Theory of Vibrationally Inelastic Electron Transport through Molecular Bridges

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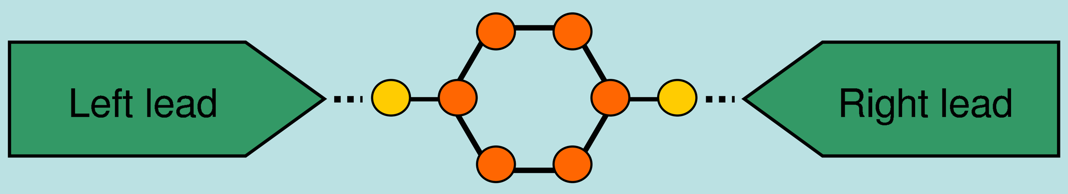
Goals of this work

To understand how the vibrations influence the electron transport through a molecular bridge.



To formulate the theory employing methods developed for description of the electron scattering from large molecules.

Theoretical description - Hamiltonian

The system is described with the following Hamiltonian

$$H_S = |\phi_d\rangle \tilde{H}_d \langle\phi_d| + \sum_{k,\alpha=L,R} \left\{ |\phi_{k\alpha}\rangle(\epsilon_{k\alpha} + \tilde{H}_0)\langle\phi_{k\alpha}| + |\phi_d\rangle V_{dk\alpha}\langle\phi_{k\alpha}| + |\phi_{k\alpha}\rangle V^*_{dk\alpha}\langle\phi_d| \right\}$$

The potential surfaces can in principle be found form quantum chemistry. Here we use harmonic potential model

$$\tilde{H}_0 = \omega_S\, a^\dagger a \quad , \quad \tilde{H}_d = \omega_S\, a^\dagger a + \lambda(a + a^\dagger) + \epsilon_d = \omega_S\, a_d^\dagger a_d + \epsilon_d - \frac{\lambda^2}{\omega_S}.$$

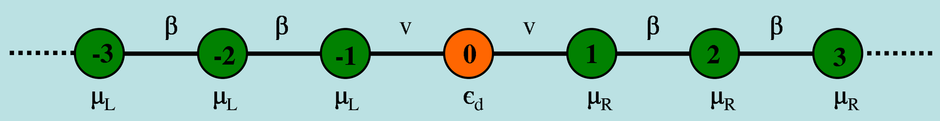
Other vibrational modes, not coupled directly to electronic motion, can be included as a bath

$$H = H_S + H_B + H_{SB}, \quad H_B = \sum_j \omega_j\, b_j^\dagger b_j, \quad H_{SB} = |\phi_d\rangle \sum_j c_j (a_d b_j^\dagger + a_d^\dagger b_j)\langle\phi_d|.$$

For this study we use Ohmic bath with exponential cut-off characterized by spectral density

$$J(\omega) = \sum_j c_j^2 \delta(\omega - \omega_j) = \eta\omega e^{-\omega/\omega_c}.$$

For this study, the electronic states in leads are found from a simple tigh-binding model:



One-electron transmission and current

Scattering theory yields (for specified final and ini.-states)

$$t_{\alpha_f\leftarrow\alpha_i}(\epsilon_f, v_f, \mathrm{v}_f, \epsilon_i, v_i, \mathrm{v}_i) = \delta(\epsilon_i + E_{\mathrm{v}_i} + E_{v_i} - \epsilon_f - E_{\mathrm{v}_f} - E_{v_f})\Gamma_{\alpha_i}(\epsilon_i)\Gamma_{\alpha_f}(\epsilon_f) \times \left| \langle \mathrm{v}_f|\langle v_f|\langle\phi_d|(\epsilon_i^+ - H)^{-1}|\phi_d\rangle|v_i\rangle|\mathrm{v}_i\rangle \right|^2,$$

Where

$$\Gamma_\alpha(\epsilon) \equiv 2\pi \sum_k \delta(\epsilon - \epsilon_{k\alpha})|V_{dk\alpha}|^2 \qquad \Sigma_\alpha(\epsilon) = \sum_k \frac{|V_{dk\alpha}|^2}{\epsilon^+ - \epsilon_{k\alpha}} \equiv \Delta_\alpha(\epsilon) - \tfrac{i}{2}\Gamma_\alpha(\epsilon).$$

It is useful to introduce integrated quantities

$$t_{\alpha_f\leftarrow\alpha_i}(\epsilon_f, \epsilon_i) \equiv \sum_{v_f,\mathrm{v}_f} t_{\alpha_f\leftarrow\alpha_i}(\epsilon_f, v_f, \mathrm{v}_f, \epsilon_i, v_i, \mathrm{v}_i), \qquad t_{\alpha_f\leftarrow\alpha_i}(\epsilon_i) = \int t_{\alpha_f\leftarrow\alpha_i}(\epsilon_f, \epsilon_i)\, d\epsilon_f.$$

The current is calculated from

$$I = \frac{1}{\pi}\int d\epsilon_i \int d\epsilon_f \left\{ t_{R\leftarrow L}(\epsilon_f, \epsilon_i) f_L(\epsilon_i)[1 - f_R(\epsilon_f)] - t_{L\leftarrow R}(\epsilon_f, \epsilon_i) f_R(\epsilon_i)[1 - f_L(\epsilon_f)] \right\}$$

Evaluation of transmission

The elastic case – exact solution

$$t_{R\leftarrow L}(\epsilon_i) = t_{L\leftarrow R}(\epsilon_i) = \frac{\Gamma_R(\epsilon_i)\Gamma_L(\epsilon_i)}{[\epsilon_i - \epsilon_d - \Delta_L(\epsilon_i) - \Delta_R(\epsilon_i)]^2 + [\Gamma_L(\epsilon_i) + \Gamma_R(\epsilon_i)]^2/4}$$

The inelastic case – numerically exact solution

$$t_{R\leftarrow L}(\epsilon_f, \epsilon_i) = \sum_{v_f} \delta(\epsilon_i - \epsilon_f - E_{v_f})\Gamma_R(\epsilon_f)\Gamma_L(\epsilon_i) \left| \langle v_f|G_d^{(S)}(\epsilon_i)|0\rangle \right|^2,$$

$$G_d^S(E) \equiv \langle\phi_d|(E^+ - H_S)^{-1}|\phi_d\rangle = \left[E^+ - \tilde{H}_d - \Sigma_L(E - \tilde{H}_0) - \Sigma_R(E - \tilde{H}_0) \right]^{-1}.$$

Inclusion of the bath – expansion in H_{SB} , i.e. in η

$$t_{R\leftarrow L}(\epsilon_f, \epsilon_i) = \sum_{m=0}^{\infty} t^{(m)}_{R\leftarrow L}(\epsilon_f, \epsilon_i),$$

$$t^{(0)}_{R\leftarrow L}(\epsilon_f, \epsilon_i) = \sum_{v_f} \delta(\epsilon_i - \epsilon_f - E_{v_f})\Gamma_R(\epsilon_f)\Gamma_L(\epsilon_i) \left| \langle v_f|G_d(\epsilon_i)|0\rangle \right|^2,$$

$$t^{(1)}_{R\leftarrow L}(\epsilon_f, \epsilon_i) = \sum_{v_f} J(\epsilon_i - \epsilon_f - E_{v_f})\Gamma_R(\epsilon_f)\Gamma_L(\epsilon_i) \left| \langle v_f|\, G_d(\epsilon_f + E_{v_f})\, a_d\, G_d(\epsilon_i)\, |0\rangle \right|^2,$$

$$G_d(E) = \langle\phi_d| \left(E^+ - H_S - |\phi_d\rangle a_d^\dagger \int d\omega\, J(\omega)\, G_d^S(E - \omega)\, a_d \langle\phi_d| \right)^{-1} |\phi_d\rangle.$$

$$G_d(E) = G_d^S(E) + G_d^S(E) \left[a_d^\dagger \int d\omega\, J(\omega)\, G_d^S(E - \omega)\, a_d \right] G_d(E)$$

Complete transmission from unitarity

In the case of zero bias and symmetric bridge one can write

$$t^{(m)}_{R\leftarrow L} = t^{(m)}_{L\leftarrow L} \text{ for all } m > 0.$$

$$t^{(0)}_{R\leftarrow L}(\epsilon_i) = \sum_{v_f=0}^{\infty} \Gamma_R(\epsilon_i - E_{v_f})\Gamma_L(\epsilon_i) \left| \langle v_f|G_d(\epsilon_i)|0\rangle \right|^2,$$

$$t^{(0)}_{L\leftarrow L}(\epsilon_i) = \left| 1 - i\Gamma_L(\epsilon_i)\langle 0|G_d(\epsilon_i)|0\rangle \right|^2 + \sum_{v_f=1}^{\infty} \Gamma_L(\epsilon_i - E_{v_f})\Gamma_L(\epsilon_i) \left| \langle v_f|G_d(\epsilon_i)|0\rangle \right|^2.$$

i.e. from unitarity condition

$$t^{(0)}_{L\leftarrow L}(\epsilon) + \sum_{m>0} t^{(m)}_{L\leftarrow L}(\epsilon) + t^{(0)}_{R\leftarrow L}(\epsilon) + \sum_{m>0} t^{(m)}_{R\leftarrow L}(\epsilon) = 1,$$

we have

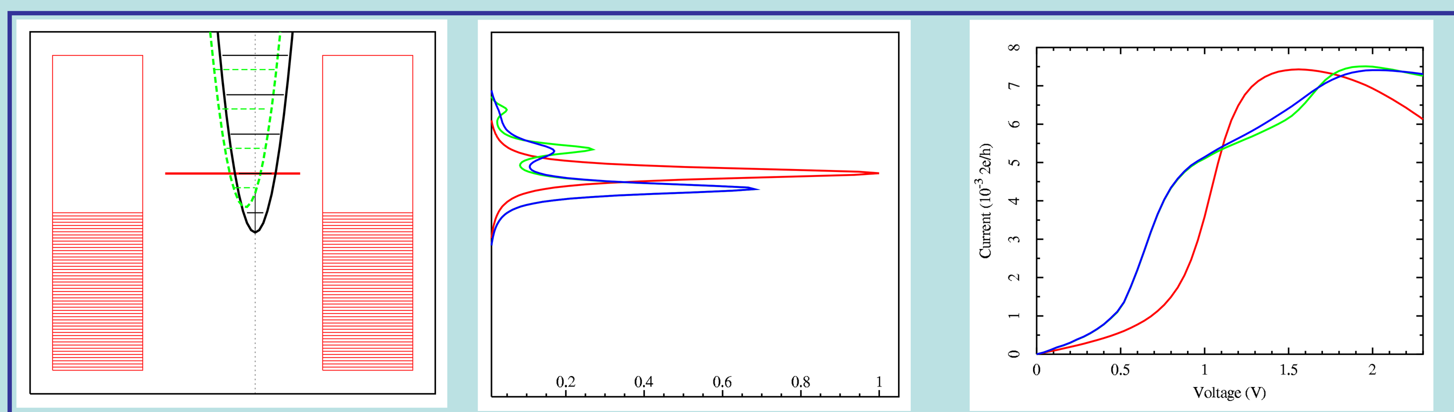
$$t_{R\leftarrow L}(\epsilon_i) = \tfrac{1}{2}\left(1 + t^{(0)}_{R\leftarrow L}(\epsilon_i) - t^{(0)}_{L\leftarrow L}(\epsilon_i) \right) = -\Gamma_L(\epsilon_i)\, \mathrm{Im}\langle 0|G_d(\epsilon_i)|0\rangle.$$

Conclusions

- The theory of the *vibrationally inelastic transport* of single electron through molecular bridge is formulated.
- The vibrations are divided into one (or few) system modes coupled directly to electronic motion and *vibrational bath*. The system mode is treated *numerically exactly* and bath is treated perturbatively (convergence checked).
- The *anharmonic effects* can be taken into account
- Wide-band limit is not assumed and sharp features can be present in density of states in leads.
- *Dissociation of the bridge* can be treated.
- Different regimes of transport are studied below on a simple tight-binding model with harmonic vibrations.

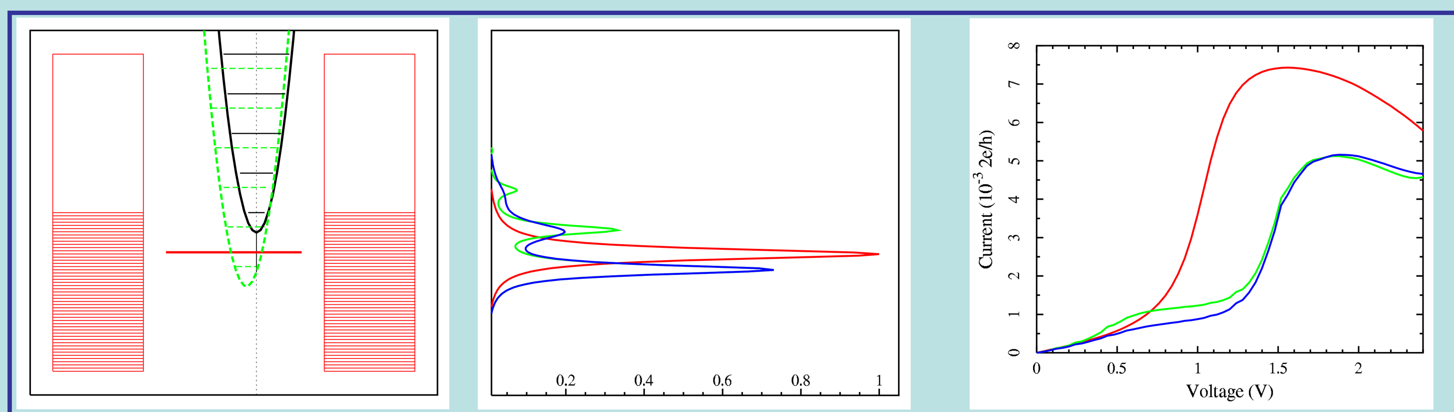
Results

Model | Transmission | Current



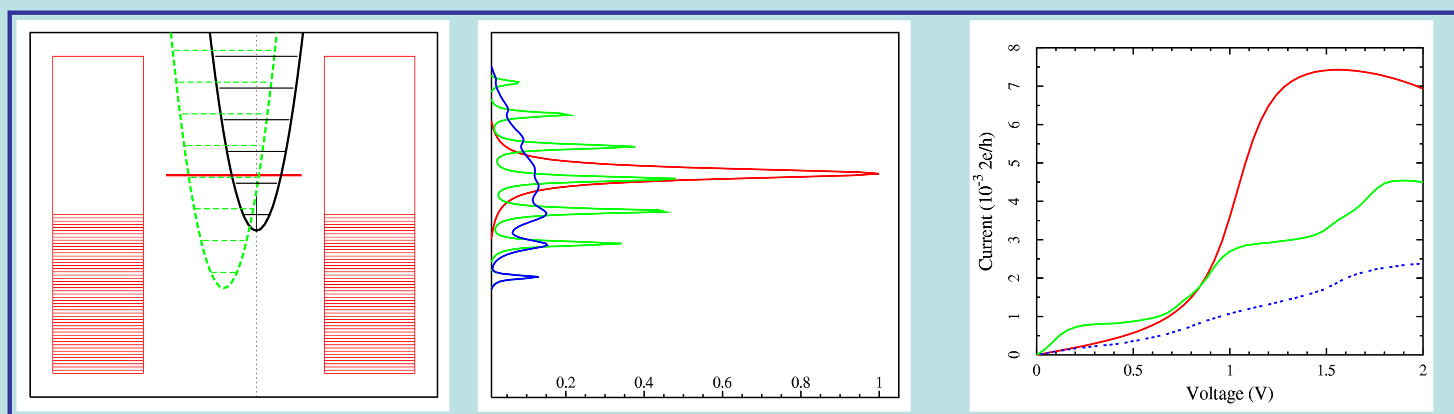
Model A

$\varepsilon_d = 0.5$
$v = 0.2$
$\omega_S = 0.5$
$\lambda = 0.3$



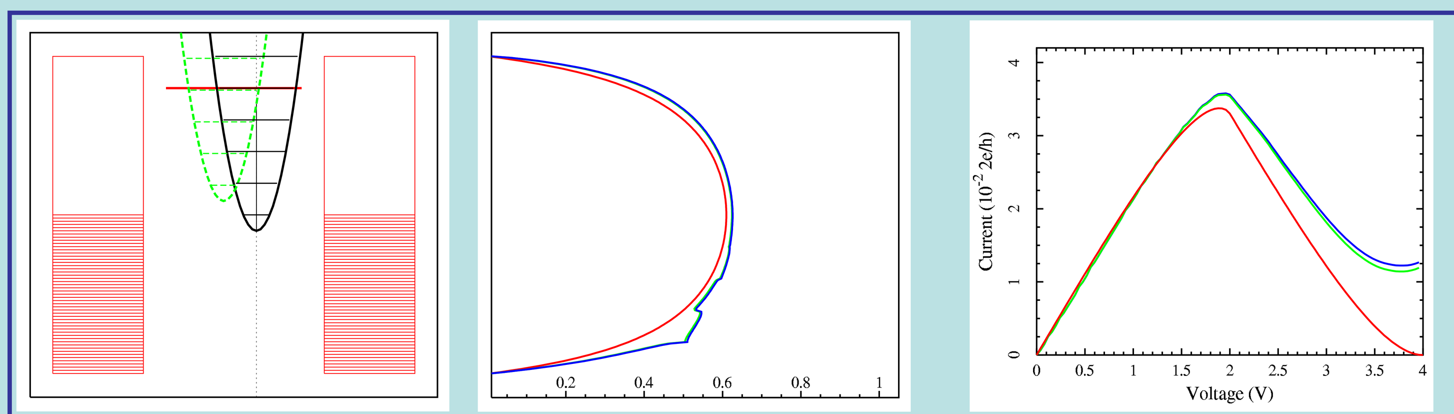
Model B

$\varepsilon_d = -0.5$
$v = 0.2$
$\omega_S = 0.5$
$\lambda = 0.3$



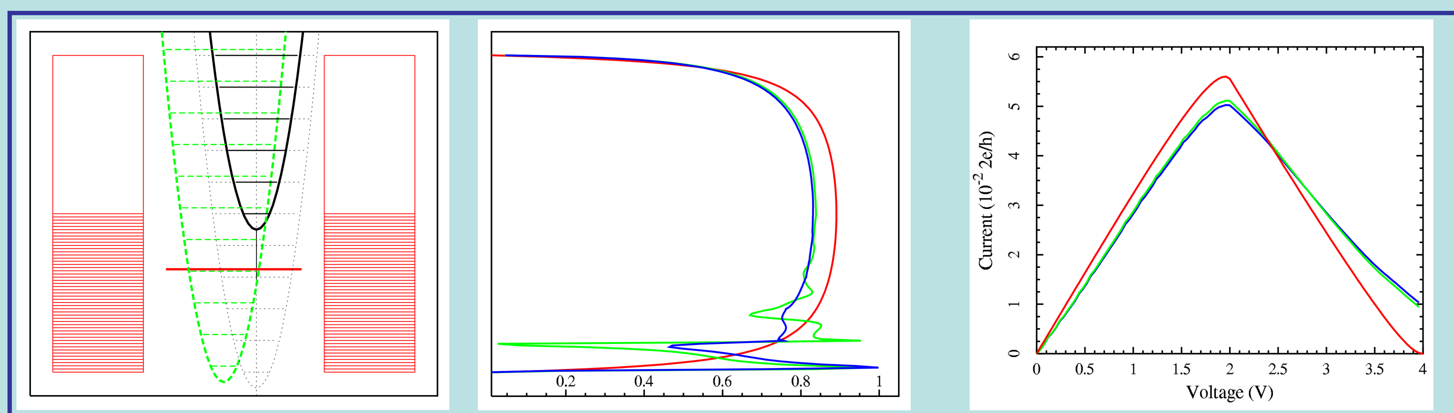
Model C

$\varepsilon_d = 0.5$
$v = 0.2$
$\omega_S = 0.4$
$\lambda = 0.7$



Model D

$\varepsilon_d = 1.6$
$v = 1.0$
$\omega_S = 0.4$
$\lambda = 0.7$

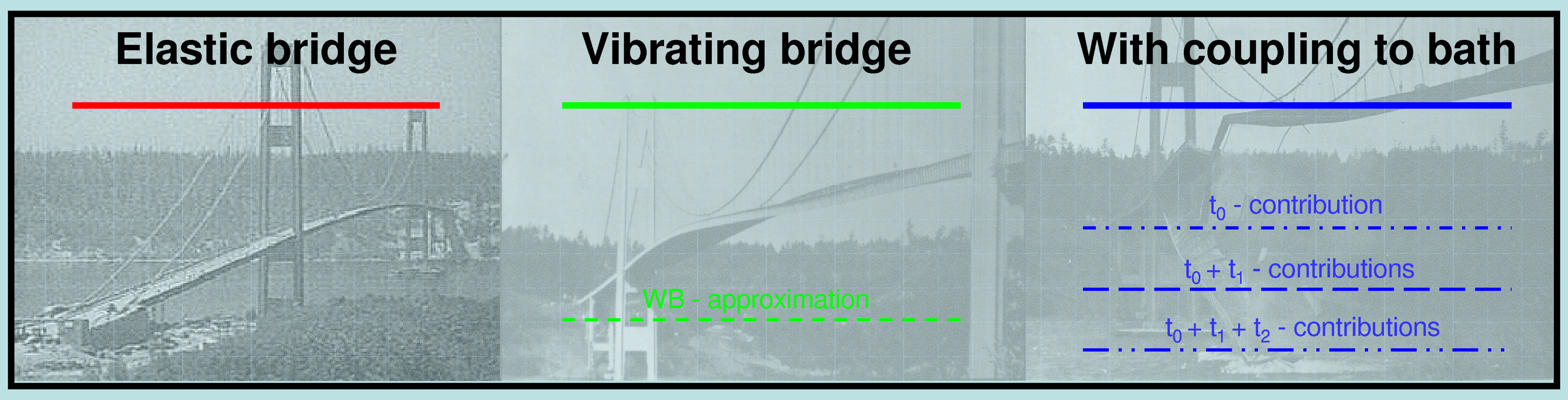


Model E

$\varepsilon_d = -0.7$
$v = 1.0$
$\omega_S = 0.4$
$\lambda = 0.7$

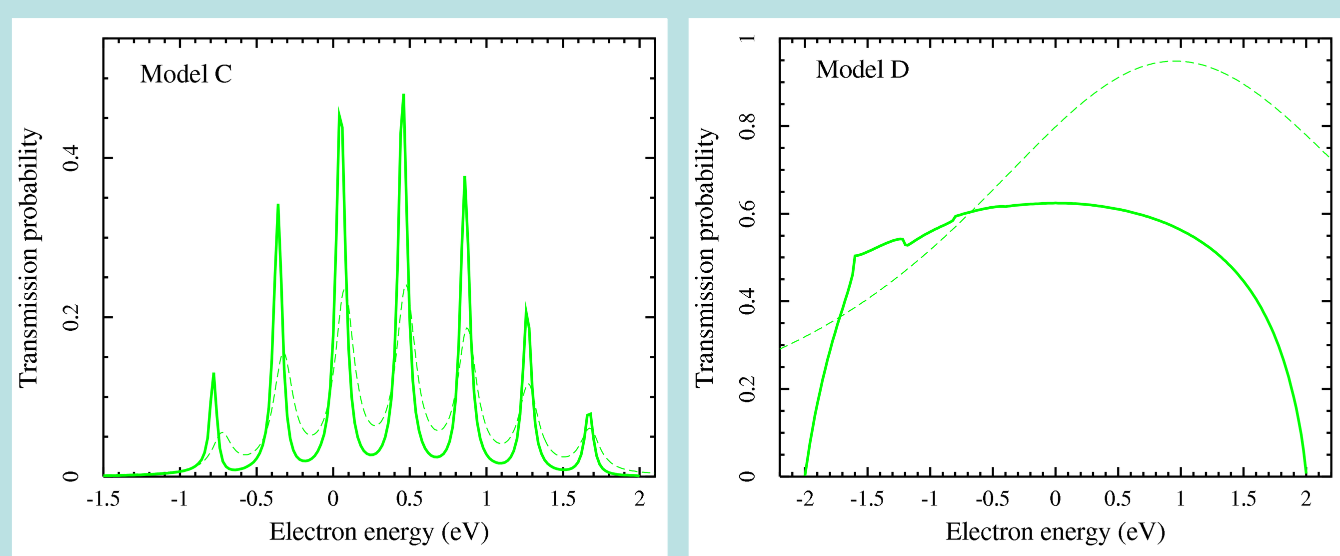
In all models: β=1eV, η=0.1, $\omega_C = \omega_S$

Legend



Further tests

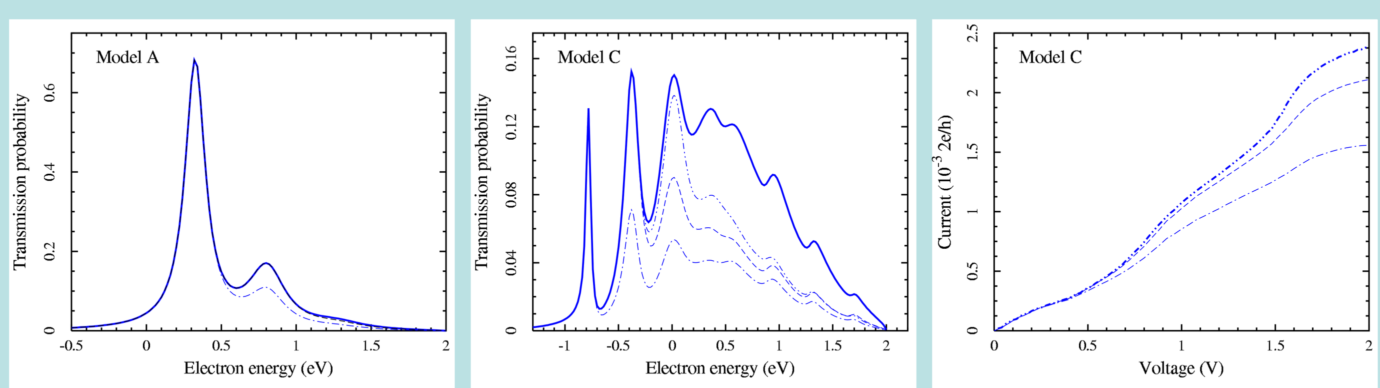
Wide-band approximation



The *width of peaks is narrowed* with respect to wide-band limit as a consequence of resonance overlap – the effect well known from electron scattering from molecules

Wide-band limit is useless for bridge strongly coupled to leads (wide resonances).

Convergence of the expansion in coupling to bath



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