Broadening of Frank-Condon steps in molecular transistors

Karsten Flensberg

Niels Bohr Institute
University of Copenhagen

Laboratory of Atomic and Solid State physics,
Cornell University


ADMOL Dresden 2004
Outline

- **Introduction**
  - Experimental motivation
  - Mechanisms for electron-phonon coupling
  - Frank-Condon steps in IV curve
  - Thermal broadening of Frank-Condon steps
- **Broadening of Frank-Condon steps I**
  - Finite Q factor of the vibrational mode
  - How to model dissipation in quantum system
  - From classical to quantum behavior
  - Realistic model of environments
- **Broadening of Frank-Condon steps II**
  - Strong tunneling coupling to the leads
  - Known results in the single particle approximation
  - Beyond the SPA:
    - Broadening suppressed near the Fermi level
- **Summary and outlook**
Single molecular devices with electron-vibron coupling
Sequential tunneling limit


C$_{60}$


Co(tpy-$(\text{CH}_2)_5$-SH)$_2$
More recent experiments

Zhitenev, Meng, Bao, PRL (02)

Pasupathy et al., condmat/0311150

(see poster 19 by Gregers Kaat)

Single molecular devices with electron-vibron coupling
Strong coupling to the leads: **Coherent transport**

Talks Monday by van Ruitenbeek and van der Zant

Semi-strong coupling devices showing Kondo effect

---

The Kondo effect in C\textsubscript{60} single-molecule transistors

Lam H. Yu and Douglas Natelson
Department of Physics and Astronomy, Rice University, 6100 Main St., Houston, TX 77005
(Dated: October 27, 2008)

condmat/0310625

---

Coulomb blockade and the Kondo effect in single-atom transistors

Jiwoong Park\textsuperscript{\dagger,†}, Abhay N. Pasupathy\textsuperscript{††}, Jonas I. Goldsmith\textsuperscript{§},
Connie Chang\textsuperscript{*,†}, Yuval Yaish\textsuperscript{*,†}, Jason R. Petta\textsuperscript{*,†}, Marie Rinkoski\textsuperscript{††},
James P. Sethna\textsuperscript{*,†}, Héctor D. Abreuña\textsuperscript{§}, Paul L. McEuen\textsuperscript{††} & Daniel C. Ralph\textsuperscript{†}

Strongly damped oscillator: Phonon blockade

Single-Electron-Phonon Interaction in a Suspended Quantum Dot Phonon Cavity

E. M. Weig, R. H. Blick, T. Brandes, J. Kirschbaum, W. Wegscheider, M. Bichler, and J. P. Kotthaus

Tunneling in: costs classical displacement energy
Tunneling out: the energy has dissipated and tunneling is blocked
Mechanisms of electron-vibron coupling: Center of mass or internal vibrations

Force due to:
1. image charges
2. static E fields

Simple model:
\[ \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 + \lambda nx \]

\( n = \text{occupation} \)
Frank-Condon steps in IV curve

**Quantum:**

\[ P_n = |\langle 0|n \rangle|^2 \]

\[ P_n(g) = \frac{e^{-g}g^n}{n!}, \quad g = \frac{1}{2} \left( \frac{\ell}{\ell_0} \right)^2, \quad \ell_0^2 = \frac{\hbar}{m\omega_0} \]

**Classical:**

Displacement energy:

\[ E_d = \lambda \ell \]
Non-equilibrium current: weak tunneling limit = rate equation

\[
\frac{dP_0}{dt} = -P_0 \Gamma_{10} + P_1 \Gamma_{01} = 0
\]

\[
P_0 + P_1 = 1
\]

\[
P_1 = \frac{\Gamma_{10}}{\Gamma_{10} + \Gamma_{01}}
\]

\[
I = -e \left( P_0 \Gamma_{10}^{\text{left}} - P_1 \Gamma_{01}^{\text{left}} \right)
\]

Fermi’s golden rule:

\[
\Gamma_{10}^{\text{left}} = \frac{2\pi \Gamma}{\hbar} \sum_{i,f} \left| \langle f | e^{i\hat{p}l} | i \rangle \right|^2 \frac{e^{-E_i/kT}}{Z_0} n_F(\epsilon_0 + E_f - E_i - eV_l)
\]

displacement operator  thermal distribution of $|i\rangle$  left Fermi function
Weak tunneling current formula

\[ I = \frac{e}{\hbar} \frac{\Gamma_L \Gamma_R \tilde{n}_L \tilde{n}_R n_L n_R}{\Gamma_L \tilde{n}_L n_R + \Gamma_R \tilde{n}_R n_L} \left( e^{(\varepsilon_0 - eV_R)/kT} - e^{(\varepsilon_0 - eV_L)/kT} \right) \]

\[ n_L = n_F(\varepsilon_0 - eV_L), \quad \tilde{n}_L = \sum_{n=-\infty}^{\infty} P_n(g) n_F(\varepsilon_0 - eV_L + n\hbar\omega_0) \]

\[ P_m(g) = \exp(-g \coth(b)) e^{mb} I_m \left( \frac{g}{\sinh(b)} \right), \quad b = \frac{\beta\omega_0}{2} \]

Other rate equations approaches: Boese and Schoeller, Europhys. Lett. 54, 668 (01); Mitra, Aleiner, Millis, condmat/0302132; McCarthy et al., PRB (03).
**IV curves**

**Symmetric device**

\[ \frac{kT}{\hbar \omega_0} = 0.025 \] and \[ 0.1 \]

\[ g = 1 \]

\[ \frac{\Gamma_L}{\Gamma_R} = 1 \]

\( I/I_N \)

\( -1 \)

\( -0.5 \)

\( 0 \)

\( 0.5 \)

\( 1 \)

\( V/\omega_0 \)

\( -8 \)

\( -4 \)

\( 0 \)

\( 4 \)

\( 8 \)

**Asymmetric device**

\[ g = 1 \]

\[ \frac{\Gamma_L}{\Gamma_R} = 0.05 \]

\( I/I_N \)

\( -1 \)

\( -0.5 \)

\( 0 \)

\( 0.5 \)

\( 1 \)

\( V/\omega_0 \)

\( -8 \)

\( -4 \)

\( 0 \)

\( 4 \)

\( 8 \)

\( V/\omega_0 \)

\( -8 \)

\( -4 \)

\( 0 \)

\( 4 \)

\( 8 \)
V-V\textsubscript{g} plots

\[ \varepsilon_0 = eV_g + \alpha eV_L \]

Symmetric

Asymmetric

\[ \frac{\Gamma_L}{\Gamma_R} = 0.05 \]

C\textsubscript{60} (Park et al. 2000)
Mechanisms for broadening of steps

Two possible mechanisms:

1. The molecular motion is damped
   $\Rightarrow$ finite lifetime of phonons

2. Strong tunnel coupling between molecular levels
   and electronic stats of the leads
   $\Rightarrow$ finite lifetime of electronic state
Broadening of the Frank-Condon steps I: Coupling to dissipative environments

Classical friction: finite Q factor

\[ \ddot{x} + \omega_0^2 x + \omega_0 \dot{x} / Q = 0 \]

Quantum mechanical: coupling to a continuum of harmonic oscillators (Caldeira, Leggett model)

\[ H = H_0 + x \sum_i C_i y_i + \sum_i \left( \frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 y_i^2 \right) \]

\[ \frac{1}{Q} = \sum_i \frac{C_i^2}{2m_i^2 \omega_i^4} \delta(\omega_0 - \omega_i) \]

Q: What happens to the Frank-Condon steps when Q is finite?
Tunneling with a dissipation

\[ x \rightarrow x - \ell \quad y_i \rightarrow y_i - \ell_i \]

\[ P_{fi} = |\langle f | \text{displacement} | i \rangle|^2 \]

\[ P(E_f - E_i) \]

Distribution of available tunneling energies

\[ P(E) = \int_{-\infty}^{\infty} e^{iEt/\hbar} \exp \left( \frac{2g}{Q\pi} \int_{-\infty}^{\infty} \frac{d\omega}{\omega} \frac{e^{-i\omega t} - 1}{1 - e^{-\hbar \omega/kT}} \frac{\omega^4}{(\omega^2 - \omega_0^2)^2 + \omega_0^2 \omega^2/Q^2} \right) \]

Related to classical response function! (Feynman-Vernon)

External force: \[ F(t) \Rightarrow x(\omega) = R(\omega)F(\omega) \]

New rate equations:

\[ P(E) \quad \text{replaces the discrete Frank-Condon function} \quad P_n(g) \]

From quantum to classical

Two parameters: \( Q \) and \( g \)

Classical energy after the tunneling event:

\[
\lambda \ell = g \hbar \omega_0
\]

- Time to “finish” tunneling:
  \[
  \frac{\hbar}{\lambda \ell}
  \]
- Time to relax to new classical state:
  \[
  \frac{Q}{\omega_0}
  \]

Cross-over from quantum to classical when:

\[
\frac{Q}{\omega_0} = \frac{\hbar}{\lambda \ell} \quad \Rightarrow \quad Q_q = \frac{1}{g}
\]
Estimate of $Q$ factor?

For $C_{60}$ on Au:

$$Q \sim \frac{m \lambda}{M a'} , \quad \lambda = \frac{v_s}{\omega_0}$$

$Q \sim 1 - 10$
IV curves with dissipation, $Q > Q_c$

$kT = 0 \quad g = 1$

Power law at small energies: $V^{2g/Q\pi}$

- $Q = 20$
- $Q = 10$
- $Q = 5$
- $Q = 2.5$
- $Q = Q_c = \frac{2}{\pi}$
IV curves with dissipation, $Q < Q_{c^{1/2}}$

Classical displacement energy

PHONON BLOCKADE
More realistic calculation (frequency dependent Q factor)

Two kinds of modes:
- Bulk phonons
- Surface modes (similar to seismic waves, so-called Rayleigh Waves)

(with Stephan Braig, Cornell)
Continuum model of electrode

Lagrangian:

\[ \mathcal{L}(\vec{r}, t) = \frac{1}{2} \rho \left[ (\partial_t \vec{u})^2 - (v_i^2 - 2v_i^2) \left( \nabla \vec{u} \right)^2 - v_i^2 (\nabla \times \vec{u})^2 - 2v_i^2 \frac{\partial u_i}{\partial x_j} \frac{\partial u_j}{\partial x_i} \right] \]

Boundary conditions:

\[ T_{zr} \bigg|_{z=0} = 0, \quad T_{zz} \bigg|_{z=0} = -\mathcal{F} f(r) \]

Force:

\[ \mathcal{F} = k_M \left[ x - \int_0^\infty 2\pi r f(r) u_z^0(r) dr \right] \]
IV curves based on “realistic” model

Frequency dependence of $Q$

Fit parameters: left and right tunneling rates.
Fixed parameters: elastic coefficient of Au
Determined from experiments: oscillator frequency and size of molecule
Broadening of the Frank-Condon steps II: Strong tunnel coupling

Exact solution for a single electron (no Fermi sea):
All levels are broadened by the same Lorentzian

(Amounts to a decoupling of electronic and vibronic degrees of freedom)

SPA approximation used in our papers:
Kuo and Change, PRB (02); Lundin and McKenzie PRB (02); Alexandrov and Bratkovsky, PRB (03).
\[ G^R(d, t) \rightarrow G^R(d, t) \exp \left[ g \left( e^{i\omega_0 t} - 1 \right) \right] \]
Many-body problem

Next tunneling “in” remembers previous events

$\Rightarrow$ electron-phonon-electron interaction

Approximation needed:

Treat the lead electrons as a Fermi distribution at all times

Other many body treatments beyond SPA:
König, Schoeller, Schön, PRL 76, 1715 (96). P. Kral PRB (97).

SCBA:
Nitzan Tuesday talk
Resonant tunneling, non-interacting

Lorentzian

\[ A(\xi) = \frac{\Gamma}{(\xi - \varepsilon_0)^2 + (\Gamma/2)^2} \]

\[ \Gamma = 2\pi |t_0|^2 \rho \]

“Two contributions”

Decaying out:

\[ \Gamma_{\text{out}} = \Gamma \left[ 1 - n_F(\varepsilon_0) \right] \]

Decaying in:

\[ \Gamma_{\text{in}} = \Gamma n_F(\varepsilon_0) \]
Resonant tunneling, with vibrations

Sum of Lorentzians:

\[ A(\xi) = \sum_n |f_{n0}|^2 \frac{\Gamma_n}{(\xi - \varepsilon_0 - E_n)^2 + (\Gamma_n/2)^2} \]

“Two contributions”

Decaying out:

\[ \Gamma_{n,\text{out}} = \Gamma \sum_m |f_{mn}|^2 [1 - n_F(\varepsilon_0 + E_n - E_m)] \]

Decaying in:

\[ \Gamma_{n,\text{in}} = \Gamma \sum_m |f_{m0}|^2 n_F(\varepsilon_0 + E_m - E_0) \]

\[ n_F = 0 \quad \text{single particle approximation (exact results)} \]
Details of calculation

Hamiltonian

\[ H = \varepsilon_0 \hat{d} \hat{\hat{d}} + H_{\text{leads}} + H_{\text{osc}} + \sum_k \left( c_k^\dagger e^{i p \ell} + d_k^\dagger c_k e^{-i p \ell} \right) \]

Green's function

\[ G^R = -i \theta(t) \langle \{ (e^{i p \ell} \hat{d})(t), d^\dagger e^{-i p \ell}\} \rangle = \sum_{n n' m m'} G^R_{n n' m m'} \langle n | e^{i p \ell} | n' \rangle \langle m' | e^{-i p \ell} | m \rangle \]

Use propagator for many-body eigenstates in presence of leads

\[ G^R_{n n' m m'} = -i \theta(t) \langle \{ | n \rangle \langle n' | \hat{d}(t), d^\dagger | m' \rangle \langle m | \} \rangle \]

Set up equations of motion:

\[ i \partial_t G^R_{n n' m m'} = \ldots \quad \text{need:} \quad [H, | n \rangle \langle n' | \hat{d}] \]

Truncate EOMs: neglect correlations in the leads

\[ c_{k'}^\dagger c_k^\dagger \hat{d} \approx \langle c_{k'}^\dagger c_k^\dagger \rangle \hat{d} \]
Tunneling spectrum on resonance

Differential conductance

Current

\[ \frac{g}{\hbar \omega_0} = 2 \]

\[ \frac{\Gamma}{\hbar \omega_0} = 0.5 \]

\[ \varepsilon_0 = 0 \]

On resonance
Reduction of width

\[ g = 2 \]
\[ \frac{\Gamma}{\hbar \omega_0} = 1 \]
\[ \varepsilon_0 = 0 \]

Differential conductance

Width:

\[ \Gamma \mapsto \Gamma \left| \langle 0|0' \rangle \right|^2 \]
Tunneling spectrum, off resonance

Approaches the SPA when off resonance!

\[
\begin{align*}
g &= 2 \\
\frac{\Gamma}{\hbar \omega_0} &= 0.5 \\
\varepsilon_0 &= 1.5\hbar \omega_0
\end{align*}
\]
Summary and outlook

1. Dissipative molecular motion:
   \[ \Rightarrow \text{Cross-over from quantum to classical regime at } Q \sim Q_q \]
   \[ \Rightarrow \text{Realistic model with gold electrodes gives good agreement} \]
   \[ \Rightarrow \text{Experimentally } Q \approx 5 \text{ (but frequency dependent)} \]

2. Tunneling broadening
   \[ \Rightarrow \text{Single particle approximation only valid far from the Fermi surface} \]
   \[ \Rightarrow \text{Frank-Condon steps sharpest near zero energy} \]

3. Outlook
   \[ \Rightarrow \text{Does the sidebands survive into the Kondo regime?} \]
   \[ \text{No suppression expected because fixed charge state!} \]
   \[ \Rightarrow \text{Internal vibrations: asymmetric IV curves because of polaron formation or confirmational changes.} \]