Theory of vibrationally inelastic electron transport through molecular bridges

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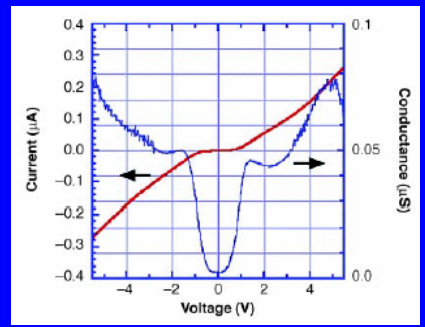
Motivation I: Molecular electronics

as ultimate solution for miniaturization of electronic devices

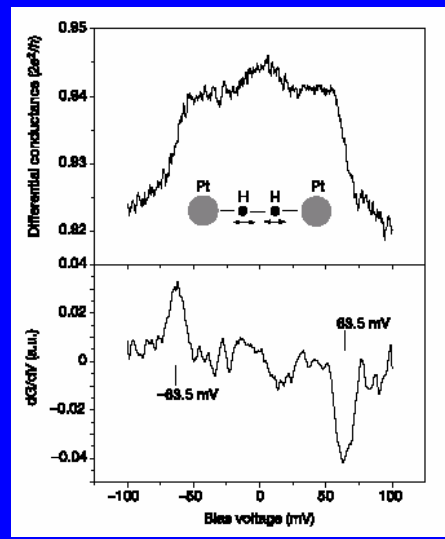
Experiments: conduction properties of individual molecules

- M. A. Reed et al. Science 278 (1997) 252:
  Conductance of a molecular junction.



- H. Park et al. Nature 407 (2000) 57:
  Nanomechanical oscillations in a single-C_{60} transistor.

- R. H. M. Smit et al. Nature 419 (2002) 906:
  Measurement of the conductance of a hydrogen molec.



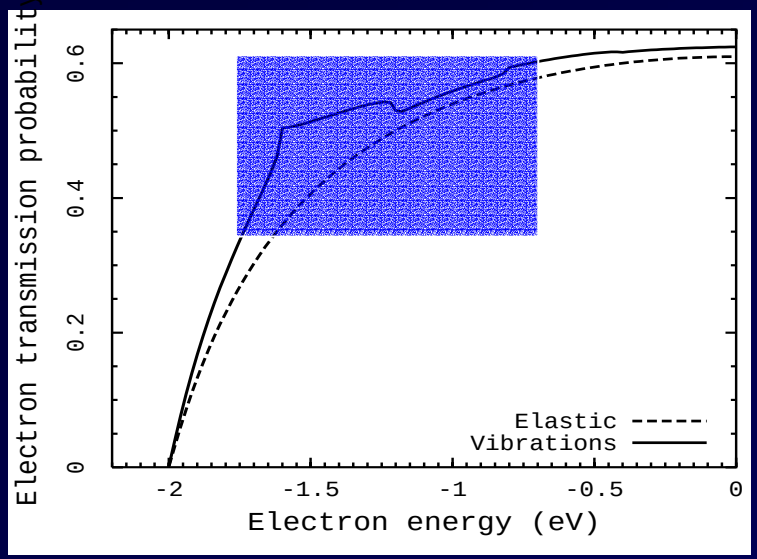
Motivation II

A.Nitzan, M.A.Ratner, *Science* **300** (2003) 1384:

> 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.

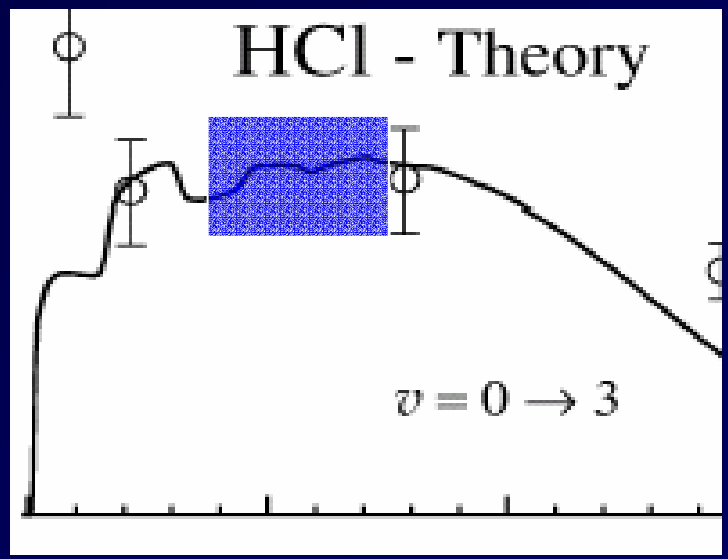
Goal of this work: To understand role of the molecular vibrations in the transmission of electrons through a molecular bridge

Motivation III



B.Y.Gelfand, S.Schmitt-Rink, A.F.J.Levi
Phys. Rev. Lett. **62** (1989) 168

Tunneling in the presence of phonons: A solvable model.

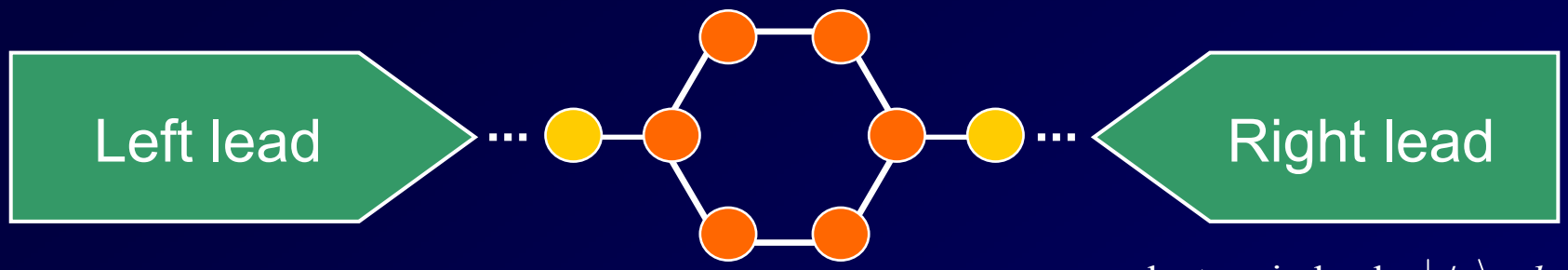


W.Domcke, C. Mundel
Phys. Rev. A **18** (1985) 4491

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)

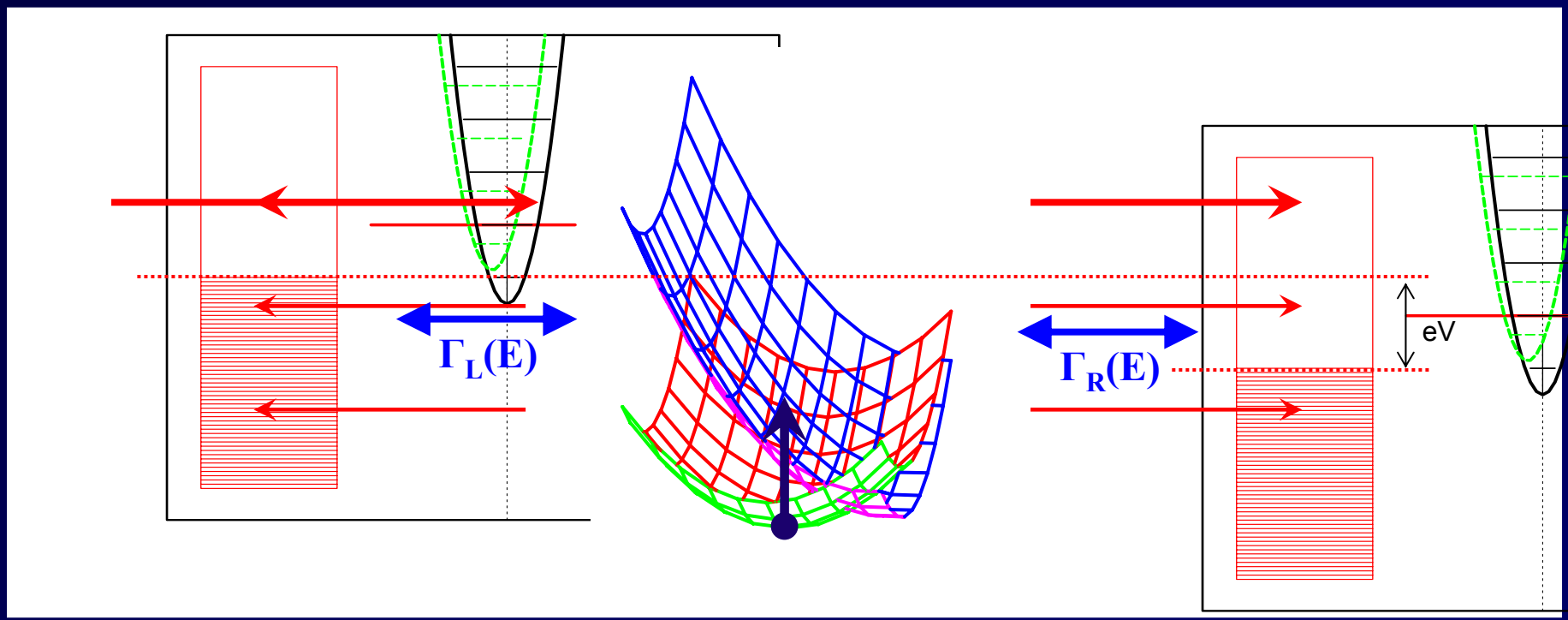
Theoretical model – outline



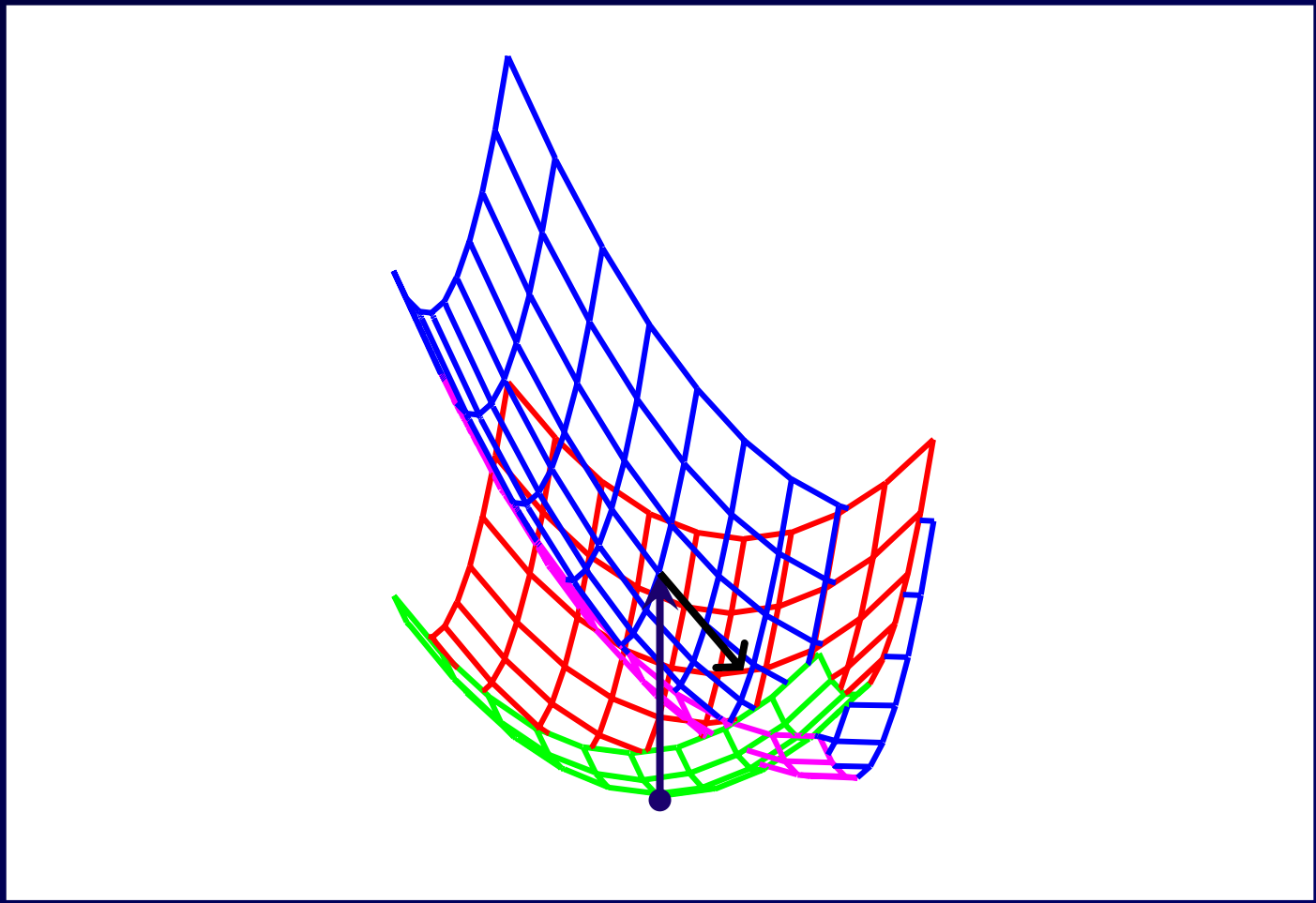
electron in lead ... $|\phi_k\rangle$ $k \in L$

electron in molecular orbital $|\phi_d\rangle$

electron in lead ... $|\phi_k\rangle$ $k \in R$



Separation of vibrations to system and bath degrees of freedom



M. Thoss and W. Domcke, J. Chem. Phys. 109 (1998) 6577.

Theoretical model – single particle description

$$H = H_{\mathrm{S}} + H_{\mathrm{B}} + H_{\mathrm{SB}}$$

System Hamiltonian:

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

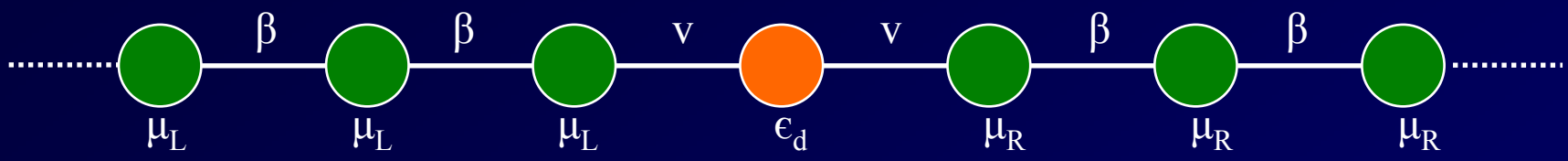
$$H_d = \omega_S a^+ a + \lambda(a + a^+) + \varepsilon_d$$

$$H_0 = \omega_S a^+ a$$

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: $$\Gamma(E) = \frac{v^2}{\beta^2}\sqrt{4\beta^2 - (E-\mu_\alpha)^2}$$

Selfenergy function (level shift):

$$\Sigma(E) = \Delta(E) - \tfrac{i}{2}\Gamma(E) = \frac{2v^2}{E-\mu_\alpha + \sqrt{(E-\mu_\alpha)^2 - 4\beta^2}}$$

Transmission through molecular bridge

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

$$t_{R\leftarrow L}(\varepsilon) = t_{L\leftarrow R}(\varepsilon) = \frac{\Gamma_L(\varepsilon)\Gamma_R(\varepsilon)}{\left[\varepsilon - \varepsilon_d - \Delta(\varepsilon)\right]^2 + \frac{1}{4}\Gamma(\varepsilon)^2}$$

Transmission through molecular bridge

Including vibrations (no bath): Exact numerical solution

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

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

Transmission through molecular bridge

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

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

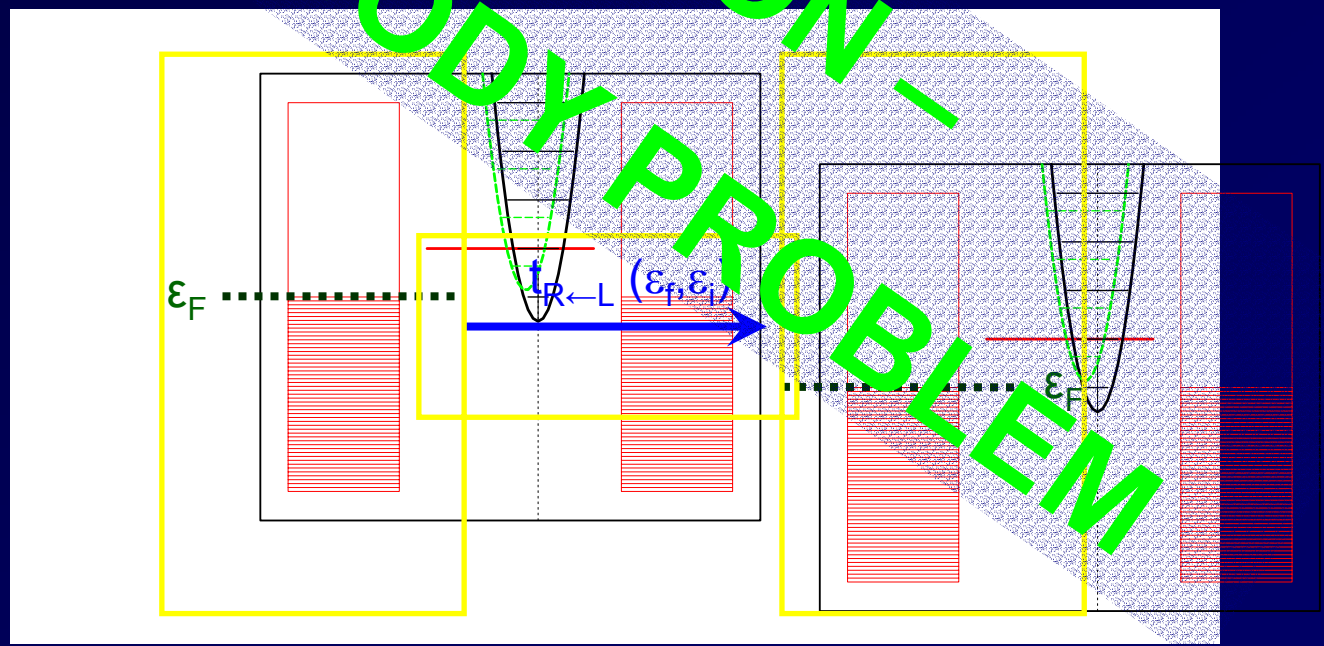
Can be summed to all orders for symmetric bridge under zero bias (unitarity).

Calculation of the current

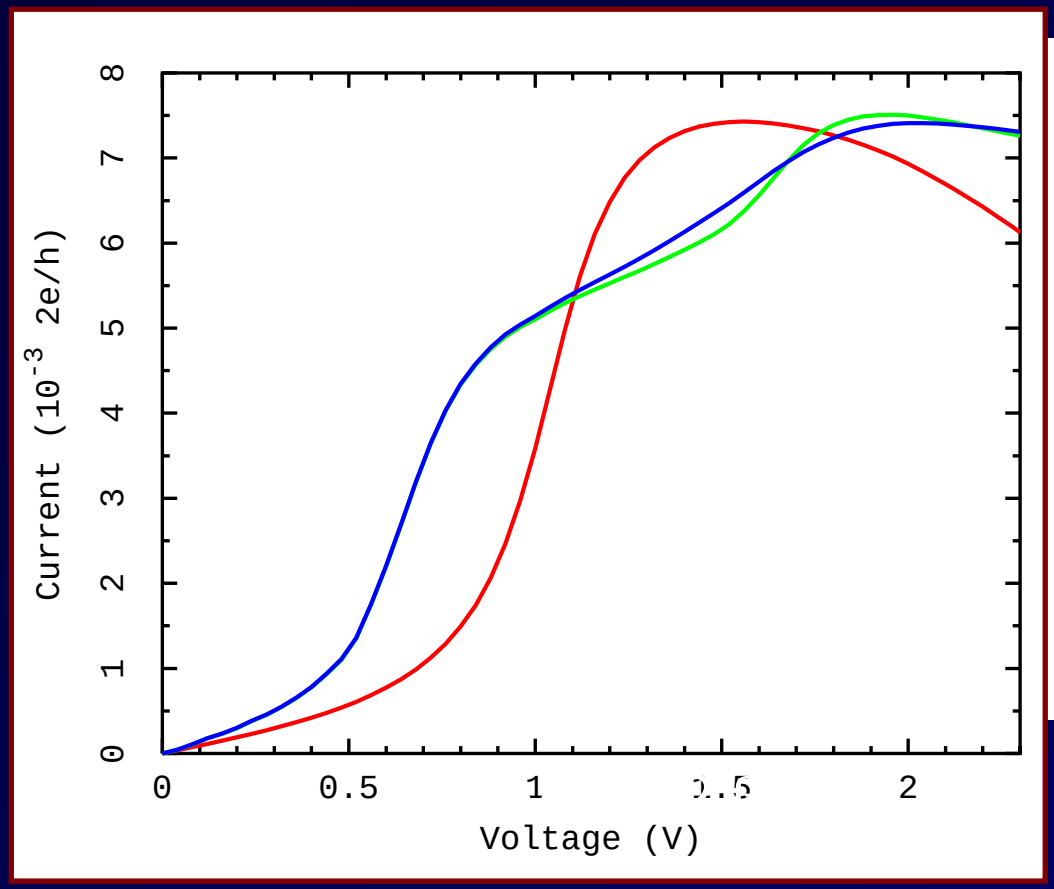
$$I = \frac{1}{\pi}\int d\varepsilon_i \int d\varepsilon_f \left\{ t_{R\leftarrow L}(\varepsilon_f,\varepsilon_i) f_L(\varepsilon_i)\left[1 - f_R(\varepsilon_f)\right] \right\}$$

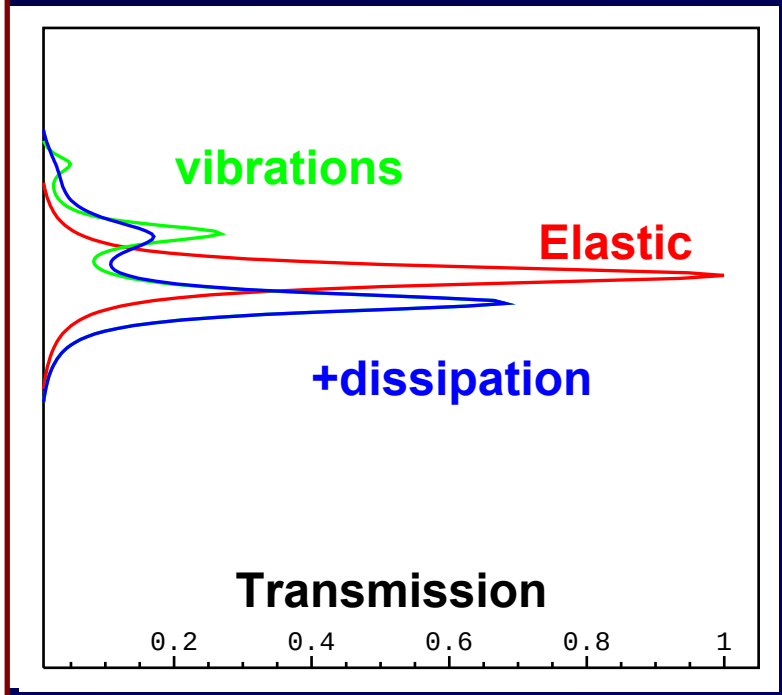
$$- \frac{1}{\pi}\int d\varepsilon_i \int d\varepsilon_f \left\{ t_{L\leftarrow R}(\varepsilon_f,\varepsilon_i) f_R(\varepsilon_i)\left[1 - f_L(\varepsilon_f)\right] \right\}$$

CAUTION – MANY BODY PROBLEM

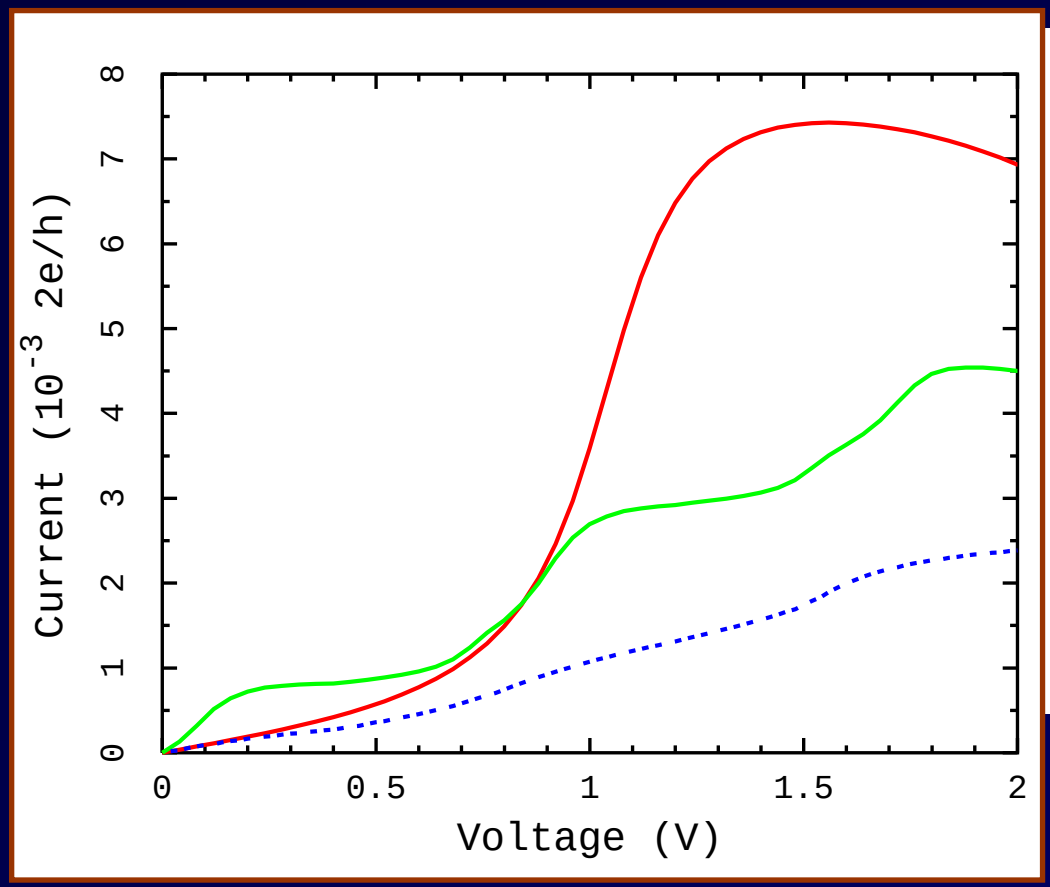


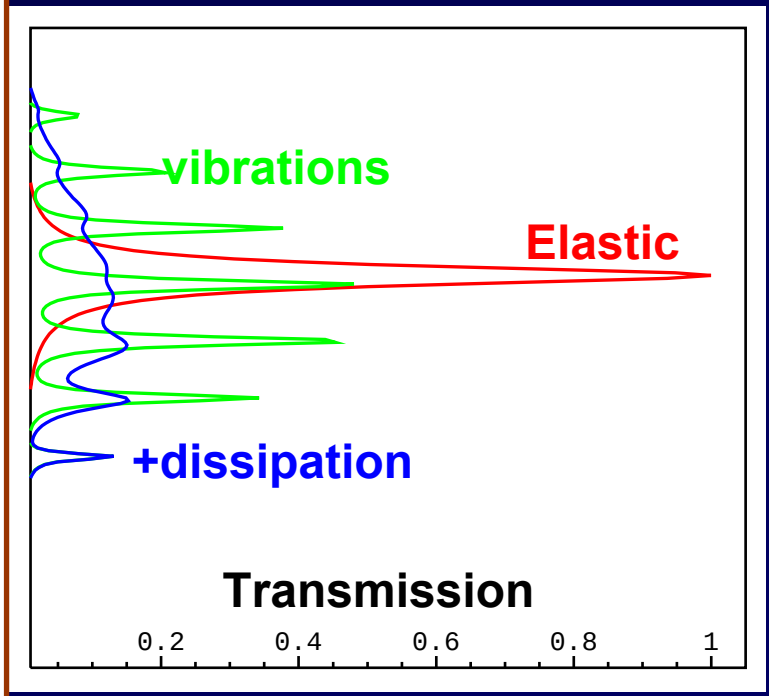
Results – weakly coupled case





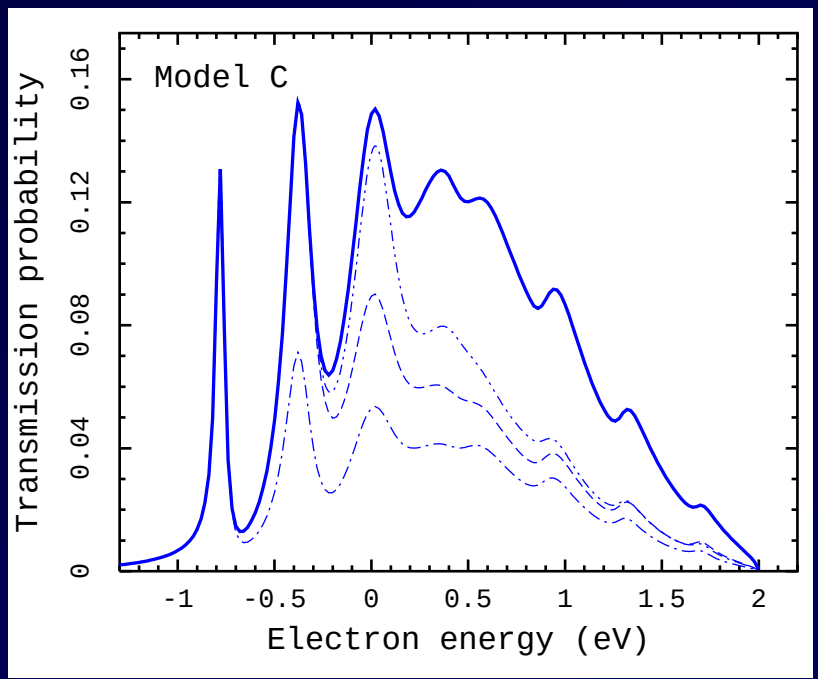
Results – strongly coupled vibrations

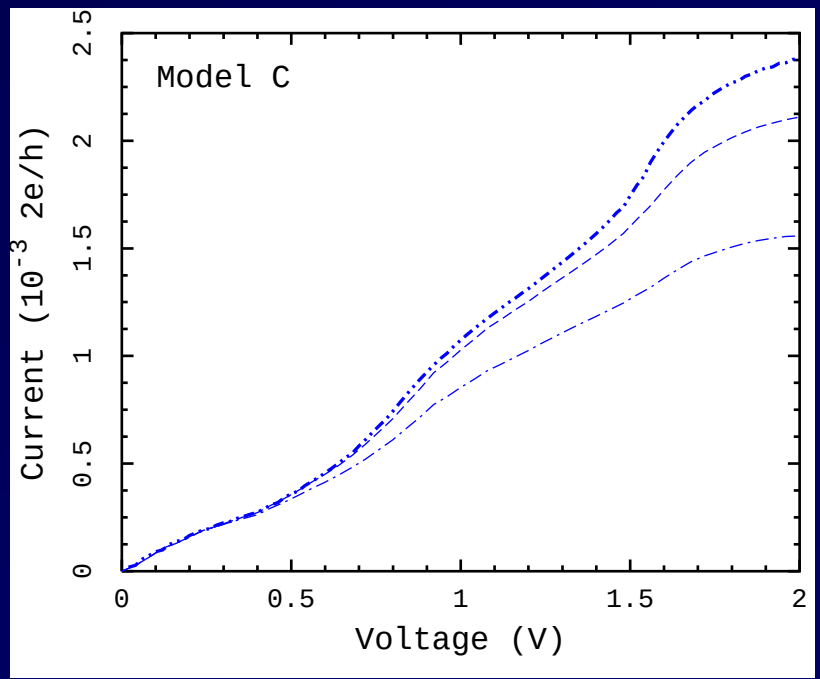




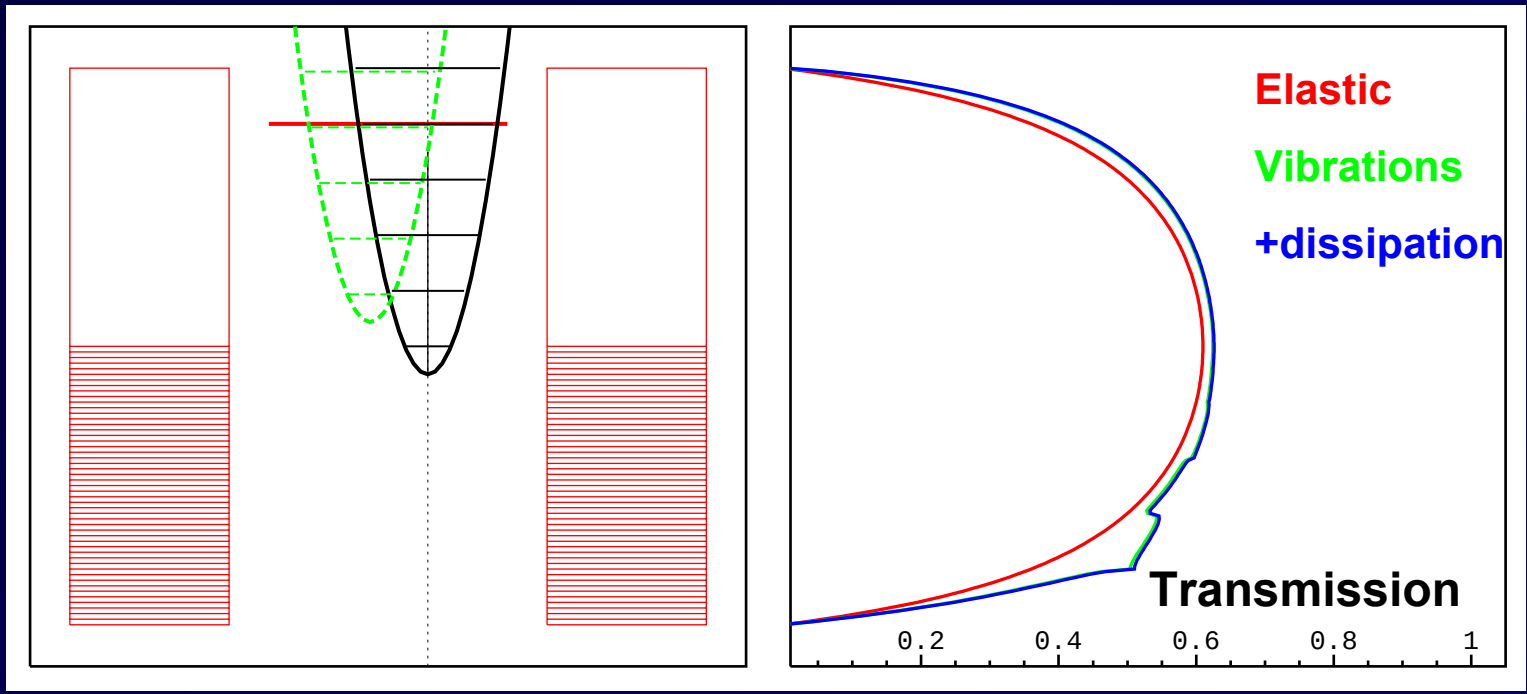
Convergence of the expansion in the system-bath coupling

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



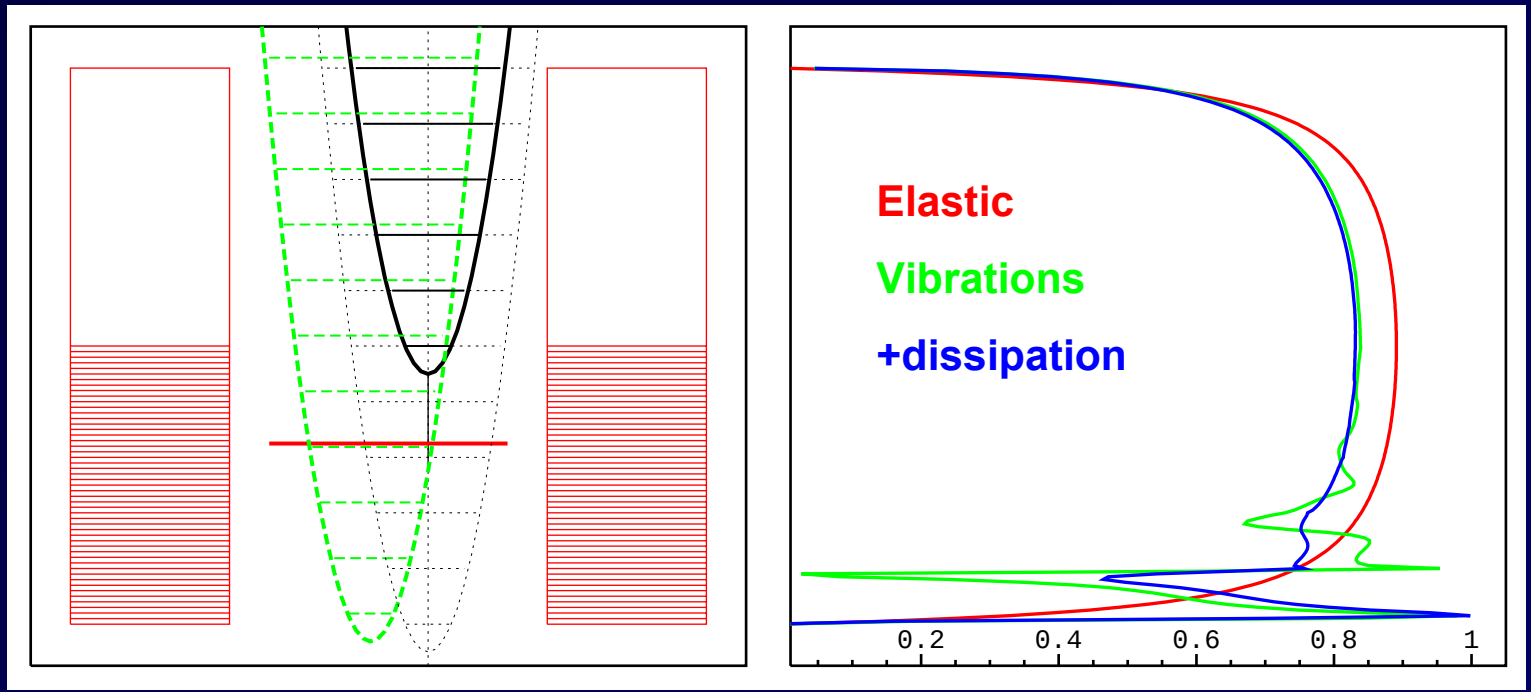


Results – strongly coupled leads



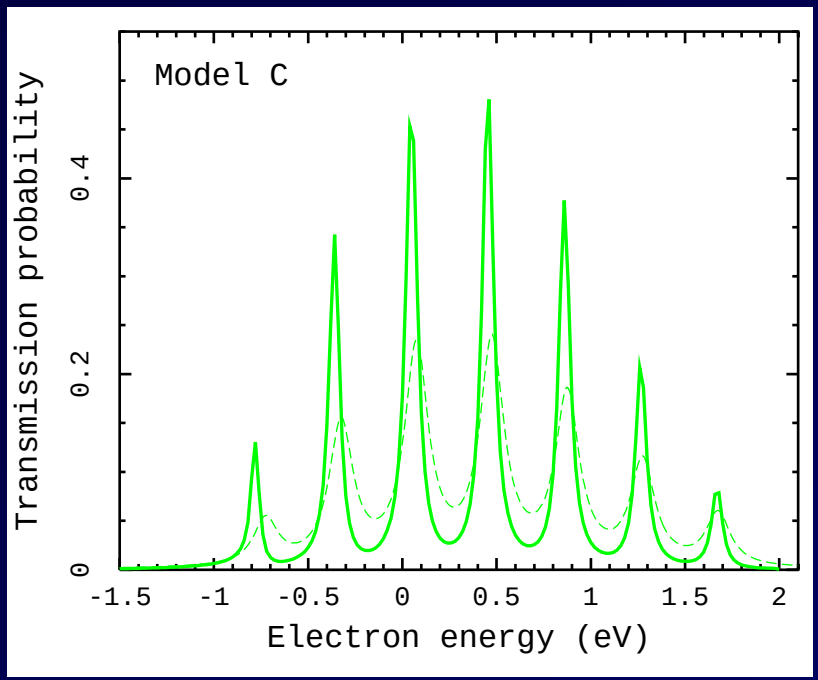
$v = \beta$

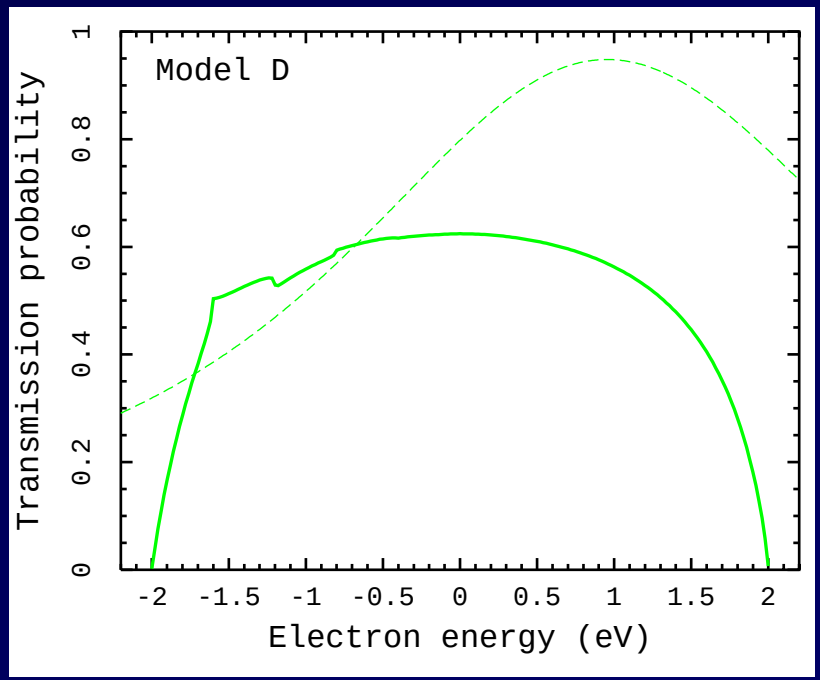
Results – strongly coupled leads



$v = \beta$

Wide-band approximation
$\Gamma(E)$=const.





Conclussions 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.

Acknowledgements

Wolfgang Domcke, Michael Thoss

Financial support:

Alexander von Humboldt foundation

The detailed description of this work can be found in

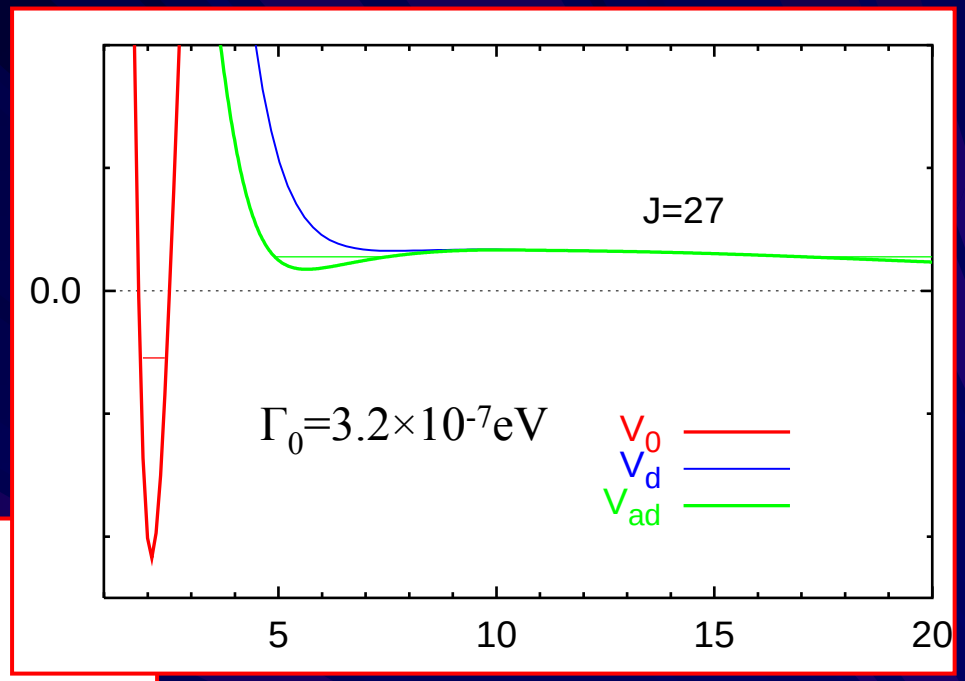
http://arxiv.org/abs/cond-mat/0312080

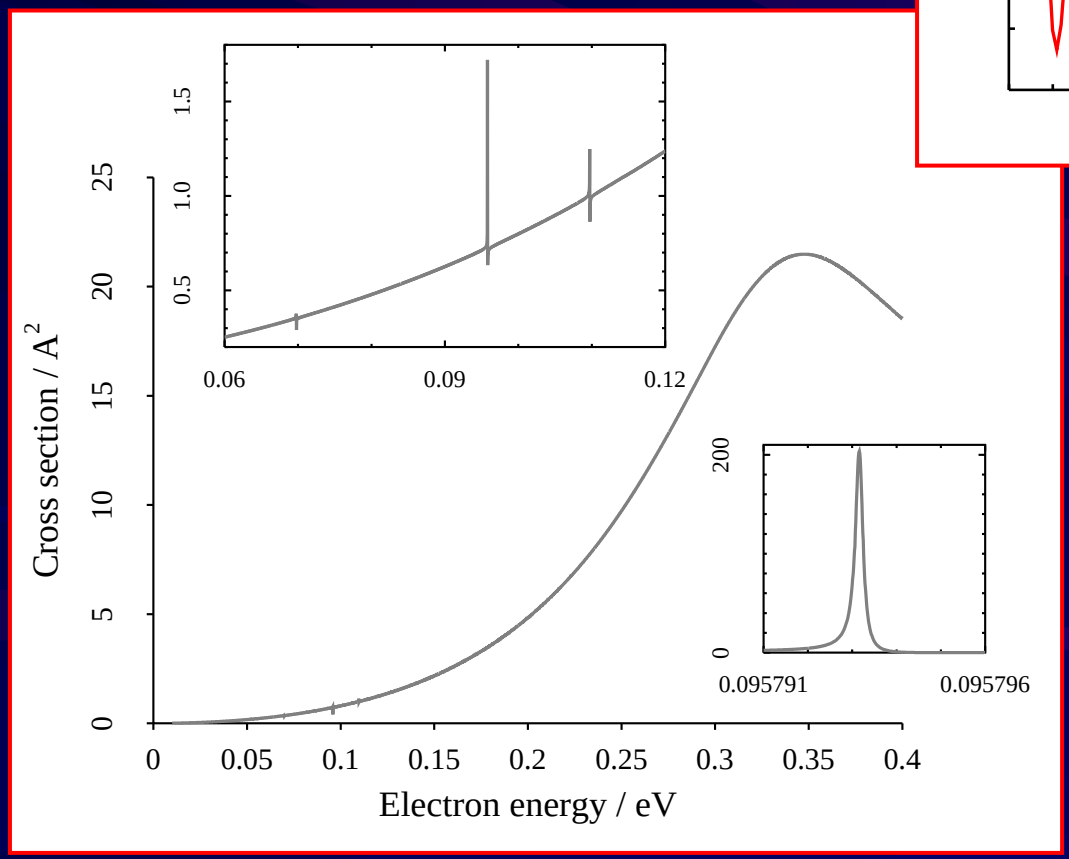
Phys. Rev. B (2004) in press

Narrow resonances in VE on H2:

$e^- + H_2$(**J=22-27**) → $\Gamma \sim 10^{-7}$ eV

$e^- + D_2$(**J=30-39**) → $\Gamma \sim 10^{-11}$ eV





Long lived states

H^-_2(**J=27**) → $\tau \sim$ ns

D^-_2(**J=38**) → $\tau \sim 10\mu$s