Molecular transport junctions: Current from electronic excitations in the leads

Michael Galperin,[1] Abraham Nitzan,[2] and Mark A. Ratner[1]

[1]*Department of Chemistry and Nanotechnology Center, Northwestern University, Evanston IL 60208*
[2]*School of Chemistry, The Sackler Faculty of Science, Tel Aviv University, Tel Aviv 69978, Israel*
(Dated: November 18, 2005)

Using a model comprising a 2-level bridge connecting free electron reservoirs we show that coupling of a molecular bridge to electron-hole excitations in the leads can markedly effect the source-drain current through a molecular junction. In some cases, e.g. molecules that exhibit strong charge transfer transitions, the contribution from electron-hole excitations can exceed the Landauer elastic current and dominate the observed conduction.

Introduction. Electron transport in molecular tunnel junctions has been the focus of intense recent research[1,2,3,4]. Theoretical modeling of tunnel conduction[5,6] starts from Hamiltonians that contain electron transfer (tunneling) interactions between molecule and leads as essential elements for current transport in such junctions. At the same time, energy transfer interactions — excitation/de-excitation of the molecule accompanied by electron-hole (EH) pair annihilation/creation in the metal — are known to strongly affect the lifetime of excited molecules near metal surfaces[7]. An essential difference between these interactions is that electron transfer is a tunneling process that depends exponentially on the molecule-metal distance, while energy transfer is associated with dipolar coupling that scales like the inverse cube of this distance, and can therefore dominate at larger distances.

How will such dipolar interactions affect the conduction properties of molecular junctions? Here we address this question by using the non-equilibrium Green function (NEGF) formalism to derive an expression for the conduction in junction model that contains both electron and energy transfer interactions, then analyze several examples with reasonable parameters. We conclude that current caused by electron-hole excitations in the leads may be significant, sometimes even dominant, in situations when strong asymmetry, of a particular type explained below, in the molecule-lead coupling is present. As a simple extreme example consider the case where the highest occupied molecular orbital (HOMO) is coupled only to one lead, while the lowest unoccupied molecular orbital (LUMO) is coupled only to the other. Such a junction cannot pass current (in the absence of electronic correlations) if the dipolar interaction is absent. Realistic situations will not be that extreme, still whenever the HOMO-LUMO transition is of the charge transfer type, we expect some degree of such asymmetry. We have recently shown[8] that such situations may give rise to light induced current under zero voltage. We show below that also the current-voltage characteristic of such junctions is strongly affected by dipolar energy transfer interactions between molecule and leads.

Model and Method. We consider a tunneling junction consisting of a molecule positioned between two metal contacts (L and R). The molecule is represented by its highest occupied molecular orbital (HOMO), $|1>$, and lowest unoccupied molecular orbital (LUMO), $|2>$, with energies ε_1 and ε_2 and gap $\varepsilon_{21} = \varepsilon_2 - \varepsilon_1$. The contacts are assumed to be free electron reservoirs, each at its own equilibrium, characterized by electronic chemical potentials μ_L and μ_R, where the difference $\mu_L - \mu_R = e\Phi$ is the imposed voltage. The corresponding Hamiltonian is

$$\hat{H} = \hat{H}_0 + \hat{V}_M + \hat{V}_N \tag{1}$$

$$\hat{H}_0 = \sum_{m=1,2} \varepsilon_m \hat{c}_m^\dagger \hat{c}_m + \sum_{k \in \{L,R\}} \varepsilon_k \hat{c}_k^\dagger \hat{c}_k \tag{2}$$

$$\hat{V}_M = \sum_{K=L,R} \sum_{m=1,2; k \in K} \left(V_{km}^{(MK)} \hat{c}_k^\dagger \hat{c}_m + \text{H.c.} \right) \tag{3}$$

$$\hat{V}_N = \sum_{K=L,R} \sum_{k \neq k' \in K} \left(V_{kk'}^{(NK)} \hat{c}_k^\dagger \hat{c}_{k'} \hat{c}_2^\dagger \hat{c}_1 + \text{H.c.} \right) \tag{4}$$

where H.c. denotes Hermitian conjugate. Here the operators $\hat{c}_m$ and $\hat{c}_m^\dagger$ are annihilation and creation operators of electrons in the bridge ($m = 1, 2$), while $\hat{c}_k$ and $\hat{c}_k^\dagger$ are annihilation and creation operators of electrons in the leads. The Hamiltonian $\hat{H}_0$ is a sum of terms that correspond to the isolated molecule (represented by its HOMO-LUMO levels in our model) and free contacts. $\hat{V}_M$ describes the electron transfer (tunneling) process between these subsystems. This is the term usually employed to treat current in the biased junction. $\hat{V}_N$ represents coupling of the molecular HOMO-LUMO transition to electron-hole excitations in the contacts and is often used in models of energy transfer between the molecule and the contacts.

In the Keldysh NEGF formalism[9] the steady-state current through the junction is given by[10]

$$I_{sd} = \pm \frac{e}{\hbar} \int \frac{dE}{2\pi} \text{Tr} \left[\mathbf{\Sigma}_{\mathbf{MK}}^< (E) \mathbf{G}^> (E) - \mathbf{\Sigma}_{\mathbf{MK}}^> (E) \mathbf{G}^< (E) \right] \tag{5}$$

calculated at the left ($K = L$ with "+" sign) or right ($K = R$ with "−" sign) contact, where the direction from left to right chosen positive.

The lesser and greater Green functions, $G^{<,>}$, needed in (5) can be obtained from the Keldysh equation

$$\mathbf{G}^{<,>}(E) = \mathbf{G}^{\mathbf{r}}(E) \, \mathbf{\Sigma}^{<,>}(E) \, \mathbf{G}^{\mathbf{a}}(E) \tag{6}$$

where the retarded and advanced Green functions, $G^{r,a}$, are given by the Dyson equation

$$\mathbf{G^r}(E) = [E - \mathbf{H_0^m} - \mathbf{\Sigma^r}(E)]^{-1}; \quad \mathbf{G^a}(E) = [\mathbf{G^r}(E)]^\dagger \tag{7}$$

Here $\mathbf{H_0^m}$ is a matrix that corresponds to the molecular part (first term on the right) of the Hamiltonian (2) and $\mathbf{\Sigma^r}(E)$ is the retarded self-energy matrix due to both direct and dipolar coupling to the leads. Here and below the matrices are given in the basis $\{|1>, |2>\}$.

The self-energies needed in Eqs.(5)-(7) are obtained within the usual diagrammatic technique on the Keldysh contour. In the non-crossing approximation (NCA)[11] this leads to

$$\mathbf{\Sigma} = \mathbf{\Sigma^{(ML)}} + \mathbf{\Sigma^{(MR)}} + \mathbf{\Sigma^{(NL)}} + \mathbf{\Sigma^{(NR)}} \tag{8}$$

On the Keldysh contour these self energies are[12,13] 2×2 matrices in the bridge space

$$\Sigma_{mm'}^{(MK)}(\tau_1, \tau_2) = \sum_{k \in K} V_{mk}^{(MK)} g_k(\tau_1, \tau_2) V_{km'}^{(MK)} \tag{9}$$

$$\Sigma_{mm'}^{(NK)}(\tau_1, \tau_2) = \delta_{mm'} \sum_{k \neq k' \in K} \left| V_{kk'}^{(NK)} \right|^2$$
$$\times g_k(\tau_2, \tau_1) g_{k'}(\tau_1, \tau_2) G_{\bar{m}\bar{m}}(\tau_1, \tau_2) \tag{10}$$

Here and below we use $\Sigma_{mm'}^{(PK)}$ to denote mm' matrix element $(m, m' = 1, 2)$ of the self energy, $P = M$ or N corresponds to the physical process (electron or energy transfer to the metal, respectively) and $K = L$ or R denotes the left and right leads, respectively. g_k is the free electron Green function in state k, and $\bar{m} = 2\delta_{m,1} + \delta_{m,2}$, i.e. $\bar{m} = 1$ if $m = 2$ and vice versa.

After projection onto the real time axis we get the retarded, advanced, lesser, and greater components of these self-energies, which in steady state situations can be expressed in energy space. In the wide-band approximation (see e.g. Ref. 14) the self-energies associated with electron exchange between molecule and leads have the familiar forms[13]

$$\Sigma_{mm'}^{(MK)\,r} = \left[\Sigma_{m'm}^{(MK)\,a}\right]^* = -i\delta_{mm'}\Gamma_m^{(MK)}/2 \tag{11a}$$

$$\Sigma_{mm'}^{(MK)\,<} = i\delta_{mm'} f_K(E) \Gamma_m^{(MK)} \tag{11b}$$

$$\Sigma_{mm'}^{(MK)\,>} = -i\delta_{mm'}[1 - f_K(E)] \Gamma_m^{(MK)} \tag{11c}$$

$$\Gamma_m^{(MK)} = 2\pi \sum_{k \in K} \left| V_{km}^{(MK)} \right|^2 \delta(E - \varepsilon_k) \tag{11d}$$

$$f_K(E) = [\exp\{(E - \mu_K)/k_B T\} + 1]^{-1} \tag{11e}$$

(we neglect level mixing due to coupling to the contacts) where μ_K is the chemical potential of the leads and $K = L, R$ denotes the left and right electrode, respectively.

The Langreth projection rules[15] give the lesser and greater projections of the self-energies due to electron-hole excitations, Eq.(10), in the (diagonal) form[8]

$$\Sigma_{mm}^{(NK)\,<}(E) = \int \frac{d\omega}{2\pi} B^{(K)}(\omega, \mu_K) G_{\bar{m}\bar{m}}^<(E + \omega) \tag{12a}$$

$$\Sigma_{mm}^{(NK)\,>}(E) = \int \frac{d\omega}{2\pi} B^{(K)}(\omega, \mu_K) G_{\bar{m}\bar{m}}^>(E - \omega) \tag{12b}$$

$$B^{(K)}(\omega, \mu_K) = 2\pi \int dE \sum_{k \neq k' \in K} \left| V_{kk'}^{(NK)} \right|^2 \tag{12c}$$
$$\times \delta(E - \varepsilon_k)\delta(E + \omega - \varepsilon_{k'}) f_K(E)[1 - f_K(E + \omega)]$$
$$\equiv 2\pi \left| V^{(NK)} \right|^2 \rho_K^{e-h}(\omega) \tag{12d}$$

Here $\rho_K^{e-h}(\omega)$ is density of electron-hole excitations in the lead K, $\rho_K^{e-h}(\omega) = \int dE\, C^{(K)}(E, \omega) f_K(E)[1 - f_K(E + \omega)]$, with $C^{(K)}(E, \omega) = \sum_{k \neq k' \in K} \delta(E - \varepsilon_k)\delta(E + \omega - \varepsilon_{k'}) \approx \rho(E)\rho(E + \omega)$, where $\rho(E)$ is the density of lead electronic states. In the spirit of the wide-band approximation one can assume $C^{(K)}$ to be constant. This leads to $\rho_K^{e-h}(\omega) = \omega\, C^{(K)} / \left[1 - e^{-\beta\omega}\right]$. Below we will use this expression in (12d) to get $B^{(K)}(\omega, \mu_K)$. The retarded and advanced self-energies, $\Sigma^{(NK)\,r,a}$, are difficult to calculate from the Langreth rules. For simplicity we assume, in the spirit of the wide band approximation, that all diagonal components of $\mathbf{\Sigma^{(NK)\,r}}$ and $\mathbf{\Sigma^{(NK)\,a}}(E) = \left[\mathbf{\Sigma^{(NK)\,r}}(E)\right]^\dagger$ are purely imaginary. Then[8]

$$\mathbf{\Sigma^{(NK)\,r}}(E) = \frac{\left[\mathbf{\Sigma^{(NK)\,>}}(E) - \mathbf{\Sigma^{(NK)\,<}}(E)\right]}{2} \equiv -\frac{i}{2}\mathbf{\Gamma^{(NK)}} \tag{13}$$

Eqs. (6), (7), (12a), (12b) and (13) have to be solved self-consistently until convergence is achieved. We use the level populations, $n_m = -i \int \frac{dE}{2\pi} G_{mm}^<(E)$ $(m = 1, 2)$, as a test for convergence. Convergence is declared when the population values at subsequent iteration steps change no more than the predefined tolerance, taken below 10^{-6}.

The additive structure of the self-energy, Eq.(8), makes it possible to separate the lesser and greater Green functions, Eq.(6), and consequently also the source-drain current, Eq.(5), into contributions due to direct electron transfer to the leads and coupling to the electron-hole excitations.

$$I_{sd} = I_{sd}^L + I_{sd}^{e-h} \tag{14}$$

I_{sd}^L, is the usual Landauer expression for elastic current

$$I_{sd}^L = \frac{e}{\hbar} \int_{-\infty}^{+\infty} \frac{dE}{2\pi} \sum_{m=1,2} \Gamma_m^{(ML)} G_{mm}^r(E) \Gamma_m^{(MR)} G_{mm}^a(E)$$
$$\times [f_L(E) - f_R(E)] \tag{15}$$

while I_{sd}^{e-h} is the contribution from the electron-hole excitation. A simple expression for this current can be obtained when $\Gamma_m^{(MK)} \ll \varepsilon_{21}$, where $\Sigma^{(NK)\,<,>}$ takes an

approximate form

$$\mathbf{\Sigma}^{(\mathbf{NK})<}(E) = iB^{(K)} \begin{bmatrix} n_2 & 0 \\ 0 & 0 \end{bmatrix} \qquad (16a)$$

$$\mathbf{\Sigma}^{(\mathbf{NK})>}(E) = -iB^{(K)} \begin{bmatrix} 0 & 0 \\ 0 & 1-n_1 \end{bmatrix} \qquad (16b)$$

Here $B^{(K)}$ is assumed to be a constant. Note that using $B^{(K)}$ as a parameter in the full self-consistent calculations below means that in fact we take $|V^{(NK)}|^2 C^{(K)} = B^{(K)}/2\pi\varepsilon_{21}$. Using (16) in (5) leads to the electron-hole excitations part of the flux in the form

$$I_{sd}^{e-h} = \frac{e}{\hbar}B\times \qquad (17)$$

$$\left[n_2^{(ML)}\left(\frac{\Gamma_1^{(MR)}}{\Gamma_1} - n_1^{(MR)} \right) - n_2^{(MR)}\left(\frac{\Gamma_1^{(ML)}}{\Gamma_1} - n_1^{(ML)} \right) \right]$$

where $\Gamma_m = \Gamma_m^{(ML)} + \Gamma_m^{(MR)} + \Gamma_m^{(NL)} + \Gamma_m^{(NR)}$ ($\Gamma_1^{(NK)} = B^{(K)}n_2$ and $\Gamma_2^{(NK)} = B^{(K)}[1-n_1]$) and $n_m^{(MK)} = -i\int \frac{dE}{2\pi} |G_{mm}^r(E)|^2 \Sigma_{mm}^{(MK)<}(E)$ ($m=1,2$).

Further simplification of Eqs. (15) and (17) is achieved for strong bias, e.g. for negatively biased left electrode where $\mu_L \gg \varepsilon_2$ and $\mu_R \ll \varepsilon_1$ so that $f_L = 1$ and $f_R = 0$ in the energy range relevant to the integral in Eq.(15). Also in this case $n_m^{(MR)} = 0$ and $n_m^{(ML)} = \Gamma_m^{(ML)}/\Gamma_m$ ($m = 1, 2$) cam be used in (17). Similar consideration apply in the opposite bias, leading finally to

$$I_{sd}^L = \frac{e}{\hbar}\sum_{m=1,2} \frac{\Gamma_m^{(ML)}\Gamma_m^{(MR)}}{\Gamma_m}\mathrm{sgn}(\mu_L - \mu_R) \qquad (18)$$

$$I_{sd}^{e-h} = \frac{e}{\hbar}B\times \qquad (19)$$

$$\left[\frac{\Gamma_2^{(ML)}\Gamma_1^{(MR)}}{\Gamma_1\Gamma_2}\theta(\mu_L - \mu_R) - \frac{\Gamma_1^{(ML)}\Gamma_2^{(MR)}}{\Gamma_1\Gamma_2}\theta(\mu_R - \mu_L) \right]$$

where θ is the step function $\theta(x) = 1$ for $x > 0$ and 0 for $x < 0$. Note that $\left|I_{sd}^{e-h}\right|$ can be asymmetric to bias reversal (see also Fig. 1 and discussion below). For, e.g., $\mu_L > \mu_R$ we see that the magnitude of I_{sd}^{e-h} is determined both by the value of $B = B^{(L)} + B^{(R)}$ and by the product $\Gamma_2^{(ML)}\Gamma_1^{(MR)}$ while I_{sd}^L is determined by the product $\Gamma_m^{(ML)}\Gamma_m^{(MR)}$ ($m = 1, 2$). The electron-hole contribution to the source-drain current is significant when $\Gamma_2^{(ML)} > \Gamma_2^{(MR)}$ and/or $\Gamma_1^{(MR)} > \Gamma_1^{(ML)}$. Below we compare the magnitude of the two contributions to the current for different junctions parameters.

Numerical results. In the calculations reported below we used the following 'standard' choice of parameters: $T = 300$ K, $\varepsilon_1 = 0$ eV, $\varepsilon_2 = 2$ eV, $\Gamma_1^{(M)} = \Gamma_2^{(M)} = 0.2$ eV. Values of other parameters are indicated in the figures. The Fermi energy is taken in the middle of the HOMO-LUMO gap. Chemical potentials in the left and right leads are assumed to shift with the voltage bias symmetrically relative to the Fermi energy. Numerical integration was done on the energy grid spanning range from -3 to 5 eV with the step 10^{-3} eV.
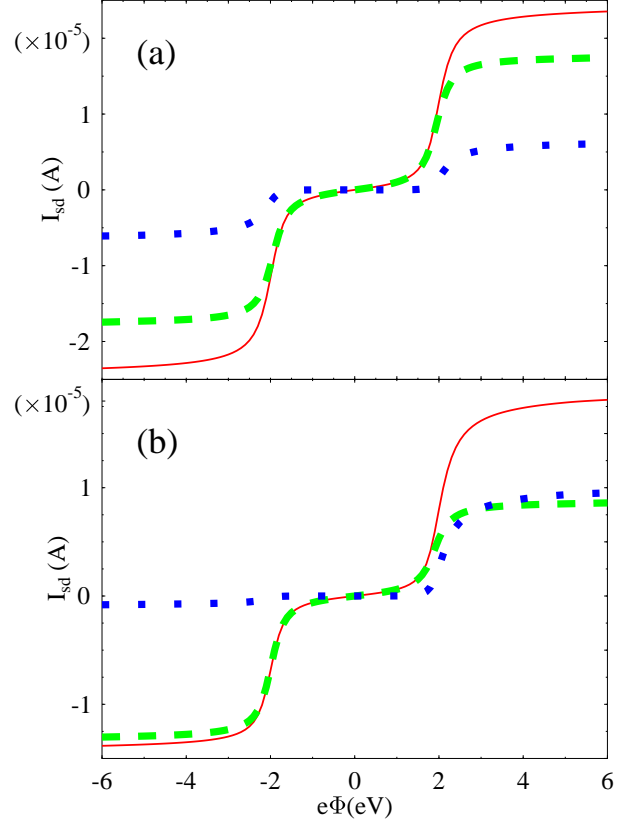

FIG. 1: The source-drain current I_{sd} vs. applied voltage Φ. Shown are the total current I_{sd} (full line, red) as well as contributions due to direct electron transfer I_{sd}^L (dashed line, green) and electron-hole excitations I_{sd}^{e-h} (dotted line, blue) for symmetric $\Gamma_{1,2}^{(ML)} = \Gamma_{1,2}^{(MR)} = 0.1$ eV (a) and asymmetric $\Gamma_1^{(ML/R)} = 0.1$ eV, $\Gamma_2^{(ML)} = 0.19$ eV, and $\Gamma_2^{(MR)} = 0.01$ eV (b) cases.

Figure 1 depicts the current-voltage characteristic of the junction for the cases of symmetric and asymmetric coupling between the molecular LUMO and the contacts. Shown are the total current and its two components. In the symmetric case the current is dominated by the usual elastic electron (hole) transport through the LUMO (HOMO), and is symmetric relative to voltage reversal. The asymmetric case shows a significant contribution of the current associated with electron-hole excitations. The following points are noteworthy: (1) I_{sd}^{e-h} is significant when the LUMO is coupled asymmetrically to the two electrodes (2) This effect is particularly strong when the LUMO is coupled more strongly to the negatively biased electrode (i.e. $\Phi < 0$ when the LUMO couples strongly to the left). Indeed, I_{sd}^{e-h} is expected to be pronounced when the LUMO is populated and the HOMO is empty, which happens at such bias. Note also that the total current is asymmetric relative to bias reversal in this case.

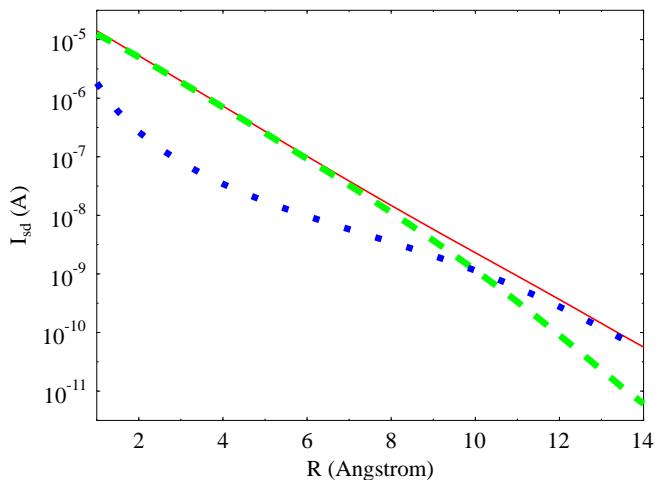Figure 2 shows the results of a model study

FIG. 2: Source-drain current I_{sd} at $\Phi = 3$ V vs. molecule-contacts distance R. See text for choice of the coupling parameters. Shown are the total I_{sd} current (full line, red) as well as contributions due to direct electron transfer I_{sd}^L (dashed line, green) and electron-hole excitations I_{sd}^{e-h} (dotted line, blue).

of the dependence of the source-drain current on the molecule-lead distance R. We take $\Gamma_m^{(MK)} = A_m^{(MK)} \exp\left[-\alpha_m^{(MK)} R\right]$ to reflect a tunneling transition, while $B^{(K)}(R)$ is assumed to have a dipolar distance dependence[7], $B^{(K)} = \beta^{(K)}/R^3$. The parameters used are $A_1^{(ML)} = A_1^{(MR)} = 0.27$ eV, $A_2^{(ML)} = 0.52$ eV, $A_2^{(MR)} = 0.027$ eV, $\alpha_m^{(MK)} = 1$ Å^{-1}, and $\beta^{(K)} = 0.01$ eV A^3 ($K = L, R$ and $m = 1, 2$). The choice of $A_m^{(MK)}$ reflects a total lifetime broadening for electron transfer into the electrodes of 0.2 eV at a distance (from each electrode) of 1 Å. The choice of $\beta^{(K)}$ corresponds to taking $B^{(K)} = 0.01$ eV at this distance. The relative importance of the I_{sd}^L and I_{sd}^{e-h} components of I_{sd} depends on the details of the molecule-leads couplings. In

particular, when $R \to \infty$ for both leads $\Gamma_m^{(M)}/B \to 0$ ($m = 1, 2$). In this limit I_{sd}^{e-h} can become larger than I_{sd}^L. As a specific example consider the situation where $\Gamma_1^{(M)} = \Gamma_2^{(M)}$ and denote $\xi_m = \Gamma_m^{(ML)}/\Gamma_m^{(M)}$. Then using Eqs. (8), (16), (18), and (19) for the case $\mu_R \ll \varepsilon_1 < \varepsilon_2 \ll \mu_L$ we obtain $I_{sd}^{e-h}/I_{sd}^L \to \xi_2/\xi_1(1 - \xi_1 - \xi_2)$, ∞ and $(1 - \xi_1)/(1 - \xi_2)|1 - \xi_1 - \xi_2|$ when $\xi_2 < 1 - \xi_1$, $\xi_2 = 1 - \xi_1$ and $\xi_2 > 1 - \xi_1$, respectively. Our choice of parameters in Figure 2 corresponds to the third case and yields ultimate dominance of I_{sd}^{e-h} at large distances with $I_{sd}^{e-h}/I_{sd}^L \sim 100$ as $R \to \infty$. Note that this limiting behavior is obtained only when both left and right molecule-metal couplings decrease together. Experimentally one of these distances can be controlled by moving a tip while the other can be changed by adding insulating layers between molecule and substrate[16,17].

Conclusion. We have studied, within a simple model, the effect of dipolar energy-transfer interaction between molecule and leads on molecular conduction. We found that such interaction, that leads to electron-hole excitations in the contacts, can affect the current voltage characteristic of the junction in a substantial way and can not in general be disregarded. The contribution of this interaction can dominate the overall conduction for particular asymmetric coupling where the molecular LUMO and/or HOMO are coupled differently to different leads. In addition, because of the different dependence of electron and energy transfer on the molecule-leads distance, the relative importance of I_{sd}^L and I_{sd}^{e-h} depends on this distance, and can, in some cases, result in strong dominance of I_{sd}^{e-h} at large molecule-lead separations.

[1] *Molecular Electronics II*, Eds. A. Aviram, M. Ratner, V. Mujica, Ann. N.Y. Acad. Sci., vol. 960 (2002); *Molecular Electronics III*, Eds. J. R. Reimers, C. A. Picconatto, J. C. Ellenbogen, R. Shashidhar, Ann. N.Y. Acad. Sci., vol. 1006 (2003).
[2] A. Nitzan, Ann. Rev. Phys. Chem. **53**, 681 (2001).
[3] J. R. Heath and M. A. Ratner, Physics Today **56**, 43 (2003).
[4] *Molecular Nanoelectronics*, Eds. M. A. Reed and T. Lee, American Scientific Publishers (2003).
[5] A. Nitzan and M. A. Ratner, Science **300**, 1384 (2003).
[6] S. Datta, *Quantum Transport: Atom to Transistor*, Cambridge University Press (2005).
[7] R. Chance, A. Prock, and R. Silbey, Adv. Chem. Phys. **31**, 1 (1978).
[8] M. Galperin and A. Nitzan, Phys. Rev. Lett. **95**, 206802

(2005) and to be published.
[9] L. V. Keldysh, Sov. Phys. JETP **20**, 1018 (1965).
[10] Y. Meir and N. S. Wingreen, Phys. Rev. Lett. **68**, 2512 (1992).
[11] N. E. Bickers, Rev. Mod. Phys. **59**, 845 (1987).
[12] G. D. Mahan, *Many-Particle Physics.* (Third edition, Kluwer Academic/Plenum Publishers, New York, 2000).
[13] H. Haug and A.-P. Jauho, *Quantum Kinetics in Transport and Optics of Semiconductors.* (Springer, Berlin, 1996).
[14] W. Tian, S. Datta, S. Hong et al., J. Chem. Phys. **109**, 2874 (1998).
[15] D. C. Langreth, *Linear and Nonlinear Response Theory with Applications*, p. 3–32 in: *Linear and Nonlinear Electron Transport in Solids*, Eds. J. T. Devreese and D. E. Doren (Plenum Press, New York and London, 1976).
[16] N. A. Pradhan, N. Liu, and W. Ho, J. Phys. Chem. B **109**,

8513 (2005).

[17] J. Repp, G. Meyer, S. M. Stojkovic, A. Gourdon, and C. Joachim, Phys. Rev. Lett. **94**, 026803 (2005).