Theory of electron transport through a flexible molecular bridge

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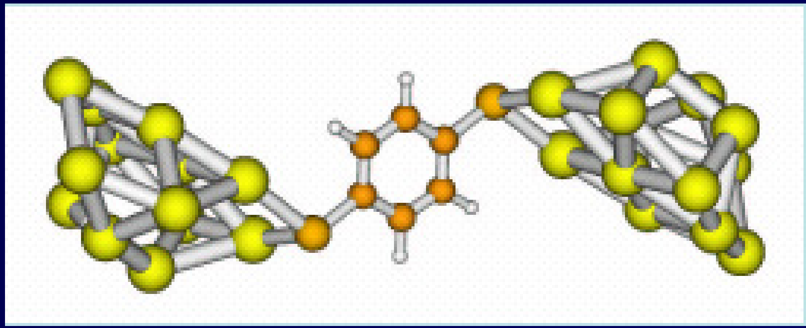
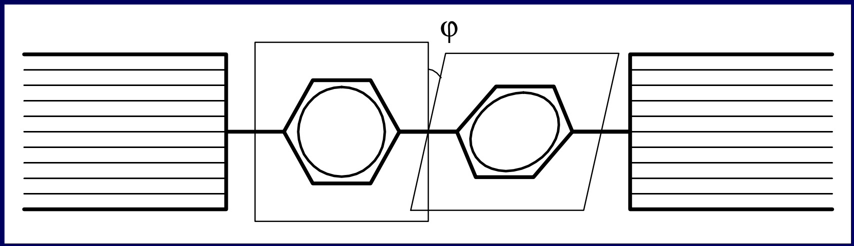




Contents of the talk

- Introduction (*my previous work and relation to molecular electronics*)
- Generic model and methods of solution
- Results for harmonic mode and bath
- Results for biphenyl molecule (model)
- Conclusions

My contributions to theory of resonance electron-molecule collisionsv

(as PhD student and postdoc of Jiří Horáček in Prague)

1997 with **Wolfgang Domcke** (Duesseldorf)

numerical methods for $HX + e^- $ ❄ $HX(v) + e^-$

$\leftrightarrow H + X^-$

X=H: *J. Phys.* B **31** (1998) 2571,

X=Cl: *Phys. Rev.* A **60** (1999) 2873,

X=Br: *Phys. Rev.* A **63** (2001) 062710.

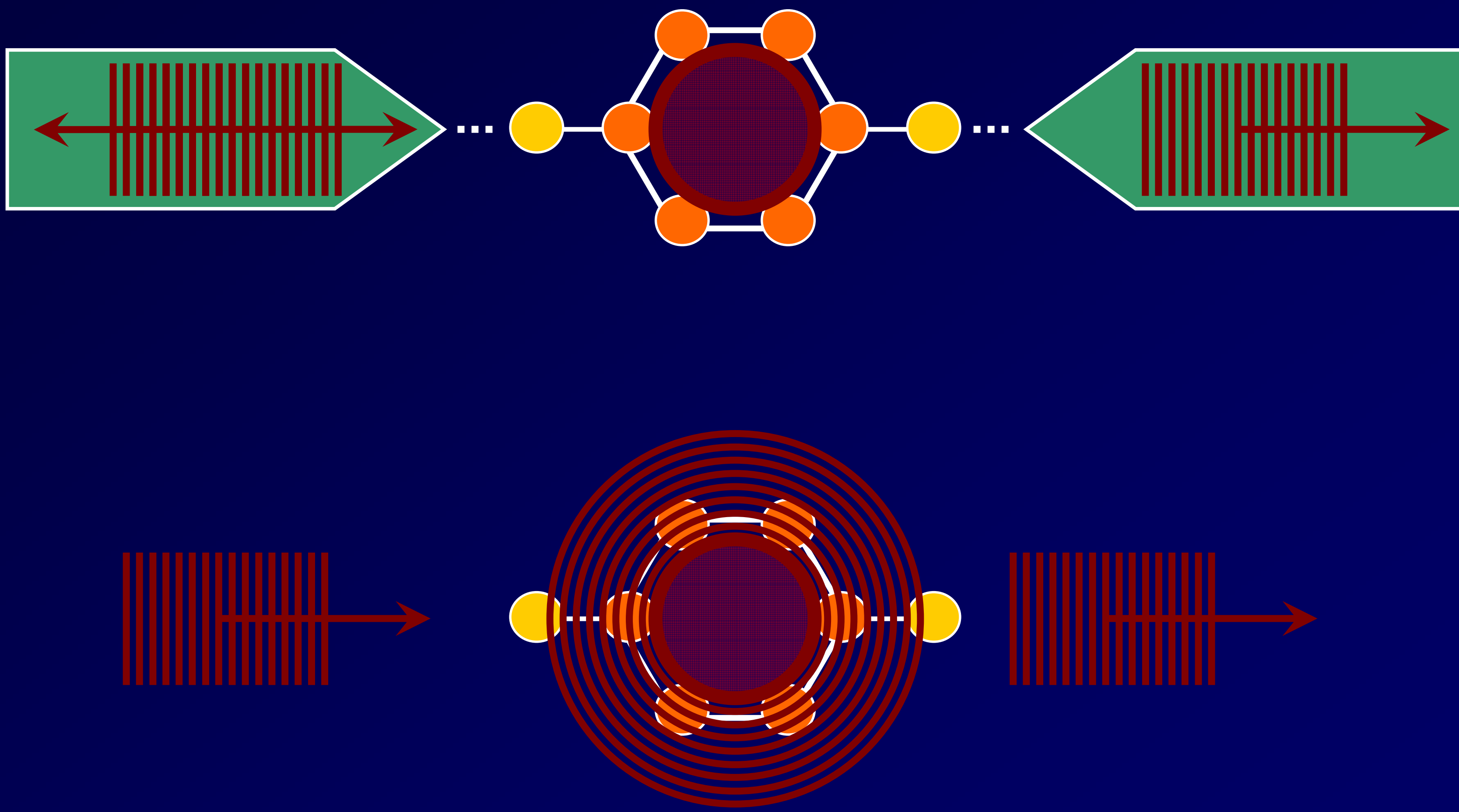
1999-2002 with **Hartmut Hotop** (Kaiserslautern), with **Michael Allan** (Fribourg)

simulation of $H + X^-$ ❄ $HX + e^-$, X=F, Cl, Br

J. Phys. B **34** (2001) 983, *Phys. Rev. Lett.* **89** (2002) 073201,

J. Phys. B **36** (2003) 3513.

Molecular conduction / electron scattering in vacuum

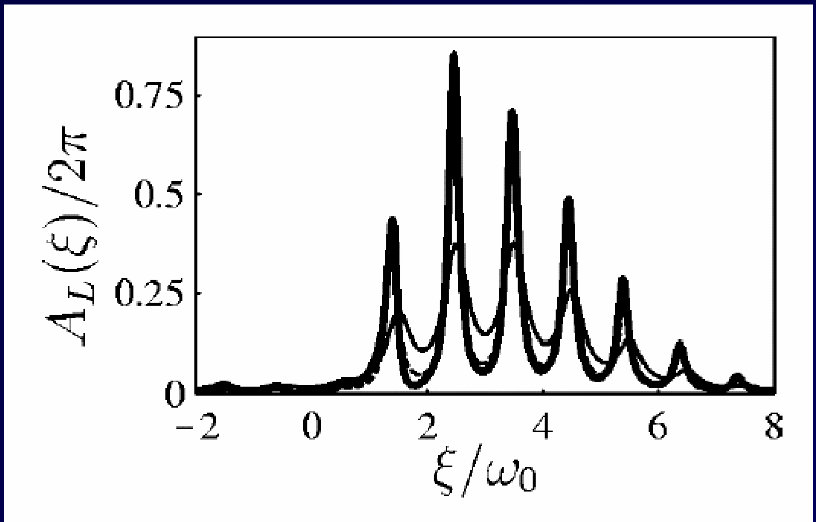


Molecular conduction / electron scattering in vacuum

Tunneling broadening of vibrational sidebands in molecular transistors

Karsten Flensberg

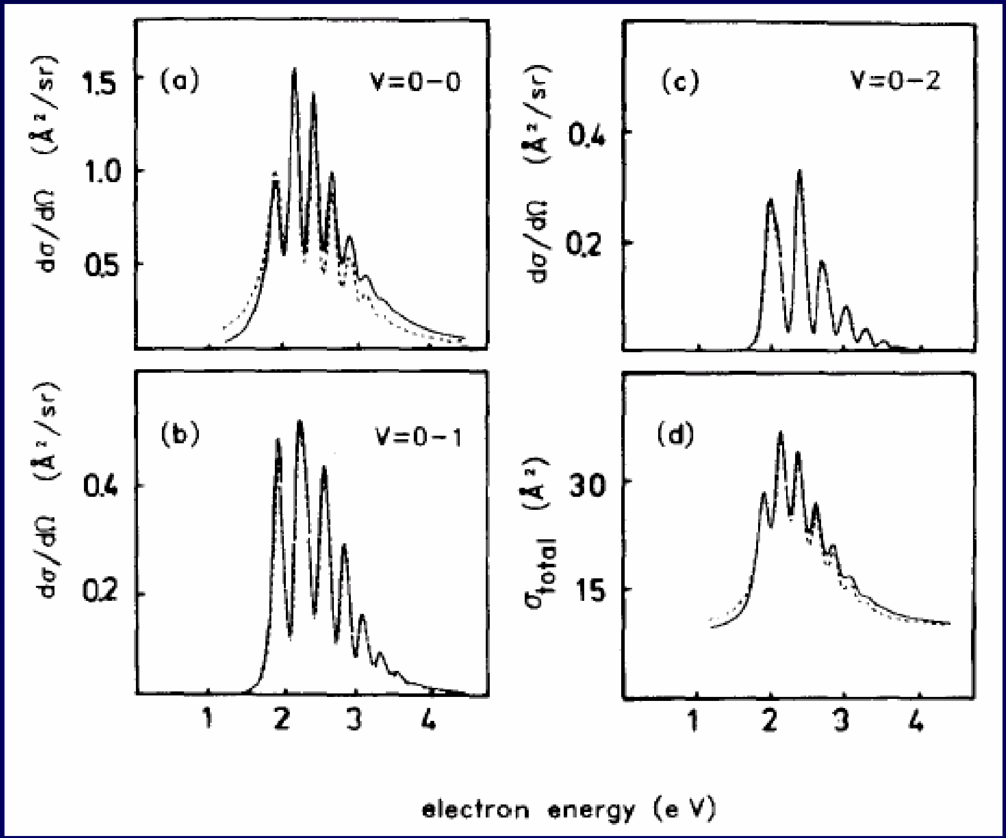
PRB **68** (2003) 205323



Vibrational excitation of N_2 by electron impact

Wolfgang Domcke

Phys. Rep. **208** (1991) 97



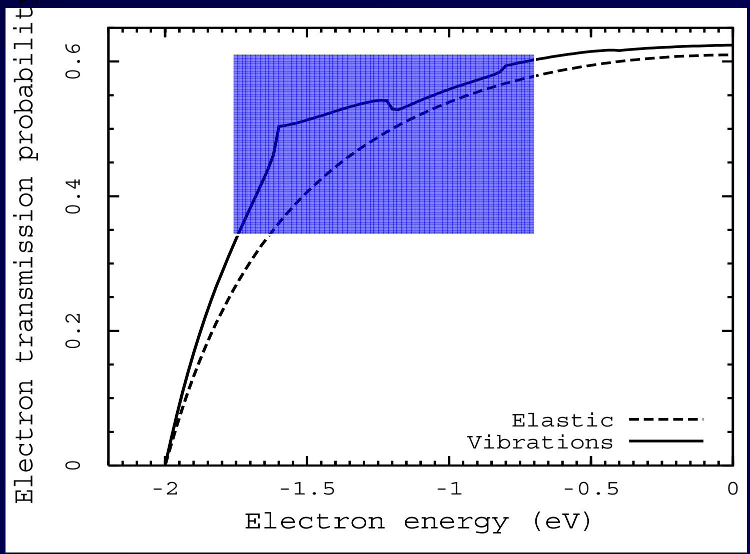
Molecular conduction / electron scattering in vacuum

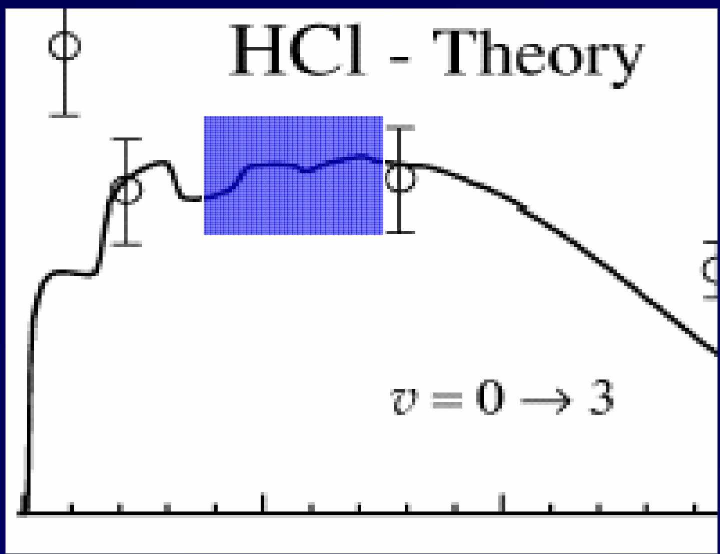
Tunneling in the presence of phonons:
A solvable model.

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

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

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





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Generic model

$$H = \hbar\omega\, a^+ a + \left[\varepsilon_d + \lambda\left(a + a^+\right)\right] d^+ d + \sum_k \left\{ \varepsilon_k c_k^+ c_k + V_{dk} d^+ c_k + V_{dk}^* c_k^+ d \right\}$$

↓

$$1 = d^+ d + d\, d^+$$

$$H = h_0\, d\, d^+ + h_d\, d^+ d + \sum_k \left\{ \varepsilon_k c_k^+ c_k + V_{dk} d^+ c_k + V_{dk}^* c_k^+ d \right\}$$

h_0 = vibrational hamiltonian for *neutral* molecule

$h_0 = \hbar\omega\, a^+ a$

h_d = vibrational hamiltonian for *anionic* molecule

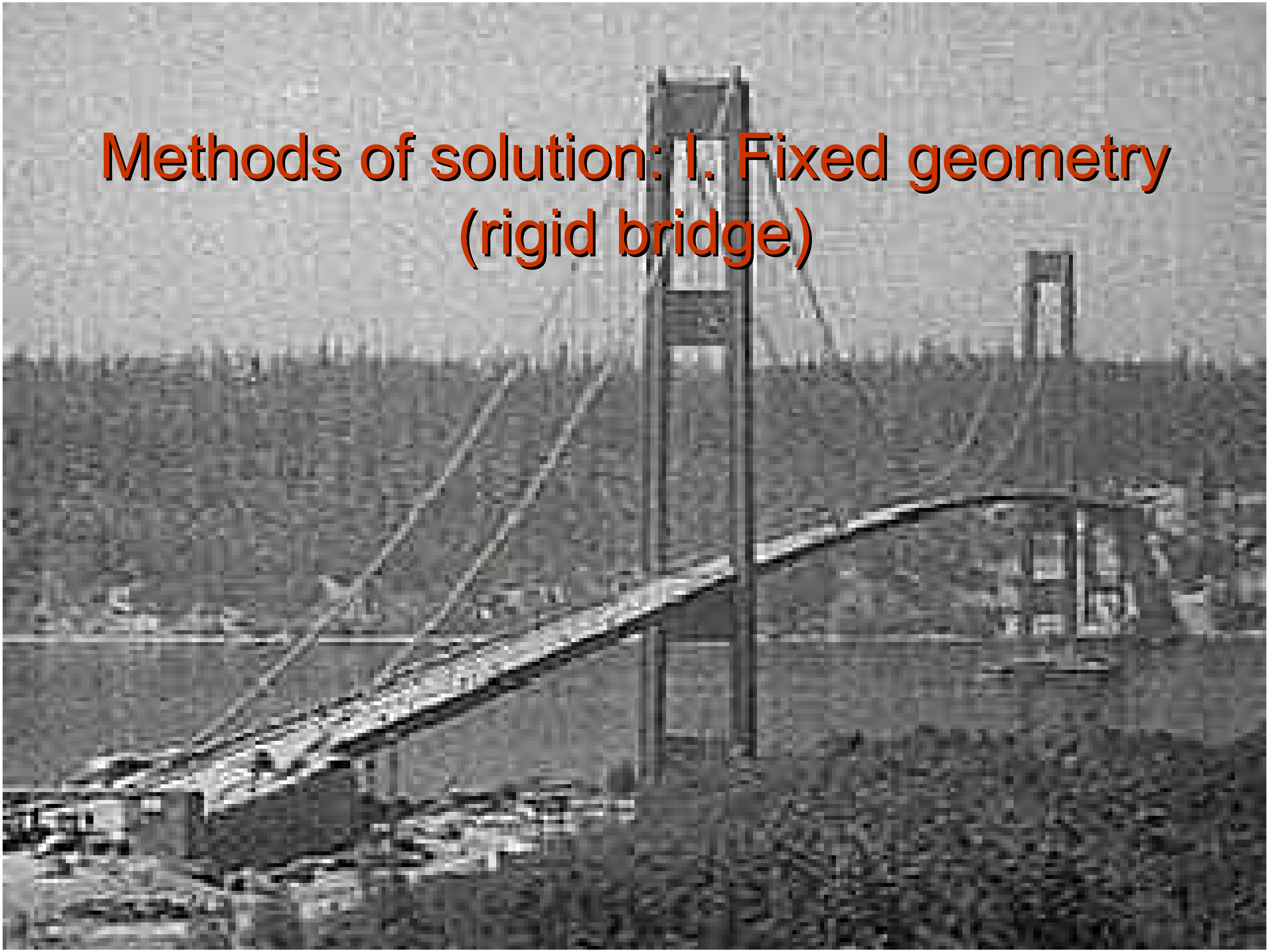
$h_d = \hbar\omega\, a^+ a + \varepsilon_d + \lambda\left(a + a^+\right)$

One-electron subspace:

$$n = 1 = d^+ d + \sum_k c_k^+ c_k = d^+ d + d\, d^+ \;\Rightarrow\; \sum_k c_k^+ c_k = d\, d^+$$

$$H = \left|\phi_d\right\rangle h_d \left\langle\phi_d\right| + \sum_k \left\{ \left|\phi_k\right\rangle \left(\varepsilon_k + h_0\right) \left\langle\phi_k\right| + \left|\phi_d\right\rangle V_{dk} \left\langle\phi_k\right| + \left|\phi_k\right\rangle V_{dk}^* \left\langle\phi_d\right| \right\}$$

Methods of solution: I. Fixed geometry (rigid bridge)



Solution of scattering problem

$$H = |\phi_d\rangle \varepsilon_d \langle \phi_d| + \sum_{k,\alpha=L,R} \left\{ |\phi_{k\alpha}\rangle \varepsilon_{k\alpha} \langle \phi_{k\alpha}| + |\phi_d\rangle V_{dk\alpha} \langle \phi_{k\alpha}| + |\phi_{k\alpha}\rangle V^*_{dk\alpha} \langle \phi_d| \right\}$$

$$|\Psi\rangle = |\Psi_i\rangle + \left(E^+ - \mathcal{H}_0\right)^{-1} \mathcal{H}_I |\Psi\rangle$$

$$|\Psi\rangle = \psi_d |\phi_d\rangle + \sum_{k,\alpha=L,R} \psi_k |\phi_k\rangle$$

$$\psi_d = \left(E^+ - \varepsilon_d\right)^{-1} \sum_k V_{dk} \psi_k$$

$$\psi_k = \delta(\varepsilon_i - \varepsilon_k) + \left(E^+ - \varepsilon_k\right)^{-1} V_{dk}{}^* \psi_d$$

$$\psi_d = \psi_0 + (E^+ - \varepsilon_d)^{-1} \Sigma(E) \psi_d$$

$$\Sigma(E) = \sum_k \frac{|V_{dk}|^2}{E^+ - \varepsilon_k} = \Delta(E) - \tfrac{i}{2}\Gamma(E)$$

Solution of scattering problem

$$t_{R\leftarrow L}(\varepsilon) = (2\pi)^2 \left| \left\langle \Psi_f \left| \mathcal{H}_I \right| \Psi \right\rangle \right|^2 = \Gamma_L(\varepsilon)\Gamma_R(\varepsilon) \left| \frac{1}{\varepsilon - \varepsilon_d - \Sigma(\varepsilon)} \right|^2$$

i.e. transmission probability

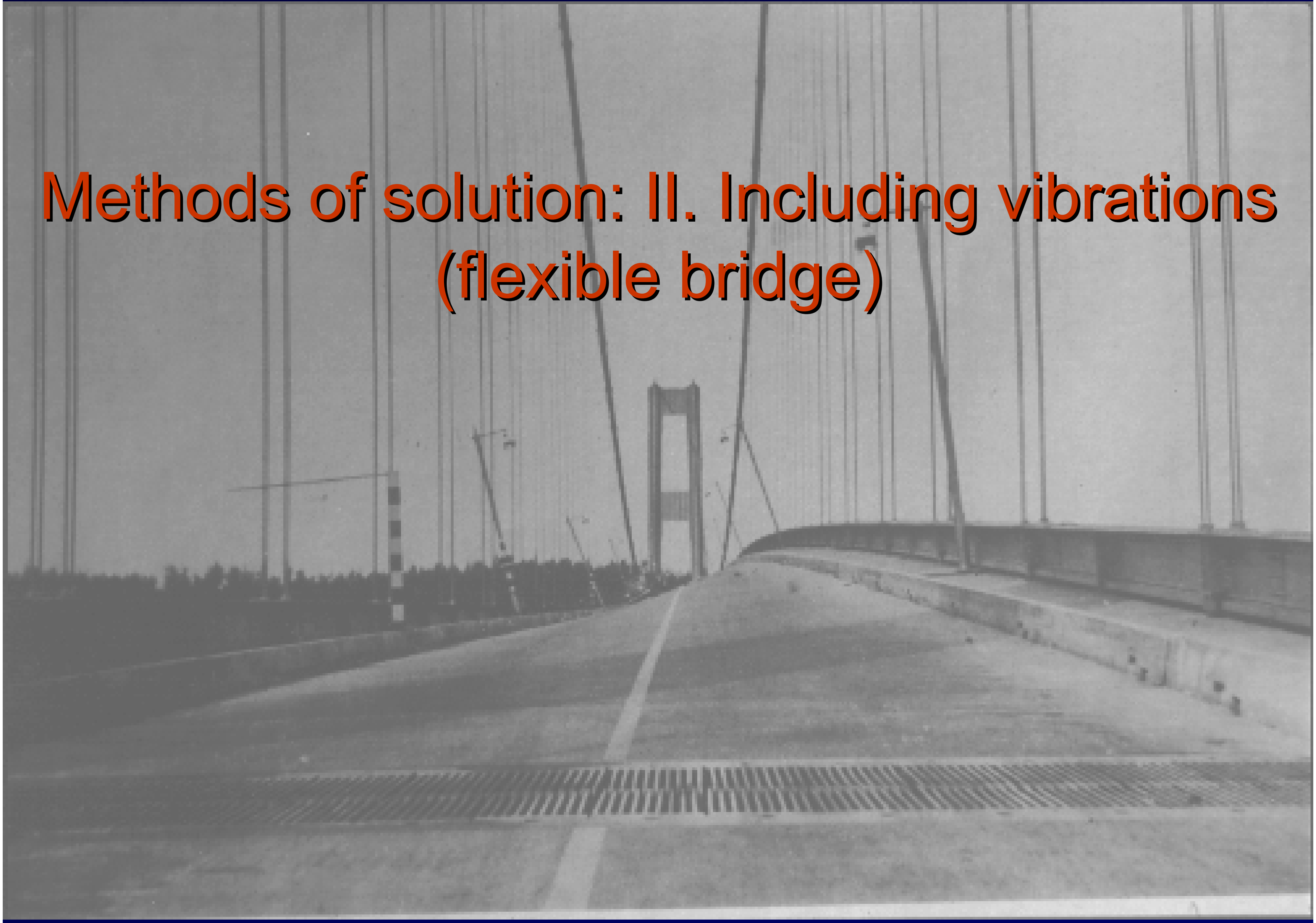
$$t_{R\leftarrow L}(\varepsilon) = t_{L\leftarrow R}(\varepsilon) = \frac{\Gamma_L(\varepsilon)\Gamma_R(\varepsilon)}{\left[\varepsilon - \varepsilon_d - \Delta(\varepsilon)\right]^2 + \frac{1}{4}\Gamma(\varepsilon)^2}$$

Landauer formula for current

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

Equivalent with full many-body solution using NEGF

Methods of solution: II. Including vibrations (flexible bridge)



Solution of scattering problem

$$H = |\phi_d\rangle h_d \langle\phi_d| + \sum_{k,\alpha=L,R} \left\{ |\phi_{k\alpha}\rangle (\varepsilon_{k\alpha} + h_0) \langle\phi_{k\alpha}| + |\phi_d\rangle V_{dk\alpha} \langle\phi_{k\alpha}| + |\phi_{k\alpha}\rangle V^*_{dk\alpha} \langle\phi_d| \right\}$$

$$|\Psi\rangle = |\Psi_i\rangle + \left(E^+ - \mathcal{H}_0\right)^{-1} \mathcal{H}_I |\Psi\rangle$$

$$|\Psi\rangle = \psi_d(q) |\phi_d\rangle + \sum_{k,\alpha=L,R} \psi_k(q) |\phi_k\rangle$$

$$\psi_d(q) = \left(E^+ - h_d(q)\right)^{-1} \sum_k V_{dk}(q) \psi_k(q)$$

$$\psi_k(q) = \delta(\varepsilon_i - \varepsilon_k) |v_i\rangle + \left(E^+ - \varepsilon_k - h_0(q)\right)^{-1} V_{dk}{}^*(q) \psi_d(q)$$

$$\psi_d(q) = \psi_0(q) + (E^+ - h_d(q))^{-1} \Sigma(E - h_0(q)) \psi_d(q)$$

$$\Sigma(E - h_0) = \sum_k V_{dk}(q) \frac{1}{E^+ - \varepsilon_k - h_0(q)} V_{dk}(q)^*$$

Solution of scattering problem

i.e. transmission probability

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

$$G_d^S(E)\equiv\left\langle\phi_d\left|(E^+-H)^{-1}\right|\phi_d\right\rangle=\boxed{\left[E^+-h_d-\Sigma(E-h_0)\right]^{-1}}$$

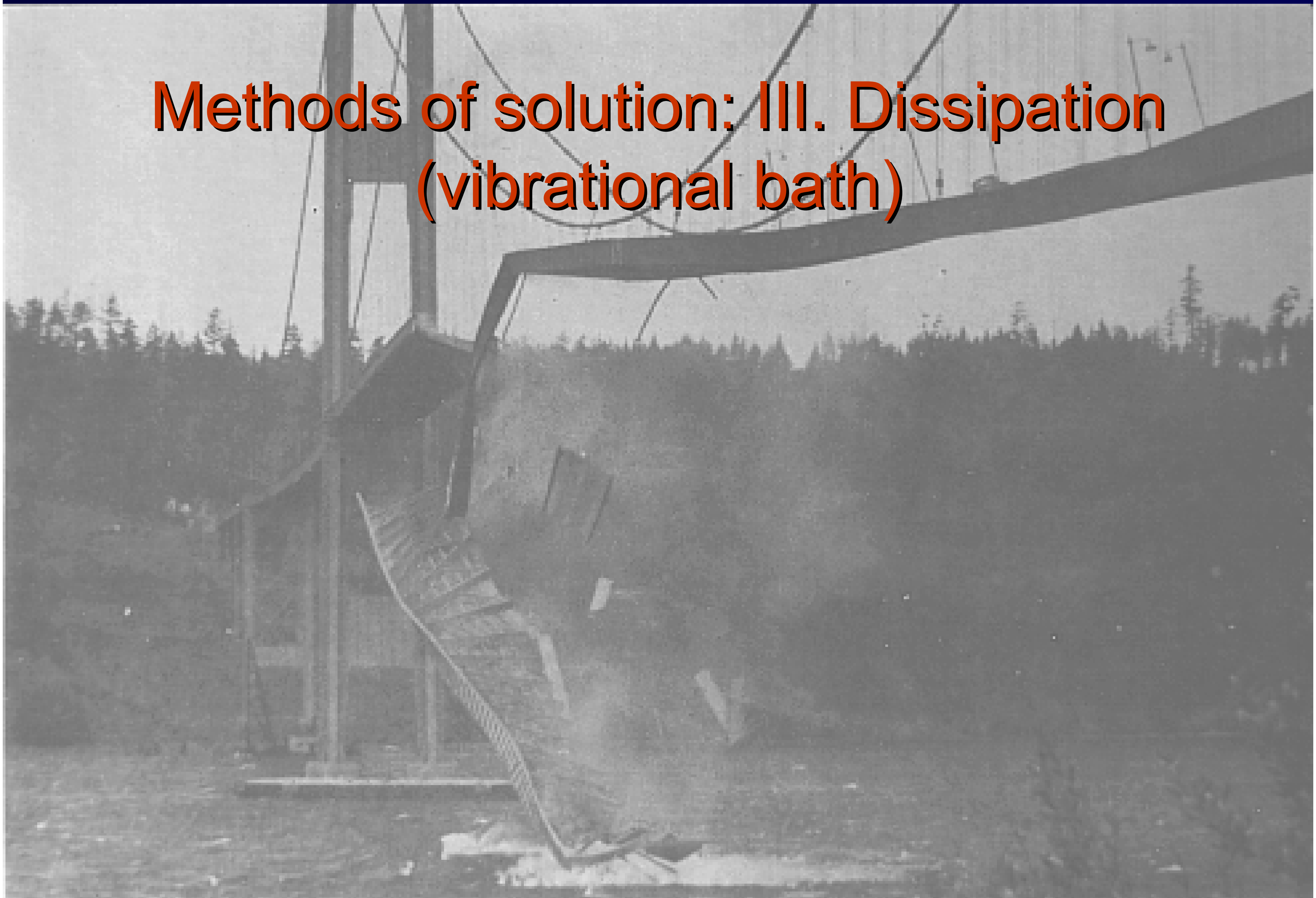
Compare

$$t_{R\leftarrow L}(\varepsilon_i,\varepsilon_f)=\delta(\varepsilon_i-\varepsilon_f)\Gamma_L(\varepsilon)\Gamma_R(\varepsilon)\left|\frac{1}{\varepsilon-\varepsilon_d-\Sigma(\varepsilon)}\right|^2$$

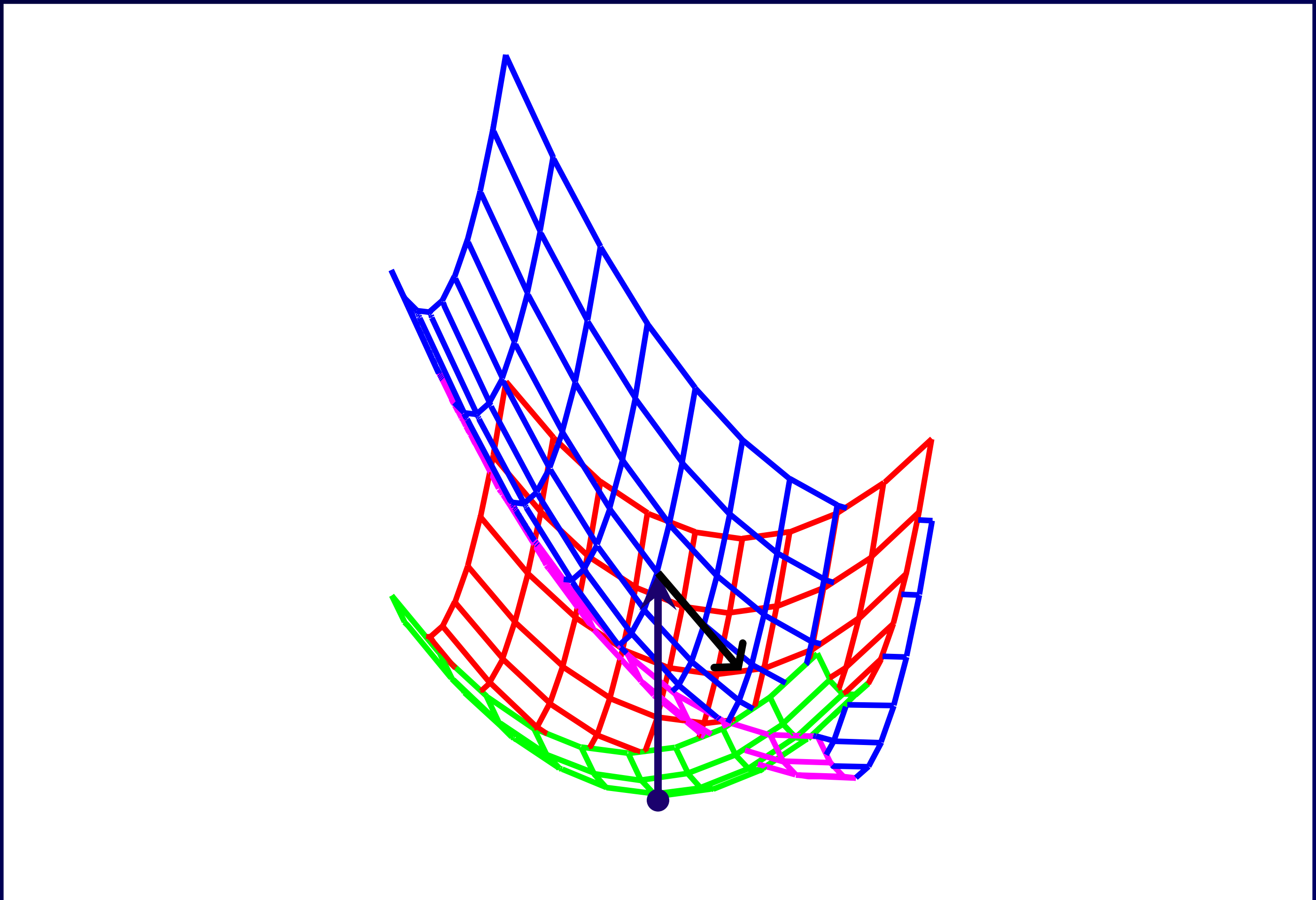
Method: variational principle for $\left|\psi\right\rangle=G_d^S(E)\left|v_i\right\rangle$

$$G_d^S(E)\left|v_i\right\rangle=\left(E^+-h_d\right)^{-1}\left|v_i\right\rangle+\left(E^+-h_d\right)^{-1}\Sigma(E-h_0)G_d^S(E)\left|v_i\right\rangle$$

Methods of solution: III. Dissipation (vibrational bath)



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 ... vibrations of the anion in system mode

h_0 ... vibrations of the neutral in system mode

Bath Hamiltonian: $H_B = \sum_j \omega_j b_j^{+} b_j$

System-bath coupling: $H_{SB} = |\phi_d\rangle \sum_j c_j \left(a_d^{+} b_j + b_j^{+} a_d\right)\langle\phi_d|$

Transmission through molecular bridge

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

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

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

$$J(\omega)=\sum_j c_j^2\delta\left(\omega-\omega_j\right)$$

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

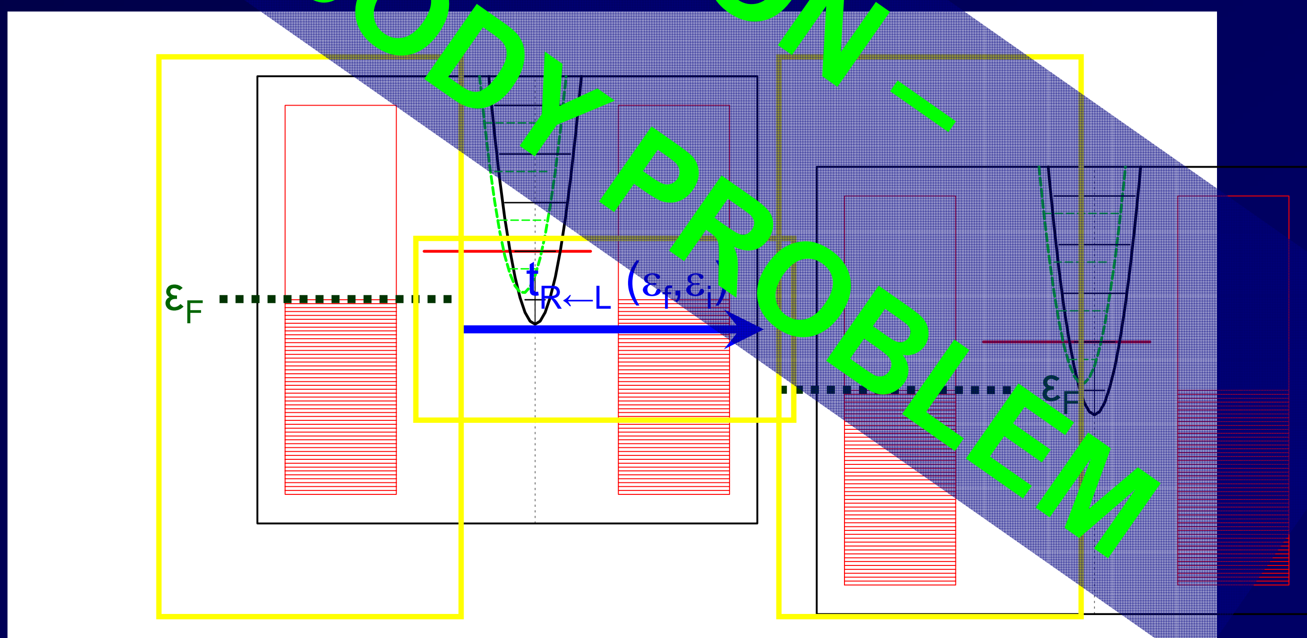
Can be summed to all orders for symmetric bridge under zero bias (unitarity).

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



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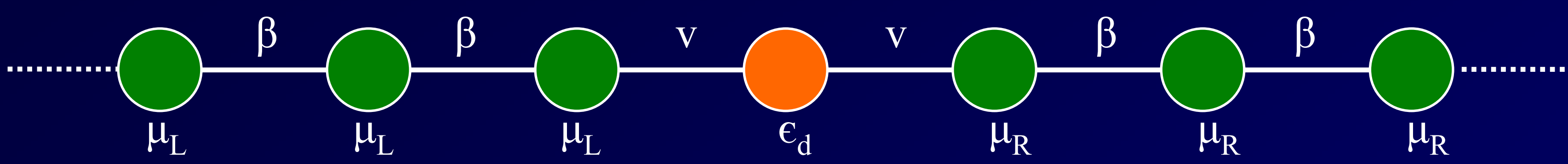
Model: Electronic degrees of freedom



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

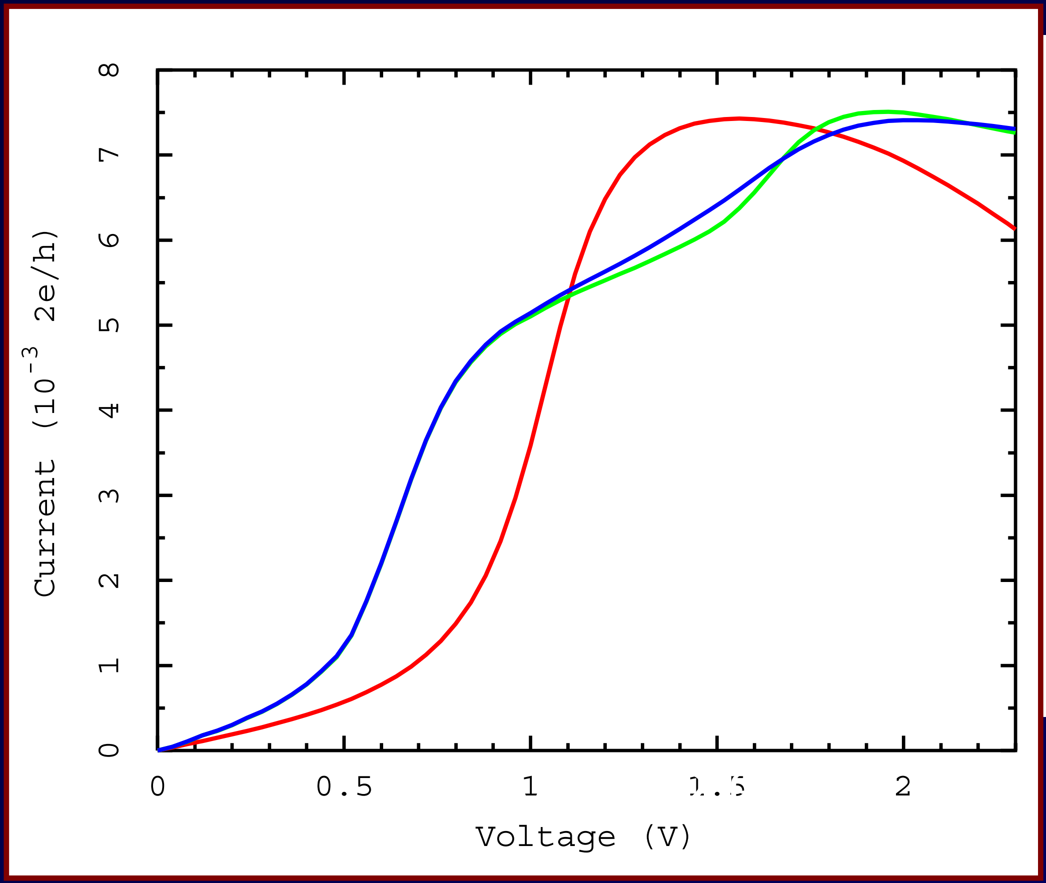
Conduction band in leads: $\mu_\alpha - 2\beta < E < \mu_\alpha + 2\beta$

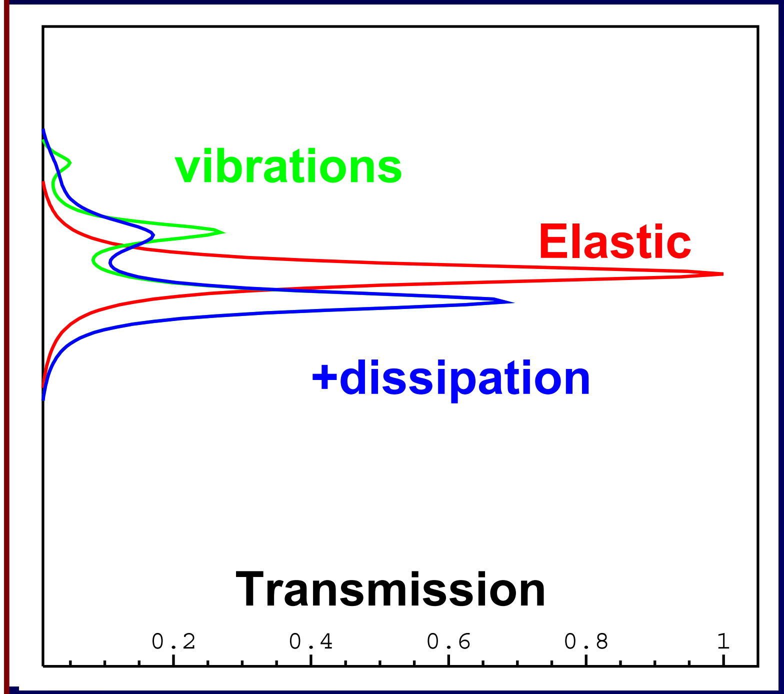
Energy dependent width: $$\Gamma(E) = \frac{v^2}{\beta^2}\sqrt{4\beta^2 - \left(E - \mu_\alpha\right)^2}$$

Selfenergy function (level shift):

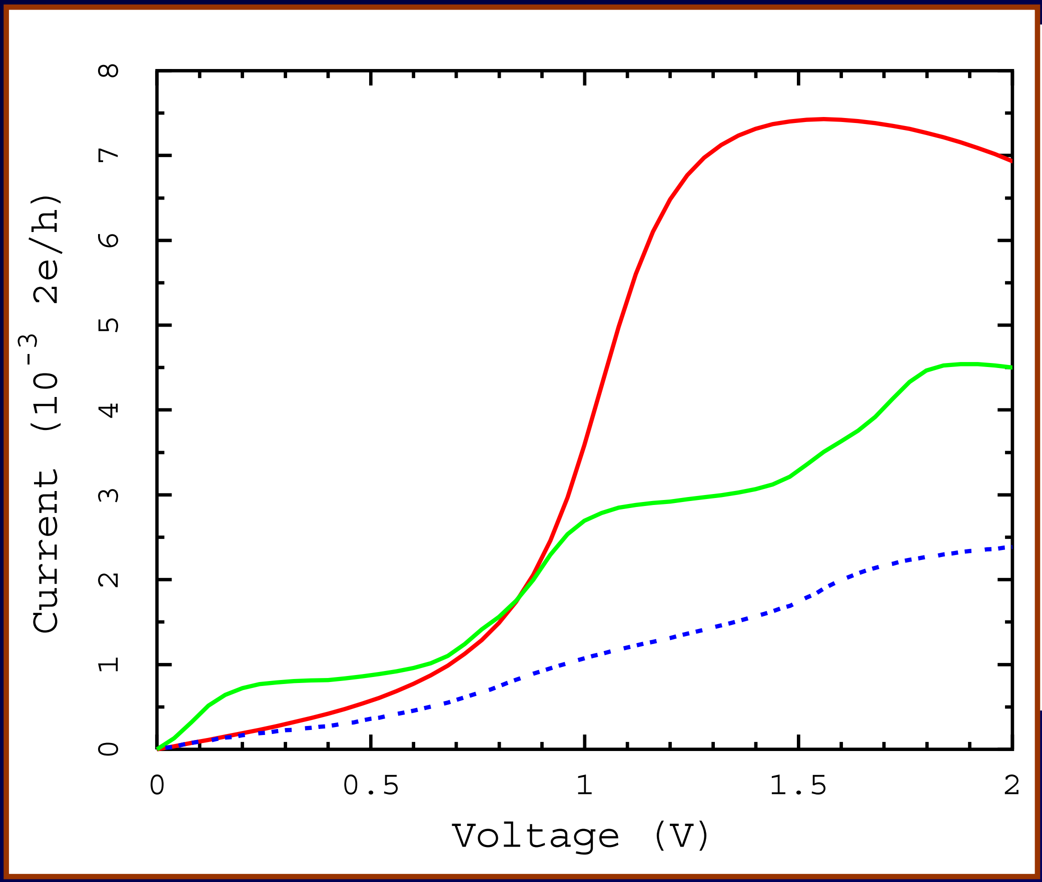
$$\Sigma(E) = \Delta(E) - \tfrac{i}{2}\Gamma(E) = \frac{2v^2}{E - \mu_\alpha + \sqrt{\left(E - \mu_\alpha\right)^2 - 4\beta^2}}$$

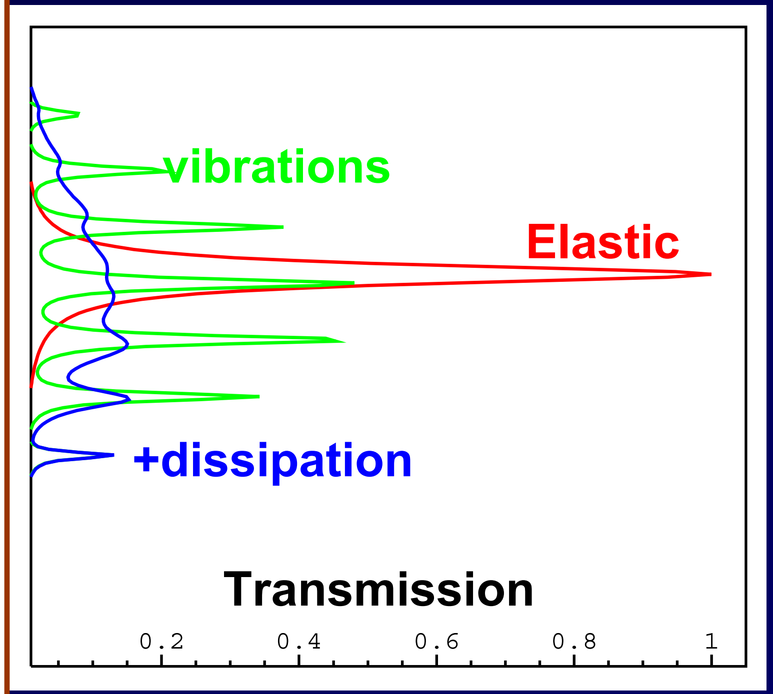
Results – weakly coupled case





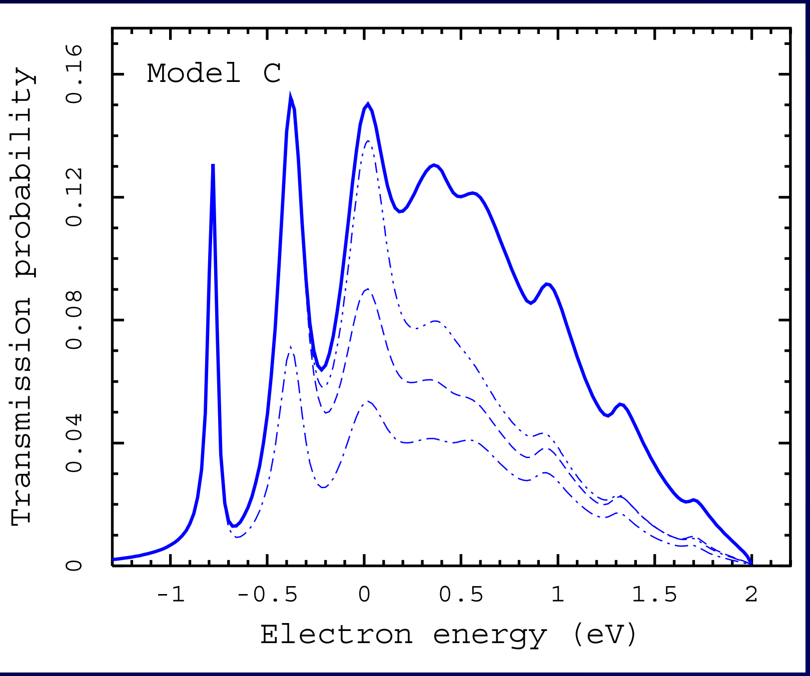
Results – strongly coupled vibrations

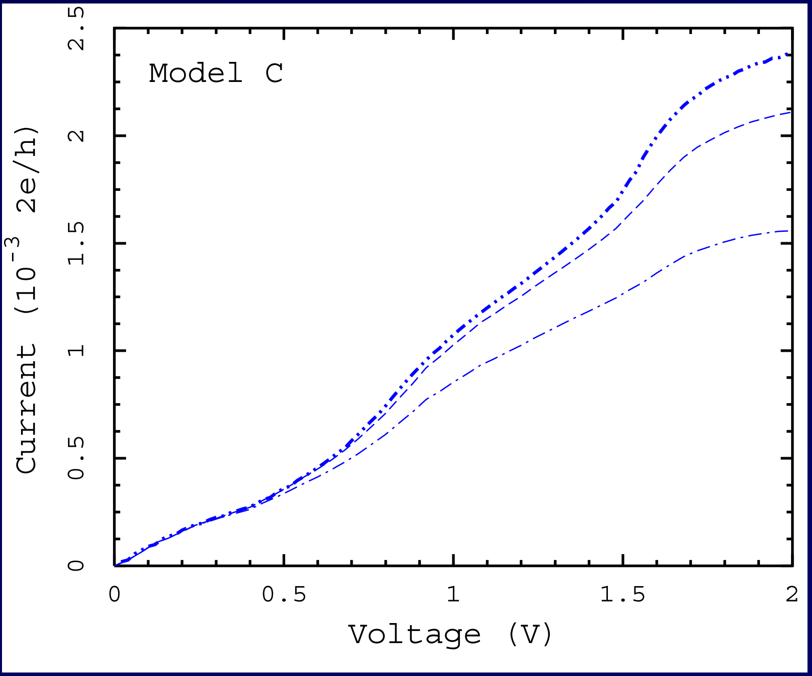




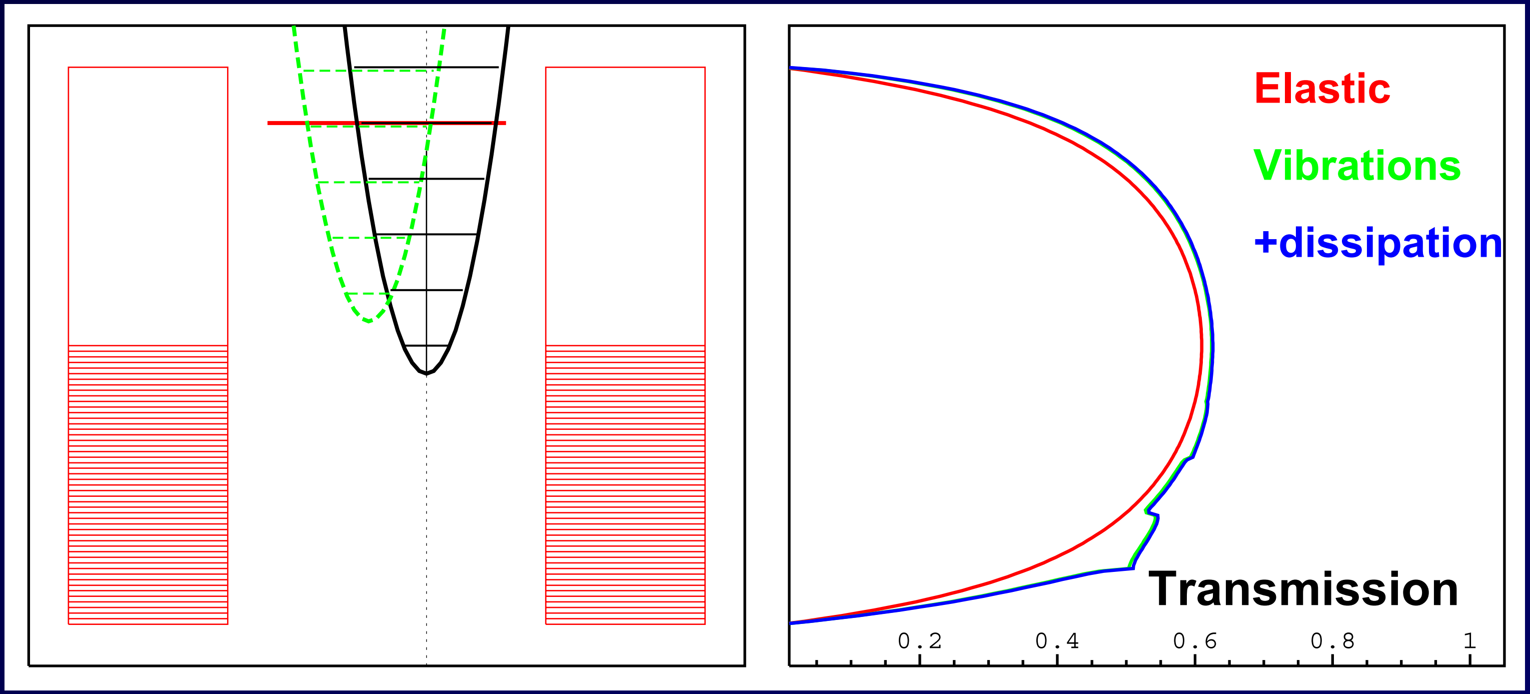
Convergence of the expansion in the system-bath coupling

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



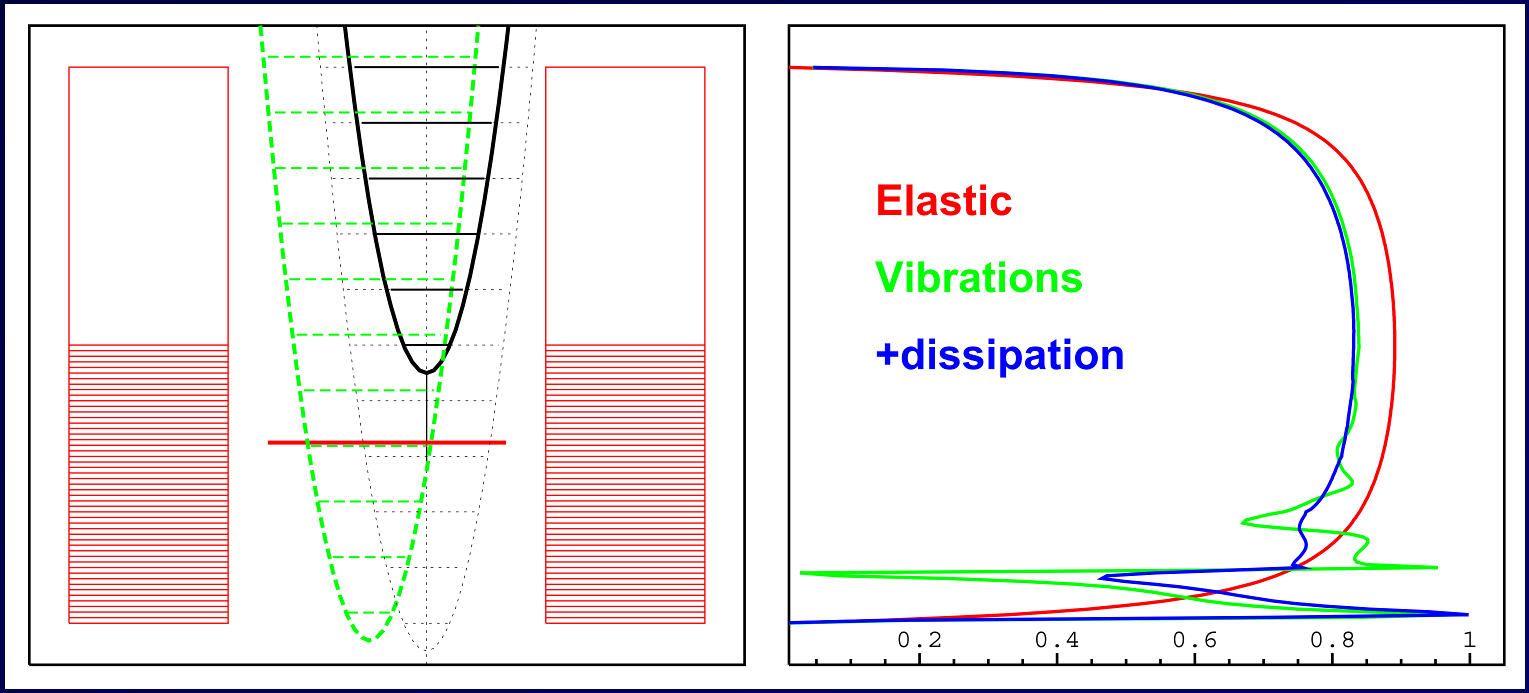


Results – strongly coupled leads



v = β

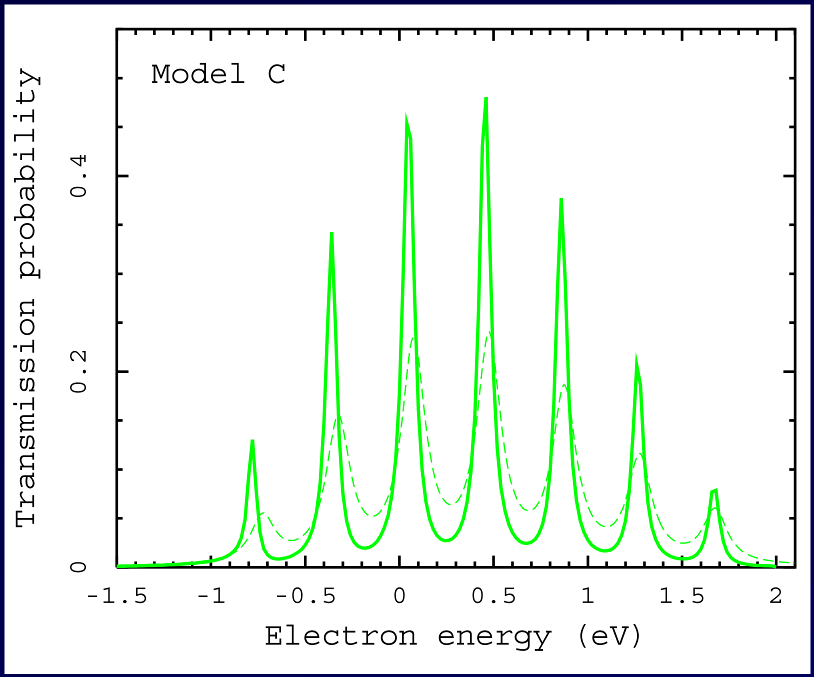
Results – strongly coupled leads

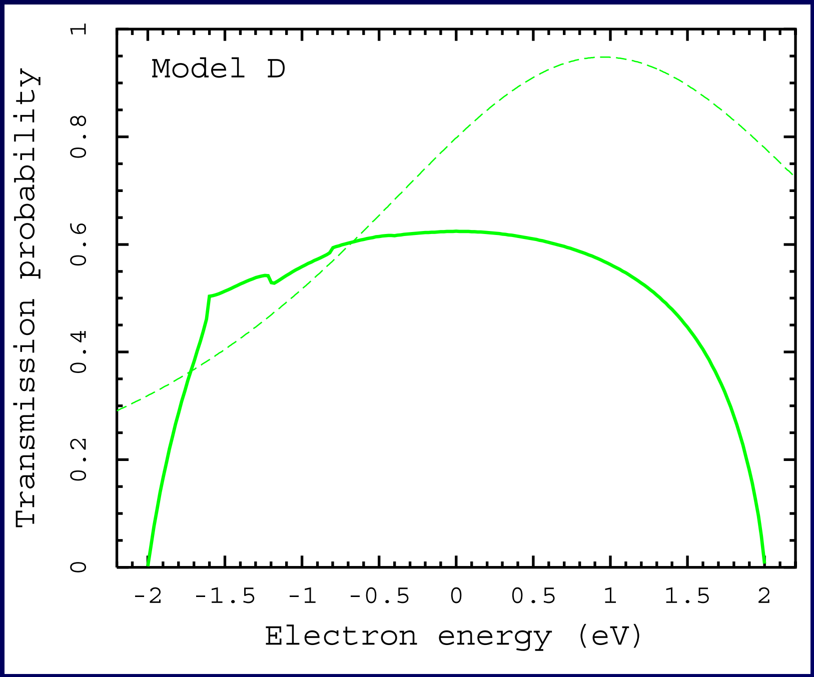


$v = \beta$

Transmission

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





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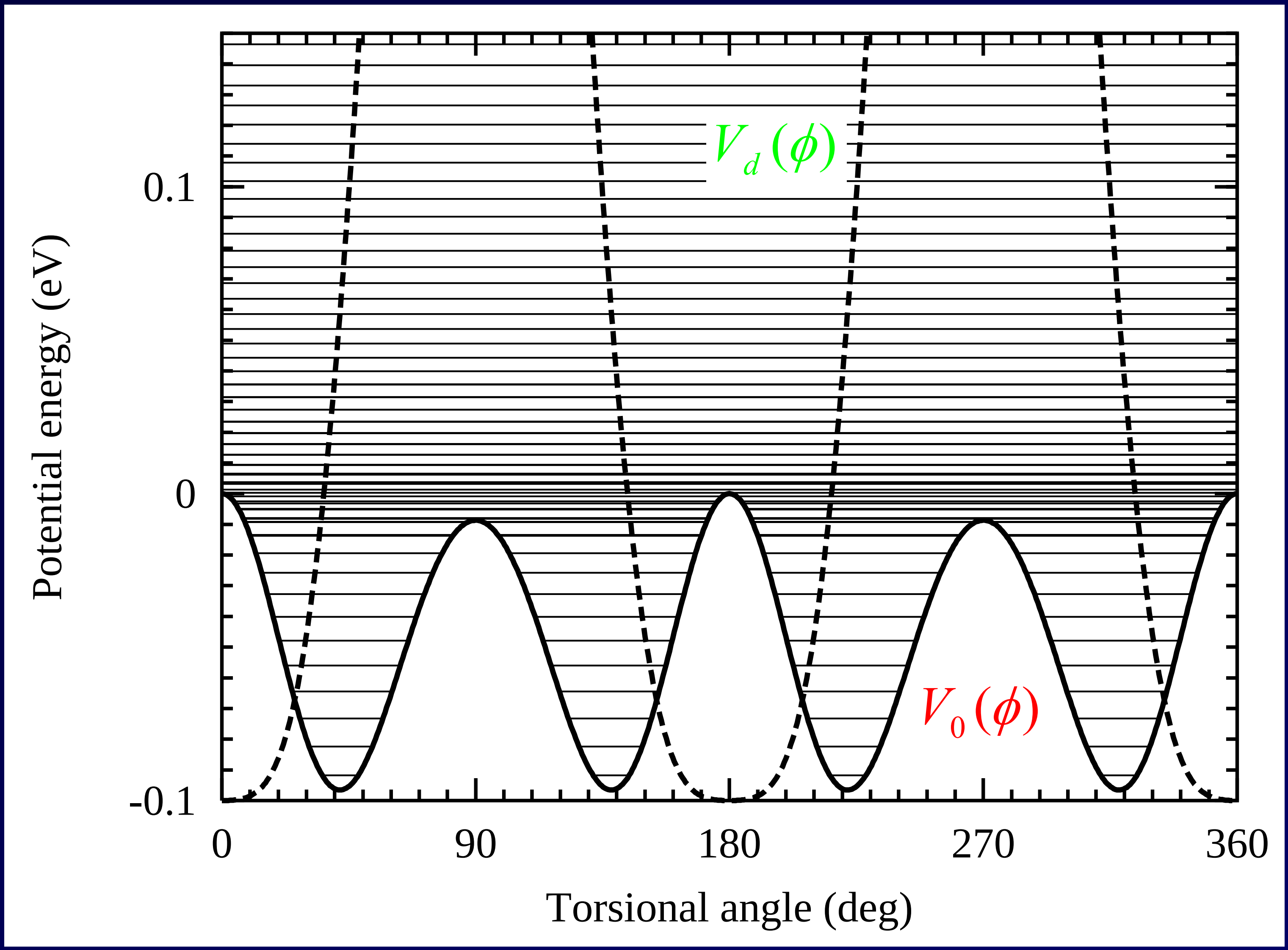
Model for biphenyl – anharmonic vibrations

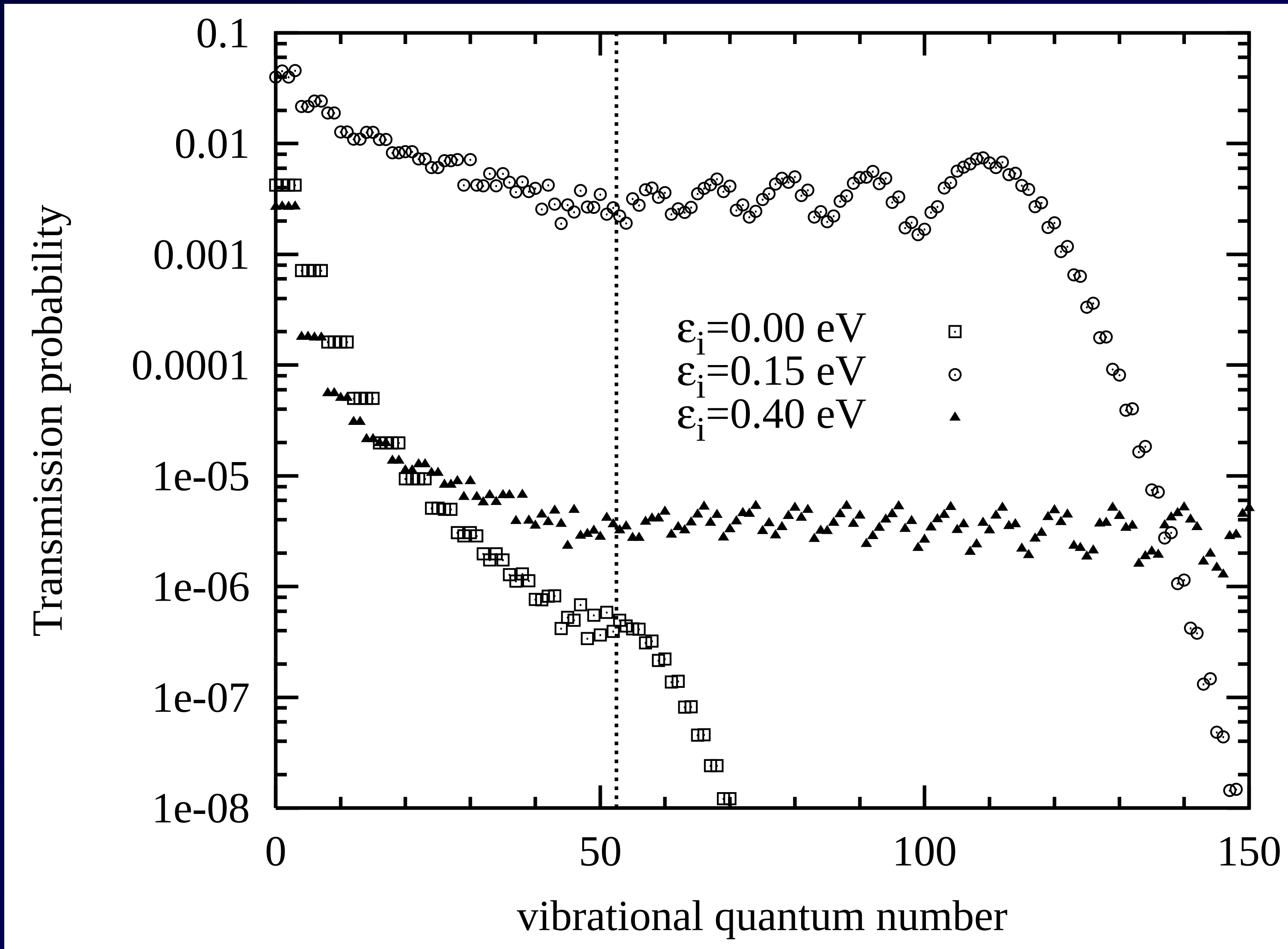


Adiabatic-nuclei approximation

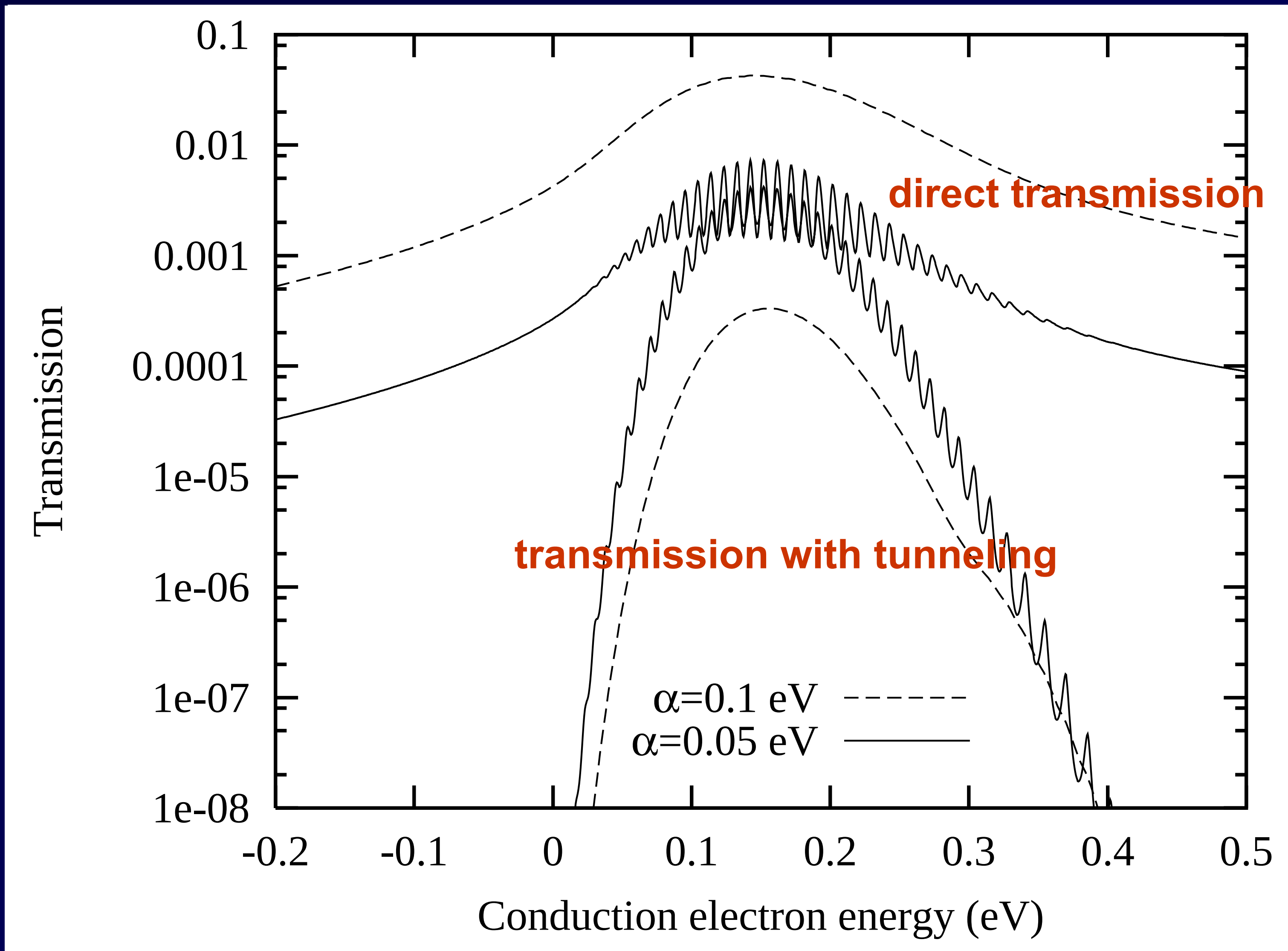
$$t_{AN}(\varepsilon) = \int dq \sum_i p_i \left| v_i(q) \right|^2 t_{el}(q, \varepsilon)$$

$$p_i = \tfrac{1}{z} \exp\left\{ -E_i / kT \right\}$$

Model for biphenyl – anharmonic vibrations



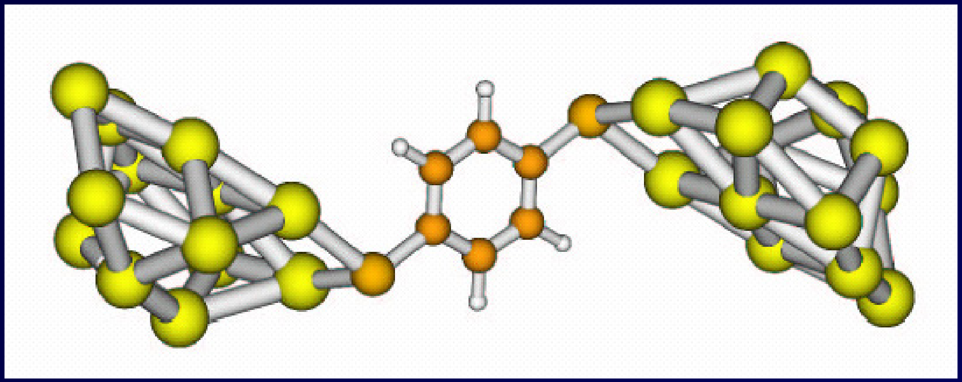
Model for biphenyl – electron assisted tunneling

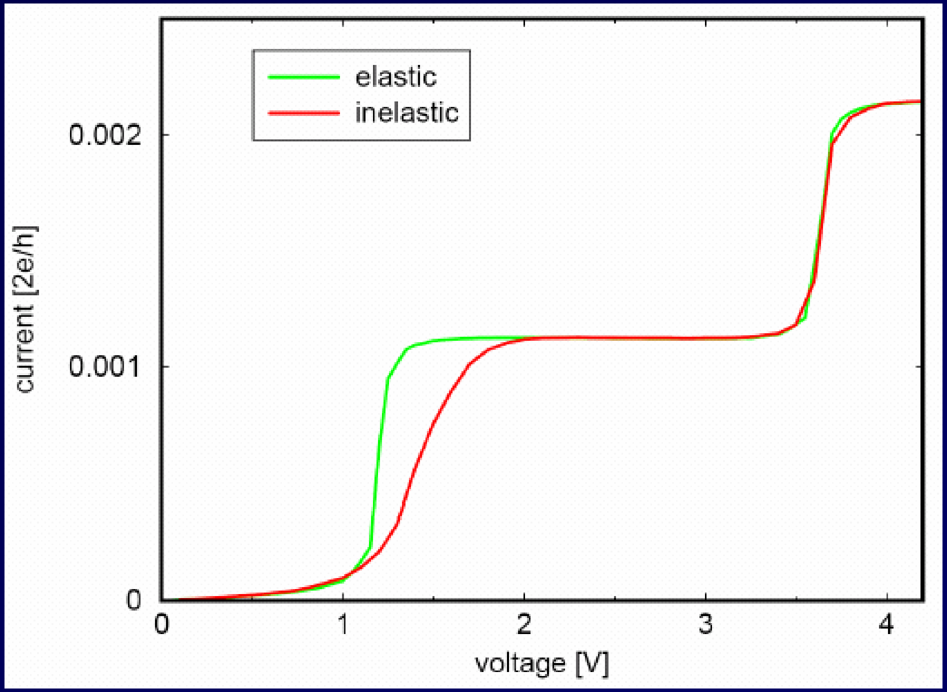


Conclussions and outlook

- 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.

Preliminary results – model motivated by DFT calculation





Acknowledgements

Michael Thoss, Wolfgang Domcke
(coauthors)

Financial support:
Alexander von Humboldt foundation, GAČR

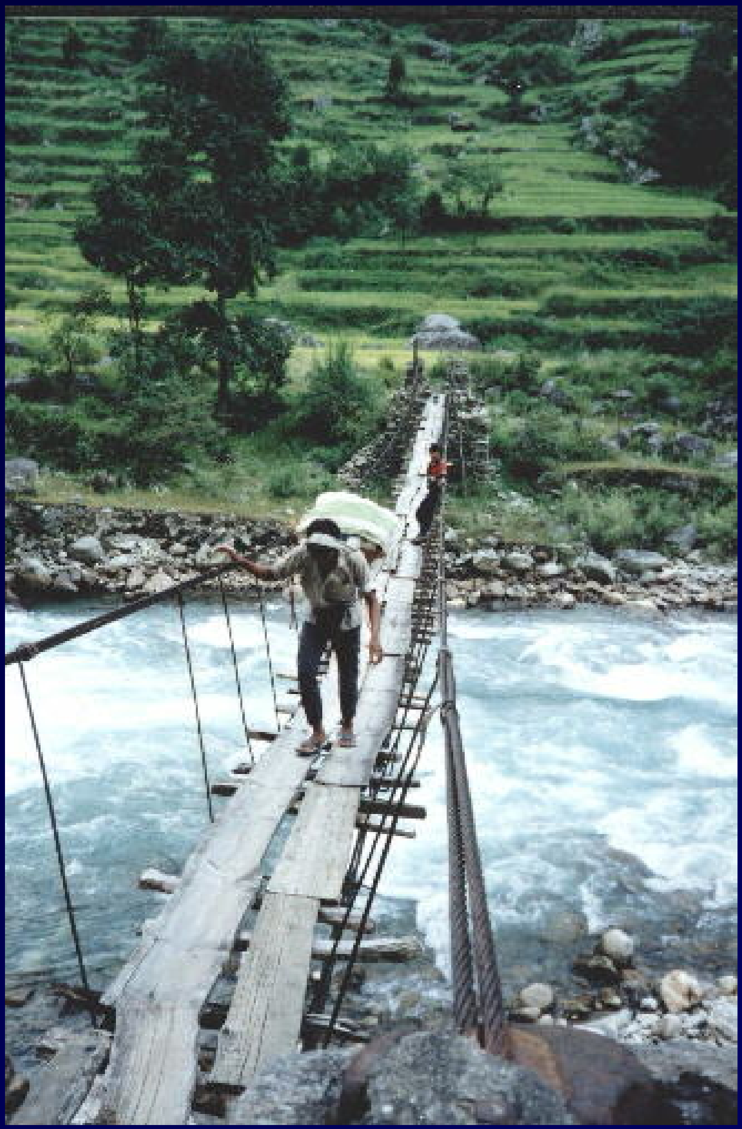
The detailed description of this work:

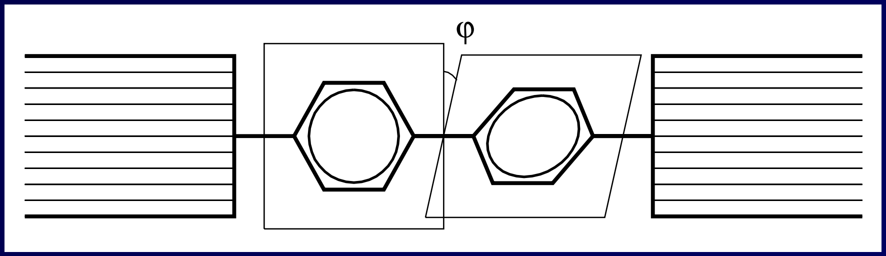
Phys. Rev. B 70 (2004) 125406 (harmonic models)

http://arxiv.org/abs/cond-mat/0411064, (biphenyl)

Contact: cizek@mbox.troja.mff.cuni.cz
http://utf.mff.cuni.cz/~cizek

Ladungstransport űber flexibele Brűcken





To be continued …