Molecular Transport Junctions: Current from Electronic Excitations in the Leads

Michael Galperin,1 Abraham Nitzan,2 and Mark A. Ratner1
1Department of Chemistry and Nanotechnology Center, Northwestern University, Evanston, Illinois 60208, USA
2School of Chemistry, The Sackler Faculty of Science, Tel Aviv University, Tel Aviv 69978, Israel
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Using a model comprising a two-level bridge connecting free electron reservoirs we show that coupling of a molecular bridge to electron-hole excitations in the leads can markedly affect 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.

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Introduction.—Electron transport in molecular tunnel junctions has been the focus of intense recent research [1–4]. 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 (deexcitation) of the molecule accompanied by electron-hole 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 nonequilibrium Green function (NEGF) formalism to derive an expression for the conduction in a 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 in the molecule-lead coupling, of a particular type explained below, is present.

As an 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. However, mixing of the HOMO and LUMO orbitals by dipolar coupling to the leads makes conduction possible. Realistic situations will not be that extreme; still, whenever the HOMO-LUMO transition is associated with electronic charge transfer along the molecular bridge, we expect some degree of such asymmetry. For example, the dipole moment of DMEANS (4-Dimethylamino-4’-nitrostilbene) is 7 D in the ground state and 31 D in the first excited singlet state [8], and 40 Å CdSe nanocrystals change their dipole from 0 to 32 D upon transition from their ground to the first excited state [9]. We have recently shown [10] that such situations may give rise to light induced current under zero voltage. We show below that another manifestation of this charge transfer property is the increasing importance of dipolar energy-transfer interactions between molecule and leads in determining the junction conduction properties.

Model and method.—We consider a tunneling junction (Fig. 1) consisting of a molecule positioned between two metal contacts (L and R). The molecule is represented by its HOMO, |1⟩, and LUMO, |2⟩, with energies ε1 and ε2 and gap ε21 = ε2 − ε1. The contacts are assumed to be free electron reservoirs, each at its own equilibrium, characterized by electronic chemical potentials µL and µR, where the difference µL − µR = eΦ is the imposed voltage. The corresponding Hamiltonian is

\[ \hat{H} = \hat{H}_0 + \hat{V}_M + \hat{V}_N, \]

FIG. 1. The junction model. The dark and light gray areas denote occupied and unoccupied leads states that are connected via the molecular bridge. The latter is represented by its HOMO (1) and LUMO (2) levels. The solid-line double arrows represent the electron transfer interactions, the dashed double arrows, the energy-transfer interactions, and the vertical open arrows, the electron excitation/deexcitation processes in the molecule and the metals (see text for notations).
\[ \hat{H}_0 = \sum_{m=1,2} \epsilon_m c_m^\dagger c_m + \sum_{k \in \{L,R\}} \epsilon_k c_k^\dagger c_k, \quad (2) \]

\[ \hat{V}_M = \sum_{K=L,R \atop m=1,2, k \in K} (V_{km}^{(MK)} c_k^\dagger c_m + \text{H.c.}), \quad (3) \]

\[ \hat{V}_N = \sum_{K=L,R \atop k \neq k' \in K} (V_{kk'}^{(NNK)} c_k^\dagger c_{k'} + \text{H.c.}), \quad (4) \]

where H.c. denotes the Hermitian conjugate. Here the operators \( \hat{c}_m \) and \( \hat{c}_m^\dagger \) are annihilation and creation operators of electrons in the bridge, 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 electron reservoirs representing the leads. \( \hat{V}_M \) describes the electron transfer (tunneling) process between these subsystems. \( \hat{H}_0 + \hat{V}_M \) is the standard Hamiltonian used in simple models of molecular conduction that yield the Landauer conductor expression [Eq. (11) below]. The additional term \( \hat{V}_N \) represents coupling of the molecular HOMO-LUMO transition to electron-hole excitations in the leads which is often used in models of energy transfer between the molecule and the metals. The effect of this interaction on the junction transport properties is the subject of our discussion. Effects of electron-hole recombinon on the bridge were previously considered [11] at the level of master equation approach to transport.

In the Keldysh NEGF formalism [12] the steady-state current through the junction is given in terms of the lesser and greater Green functions (GFs), \( \hat{G}^{<} \), and the corresponding self-energies (SEs) associated with the electron transfer process, \( \Sigma_{MK} \), by [13]

\[ I_{sd} = \pm \frac{e}{h} \int \frac{dE}{2\pi} \text{Tr}[\Sigma_{MK}^{<}(E)\hat{G}^{>}(E) - \Sigma_{MK}^{>}(E)\hat{G}^{<}(E)] \quad (5) \]

calculated at the left (\( K = L \) with “+” sign) or right (\( K = R \) with “−” sign) contact, where the direction from left to right is chosen to be positive. The GFs \( \hat{G}^{<} \) needed in (5) can be obtained from the Keldysh equation

\[ \hat{G}^{<}(E) = \hat{G}^{r}(E)\Sigma^{<}(E)\hat{G}^{a}(E) \quad (6) \]

where the retarded and advanced GFs, \( \hat{G}^{r,a} \), are given by the Dyson equation

\[ \hat{G}^{r}(E) = [E - \hat{H}_0^m - \Sigma^{r}(E)]^{-1}, \quad \hat{G}^{a}(E) = [\hat{G}^{r}(E)]^{\dagger}. \quad (7) \]

Here \( \hat{H}_0^m \) is a matrix that corresponds to the molecular part (first term on the right) of the Hamiltonian (2) and \( \Sigma^{r}(E) \) is the retarded self-energy matrix due to both electron transfer and dipolar coupling to the leads. These are \( 2 \times 2 \) matrices in the representation of molecular states [1] and [2].

The SEs needed in Eqs. (5)–(7) are obtained within the usual diagrammatic technique on the Keldysh contour. In the noncrossing approximation [14] they contain additive contributions associated with the electron and energy-transfer processes at the two leads (\( L \) and \( R \)): \( \Sigma = \Sigma^{(ML)} + \Sigma^{(MK)} + \Sigma^{(NL)} + \Sigma^{(NR)} \). (8)

The evaluation of these self-energies and their corresponding retarded, advanced, lesser, and greater projections on the real time axis is described in detail in Ref. [15]. The additive structure [Eq. (8)] translates into additive expressions for the corresponding projections and 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, \( I_{sd}^\text{dir} \), and due to the electron-hole excitations, \( I_{sd}^\text{eh} \).

\[ I_{sd} = I_{sd}^\text{dir} + I_{sd}^\text{eh}. \quad (9) \]

In particular, the self-energies associated with the electron transfer processes are obtained in the wide band approximation in the familiar forms [16,17]

\[ \Sigma_{mn}^{(MK)} = \left[ \Sigma_{mn}^{(MK)} \right]^* = -i \delta_{mn} \Gamma_{m}^{(MK)}/2, \quad (10a) \]

\[ \Sigma_{mn}^{(MK)} = i \delta_{mn} f_K(E) \Gamma_{m}^{(MK)}, \quad (10b) \]

\[ \Sigma_{mn}^{(MK)} = -i \delta_{mn} [1 - f_K(E)] \Gamma_{m}^{(MK)}, \quad (10c) \]

\[ \Gamma_{m}^{(MK)} = 2 \pi \sum_{k \in K} |V_{km}^{(MK)}|^2 \delta(E - e_k), \quad (10d) \]

\[ f_K(E) = \left[ \exp\{-(E - \mu_K)/k_B T\} + 1 \right]^{-1} \quad (10e) \]

(note that the matrix \( \Gamma_{m}^{(MK)} \) was assumed diagonal, disregarding possible level mixing due to coupling to the leads), where \( \mu_K, K = L, R \) are the chemical potentials of the left and right leads, respectively. This results in the standard Landauer expression for \( I_{sd}^\text{dir} \).

\[ I_{sd}^\text{dir} = \frac{e}{h} \int_{-\infty}^{+\infty} \frac{dE}{2\pi} \left[ \sum_{m=1,2} \Gamma_{mn}^{(MK)} \hat{G}_{mn}^{<}(E) \hat{G}_{mn}^{>}(E) [f_L(E) - f_K(E)] \right] \quad (11) \]

The evaluation of \( I_{sd}^\text{eh} \) is more involved. The SEs associated with the energy-transfer processes can be expressed in terms of the GFs [see Eqs. (19), (22), and (36) of Ref. [15]], and the self-consistent solutions of the resulting coupled equations are found by iterations. We use the level populations, \( n_m = -i \int \frac{dE}{2\pi} \hat{G}_{mn}^{<}(E) (m = 1, 2) \), as a test for convergence, which is declared when the population values at subsequent iteration steps do not change within a pre-defined tolerance, chosen below as \( 10^{-6} \).

The results shown in Figs. 2 and 3 were obtained from this procedure. A simple analytical expression for \( I_{sd}^\text{eh} \) can be obtained when \( \Gamma_{m}^{(MK)} = \Gamma_{m}^{(MK)} + \Gamma_{m}^{(NNK)} \ll \epsilon_{21} \) (where \( \Gamma_{m}^{(MK)} = \Gamma_{m}^{(MK)} + \Gamma_{m}^{(NNK)} \) with \( \Gamma_{m}^{(NNK)} = -2 \text{Im} \Sigma_{mn}^{(NNK)} \)).
strong bias limit. “Strong bias” implies, e.g., for negatively biased left electrode, that \( \mu_L \gg \epsilon_2 \) and \( \mu_R \ll \epsilon_1 \) so that \( f_L = 1 \) and \( f_R = 0 \) in the relevant energy range. Under these conditions the results for the Landauer current \( I_{sd}^{\text{el}} \) and for the electron-hole excitations induced current \( I_{sd}^{\text{eh}} \) are obtained [15] in the forms

\[
I_{sd}^{\text{el}} = \frac{e}{h} \sum_{m=1,2} \frac{\Gamma_m^{(ML)} \Gamma_m^{(MR)}}{\Gamma_m} \text{sgn}(\mu_L - \mu_R),
\]

(12)

\[
I_{sd}^{\text{eh}} = \frac{e}{h} \left[ \frac{\Gamma_2^{(ML)} \Gamma_1^{(MR)}}{\Gamma_1 \Gamma_2} \theta(\mu_L - \mu_R) \right.
- \left. \frac{\Gamma_1^{(ML)} \Gamma_2^{(MR)}}{\Gamma_1 \Gamma_2} \theta(\mu_R - \mu_L) \right],
\]

(13)

where \( \theta(x) = 1 \) for \( x > 0 \) and 0 for \( x < 0 \), and where \( B = B^{(L)} + B^{(R)} \) is the function

\[
B^{(K)}(\omega, \mu_K) = 2\pi \int dE \sum_{k+k'=K} |V_{kk'}^{(NK)}|^2 \delta(E - \epsilon_k)
\]

\[
\times \delta(E + \omega - \epsilon_{k'}) f_K(E) [1 - f_K(E + \omega)]
\]

\[
= 2\pi |V_{kk'}^{(NK)}|^2 \rho_{K,\omega}^{\text{eh}}(\omega)
\]

(14)
evaluated at \( \omega = \epsilon_2 - \epsilon_1 \). Here \( \rho_{K,\omega}^{\text{eh}}(\omega) \) is density of electron-hole excitations in the lead K. Equations (12) and (13) show that the magnitude of \( I_{sd}^{\text{el}} \) depends on the product \( \Gamma_1^{(ML)} \Gamma_2^{(MR)} \) (\( n = 1, 2 \)), while \( I_{sd}^{\text{eh}} \) is determined by the mixed products \( \Gamma_2^{(ML)} \Gamma_1^{(MR)} \) or \( \Gamma_1^{(ML)} \Gamma_2^{(MR)} \). The relative contribution of the latter current component will be significant in asymmetric coupling situations, e.g., for \( \mu_L > \mu_R \) when \( \Gamma_2^{(ML)} > \Gamma_2^{(MR)} \) and/or \( \Gamma_1^{(ML)} > \Gamma_1^{(MR)} \). Note that, since \( \Gamma_2^{(ML)} \Gamma_1^{(MR)} \) can be different from \( \Gamma_1^{(ML)} \Gamma_2^{(MR)} \), \( |I_{sd}^{\text{eh}}| \) can be asymmetric to bias reversal (see also Fig. 2). Below we compare the magnitude of the two contributions to the current for different junction parameters.

Numerical results.—In the calculations reported below we used the following “standard” choice of parameters: \( T = 300 \) K, \( \epsilon_1 = 0 \) eV, \( \epsilon_2 = 2 \) eV, and \( \Gamma_1^{(ML)} = \Gamma_2^{(MR)} = 0.2 \) eV. Values of other parameters are indicated in the figures. The Fermi energy is taken at the midpoint of the HOMO-LUMO gap and the electrochemical potentials in the left and right leads are assumed to shift with the voltage bias symmetrically relative to this point. Numerical integration was done on the energy grid spanning range from \(-3 \) to \( 5 \) eV using integration step \( 10^{-3} \) eV.

Figure 2 depicts the current-voltage characteristic of the junction for the cases of symmetric and asymmetric coupling between the leads and the molecular LUMO. Shown are the total current and its two components. The following points are noteworthy: (1) In the symmetric case the current is dominated by the usual electron and/or hole transport through the LUMO and/or HOMO, respectively, and is symmetric with respect to voltage reversal. (2) The asymmetric case shows a significant contribution of the current associated with electron-hole excitations when the LUMO is coupled more strongly to the negatively biased electrode. Indeed, \( I_{sd}^{\text{eh}} \) is expected to be pronounced when the LUMO is populated and the HOMO is empty, which happens at such bias. (3) The asymmetric LUMO coupling leads to asymmetry in \( I_{sd}^{\text{el}} \) and consequently in the total current with respect to bias reversal.

Figure 3 shows the results of a model study of the dependence of the source-drain current on the molecule-lead distance \( R \). These results are obtained using \( \Gamma_m^{(MK)} = A_{m}^{(MK)} \exp[-\alpha_{m}^{(MK)} R] \), which accounts for the tunneling nature of electron transfer, and taking \( B^{(K)} = \beta^{(K)}/R^2 \), which reflects a dipolar distance dependence of the energy transfer to the leads [7]. The parameters used are \( A_{1}^{(ML)} = A^{(MR)} = 0.27 \) 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 Å\(^3 \) (\( K = L, R \) and \( m = 1, 2 \)). The choice of \( A_{m}^{(MK)} \) corresponds to 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. Both choices reflect the orders of lifetimes ob-
FIG. 3 (color online). The source-drain current $I_{sd}$ at voltage $\Phi = 3$ V vs molecule-leads distance $R$. See text for the choice of coupling parameters. Shown are the total current $I_{sd}$ (solid red line) as well as its $I_{sd}^{et}$ (dashed green line) and $I_{sd}^{eh}$ (dotted blue line) components.

served for the corresponding processes for molecules adsorbed on metal surfaces.

The results shown in Fig. 3 demonstrate an important aspect of the distance dependence of the two contributions to the total current. Obviously, both $I_{sd}^{et}$ and $I_{sd}^{eh}$ involve electron transfer between molecule and leads, therefore both drop exponentially with increasing tunneling length. Their relative importance, however, depends on the details of the molecule-leads couplings. It is easily seen from Eqs. (12) and (13) that $I_{sd}^{eh}/I_{sd}^{et} \sim B/\Gamma$. For small and intermediate distances, where $\Gamma$ is dominated by the electron tunneling process, this ratio increases with increasing distances. (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 [19,20].) Detailed calculation shows that this ratio can in fact become substantially larger than 1 at large molecule-lead distances, as seen in Fig. 3. In this case the current is dominated by the contribution associated with the electron-hole excitation process.

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, which leads to electron-hole excitations in the contacts, can affect the current-voltage characteristic of the junction in a substantial way and cannot 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 $I_{sd}^{et}$ and $I_{sd}^{eh}$ depends on this distance, and can, in some cases, result in strong dominance of $I_{sd}^{eh}$ at large molecule-lead separations.

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[18] Explicit expressions for $\Gamma_m^{\text{et}}$ are obtained in this limit in terms of the level populations $n_m$ ($m = 1, 2$) [see Eq. (37) of Ref. [15]], which in turn are obtained from the self-consistent calculations.
