Effects of Inelastic Electron Transmission through Molecular Wires

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- weak electrode molecular wire coupling

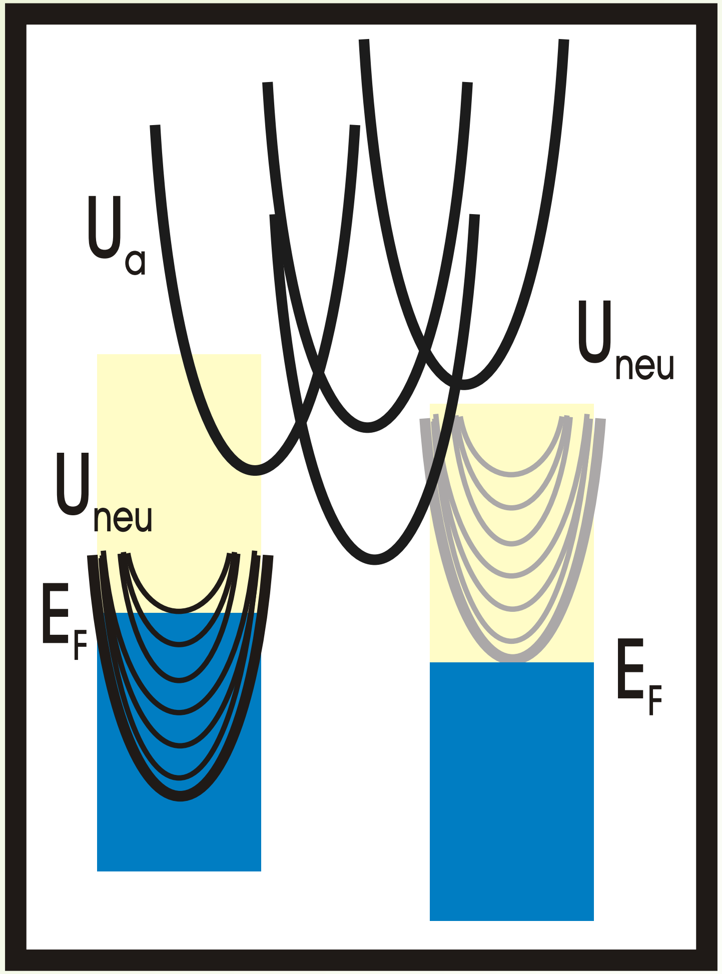
- general consideration

Nonequilibrium Green's Function Description of the Current

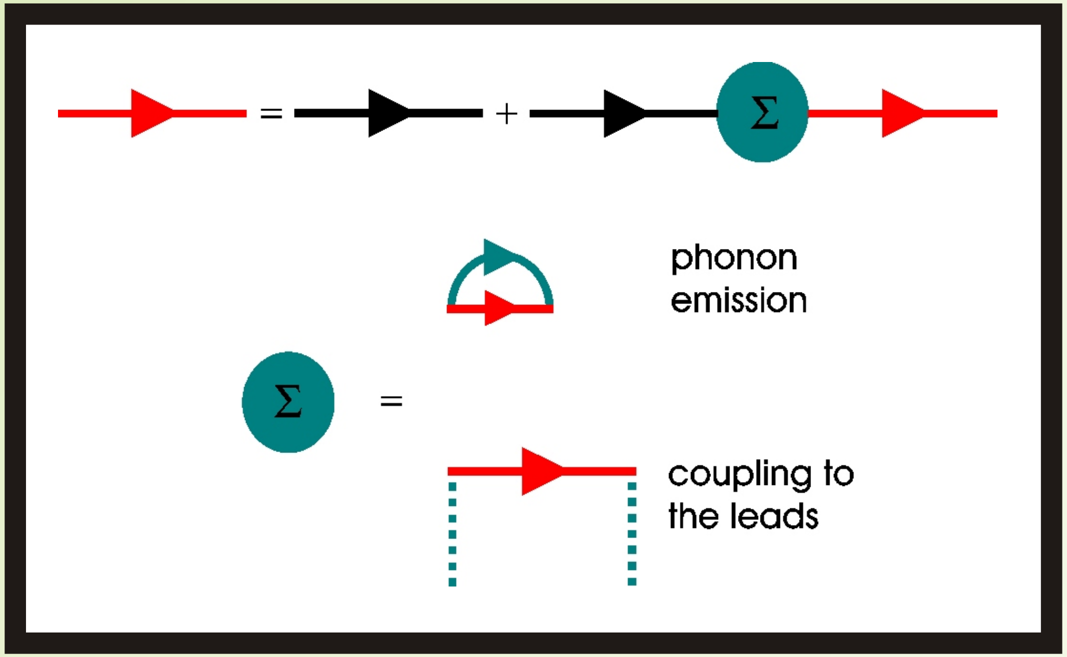
$$I = e \int d\omega \; \mathrm{tr}_{\mathrm{wire}}\{\mathbf{\Gamma}^{(R)}(\omega)\mathbf{G}^{\mathrm{ret}}(\omega)\mathbf{\Gamma}^{(L)}(\omega)\mathbf{G}^{\mathrm{adv}}(\omega)\}(f_{\mathrm{Fermi}}(\hbar\omega - \mu_L) - f_{\mathrm{Fermi}}(\hbar\omega - \mu_R))$$

$$G(\alpha_1\tau_1, \alpha_2\tau_2) = \frac{1}{i\hbar}\mathrm{tr}\{\hat{W}_{\mathrm{eq}}T_{\mathrm{C}}S_{\mathrm{C}}\; a(\alpha_1\tau_1)\; a^+(\alpha_2\tau_2)\}$$

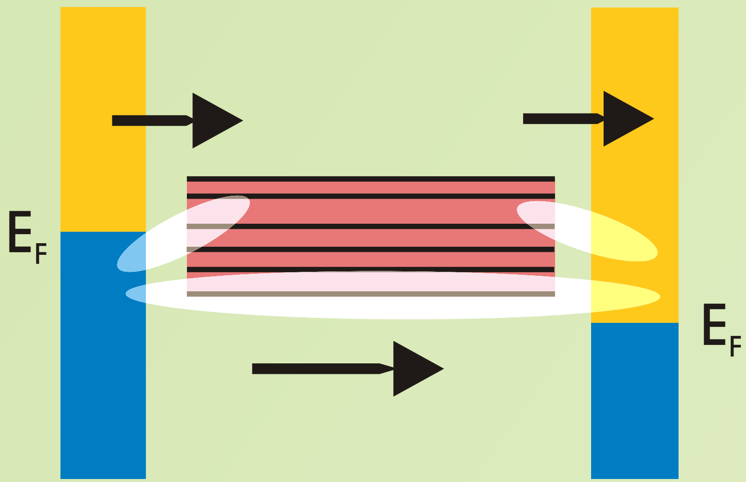
Theoretical Chemical Physics

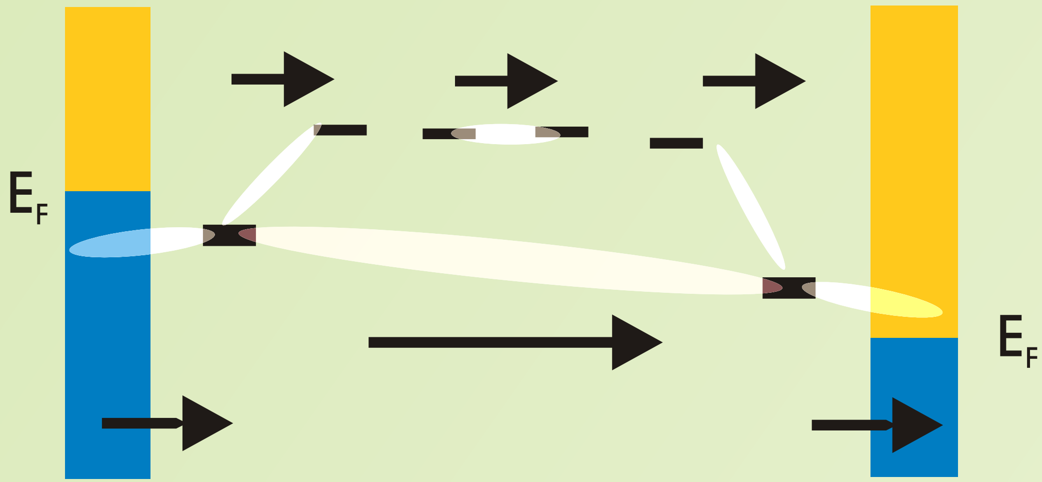


Many-Particle Theory



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

$$I = -e \frac{\partial}{\partial t} \sum_{\mathbf{k},s} P_{L\mathbf{k}s}(t)$$

Many-Electron Distribution

$$P_\alpha(t) = \langle \alpha | \mathrm{tr}_{\mathrm{vib}} \{ \hat{W}(t) \} | \alpha \rangle$$

Many-Electron Description of the Electrode-Wire System

$$|\alpha\rangle = \prod_{\mathbf{k},s} a^{+}_{L\mathbf{k}s}|0_L\rangle \times |\phi_{a(N)}\rangle \times \prod_{\mathbf{q},\bar{s}} a^{+}_{R\mathbf{q}\bar{s}}|0_R\rangle$$

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

$$H_{\text{wire}} = \sum_{m,n,s} (\delta_{m,n} H_{ms}(q) + (1-\delta_{m,n})V_{m,n}(q))a^{+}_{ms}a_{ns}$$

Projection Superoperator Approach

$$\mathcal{P}\ldots = \sum_\alpha \hat{R}_\alpha \hat{\Pi}_\alpha \mathrm{tr}\{\hat{\Pi}_\alpha \ldots\} \qquad P_\alpha(t) = \langle \alpha | \mathrm{tr}_{\mathrm{vib}}\{\mathcal{P}\hat{W}(t)\} | \alpha \rangle$$

$$\frac{\partial}{\partial t} P_\alpha(t) = -\sum_\beta \left(k_{\alpha\to\beta} P_\alpha(t) - k_{\beta\to\alpha} P_\beta(t)\right)$$

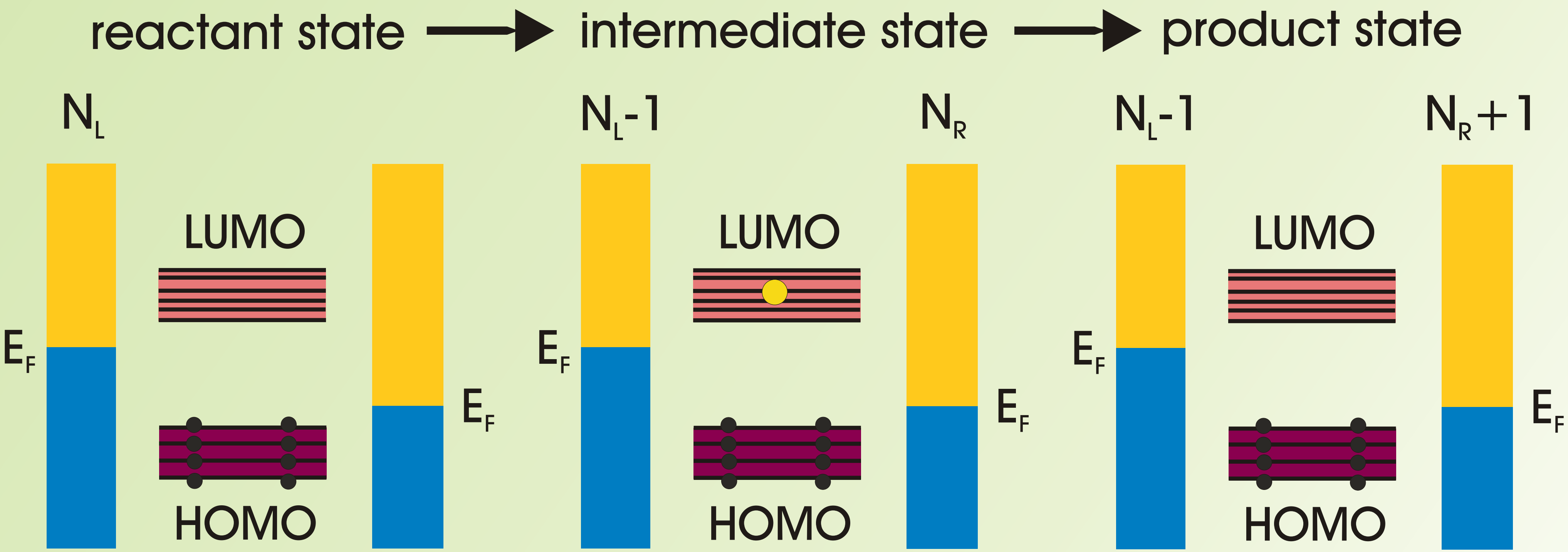
$$k_{\alpha\to\beta} = \mathrm{tr}\{\hat{\Pi}_\beta \mathcal{T}(\omega=0) \hat{R}_\alpha \hat{\Pi}_\alpha\}$$

Many-Electron Rate-Equation

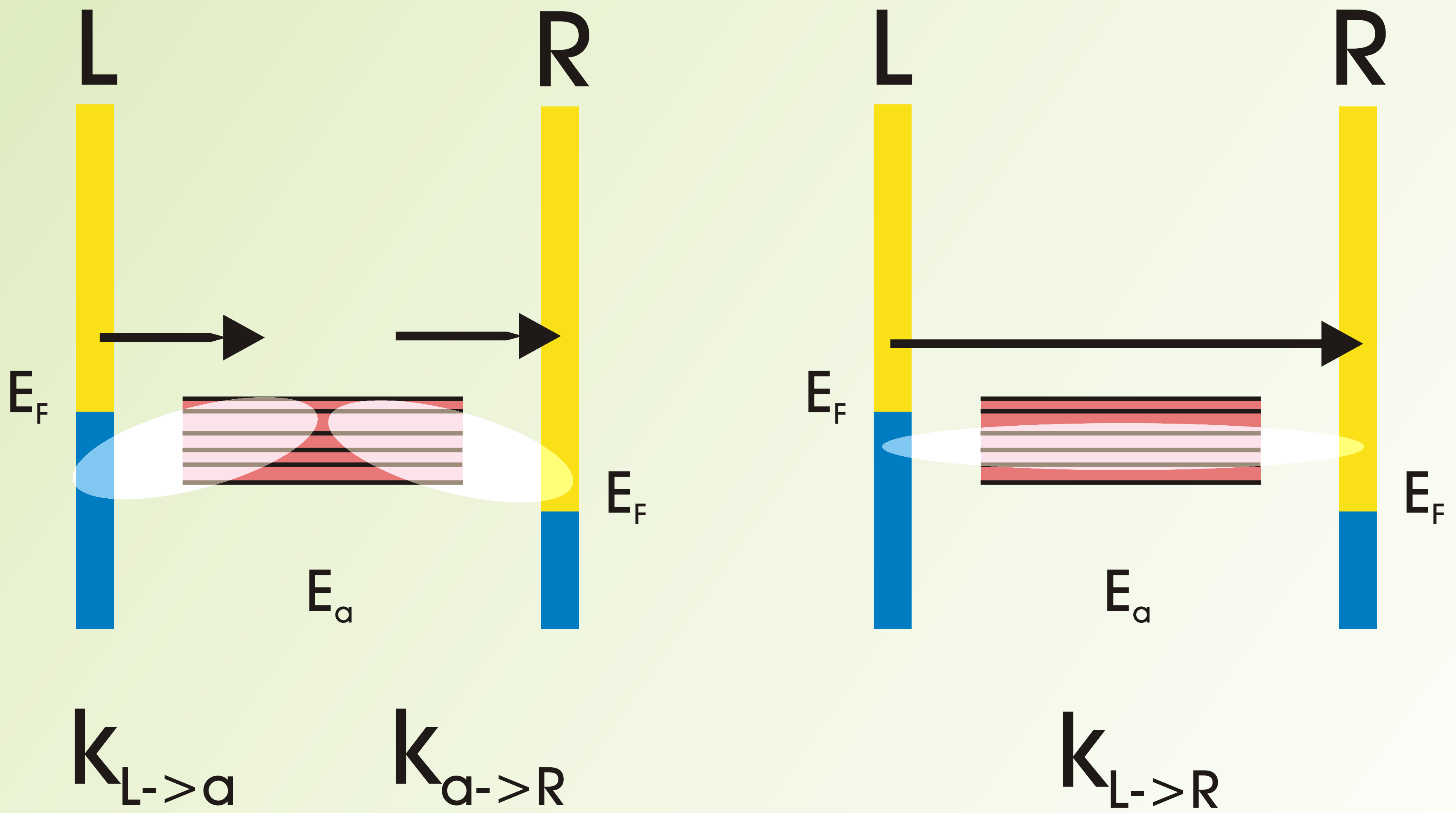
Transition Superoperator

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

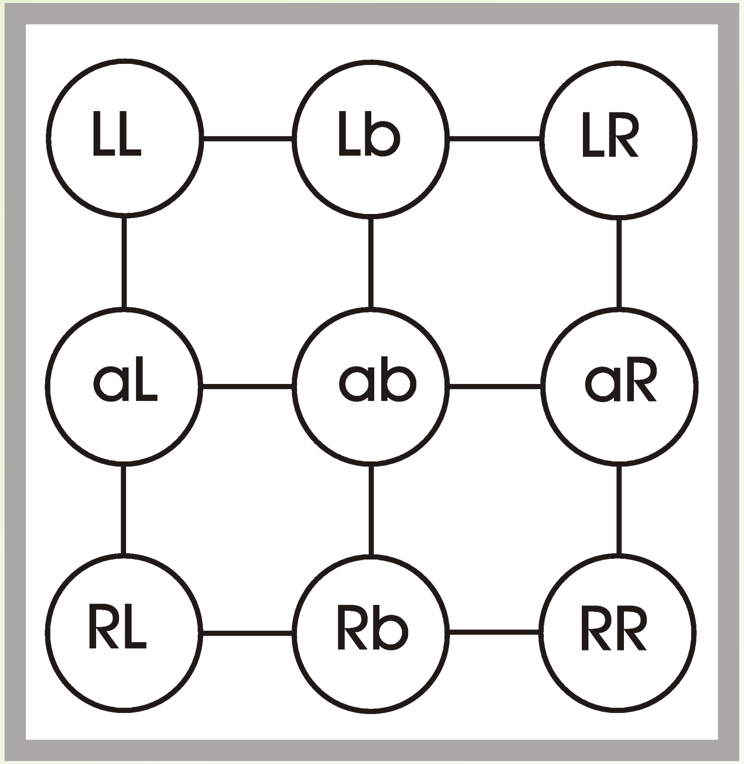
Single Electron Transmission



Sequential Transfer versus Coherent Transfer



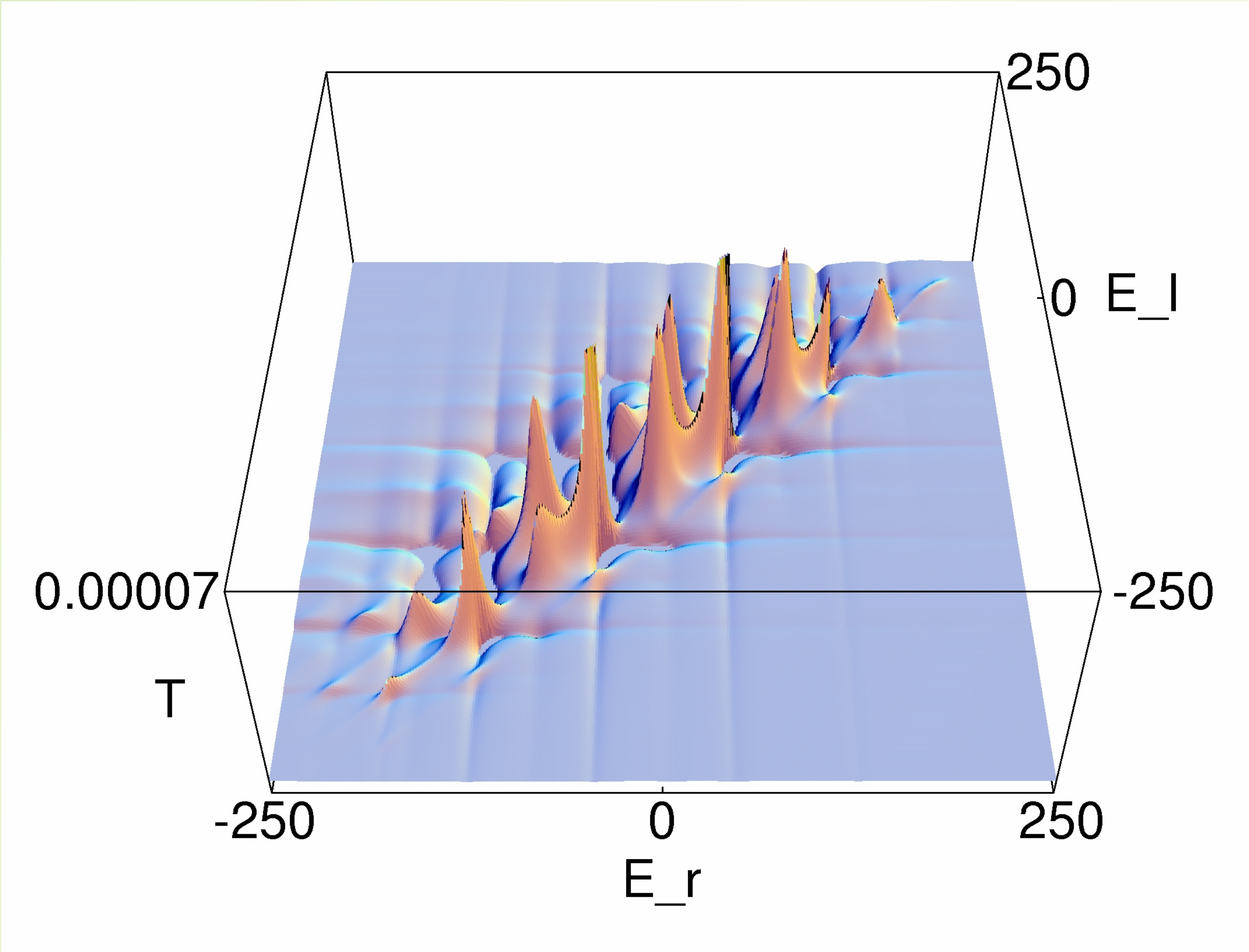
Fourth-Order Transition Rate



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

$$\mathcal{T}^{(IV)}(\Omega_1,\Omega_2) = \mathcal{T}^{(\mathrm{sx})}(\Omega_1,\Omega_2) + \mathcal{T}^{(\mathrm{seq})}(\Omega_1,\Omega_2) + \mathcal{T}^{(\mathrm{f})}(\Omega_1,\Omega_2)$$

Fourth-Order Transmission Coefficient for a Wire with Six Levels

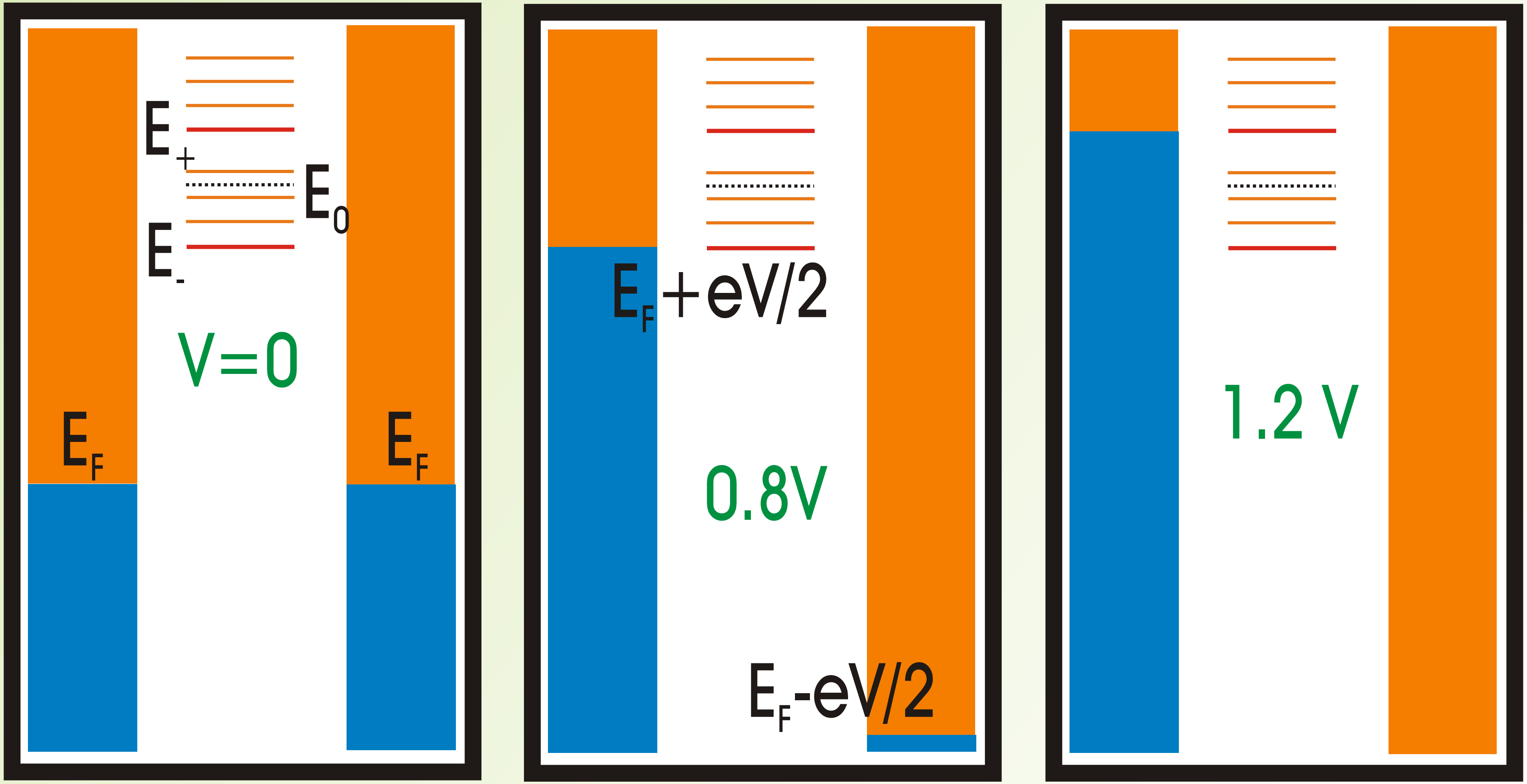


Symmetrically Applied Voltage

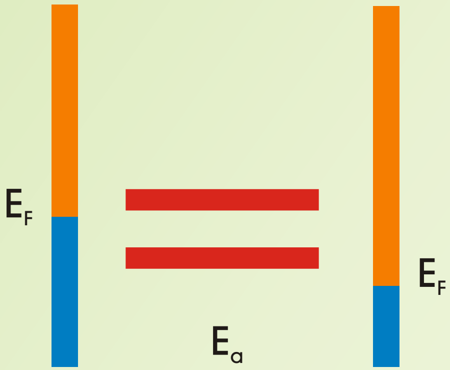
$E_0 = E_F + 0.5$ eV

$E_{+/-} = E_0 +/- 0.1$ eV

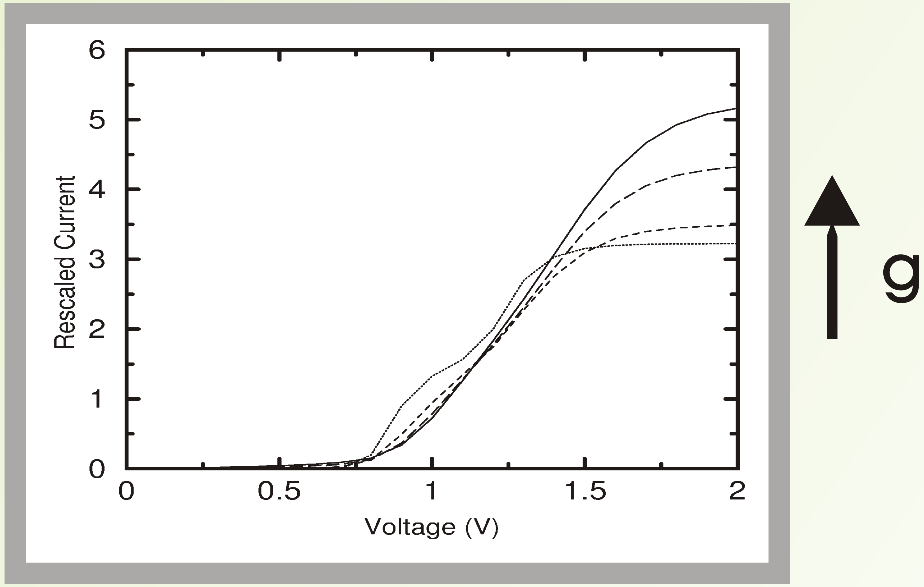
$E_{vib} = 0.04$eV



IV-Characteristics of a Two-Level Wire

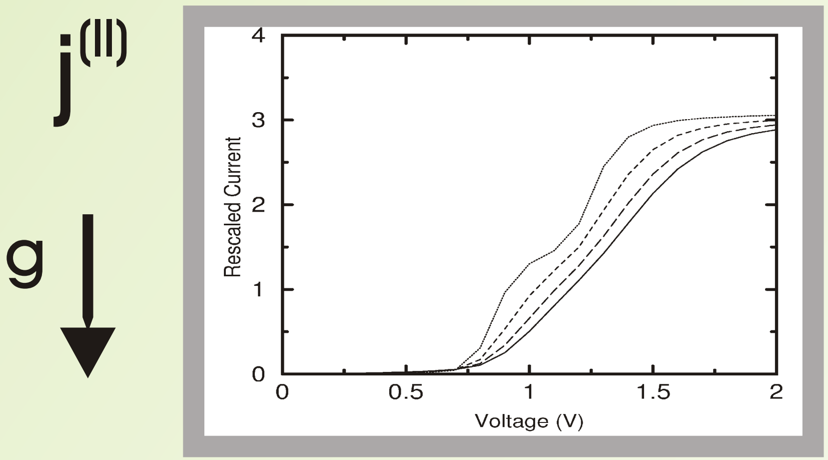


Total Current

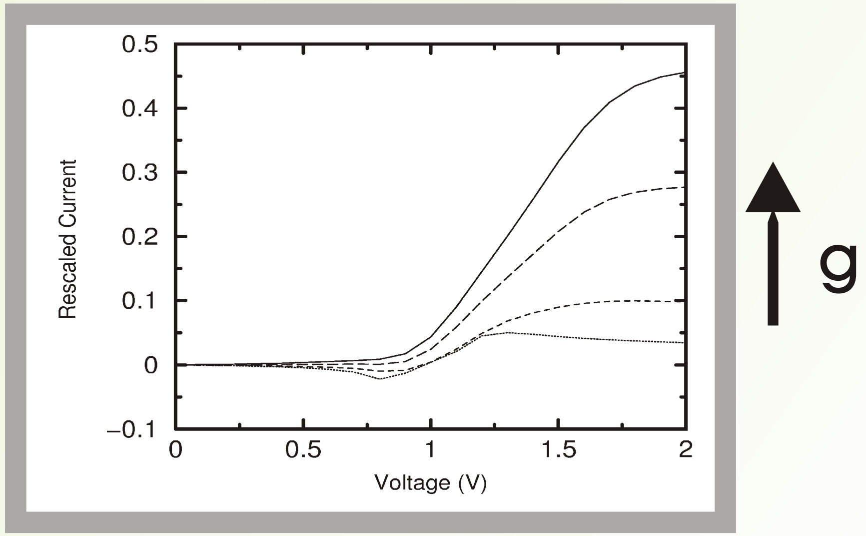


$$I/e \quad = \quad j^{(II)} \quad + \quad G_0\, j^{(IV)}$$

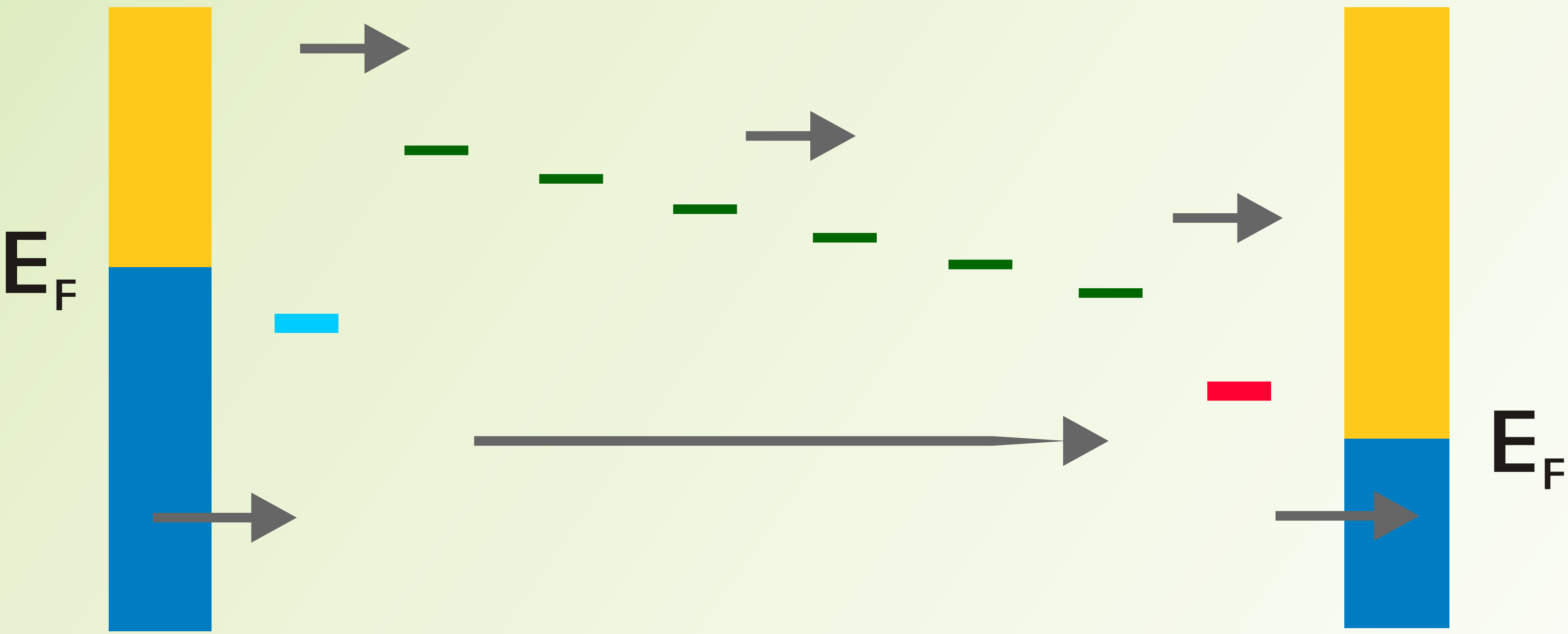
$j^{(II)}$



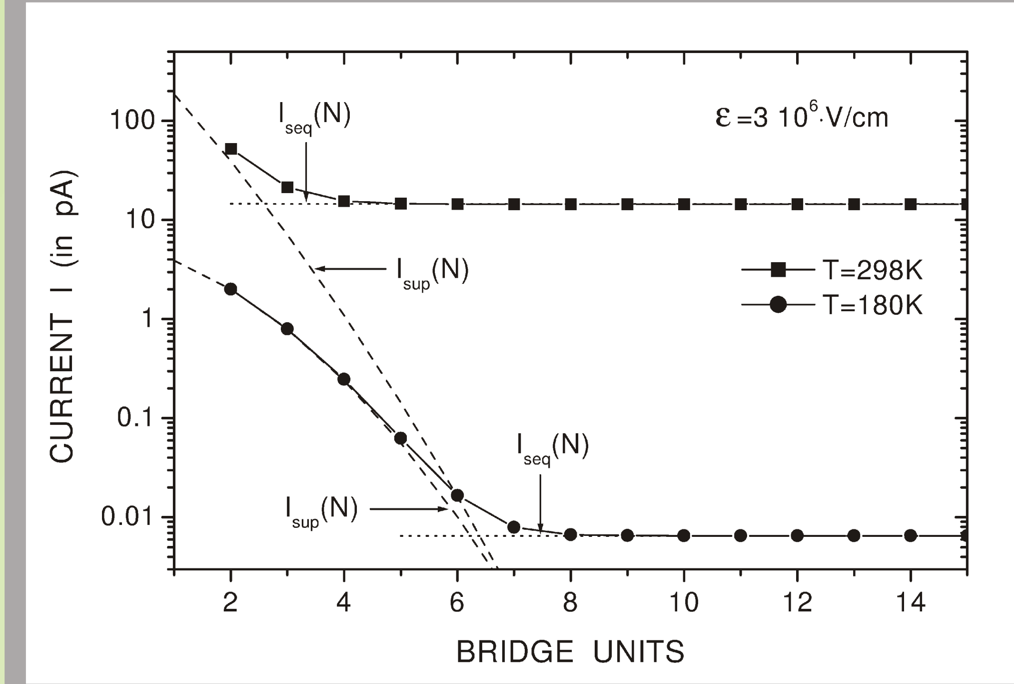
$j^{(IV)}$

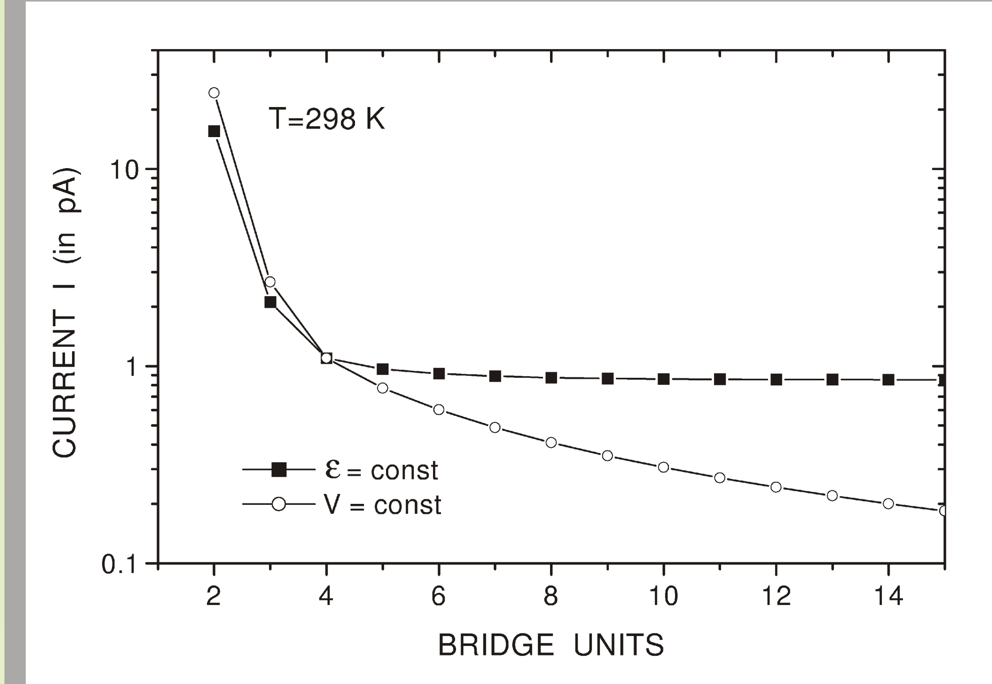


Hopping versus Superexchange Transfer



Wire-Length Dependence of the Current





$E = V/d = 3 \times 10^6$ V/cm

$E = V/d = 4.35 \times 10^5$ V/cm

$V = 0.9$ V