Theory of vibrationally inelastic electron transport through molecular bridges

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Motivation I: Molecular electronics as ultimate solution for miniaturization of electronic devices

Experiments: conduction properties of individual molecules


Motivation II


Molecular conductance junctions are structures in which single molecules or small groups of molecules conduct electrical current between two electrodes. In such junctions, the connection between the molecule and the electrodes greatly affects the current-voltage characteristics. Despite several experimental and theoretical advances, including the understanding of simple systems, there is still limited correspondence between experimental and theoretical studies of these systems.

**Goal of this work:** To understand role of the molecular vibrations in the transmission of electrons through a molecular bridge
Motivation III

Motivation

Electron transmission probability

Electron energy (eV)

Elastic Vibrations

Electron transmission probability

HCl - Theory

\( v = 0 \rightarrow 3 \)

B.Y.Gelfand, S.Schmitt-Rink, A.F.J.Levi

Tunneling in the presence of phonons:
A solvable model.

W.Domcke, C. Mundel

Calculation of cross sections for
vibrational excitation and dissociative
attachment in \{HCl\} and \{DCl\} …

Goal II: To apply methods developed for electron-
molecule scattering in gas phase (if possible)
Theoretical model – outline

- Left lead
  - electron in lead \( |\phi_k \rangle \) \( k \in L \)
  - electron in molecular orbital \( |\phi_d \rangle \)

- Right lead
  - electron in lead \( |\phi_k \rangle \) \( k \in R \)

\( \Gamma_L(E) \) and \( \Gamma_R(E) \)
Separation of vibrations to system and bath degrees of freedom

**Theoretical model – single particle description**

\[ H = H_S + H_B + H_{SB} \]

**System Hamiltonian:**

\[ H_S = |\phi_d\rangle H_d \langle \phi_d | + \sum_{k,\alpha=L,R} \left\{ |\phi_{k\alpha}\rangle (\varepsilon_{k\alpha} + H_0) \langle \phi_{k\alpha}| + |\phi_{k\alpha}\rangle V_{d\alpha} \langle \phi_{k\alpha}| + |\phi_{k\alpha}\rangle V^{*}_{d\alpha} \langle \phi_{d}| \right\} \]

\[ H_d = \omega_S a^+ a + \lambda (a + a^+) + \varepsilon_d \]

\[ H_0 = \omega_S a^+ a \]

**Bath Hamiltonian:**

\[ H_B = \sum_j \omega_j b_j^+ b_j \]

**System-bath coupling:**

\[ H_{SB} = |\phi_d\rangle \sum_j c_j \left( a_d^+ b_j + b_j^+ a_d \right) \langle \phi_d | \]
Model: Electronic degrees of freedom

Exactly solvable model: Tight-binding (Huckel-type Hamiltonian)

Conduction band in leads: \( \mu_\alpha - 2\beta < E < \mu_\alpha + 2\beta \)

Energy dependent width: \( \Gamma(E) = \frac{\nu^2}{\beta^2} \sqrt{4\beta^2 - (E - \mu_\alpha)^2} \)

Selfenergy function (level shift):
\[
\Sigma(E) = \Delta(E) - \frac{i}{2} \Gamma(E) = \frac{2\nu^2}{E - \mu_\alpha + \sqrt{(E - \mu_\alpha)^2 - 4\beta^2}}
\]
Transmission through molecular bridge

1) Elastic case (frozen vibrations): Exact analytic solution

\[ t_{R \leftarrow L}(\varepsilon) = t_{L \leftarrow R}(\varepsilon) = \frac{\Gamma_L(\varepsilon)\Gamma_R(\varepsilon)}{[\varepsilon - \varepsilon_d - \Delta(\varepsilon)]^2 + \frac{1}{4} \Gamma(\varepsilon)^2} \]
Transmission through molecular bridge

Including vibrations (no bath): Exact numerical solution

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

\[
G^S_d (E) \equiv \langle \phi_d \left| (E^+ - H_S)^{-1} \right| \phi_d \rangle = \left[ E^+ - H_d - \Sigma(E - H_0) \right]^{-1}
\]
Transmission through molecular bridge

Including vibrations and bath: Perturbation expansion in $H_{SB}$

$$t_{R \leftrightarrow L} (\varepsilon_f, \varepsilon_i) = \sum_m t^{(m)}_{R \leftrightarrow L} (\varepsilon_f, \varepsilon_i)$$

Can be summed to all orders for symmetric bridge under zero bias (unitarity).
Calculation of the current

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

\[ - \frac{1}{\pi} \int d\varepsilon_i \int d\varepsilon_f \left\{ t_{L \leftarrow R}(\varepsilon_f, \varepsilon_i) f_R(\varepsilon_i) \left[ 1 - f_L(\varepsilon_f) \right] \right\} \]
Results – weakly coupled case

- Current (10^{-3} 2e/h)
  - Voltage (V)
  - Transmissions
  - Vibrations
  - Elastic
  - Dissipation

Graph showing current and voltage relationships in a weakly coupled case with annotations for vibrations, elastic, and dissipation.
Results – strongly coupled vibrations
Convergence of the expansion in the system-bath coupling

\[ t_{R \leftrightarrow L} (\varepsilon_f, \varepsilon_i) = \sum_{m} t_{R \leftrightarrow L}^{(m)} (\varepsilon_f, \varepsilon_i) \]
Results – strongly coupled leads

$\nu = \beta$

Transmission

Elastic Vibrations +dissipation
Results – strongly coupled leads

\[ v = \beta \]
Wide-band approximation
\( \Gamma(E) = \text{const.} \)
Conclusions and outlook

- We have demonstrated ability of our approach to describe inelastic effects in molecular conduction within single particle (tunneling electron) approximation.
- Our approach is capable to treat anharmonic vibrations and dissociation of the bridge molecule. The wide band limit is not assumed – ability to describe semiconductors.
- Generalization to full many particle description is necessary – nonequilibrium Green’s function techniques. First step: self-consistent Born approximation.
- Determination of the model parameters for realistic molecular systems employing ab initio quantum chemistry methods.
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The detailed description of this work can be found in

http://arxiv.org/abs/cond-mat/0312080
Narrow resonances in VE on H2:
\[ e^- + H_2(J=22-27) \rightarrow \Gamma \sim 10^{-7} \text{ eV} \]
\[ e^- + D_2(J=30-39) \rightarrow \Gamma \sim 10^{-11} \text{ eV} \]

Long lived states
\[ H^-_2(J=27) \rightarrow \tau \sim \text{ns} \]
\[ D^-_2(J=38) \rightarrow \tau \sim 10\mu\text{s} \]