Theory vs molecular modelling of charge transfer reactions: some problems and challenges

Renat R. Nazmutdinov

Kazan National Research State Technological University

Dubna, August., 28 2012

Outline

1. Motivation

2. Medium (solvent) coordinates

3. Quantum effect of solvent on activation barrier

4. Orbital overlap (electronic transmission coefficient)

5. Some problems ahead
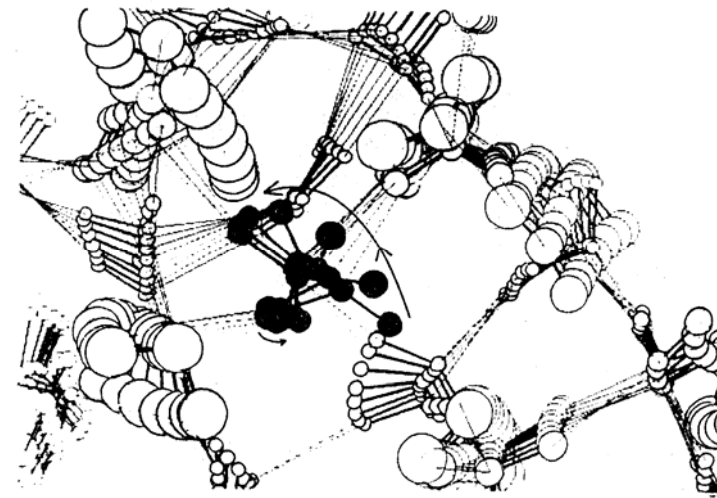
tst

Transition state theory (TST)

saddle point

Three-dimensional reaction energy surface (solvent and intramolecular coordinates)

marc

A simple way to define the solvent coordinate

(Marcus theory)

λ is the solvent reorganization energy
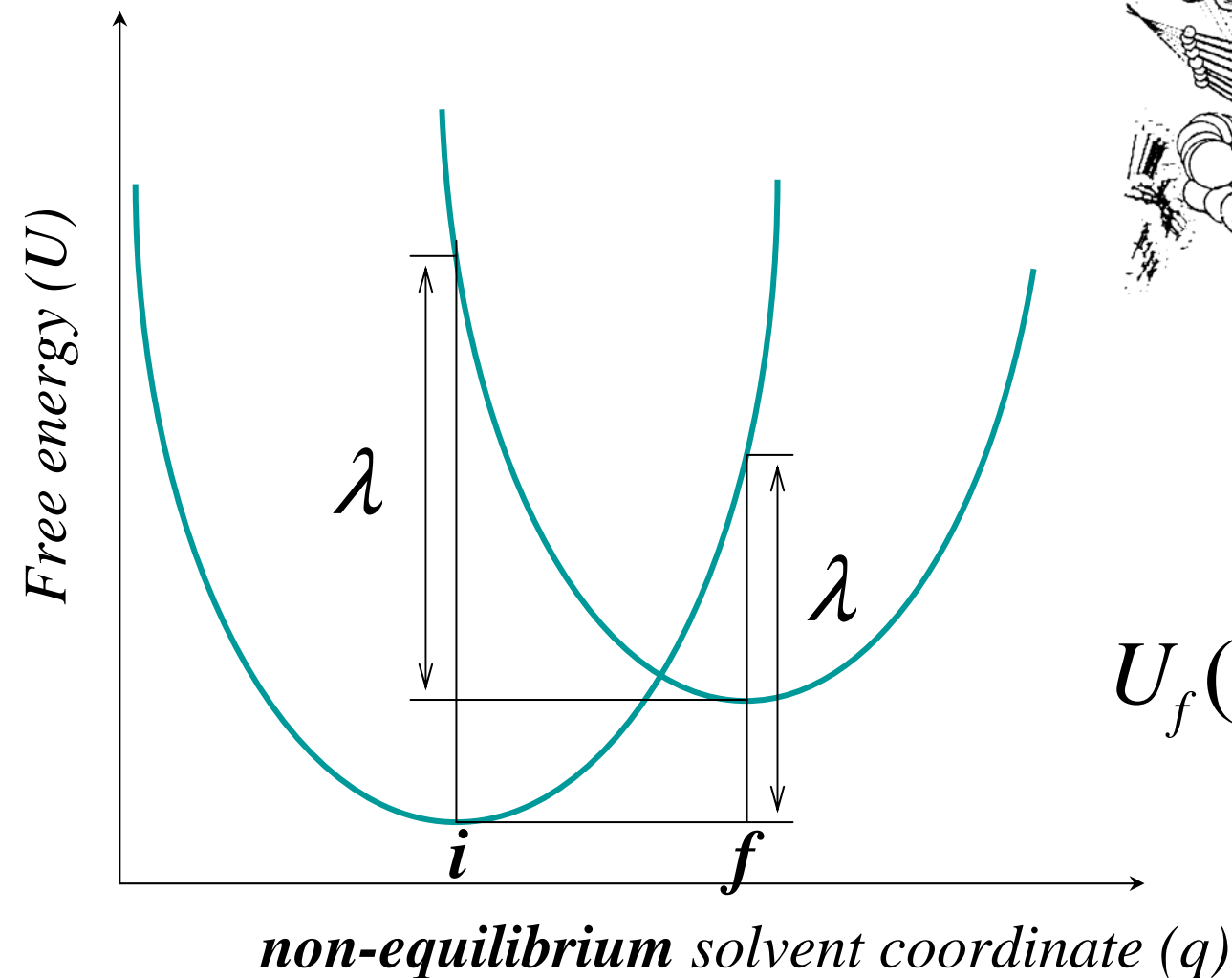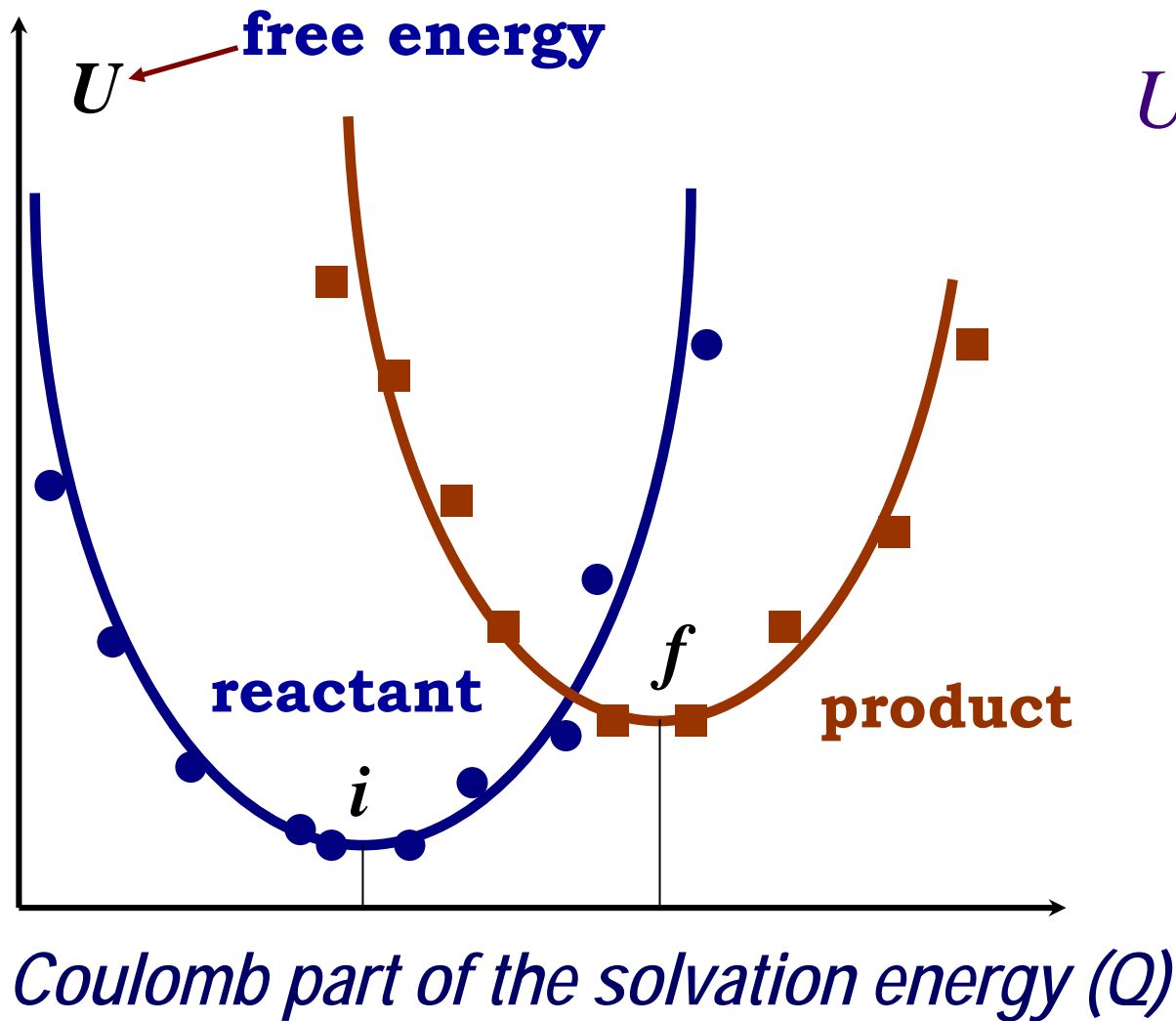

(Ohmine, 1992)

$$U_i(q) = \lambda q^2$$

$$U_f(q) = \lambda(q-1)^2 + \Delta I$$

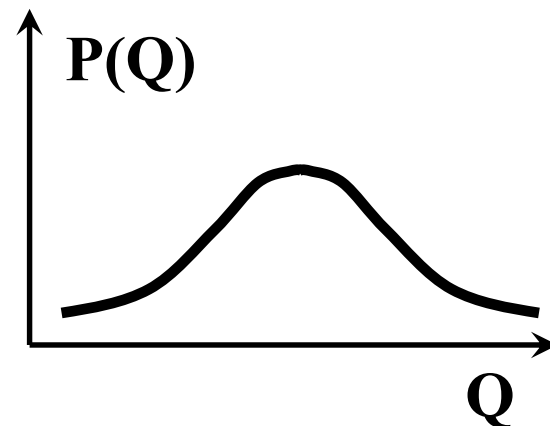$$\Delta E_a = \frac{(\lambda + \Delta I)^2}{4\lambda}$$

λ

λ

i   *f*

non-equilibrium *solvent coordinate (q)*

Free energy (U)

md

Computer simulations

free energy

U

$U(Q) = -k_B T \ln P(Q)$

$P(Q)$

Q

reactant

i

f

product

Coulomb part of the solvation energy (Q)

Umbrella sampling

kram

Stochastic theory

Reaction rate depends on <u>dynamical</u> solvent properties as well (*friction, viscosity*)

Hendrik A. Kramers
/pioneered a stochastic appoach in chemical kinetics/

Leonid D. Zusman
/extended Kramers theory to electron transfer reactions/

In terms of stochastic theory an overcoming of the activation barrier more resembles "climbing" (diffusion)

corr

Solvent correlation function

$$K(\tau) = \left\langle E_A(0), E_A(\tau) \right\rangle$$

$$K(\tau) = 2k_B T \lambda_s \frac{Q(\tau)}{Q(0)}$$

$$Q(\tau) = \frac{i}{2\pi} \int_{-\infty}^{\infty} \exp\left(-i\omega\tau\right) \left[\frac{1}{\varepsilon(\omega)} - \frac{1}{\varepsilon_\infty} \right] \frac{d\omega}{\omega}$$

S. Mukamel et al.

dielectric spectrum

spectra

Examples of dielectric spectra

sucrose solutions:

$$\varepsilon(w) = \varepsilon_\infty + \frac{\Delta\varepsilon_C}{1+(iw\tau_C)^\alpha} + \frac{\Delta\varepsilon_D}{1+iw\tau_D}$$

water-EG mixtures:

$$\varepsilon(\omega) = \frac{\Delta\varepsilon_1}{1+i2\omega\tau_1} + \frac{\Delta\varepsilon_2}{1+i2\omega\tau_2} + \frac{\Delta\varepsilon_3}{1+i2\omega\tau_3} + \varepsilon_\infty$$

series

N solvent modes   (exact expansion)

Solvent reorganization energy

correlation times

$$K(\tau) = 2k_B T \lambda \sum_{i=1}^{N} \delta_i \exp(-\tau / \tau_i^*)$$

Solvent correlation function

$$\sum_{i=1}^{N} \delta_i = 1$$

δ_i **is the contribution of *i*-th mode to the solvent reorganization energy**

**The solvent reorganization energy is "distributed" among
N solvent coordinates.**

afes

Reaction free energy surface can be described using N solvent coordinate (q_1, … q_N) and (probably) one intramolecular degree of freedom (r):

$$E_i(q_1,...,q_N;r) = \sum_{j=1}^{N} \delta_j \lambda_j q_j^2 + U_i(r)$$

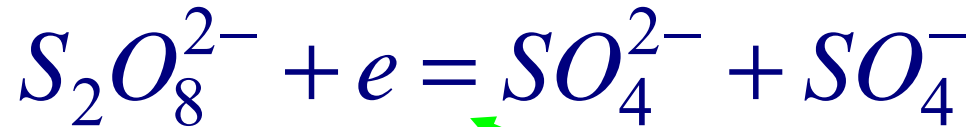*reactant*

$$E_f(q_1,...,q_N;r) = \sum_{j=1}^{N} \delta_j \lambda_j (q_j-1)^2 + U_f(r) + \Delta I$$

product

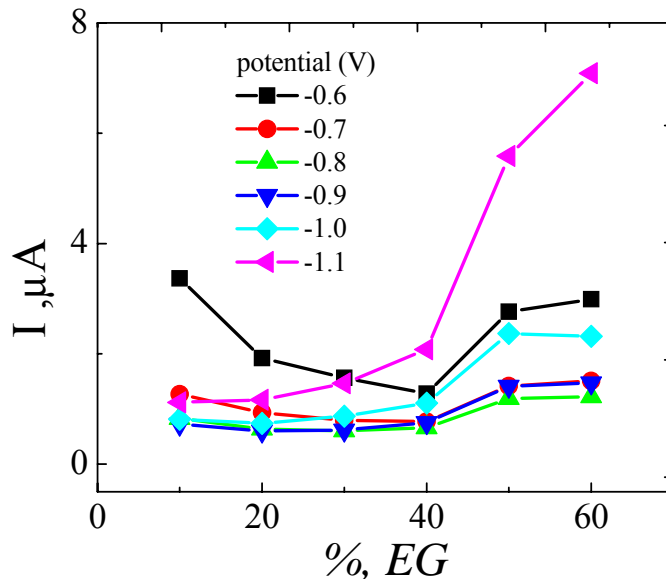**Usually N = 2 (e.g., dimethylacetamide), 3 (EG, alcohols etc)**

pers

$S_2O_8^{2-}$ reduction at a mercury electrode from water-EG mixtures

$$S_2O_8^{2-} + e = SO_4^{2-} + SO_4^{-}$$

The first ET is rate limiting

- reaction is adiabatic

- BBET reaction proceeds at large overvoltages, in the vicinity of activationless discharge, i.e. at small activation barriers
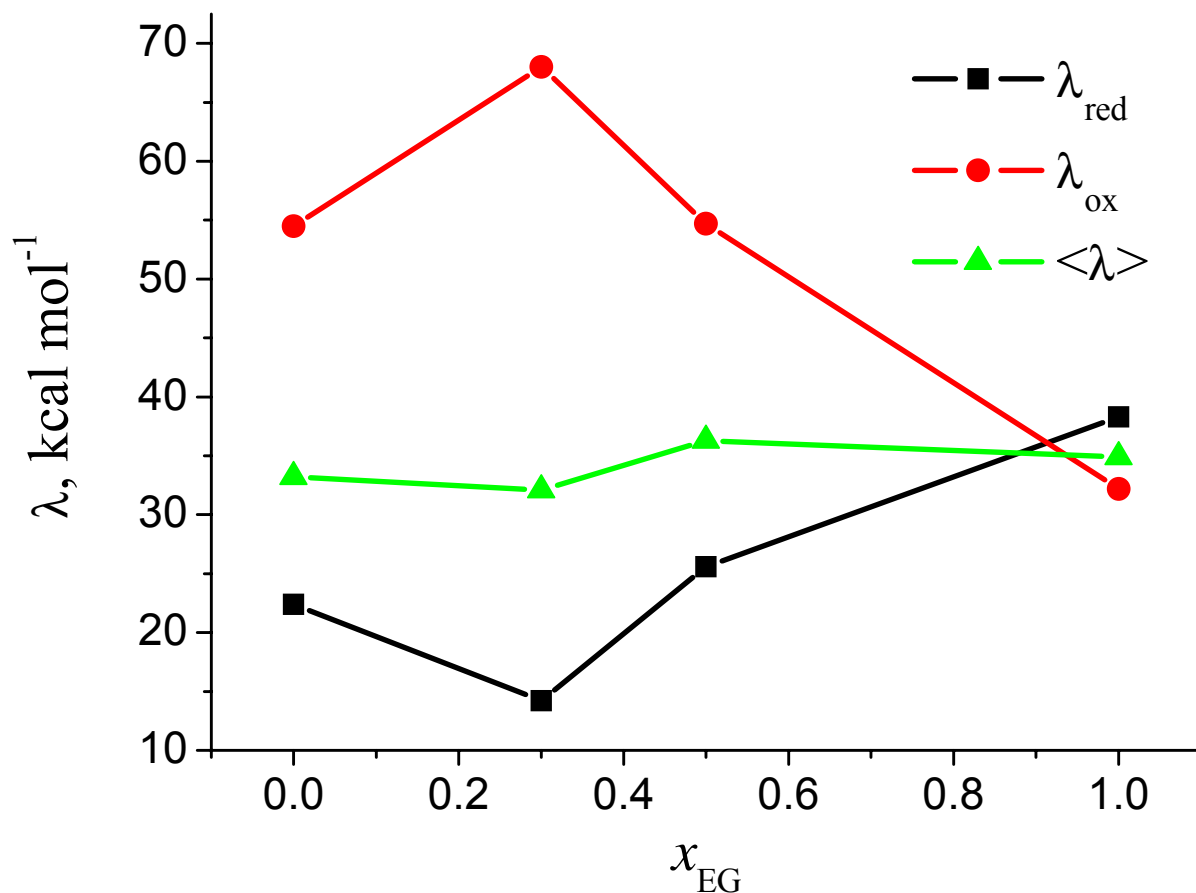
potential (V)
- -0.6
- -0.7
- -0.8
- -0.9
- -1.0
- -1.1

I , μA

%, EG

- reaction reveals an anomalous solvent viscosity effect

Exp. data (P.A. Zagrebin et al)

l, md

- Pekar factor in the solvent reorganization energy is nearly constant

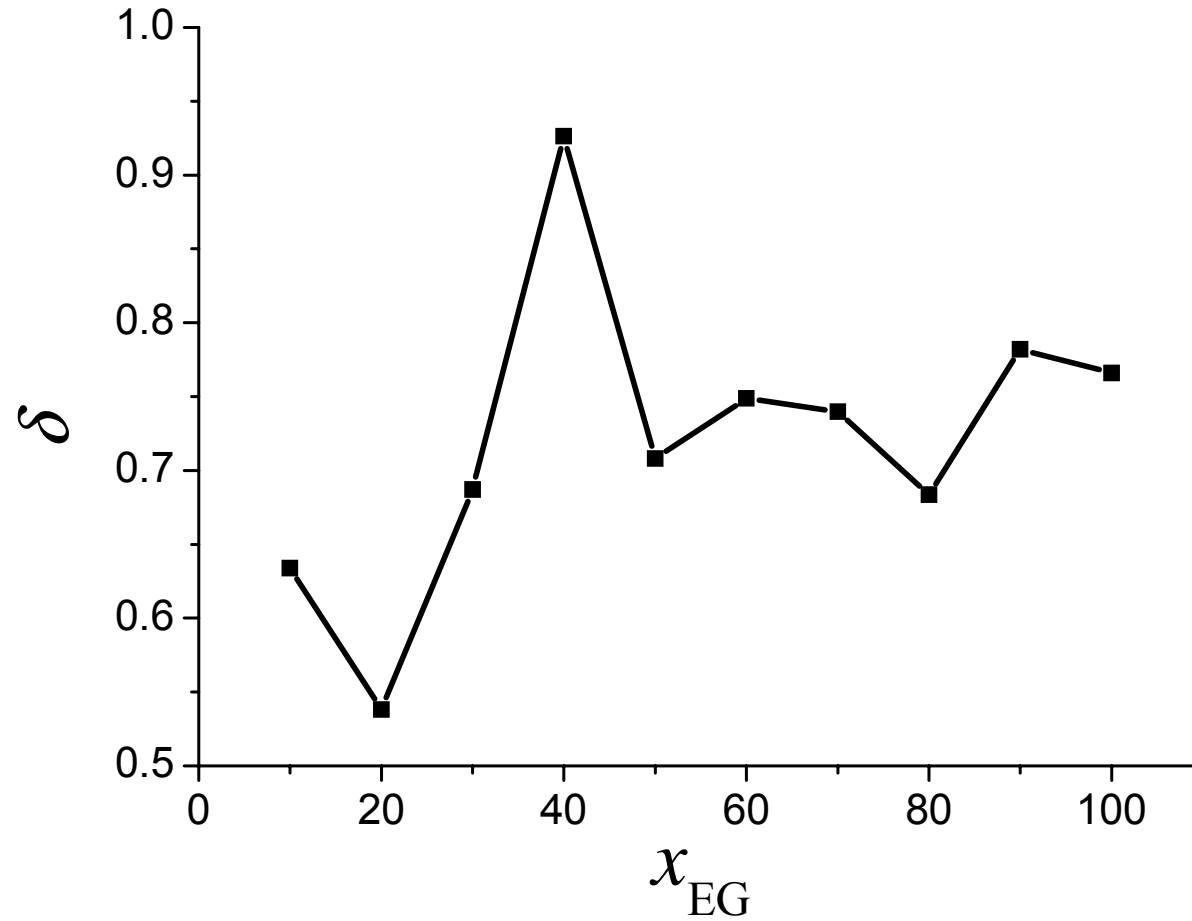**- MD simulations predict even a slight increase of $\langle\lambda\rangle$**

Bulk contributions to the solvent reorganization energy as computed form molecular dynamics (O. Ismailova, M. Probst et al)

ks
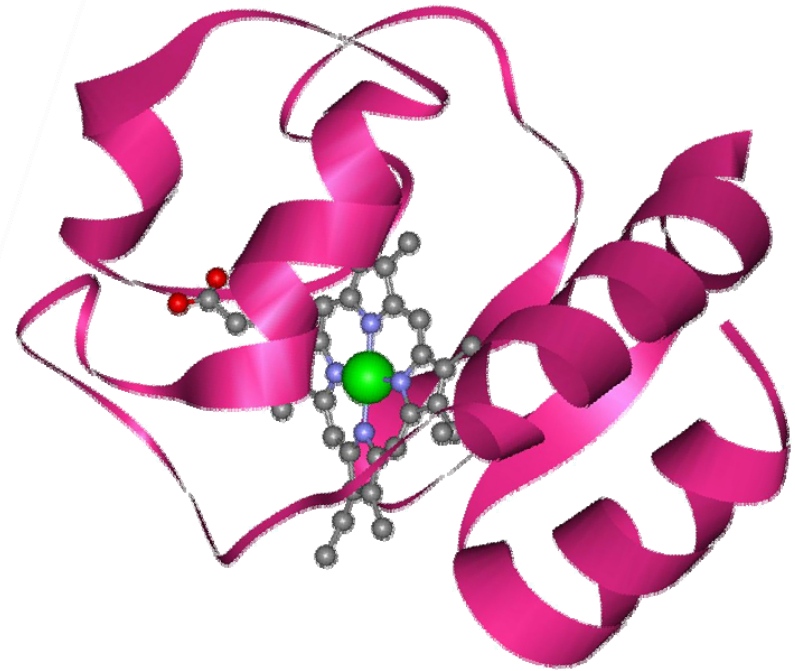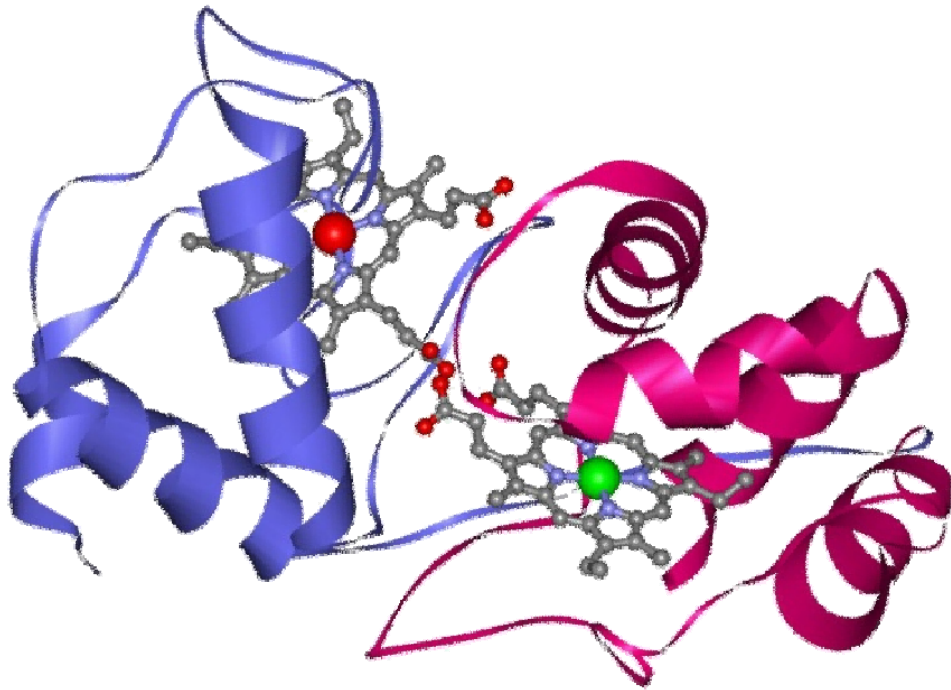
Results of Langevin molecular dynamics simulations

avoid

An attempt to explain:
saddle point avoidance
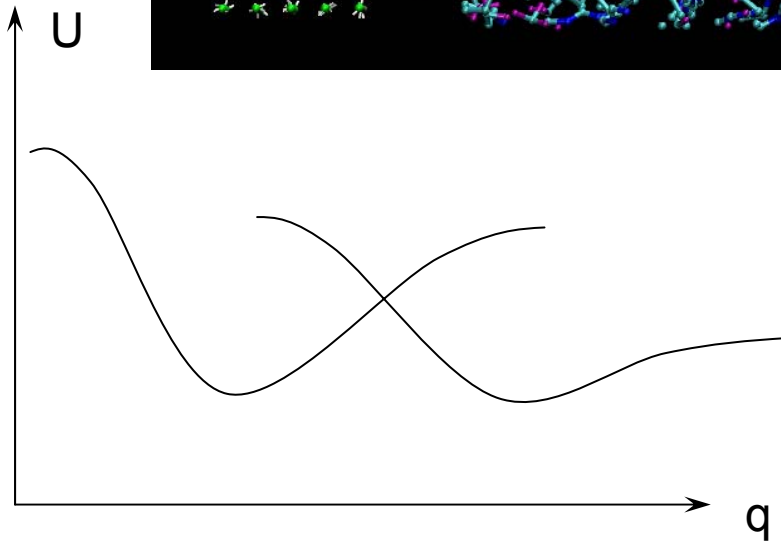

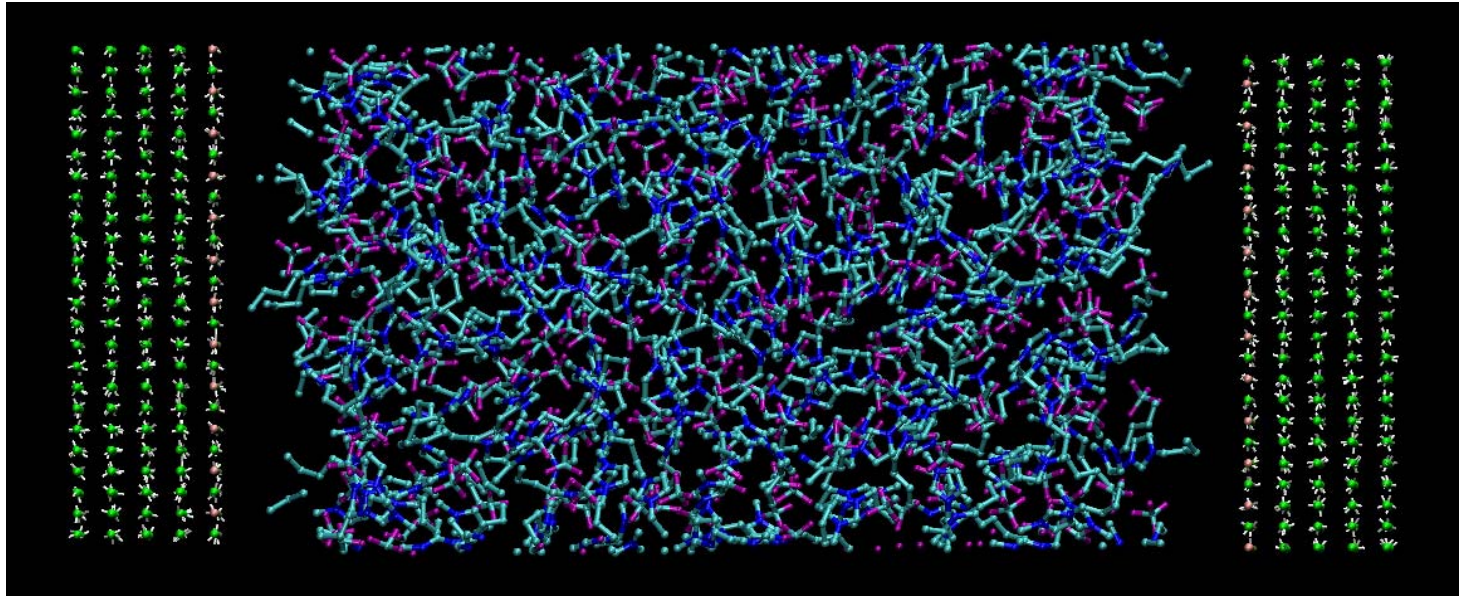
prot

Non-Gaussian fluctuations

- ferroelectric domains at a protein/water interface
 D.N. LeBard, D.V. Matyushov, PCCP, 12 (2010) 15335

IL

MD simulation of the Au(111)/[BMIM][BF$_4$] interface
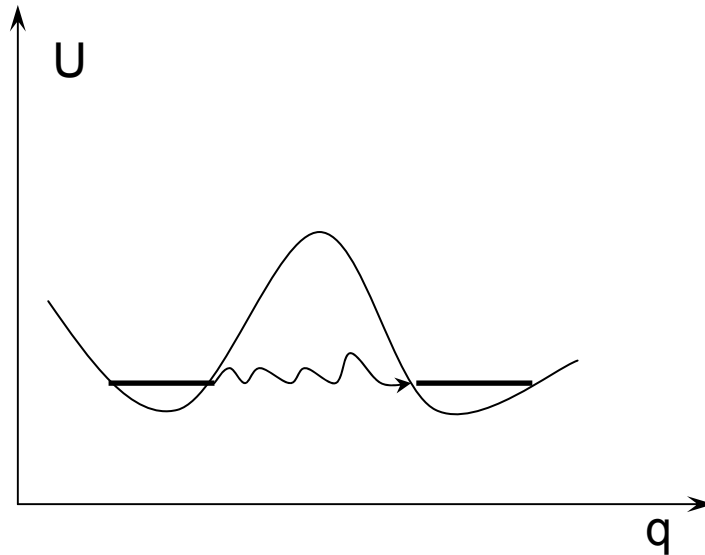
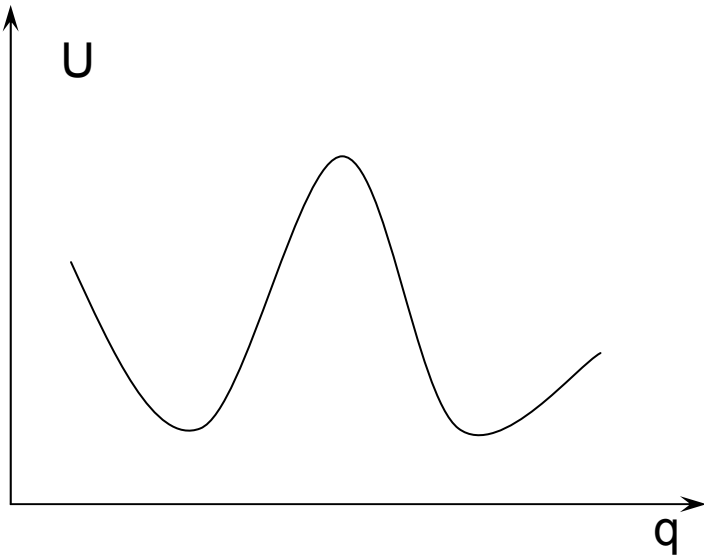## (S.A. Kislenko et al)

U

q

Non-linear response ?

quant

Solvent coordinate vs Quantum effects

- decreasing of the activation barrier ➡ increasing rate constant

- tunneling ➡ decreasing rate constant

eq

Effect of solvent quantum modes

$$k = \exp\left[-\frac{\Delta E_a^*}{k_B T}\right]\exp[-\sigma] = \exp\left[-\frac{(\lambda_s^* - \eta)^2}{4\lambda_s^* k_B T}\right]\exp[-\sigma]$$

$$\lambda_s^* = \xi \lambda_s$$

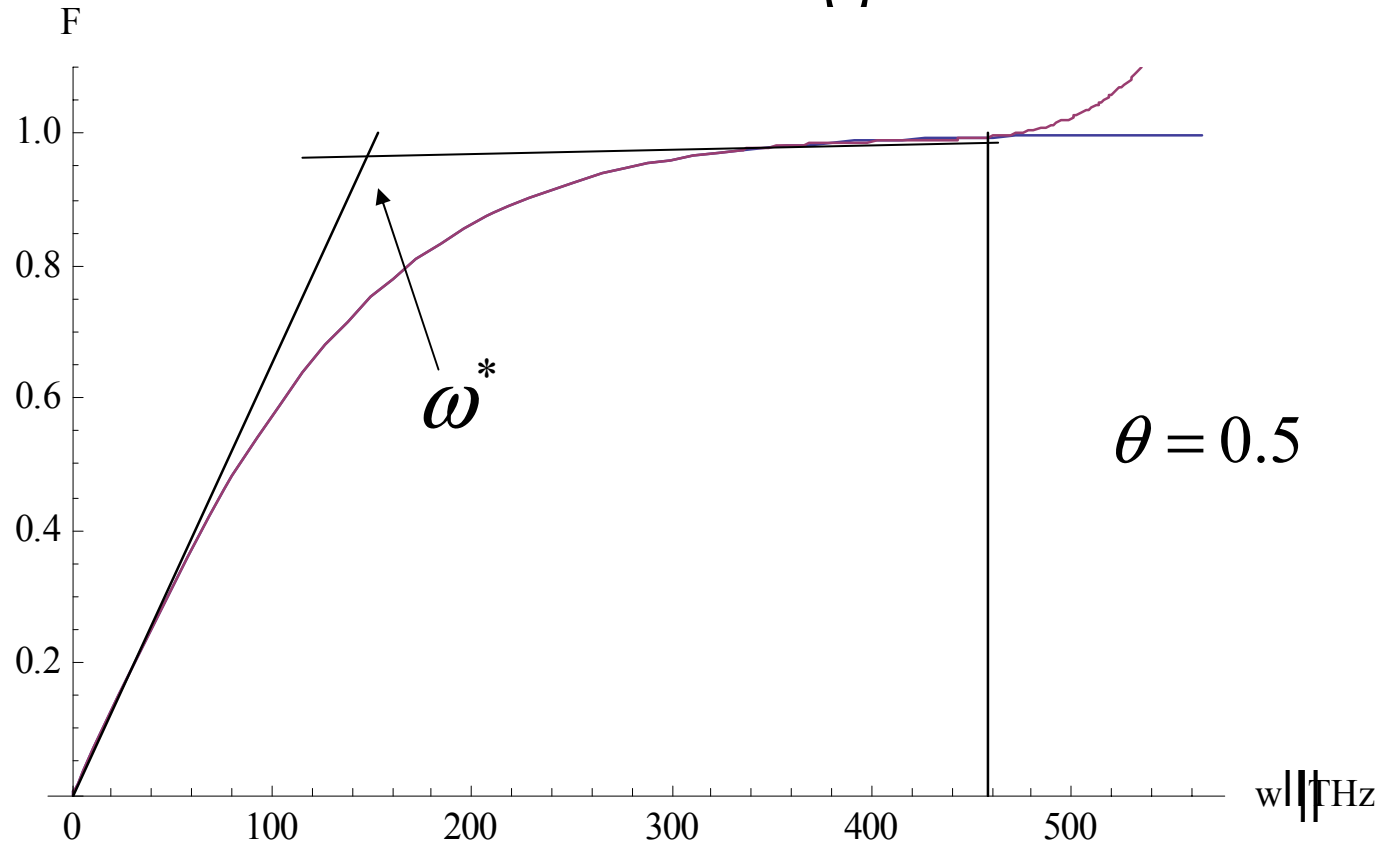$$\xi = \frac{2}{\pi C}\int_0^{\omega^*}\frac{\operatorname{Im}\varepsilon(\omega)}{\omega\|\varepsilon(\omega)\|^2}\,d\omega$$

$$C = \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_{st}}$$

$$\sigma = \frac{2\lambda_s}{\pi C}\int_{\omega^*}^{\infty}\frac{\operatorname{Im}\varepsilon(\omega)}{\omega^2\|\varepsilon(\omega)\|^2}\,d\omega$$
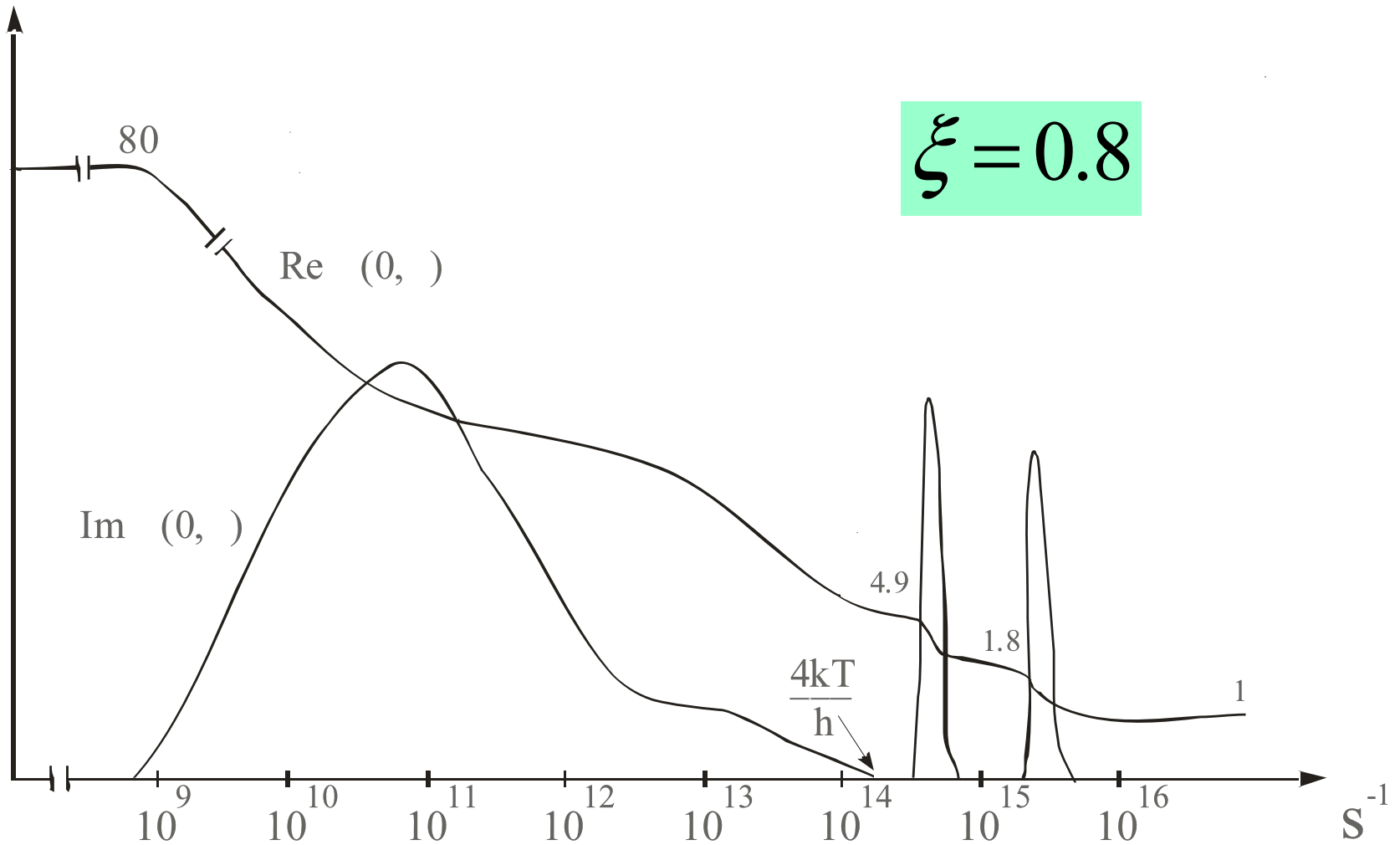
Pekar factor

tunneling factor

mdb

Interpolation ch...sh w, w^* ... by polynomial of degree 6
on the interval 0 , $3w^*$ ...

F

1.0

0.8

0.6

0.4

0.2

0   100   200   300   400   500   w THz
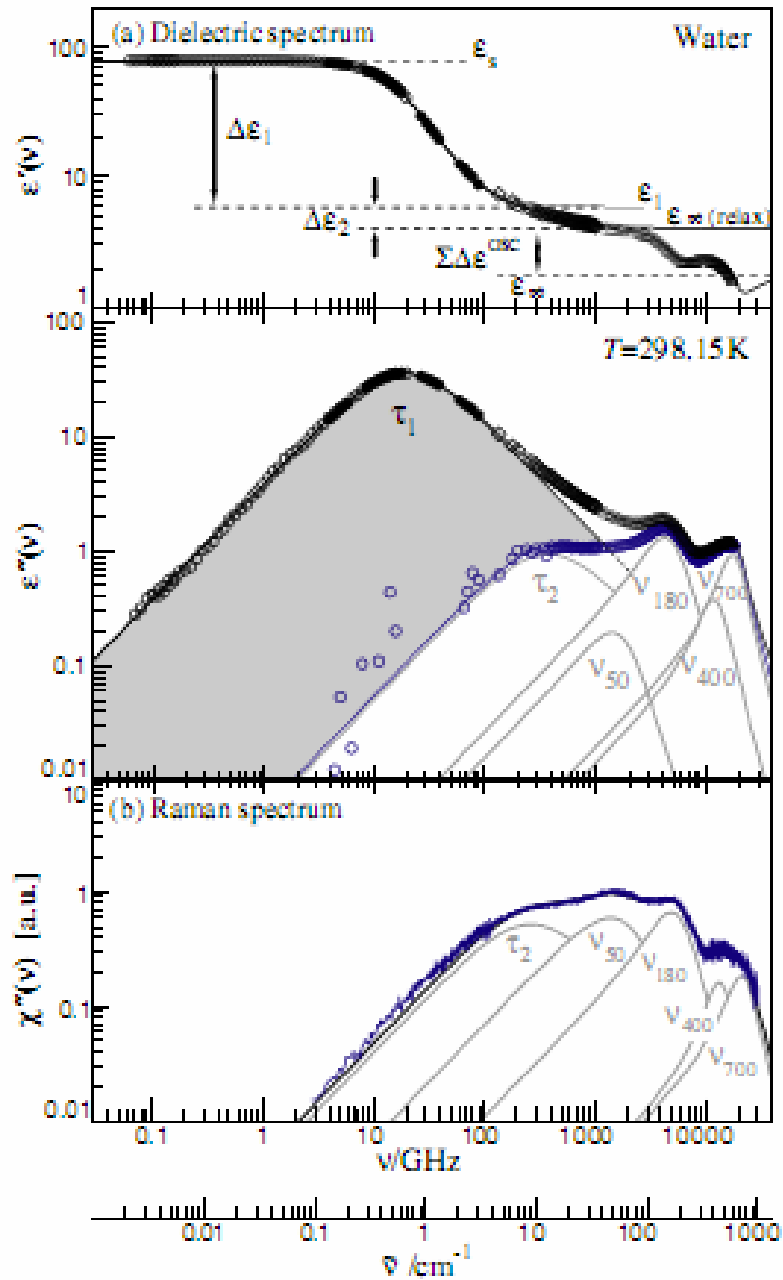
ω^*

$\theta = 0.5$

$$F(\theta, \omega) = \frac{ch\{\beta \ \omega/2\} - ch\{(1 - 2\theta)\beta \ \omega/2\}}{sh\{\beta \ \omega/2\}}$$

w   old

Dielectric spectra of water (J.A. Saxton, 1953)

$\xi = 0.8$

80

Re (0,)

Im (0,)

4.9

$\dfrac{4kT}{h}$

1.8

1

10^9 10^{10} 10^{11} 10^{12} 10^{13} 10^{14} 10^{15} 10^{16} S^{-1}

new

R. Buchner and co-workers (2005)

$$\varepsilon(v) = \varepsilon_\infty + \frac{S_1}{1 + i2\pi v\tau_1} + \frac{S_2}{1 + i2\pi v\tau_2} +$$

$$\frac{S_3}{1 + i2\pi v\tau_3} + \frac{S_4 v_4^2}{v_4^2 - v^2 + i\gamma_4 v}$$

$$+ \frac{S_5 v_5^2}{v_5^2 - v^2 + i\gamma_5 v} + \frac{S_6 v_6^2}{v_6^2 - v^2 + i\gamma_6 v} +$$

$$+ \frac{S_7 v_6^2}{v_7^2 - v^2 + i\gamma_7 v}$$

$$\xi = 0.9$$

IL

R. Buchner and co-workers (2008)

Dielectric spectra of some ionic liquids

$$\xi = 0.55$$

kapp

Electronic transmission coefficient

$$\kappa_e = \frac{1 - \exp(-2\pi\gamma_e)}{1 - (1/2)\exp(-2\pi\gamma_e)}$$

Landau-Zener factor

half of resonance splitting

$$\gamma_e = \frac{\left(\dfrac{\Delta E_e}{2}\right)^2}{\omega_{eff}}\sqrt{\frac{\pi}{(\lambda_s + \lambda_{in}) \cdot k_B T}}$$

effective frequency

Two important limiting cases:

$$\gamma_e \ll 1 \Rightarrow \kappa_e \approx \gamma_e \quad \textbf{(non-adiabatic)}$$

$$\gamma_e \gg 1 \Rightarrow \kappa_e \approx 1 \quad \textbf{(adiabatic)}$$

Vif

It is reasonable to employ the perturbation theory for large molecular systems

$$\frac{\Delta E_e}{2} \approx \int \Psi_i \hat{V} \Psi_f \, dV - \int \Psi_i \hat{V} \Psi_i \, dV \cdot \int \Psi_i \Psi_f \, dV$$
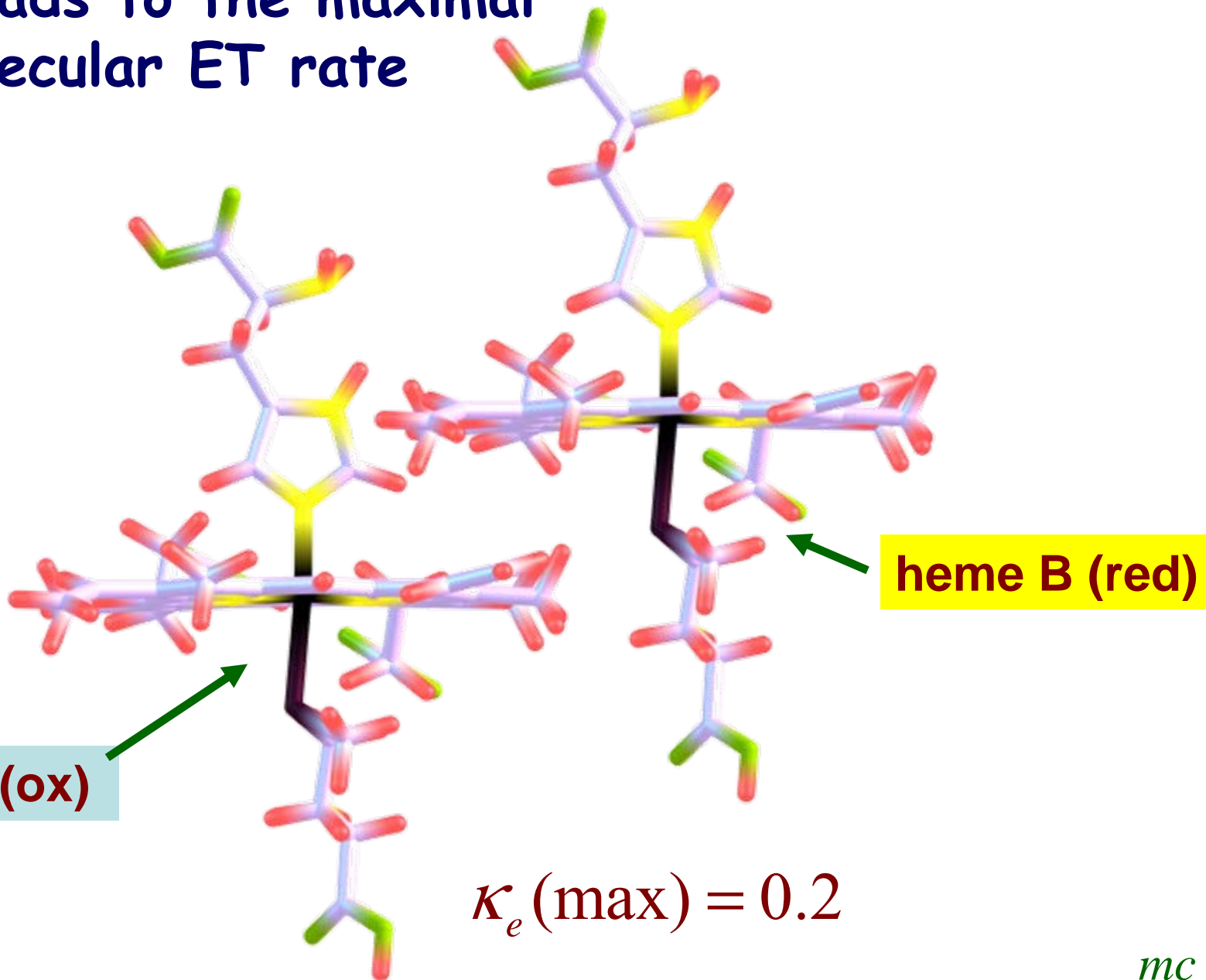
Perturbation (molecular electrostatic potential)

$$V(r) = -\sum_i \frac{Z_i}{|R_i - r|} + \sum_j \int \frac{\left|\psi_j\left(r^{/}\right)\right|^2 d\Omega^{/}}{|r^{/} - r|}$$
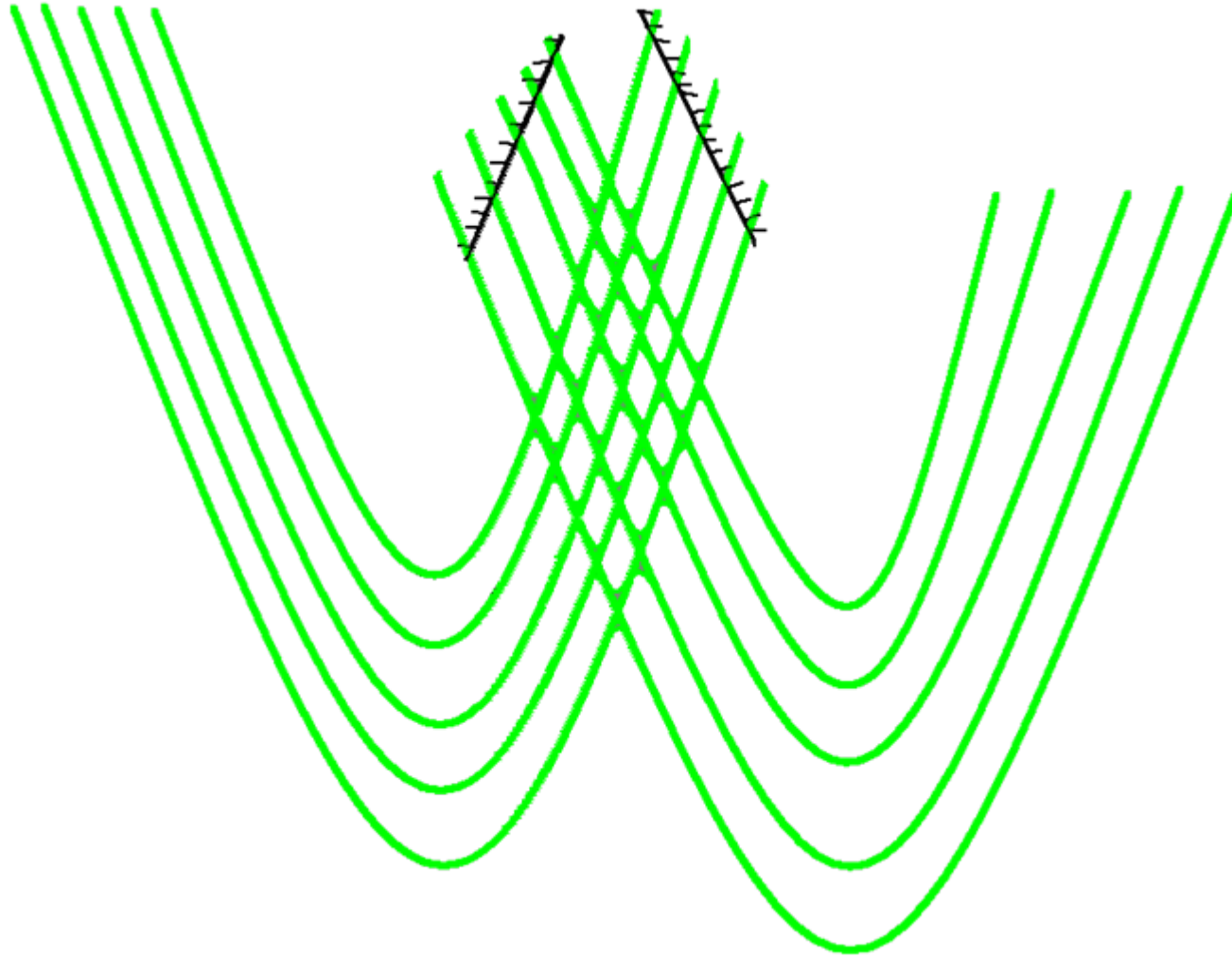
$$V(r) \approx \sum_i \frac{q_i^*}{|R_i - r|}$$

ChelpG atomic charges

cyt c4

Orientation of the cyt c₄ heme groups which leads to the maximal intramolecular ET rate

Orientation of the cyt c_4 heme groups which leads to the maximal intramolecular ET rate

heme B (red)

heme A (ox)

$$\kappa_e(\max) = 0.2$$

mc

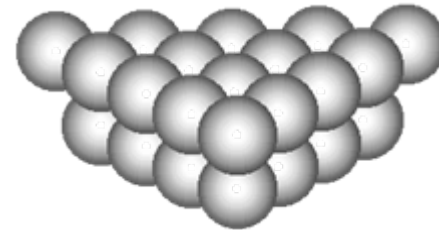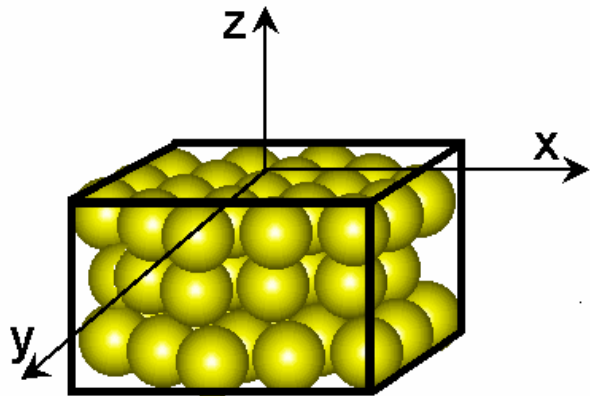# Моделирование методом Монте-Карло
(случайное блуждание по узлам двумерной решётки)

Electronic transmission coefficient vs density of electronic states calculated with the help of MC simulations at different values of γ_e

$\kappa_e^* \approx \rho(\varepsilon_F) k_B T 2\pi\gamma_e$

Legend:
- $2\pi\gamma_e = 0.999$
- $2\pi\gamma_e = 0.1$
- $2\pi\gamma_e = 0.01$
- $2\pi\gamma_e = 0.001$

Y-axis: κ_e

X-axis: N

density of electronic states

slab, cl

Model calculation of electronic transmission coefficient for interfacial reactions: some challenges.
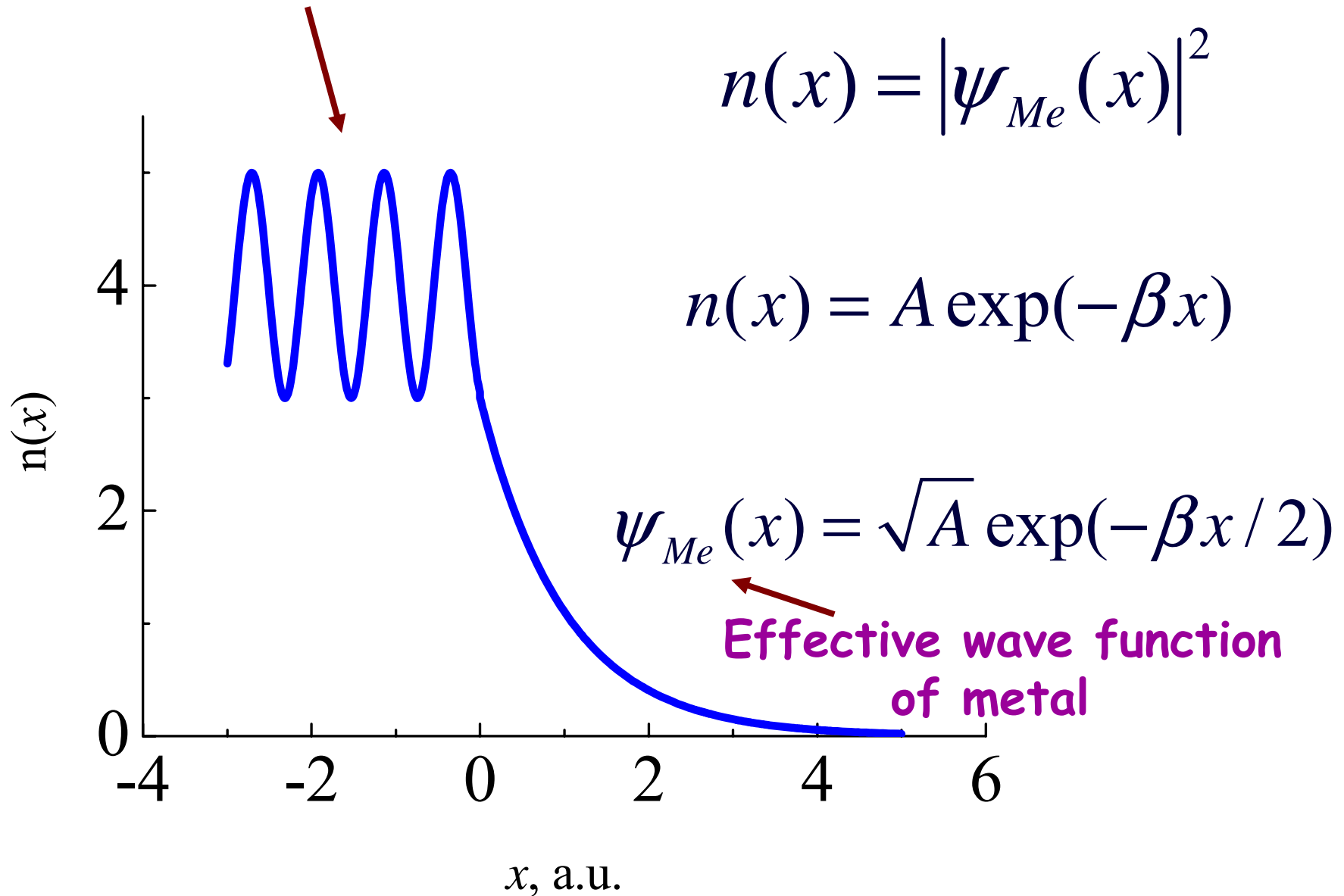
1. Model of a charged metal surface (cluster, slabs, "jellium", etc)

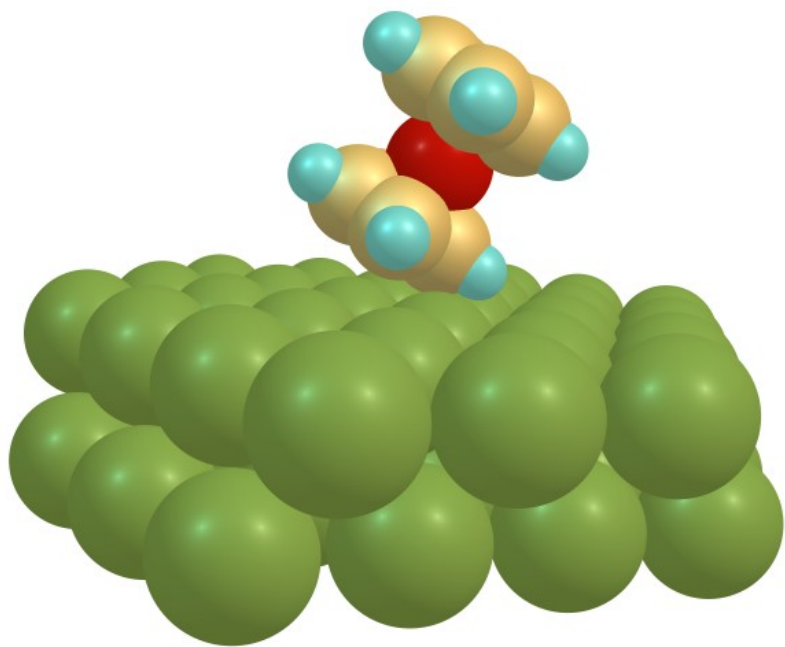2. Solvent effect on the wave functions and perturbation

3. Asymptotic behaviour of wave functions

wave

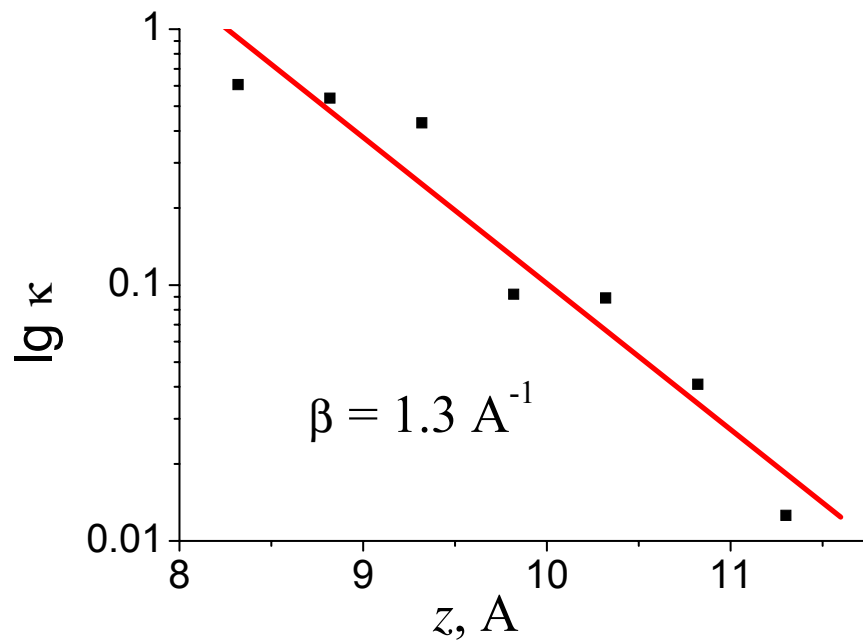# Electronic density of metal slabs vs distance

$$n(x) = \left| \psi_{Me}(x) \right|^2$$

$$n(x) = A \exp(-\beta x)$$

$$\psi_{Me}(x) = \sqrt{A} \exp(-\beta x / 2)$$

Effective wave function of metal

n(x)

-4   -2   0   2   4   6

4

2

0

x, a.u.

Fc

$$Fc^+ + e \quad\quad Fc$$

$$\kappa = \kappa_0 \exp(-\beta z)$$

Au$_{54}$ cluster
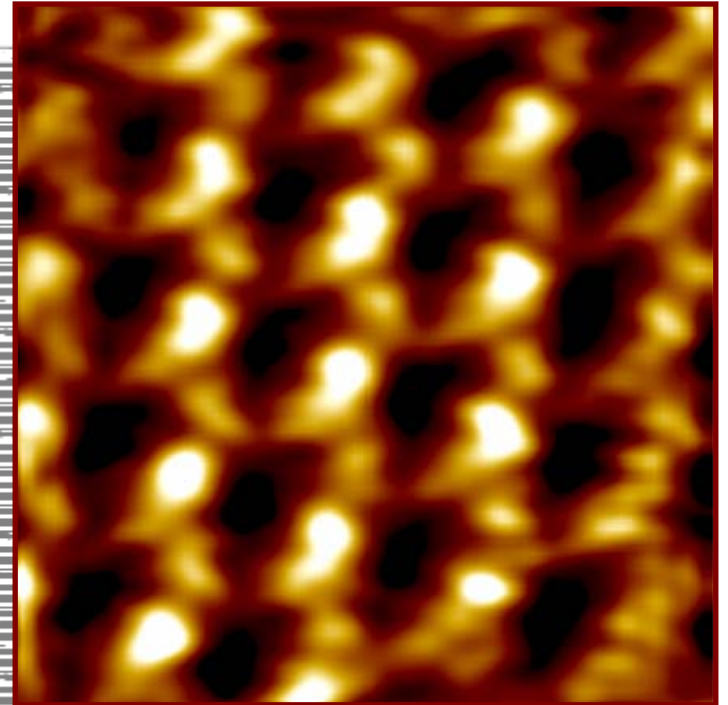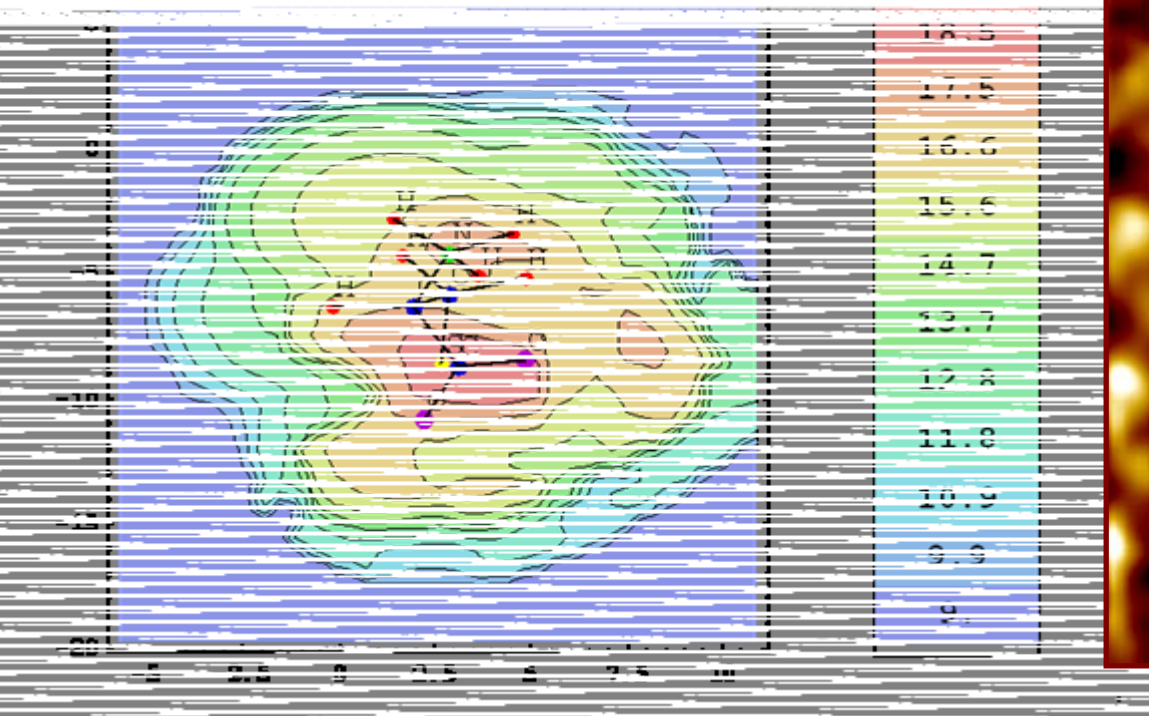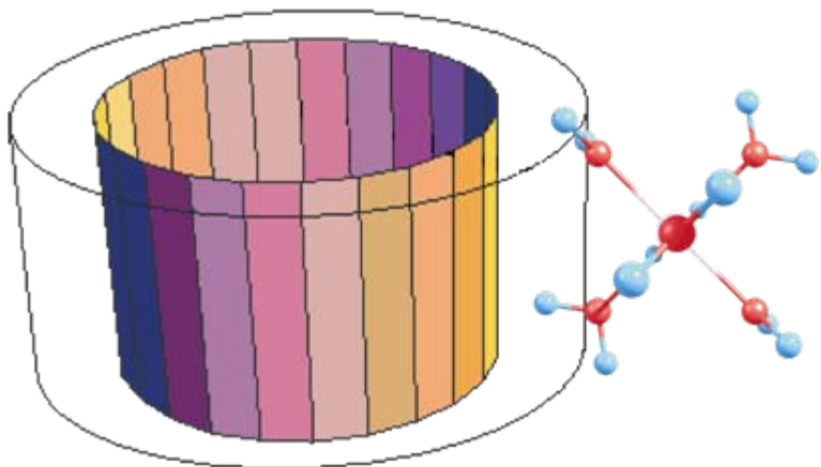
$\beta = 1.3$ A^{-1}

stm

Model STM contrast

Cysteine adsorption on Au(110) elecrode
(in situ STM images)

wire

Me(111) vs monoatomic wires
Fe(III)/Fe(II)

fin