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.

Theoretical description - Hamiltonian
The system is described with the following Hamiltonian
\[ H = H_0 + \sum_i \sum_j C_{ij} n_i n_j \]
The potential surfaces can in principle be found from quantum chemistry. Here we use harmonic potential model
\[ H_0 = \sum_i \omega_i^2 n_i^2 \]
Other vibrational modes, not coupled directly to electronic motion, can be included as a bath
\[ H_b = \sum_i \omega_i^2 n_i^2 \]
For this study we use Ohmic bath with exponential cutoff characterized by spectral density
\[ \gamma(n) = \frac{\omega_0}{e^{\gamma n} - 1} \]
For this study, the electronic states in leads are found from a simple tight-binding model:

One-electron transmission and current
Scattering theory yields (for specified final and initial states)
\[ T(E) = \frac{1}{\pi} \text{Im} \left[ \pi \sum_f \sum_i \frac{\langle i | \psi_f \rangle \langle n_i \psi_f \rangle}{E_i - E} \right] \]

Where
\[ E_k = \frac{\omega_k}{\sqrt{2}} \sum_{i=1}^N \cos \frac{\pi}{N} x_{ki} \]

It is useful to introduce integrated quantities
\[ \sum_f \sum_i \frac{\langle i | \psi_f \rangle \langle n_i \psi_f \rangle}{E_i - E} \]
The current is calculated from
\[ J = \frac{2 e}{h} \int dE \text{Re} \left[ \pi \sum_f \sum_i \frac{\langle i | \psi_f \rangle \langle n_i \psi_f \rangle}{E_i - E} \right] \]

Complete transmission from unitarity
In the case of zero bias and symmetric bridge one can write
\[ T_{ab} = \frac{1}{2} \left( 1 + \frac{2}{\pi} \text{Re} \left[ \sum_f \sum_i \frac{\langle i | \psi_f \rangle \langle n_i \psi_f \rangle}{E_i - E} \right] \right) \]

Evaluation of transmission
The elastic case - exact solution
\[ \frac{1}{2} \left( 1 + \frac{2}{\pi} \text{Re} \left[ \sum_f \sum_i \frac{\langle i | \psi_f \rangle \langle n_i \psi_f \rangle}{E_i - E} \right] \right) \]
The inelastic case - numerically exact solution
\[ \frac{1}{2} \left( 1 + \frac{2}{\pi} \text{Re} \left[ \sum_f \sum_i \frac{\langle i | \psi_f \rangle \langle n_i \psi_f \rangle}{E_i - E} \right] \right) \]

Inclusion of the bath - expansion in \( H_b \), i.e., in \( \eta \)
\[ \frac{1}{2} \left( 1 + \frac{2}{\pi} \text{Re} \left[ \sum_f \sum_i \frac{\langle i | \psi_f \rangle \langle n_i \psi_f \rangle}{E_i - E} \right] \right) \]

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

Further tests

Elastic bridge
Vibrating bridge
With coupling to bath

Wide-band approximation

Convergence of the expansion in coupling to bath