Effects of Inelastic Electron Transmission through Molecular Wires

V. May, Humboldt-University at Berlin

E. G. Petrov, Institute for Theoretical Physics, Kiev

P. Hänggi, University of Augsburg
- weak electrode molecular wire coupling
- general consideration
Nonequilibrium Green’s Function Description of the Current

\[ I = e \int d\omega \, \text{tr}_{\text{wire}}\{ \Gamma^{(R)}(\omega) G^{\text{ret}}(\omega) \Gamma^{(L)}(\omega) G^{\text{adv}}(\omega) \} (f_{\text{Fermi}}(\hbar \omega - \mu_L) - f_{\text{Fermi}}(\hbar \omega - \mu_R)) \]

\[ G(\alpha_1 \tau_1, \alpha_2 \tau_2) = \frac{1}{i\hbar} \text{tr}\{ \hat{W}_{\text{eq}} T_C S_C \, a(\alpha_1 \tau_1) \, a^+(\alpha_2 \tau_2) \} \]
Many-Particle Theory

Theoretical Chemical Physics

\[ \Sigma = \text{phonon emission} + \text{coupling to the leads} \]
Different Descriptions of the Molecular Wire

- wire characterized by adiabatic states
- adiabatic ET in the wire
- superexchange ET between the electrodes

- wire characterized by diabatic states
- nonadiabatic ET in the wire and between the wire and the electrodes
- superexchange ET between terminal units of the wire
Calculation of the Current via Level Populations

\[ I = -e \frac{\partial}{\partial t} \sum_{k,s} P_{Lks}(t) \]

Many-Electron Distribution

\[ P_\alpha(t) = \langle \alpha | \text{tr}_{\text{vib}} \{ \hat{W}(t) \} | \alpha \rangle \]
Many-Electron Description of the Electrode-Wire System

\[ |\alpha\rangle = \prod_{k,s} a_{Lk_s}^+ |0_L\rangle \times |\phi_{a(N)}\rangle \times \prod_{q,\bar{s}} a_{Rq_s}^+ |0_R\rangle \]

\[ H_{\text{wire}} = \sum_{N} \sum_{a(N)} H_{a(N)}(q) |\phi_{a(N)}\rangle \langle \phi_{a(N)} | \]

\[ H_{\text{wire}} = \sum_{m,n,s} (\delta_{m,n} H_{ms}(q) + (1 - \delta_{m,n}) V_{m,n}(q)) a_{ms}^+ a_{ns} \]
Projection Superoperator Approach

\[ P_{\alpha}(t) = \langle \alpha | \text{tr}_{\text{vib}} \{ \mathcal{P}\hat{W}(t) \} | \alpha \rangle \]

Many-Electron Rate-Equation

\[ \frac{\partial}{\partial t} P_{\alpha}(t) = -\sum_{\beta} (k_{\alpha \rightarrow \beta} P_{\alpha}(t) - k_{\beta \rightarrow \alpha} P_{\beta}(t)) \]

Transition Superoperator

\[ \mathcal{T}(\omega) = \sum_{N=1}^{\infty} \mathcal{L}_V \{ \mathcal{G}_0(\omega) \mathcal{L}_V \}^{2N-1} \quad \mathcal{G}_0(\omega) = -i \int_0^\infty dt \ e^{i\omega t} [\mathcal{U}_0 - \mathcal{P}] \]
Single Electron Transmission

reactant state $\rightarrow$ intermediate state $\rightarrow$ product state
Sequential Transfer versus Coherent Transfer

\[ E_F \rightarrow E_a \rightarrow R \]

\[ k_{L \rightarrow a} \]

\[ k_{a \rightarrow R} \]
Fourth-Order Transition Rate

\[ k_{L \rightarrow R} = \int d\Omega_1 d\Omega_2 \Gamma^{(L)}(\Omega_1) f_L(\Omega_1) \mathcal{T}^{(IV)}(\Omega_1, \Omega_2)(1 - f_R(\Omega_2)) \Gamma^{(R)}(\Omega_2) \]

\[ \mathcal{T}^{(IV)}(\Omega_1, \Omega_2) = \mathcal{T}^{(sx)}(\Omega_1, \Omega_2) + \mathcal{T}^{(seq)}(\Omega_1, \Omega_2) + \mathcal{T}^{(f)}(\Omega_1, \Omega_2) \]
Fourth-Order Transmission Coefficient for a Wire with Six Levels
$E_0 = E_F + 0.5 \text{ eV}$
$E_{+/-.} = E_0 \pm 0.1 \text{ eV}$
$E_{\text{vib}} = 0.04 \text{ eV}$

Symmetrically Applied Voltage
IV-Characteristics of a Two-Level Wire

\[ \frac{I}{e} = j^{(\text{II})} + G_0 j^{(\text{IV})} \]
Hopping versus Superexchange Transfer
Wire-Length Dependence of the Current

\[ E = \frac{V}{d} = 3 \times 10^6 \text{V/cm} \]

\[ E = \frac{V}{d} = 4.35 \times 10^5 \text{V/cm} \]

\[ V = 0.9 \text{ V} \]