Molecular transport junctions: Current from electronic excitations in the leads

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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 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. 1,2,3,4 Theoretical modeling of tunnel conduction 5 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. 6 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 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.

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 \( \varepsilon_1 \) and \( \varepsilon_2 \) 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 \( \mu_L \) and \( \mu_R \), where the difference \( \mu_L - \mu_R = e\Phi \) is the imposed voltage. The corresponding Hamiltonian is

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

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

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

\[
\hat{V}_N = \sum_{K=L,R} \sum_{k \neq k'} \left( V_{kk'}^{(NK)} \hat{c}_k^{\dagger} \hat{c}_k \hat{c}_k \hat{c}_k' + \text{H.c.} \right)
\]

where H.c. denotes Hermitian conjugate. Here the operators \( \hat{c}_m^{\dagger} \) and \( \hat{c}_k^{\dagger} \) 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 7,8 the steady-state current through the junction is given by

\[
I_{sd} = \pm \frac{e}{\hbar} \int \frac{dE}{2\pi} \text{Tr} \left[ \Sigma_{MK}(E)G^{\geq}(E) - \Sigma_{MK}^{\geq}(E)G^{\leq}(E) \right]
\]

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, \( G^{<,>}(E) \), needed in 10 can be obtained from the Keldysh equation

\[
G^{<,>}(E) = G^{\ge}(E) \Sigma^{<,>}(E) G^{\le}(E)
\]

\[
\Sigma^{<,>}(E) = \sum_{\alpha} \left( \frac{1}{E - \mu_\alpha} \delta(E - \varepsilon_\alpha^{(L)}) - \frac{1}{E - \mu_\alpha} \delta(E - \varepsilon_\alpha^{(R)}) \right)
\]

where \( \mu_\alpha^{(L)} \) and \( \mu_\alpha^{(R)} \) are chemical potentials of the left and right leads, respectively.
where the retarded and advanced Green functions, \( G^{r,a} \), are given by the Dyson equation

\[
G^{r}(E) = [E - H_{0}^{m} - \Sigma^{r}(E)]^{-1}; \quad G^{a}(E) = [G^{r}(E)]^{\dagger}
\]

Here \( H_{0}^{m} \) is a matrix that corresponds to the molecular part (first term on the right) of the Hamiltonian \( \Sigma^{r}(E) \) 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

\[
\Sigma = \Sigma^{(ML)} + \Sigma^{(MR)} + \Sigma^{(NL)} + \Sigma^{(NR)}
\]

On the Keldysh contour these self energies are\(^{12,13} \times 2 \times 2 \) matrices in the bridge space

\[
\Sigma^{(MK)}_{m_{m}'} (\tau_{1}, \tau_{2}) = \sum_{k \in K} V_{mk}^{(MK)} g_{k}(\tau_{1}, \tau_{2}) V_{km'}^{(MK)}
\]

\[
\Sigma^{(NL)}_{m_{m}'} (\tau_{1}, \tau_{2}) = \delta_{mm'} \sum_{k,k' \not\in K} \left| V_{kk'}^{(NL)} \right|^{2} \times g_{k}(\tau_{2}, \tau_{1}) g_{k'}(\tau_{1}, \tau_{2}) G^{\bar{m}\bar{m}}(\tau_{1}, \tau_{2})
\]

Here and below we use \( \Sigma^{(MK)}_{m_{m}'} \) 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\(^{12}\)

\[
\Sigma^{(MK)}_{m_{m}'} = \left[ \Sigma^{(MK)}_{m_{m}'} \right]^{a} = -i\delta_{mm'} \Gamma^{(MK)}_{m} / 2
\]

\[
\Sigma^{(NL)}_{m_{m}'} = i\delta_{mm'} f_{K}(E) \Gamma^{(NL)}_{m}
\]

\[
\Gamma^{(MK)}_{m} = 2\pi \sum_{k \in K} \left| V_{km}^{(MK)} \right|^{2} \delta(E - \varepsilon_{k})
\]

\[
f_{K}(E) = \exp \{ (E - \mu_{K})/k_{B}T \} + 1 \}^{-1}
\]

(we neglect level mixing due to coupling to the contacts) where \( \mu_{K} \) 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\(^{8}\)

\[
\Sigma_{m_{m}'}^{(NL)} - \Sigma_{m_{m}'}^{(NR)} = -\frac{i}{2} \Gamma^{(MK)}_{m}
\]

\[
\Sigma_{m_{m}'}^{(NL)} > \Sigma_{m_{m}'}^{(NR)} = 2\pi \int dE \sum_{k \not\in K} \left| V_{kk'}^{(NL)} \right|^{2} \delta(E - \varepsilon_{k}) f_{K}(E) [1 - f_{K}(E + \varepsilon_{k})] f_{K}(E + \varepsilon_{k})
\]

\[
\equiv 2\pi \left| V_{k k'}^{(NL)} \right|^{2} \rho_{K}^{-h}(\omega)
\]

Here \( \rho_{K}^{-h}(\omega) \) is density of electron-hole excitations in the lead \( K \), \( \rho_{K}^{-h}(\omega) = \int dE C^{(K)}(E, \omega) f_{K}(E)[1 - f_{K}(E + \varepsilon_{k})] \), with \( C^{(K)}(E, \omega) \), \( \omega \approx \varepsilon_{k} \approx \rho(E) \varepsilon_{k} \). Below we will use this expression in (12d) to get \( B^{(K)}(\omega, \mu_{K}) \). The retarded and advanced self-energies, \( \Sigma^{(NL),r,a}_{m} \), 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 \( \Sigma^{(NL),r,a}_{m} \) are purely imaginary. Then\(^{8}\)

\[
\Sigma_{m_{m}'}^{(NL)} r(E) = \frac{\Sigma_{m_{m}'}^{(NL)} > (E) - \Sigma_{m_{m}'}^{(NL)} < (E)}{2} = \frac{-i}{2} \Gamma^{(NL)}_{m}
\]

Eqs. (6), (7), (12a), (12b), and (13) have to be solved self-consistently until convergence is achieved. We use the level populations, \( n_{m} = -\int dE \rho_{m_{m}}^{<}(E) \), \( m = 1, 2 \), 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. (5), 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.

\[
I_{sd} = I_{sd}^{L} + I_{sd}^{e^{-}-h}
\]

\[
I_{sd}^{L} = \frac{e}{h} \int_{-\infty}^{+\infty} dE \sum_{m=1,2} \Gamma^{(MK)}_{m} (G^{r}_{m_{m}m}(E) G^{a}_{m_{m}m}(E)) \times [f_{L}(E) - f_{R}(E)]
\]
approximate form

$$\Sigma^{(NK)}(E) = i B^{(K)} \begin{bmatrix} \eta_2 & 0 \\ 0 & 0 \end{bmatrix}$$  \hspace{1cm} \text{(16a)}$$

$$\Sigma^{(NK)}(E) > (E) = -i B^{(K)} \begin{bmatrix} 0 & 0 \\ 0 & 1 - \eta_1 \end{bmatrix}$$  \hspace{1cm} \text{(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 (14) in (16) leads to the electron-hole excitations part of the flux in the form

$$I_{sd}^{e-h} = \frac{e}{h} B \times \left[ n_2^{(ML)} \left( \frac{\Gamma_1^{(MR)} + \eta_1^{(MR)}}{\Gamma_1} - n_1^{(MR)} \right) + n_2^{(MR)} \left( \frac{\Gamma_1^{(ML)} + \eta_1^{(ML)}}{\Gamma_1} - n_1^{(ML)} \right) \right]$$  \hspace{1cm} \text{(17)}$$

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

Further simplification of Eqs. (15) and (17) is achieved for strong bias, e.g., for negatively biased left electrode where $\mu_L > \varepsilon_2$ and $\mu_R < \varepsilon_1$ so that $f_L = 1$ and $f_R = 0$ in the energy range relevant to the integral in Eq. (17). Also in this case $n_m^{(MR)} = 0$ and $n_m^{(ML)} = \Gamma_1^{(ML)} / \Gamma_m$ (m = 1, 2) can be used in (17). Similar consideration apply in the opposite bias, leading finally to

$$I_{sd}^{e-h} = \frac{e}{h} \sum_{m=1,2} \Gamma_m^{(ML)} \Gamma_m^{(MR)} \frac{\theta(\mu_L - \mu_R)}{\Gamma_m}$$  \hspace{1cm} \text{(18)}$$

$$I_{sd}^{e-h} = \frac{e}{h} B \times \left[ \frac{\Gamma_1^{(ML)} \Gamma_1^{(MR)}}{\Gamma_1 \Gamma_2} \theta(\mu_L - \mu_R) - \frac{\Gamma_1^{(ML)} \Gamma_2^{(MR)}}{\Gamma_1 \Gamma_2} \theta(\mu_R - \mu_L) \right]$$  \hspace{1cm} \text{(19)}$$

where $\theta$ is the step function $\theta(x) = 1$ for $x > 0$ and 0 for $x < 0$. Note that $I_{sd}^{e-h}$ can be asymmetric to bias reversal (see also Fig. 4 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 $\Gamma_1^{(ML)} \Gamma_1^{(MR)}$ while $I_{sd}^L$ is determined by the product $\Gamma_1^{(ML)} \Gamma_1^{(MR)} (m = 1, 2)$. The electron-hole contribution to the source-drain current is significant when $\Gamma_1^{(ML)} > \Gamma_1^{(MR)}$ and/or $\Gamma_1^{(ML)} > \Gamma_1^{(MR)}$. 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: $T = 300 \text{ K}, \varepsilon_1 = 0 \text{ eV}, \varepsilon_2 = 2 \text{ eV}, \Gamma_1^{(ML)} = \Gamma_1^{(MR)} = 0.2 \text{ eV}$. 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 $5 \text{ eV}$ with the step $10^{-3} \text{ eV}$.

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 not strongly 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
of the dependence of the source-drain current on the molecule-lead distance $R$. We take $I_{sd}^{(MK)} = A_{m}^{(MK)} \exp \left[ -\alpha_{m}^{(MK)} R \right]$ to reflect a tunneling transition, while $B^{(K)}(R)$ is assumed to have a dipolar distance dependence $B^{(K)} = \beta^{(K)}/R^{3}$. The parameters used are $A_{1}^{(ML)} = A_{1}^{(MR)} = 0.27 \text{ eV}$, $A_{2}^{(ML)} = 0.52 \text{ eV}$, $A_{2}^{(MR)} = 0.027 \text{ eV}$, $\alpha_{m}^{(MK)} = 1 \text{ Å}^{-1}$, and $\beta^{(K)} = 0.01 \text{ eV} \text{ Å}^{3}$ ($K = L, R$ 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 $B^{(K)}(0) = 0.01 \text{ eV}$ at this distance. The relative importance of the $I_{sd}^{L}$ and $I_{sd}^{R-h}$ components of $I_{sd}$ depends on the details of the molecule-leads couplings. In particular, when $R \rightarrow \infty$ for both leads $I_{sd}^{(M)}/B \rightarrow 0$ ($m = 1, 2$). In this limit $I_{sd}^{R-h}$ 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. (5), (10), (18), and (19) for the case $\mu_{R} \ll \varepsilon_{1} < \varepsilon_{2} \ll \mu_{L}$ we obtain $I_{sd}^{R-h}/I_{sd}^{L} \rightarrow \xi_{2}/\xi_{1}(1 - \xi_{1} - \xi_{2})$, $\infty$ 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 $I_{sd}^{R-h}$ at large distances with $I_{sd}^{R-h}/I_{sd}^{L} \sim 100$ as $R \rightarrow \infty$. 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.

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 $I_{sd}^{R-h}$ depends on this distance, and can, in some cases, result in strong dominance of $I_{sd}^{R-h}$ at large molecule-lead separations.

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