{E - \tilde{\varepsilon}^{*}_{\mu}}. \tag{7}$$

If only the terminal sites of the molecule are coupled to the electrodes, then quantities (6) can be represented as

$$\Gamma^{(L(R))}_{\mu\mu'} = \sum_{\lambda_{1(N)}\lambda'_{1(N)}} u^{*}_{\mu'}\Big(1(N)\lambda'_{1(N)}\Big) u_{\mu}\big(1(N)\lambda_{1(N)}\big) \Gamma^{(L(R))}_{\lambda_{1(N)}} \tag{8}$$

where we have introduced the self-energies

$$\Gamma^{(L(R))}_{\lambda_{1(N)}\lambda'_{1(N)}} = 2\pi \sum_{k} V^{*}_{L(R)k\lambda'_{1(N)}} V_{L(R)k\lambda_{1(N)}} \delta\big(E - E_{L(R)k}\big) \tag{9}$$

referred to the terminal molecular sites $m = 1$ and $m = N$. Formula (7) is essentially simplified when only a single MO per site is mainly involved in the ET process (one can imagine the sites with a very large gap between the levels, for instance the sites containing the metallic ions). In this case,

$$T(E,V) = 4\Delta^{(L)}(E)\Delta^{(R)}(E) \left| \sum_{\mu} \frac{u_{\mu}(1) u^{*}_{\mu}(N)}{E - \tilde{\varepsilon}_{\mu}} \right|^{2}, \tag{10}$$

where

$$\Delta^{(L(R))} = \pi \sum_{k} \left|V_{L(R)k}\right|^{2} \delta\big(E - E_{L(R)k}\big) \tag{11}$$

is the half-width of the localized energy level related to the left (right) edge site of the molecule. Formula (10) is extremaly convenient to demonstrate the modification of the interelectrode current caused by a voltage variation. In particular, at strong intersite electronic couplings $V_{mm\pm1}$ within the molecule, when the difference $\left|\varepsilon^{(0)}_{\mu} - \varepsilon^{(0)}_{\mu'}\right|$ exceeds strongly the widths $\Delta^{(L)}$ and $\Delta^{(R)}$ as well as the gaps $|E_m - E_n|$ (E_m is the MO's energy of the molecular site m), one can derive $\varepsilon_{\mu} \approx \varepsilon^{(0)}_{\mu} + \Delta\varepsilon_{\mu}$. The quantity $\varepsilon^{(0)}_{\mu}$ corresponds to the extended zero-bias MO's energy, while $\Delta\varepsilon_{\mu} = \sum_m \left[u^{(0)}_{\mu}(m)\right]^{2} \Delta E^{(0)}_{m}$ is the addition caused by the voltage V. Bearing in mind that quantities $u^{(0)}_{\mu}(m)$ define a zero-bias transform matrix and that $E^{(0)}_{m} = eV\delta_m/\in_M l$ is the energy gap formed by a site-to-site voltage bias, it becomes possible to show that $\Delta\varepsilon_{\mu} = eV\eta$, where $\eta = (l_L + (1/2)l_m)/l$ and $\in_M$ is the permittivity of the medium around the molecule. Here, $l = l_L + l_M + l_R$ is the effective electrode-electrode distance, $l_L = \delta_L / \in_L$ and $l_R = \delta_R / \in_R$ are the effective distances between the terminal molecular sites 1 and N and the respective left and right electrodes, while $l_M = (\delta_{L1} + \delta_1 + \cdots + \delta_{N-1} + \delta_{RN}) / \in_M$ is the effective molecular length (note that actual distances in the device are denoted by symbols δ_j, cf. Fig. 1). It is clear that the fraction η is equal to 1/2 only for the symmetric case ($\delta_{L1} = \delta_{RN}, \delta_L = \delta_R, \in_L = \in_R$). Taking into account that the identity $\sum_\mu \left[u_\mu(1) u_\mu^*(N) / (E - \tilde{\varepsilon}_\mu)\right] = \prod_{m=1}^{N-1} V_{mm+1} / \prod_\mu (E - \tilde{\varepsilon}_\mu)$ is satisfied even for an irregular linear chain [20] and bearing in mind that, in the case under consideration, $\varepsilon_\mu \approx \varepsilon_\mu^{(0)} + eV\eta$, we come to relation (3) with

$$T(E) = 4\Delta^{(L)}\Delta^{(R)} \frac{\prod_{m=1}^{N-1} |V_{mm+1}|^2}{\prod_\mu \left[\left(E - \varepsilon_\mu^{(0)}\right)^2 + \left(\gamma_\mu^{(0)}\right)^2\right]} \tag{12}$$

Here, the energy width $\gamma_\mu^{(0)}$ is derived at zero-bias voltage. [Following the most theoretical approaches (cf., for instance, [2,4,5,9,13], we omit (hereafter) the dependence of the widths $\Delta^{(L)}$ and $\Delta^{(R)}$ on the transmission energy E.]

Formula (12) is true until a voltage bias does not shift strongly the energy positions of localized MOs and thus does not destroy the extended MOs of the molecule. At large V, the extended MOs and energies $\tilde{\varepsilon}_\mu$ are transformed into the localized MOs and energies E_m, respectively (cf. Fig. 2). This circumstance can bring to the essential modification of the $I-V$ characteristics of the molecule. Below, we consider this important problem in more details.

III. I–V CHARACTERISTICS OF A TWO-SITE MOLECULE

To gain analytic simplicity, we consider the formation of a current through a molecule with only two sites of electron localization which are connected by a superexchange coupling V_{12}. The energy of each localized state m can be written as

$$\tilde{E}_1 = E_1 - i\Delta^{(L)}, \qquad \tilde{E}_2 = E_2 - i\Delta^{(R)}, \tag{13}$$

where (the right electrode is assumed to be held at a zero voltage)

$$E_1 = E_1^{(0)} + eV(1 - \eta_1), \qquad E_2 = E_2^{(0)} + eV\eta_2. \tag{14}$$

In Eq. (14), the quantities $E_1^{(0)}$ and $E_2^{(0)}$ include the real parts of the corresponding self-energies, and we have also introduced the local voltage division factors (cf. Fig. 1)

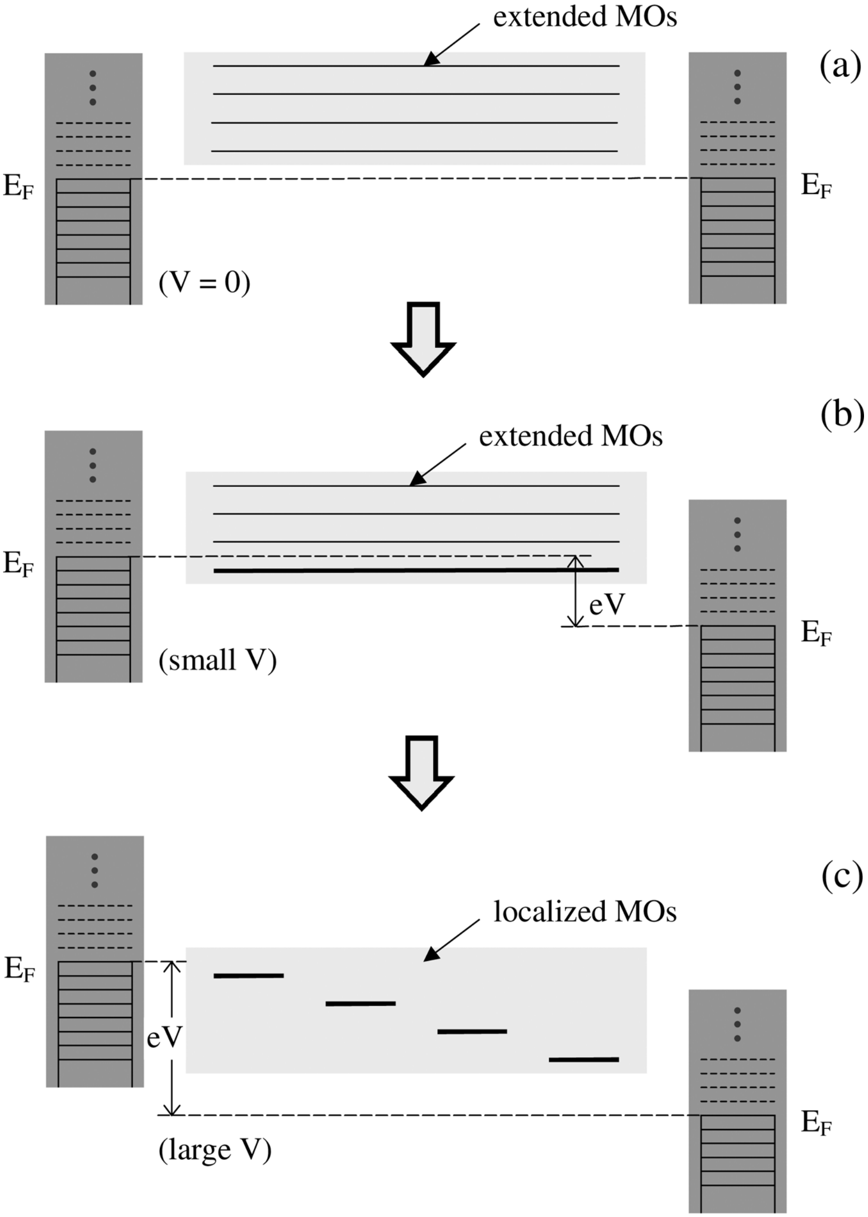

FIGURE 2 Transformation of the extended molecular states into the localized molecular states under the applied voltage.

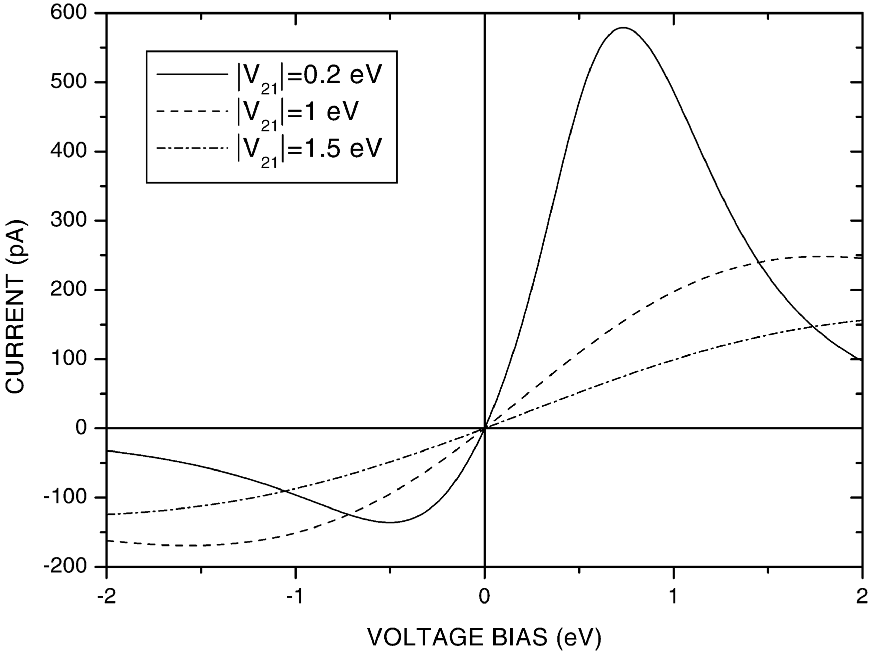

FIGURE 3 Current–voltage characteristics of the two-site molecule. The calculations are based on Eq. (20) by choosing the following parameters: $E_1^{(0)} - E_F = 0.3\,eV$, $E_2^{(0)} - E_F = 0.5\,\text{eV}$, $\eta_1 = 0.2$, $\eta_2 = 0.1$, $\Delta^{(L)} = 0.1$, $\Delta^{(R)} = 0.2$.

$$\eta_1 = (l_L + l_{L1})/l, \qquad \eta_2 = (l_R + l_{R2})/l. \tag{15}$$

As to the energy width $\Delta^{(L(R))}$, it is determined by Eq. (11). Introducing the symbols $\mu = +$ and $\mu = -$ for the upper and lower extended MOs, respectively, we derive

$$\begin{aligned} \tilde{\varepsilon}_\pm &= \varepsilon_\pm - i\gamma_\pm, \qquad \varepsilon_\pm = \frac{1}{2}(E_1 + E_2 \pm \rho\cos\varphi), \\ \gamma_\pm &= \frac{1}{2}\left(\Delta^{(L)} + \Delta^{(R)} \mp \rho\sin\varphi\right) \end{aligned} \tag{16}$$

where (we note that $\Delta_{21} = \Delta^{(R)} - \Delta^{(L)}$, $\Delta E_{21} \equiv E_2 - E_1$)

$$\tan\varphi = \frac{\rho^2 - \left(D^2 - \Delta_{21}^2\right)}{2\Delta_{21}\,\Delta E_{21}}, \tag{17}$$

and

$$\rho = \left[\left(D^2 - \Delta_{21}^2\right)^2 + 4\Delta_{21}^2\,\Delta E_{21}^2\right]^{1/4}, \qquad D = \left[\Delta E_{21}^2 + 4|V_{21}|^2\right]^{1/2}. \tag{18}$$

Now, substituting the transmission function

$$T(E,V) = \frac{4\Delta^{(L)}\Delta^{(R)}|V_{12}|^2}{\left[(E-\varepsilon_+)^2+\gamma_+^2\right]\left[(E-\varepsilon_-)^2+\gamma_-^2\right]} \tag{19}$$

in the basic equation (1), we derive the following analytic form for the interelectrode current:

$$\begin{aligned} I = &-\frac{e}{\pi\hbar}\frac{\Delta^{(L)}\Delta^{(R)}|V_{12}|^2}{\gamma_+\gamma_-} \\ &\times\Bigg\{\Bigg[\frac{1}{(\varepsilon_+-\varepsilon_-)-i(\gamma_+-\gamma_-)}\ln\left[\frac{[(\varepsilon_--E_F)-i\gamma_-]\left[(\varepsilon_+-E_F-eV)-i\gamma_+\right]}{[(\varepsilon_--E_F-eV)-i\gamma_-]\left[(\varepsilon_+-E_F)-i\gamma_+\right]}\right] \\ &-\frac{1}{(\varepsilon_+-\varepsilon_-)-i(\gamma_++\gamma_-)}\ln\left[\frac{[(\varepsilon_--E_F)+i\gamma_-]\left[(\varepsilon_+-E_F-eV)-i\gamma_+\right]}{[(\varepsilon_--E_F-eV)+i\gamma_-]\left[(\varepsilon_+-E_F)-i\gamma_+\right]}\right]\Bigg] + c.c.\Bigg\}. \end{aligned} \tag{20}$$

IV. RESULTS AND DISCUSSION

The derivation of the analytic form for both the transmission function, Eq. (19), and the interelectrode current, Eq. (20), valid for a molecule with two active sites can be referred to the main result of the present communication. It is important that expressions (19) and (20) allows one to analyze the $I-V$ characteristics at an arbitrary relation between the self-energies $\Delta^{(L)}$ and $\Delta^{(R)}$, zero-bias energy gap $E_2^{(0)} - E_1^{(0)}$, and site-site coupling V_{21}. Here, we only discuss the role of the latter factor responsible for the creation of extended MOs. Figure 3 manifests a serious modification of the $I-V$ characteristics caused by a site-site coupling. At large $|V_{21}|$, the current exhibits a monotonous dependence on voltage V, while at a small site-site coupling, the current behaviour acquires a specific feature. In particular, at a positive voltage, the current reaches a maximal value. In addition, one can observe the rectification effect caused by an asymmetric position of the zero-bias energy levels $E_1^{(0)}$ and $E_2^{(0)}$ relative to the

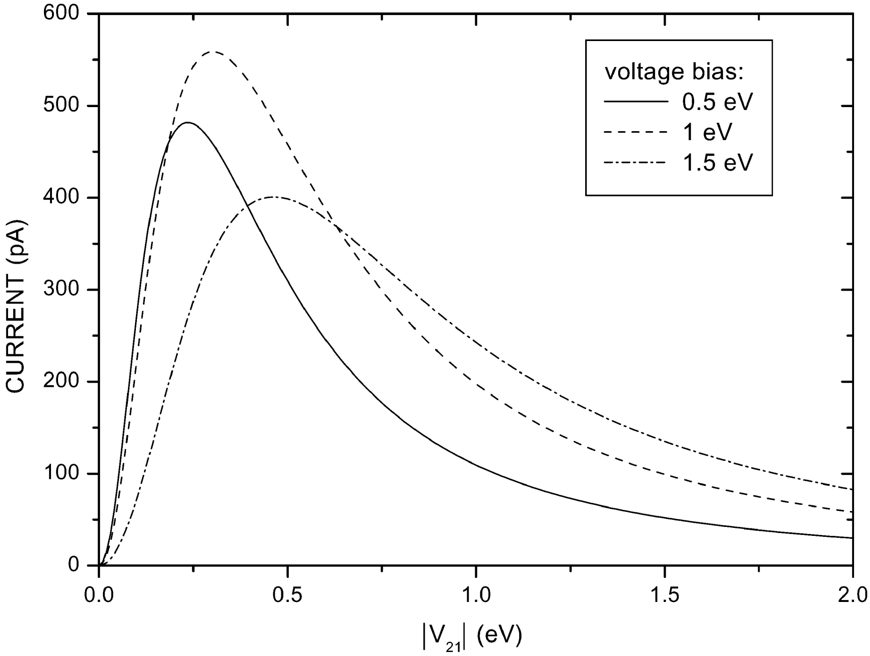

FIGURE 4 Current vs. inter-site coupling. The calculations have been done with the same parameters as in Figure 3.

Fermi level. The role of the site-site coupling is represented more clearly in Figure 4. Our results allows us to conclude that the localization of molecular states favors the molecular rectification effect.

REFERENCES

[1] Reed, M. (1999). *Proc. IEEE*, *87*, 652.
[2] Nitzan, A. (2001). *Annu. Rev. Phys. Chem.*, *52*, 681.
[3] Nitzan, A. & Ratner, M. (2003). *Science*, *300*, 1384.
[4] Zahid, F., Paulsson, M., & Datta, S. (2003). Electron conductance through molecules. In: *Advanced Semiconductors and Organic Nano–techniques*, H. Morkos (Ed.), Academic Press: New York, Chapter 2, 41.
[5] Tian, W., Datta, S., Hong, S., Reifenberger, R., Henderson, J. I., & Kubiak, C. P. (1998). *J. Chem. Phys.*, *111*, 6997.
[6] Weber, H. B., Reichert, J., Weigend, F., Ochs, R., Beckmann, D., Mayor, M., Ahlrichs, R., & Lohneysen, V. H. (2002). *Chem. Phys.*, *281*, 113.
[7] Chen, J. & Reed, M. A. (2002). *Chem. Phys.*, *281*, 127.
[8] Krzeminski, C., Delerue, C., Allan, G., & Vuillaume, D. (2001). *Phys. Rev. B*, *64*, 085405-1.

[9] Hall, L. E., Reimers, J. R., Hush, N. S., & Silverbrook, K. (2000). *J. Chem. Phys.*, *112*, 1510.

[10] Peterson, I. R., Vuillaume, D., & Proehl, H. (2002). *Phys. Rev. B*, *65*, 245422-1.

[11] Chen, H., Lu, J. Q., Wu, J., Note, R., & Kawazoe, Y. (2003). *Phys. Rev. B*, *67*, 113408-1.

[12] Mujica, V., Nitzan, A., Datta, S., Ratner, M. A., & Kubiak, C. P. (2003). *J. Phys. Chem. B*, *107*, 91.

[13] Di Ventra, M., Lang, N. D., & Pantelides, S. T. (2002). *Chem. Phys.*, *281*, 189.

[14] Mair, Y. & Wingreen, N. S. (1992). *Phys. Rev. Lett.*, *68*, 2512.

[15] Taylor, J., Brandbyge, M., & Stokbro, K. (2002). *Phys. Rev. Lett.*, *89*, 13830-1.

[16] Petrov, E. G. & Hanggi, P. (2001). *Phys. Rev. Lett.*, *86*, 2862.

[17] Petrov, E. G., May, V., & Hanggi, P. (2002). *Chem. Phys.*, *281*, 211.

[18] Petrov, E. G., May, V., & Hanggi, P. (2004). *Chem. Phys.*, *296*, 251.

[19] Petrov, E. G., Tolokh, I. S., Demidenko, A. A., & Gorbach, V. V. (1995). *Chem. Phys.*, *193*, 237.