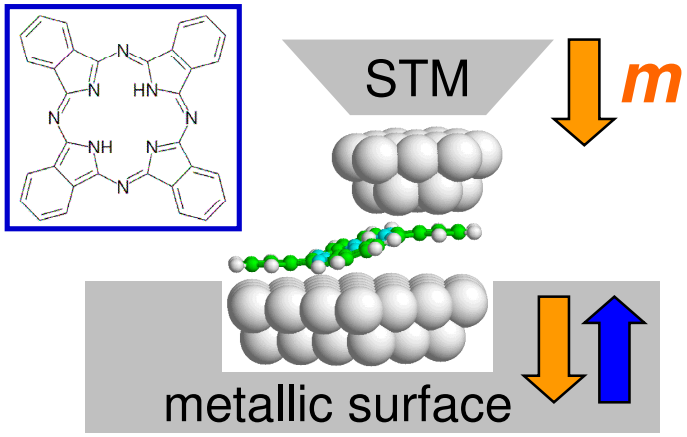

Electron transport through molecular junctions *and FHI-aims*

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@ Karlsruhe Institute of Technology (KIT), Germany

Why transport calculations for molecules ?

Technological reason (*molecular electronics*)

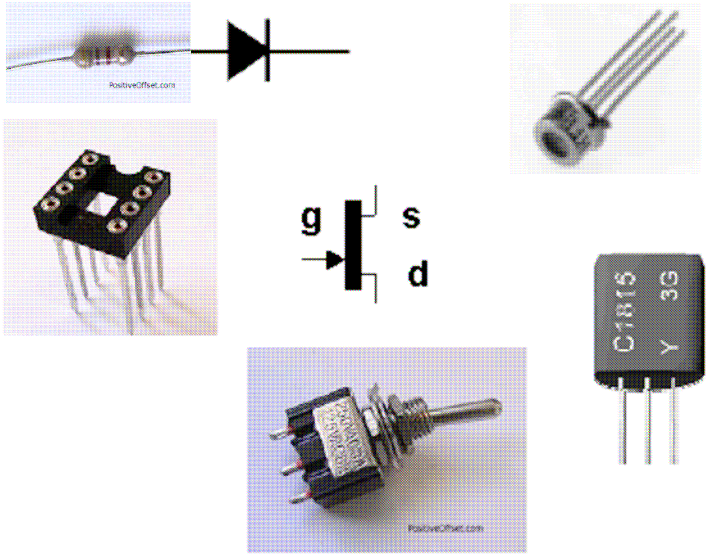
- use of molecular building blocks for the fabrication of electronic components
- design suitable molecular complexes with required functionality, e.g. *memory elements, switches, diods* or *transistors*
- data trasnfer by charge (or spin) transport

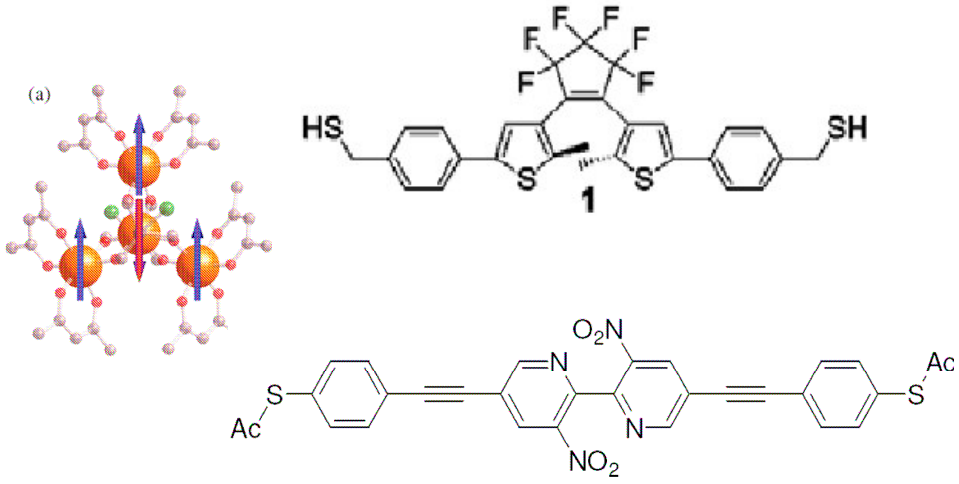
- required (transport) theories with predicative power: computer aided device design

(Fundamental) scientific reason

- molecules are „quantum dots“ with unexplored parameters regimes and symmetry properties

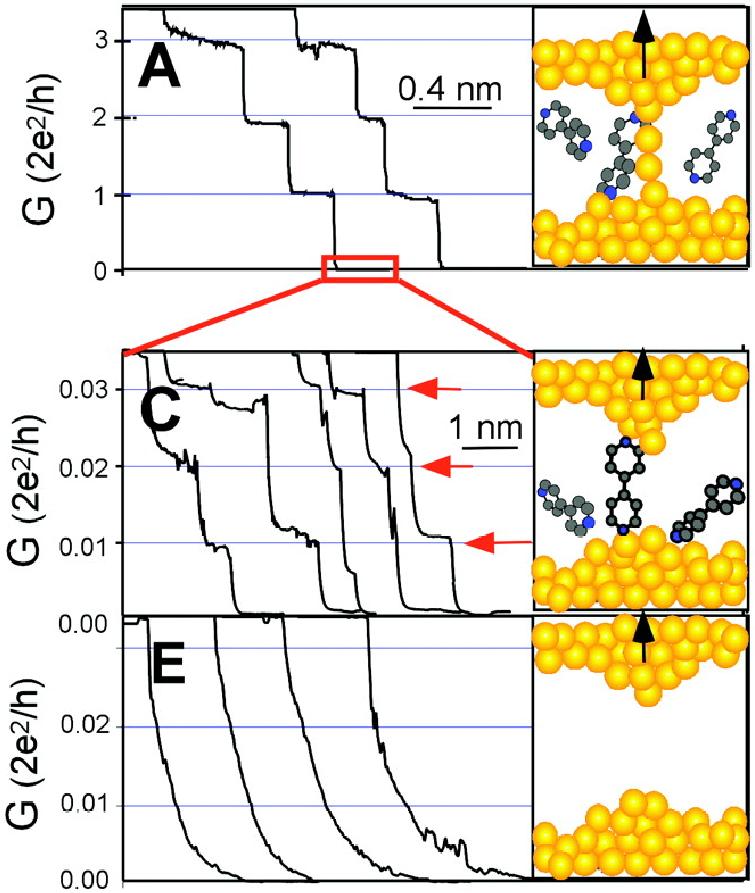
- attempt to understand and predict qualitatively new transport phenomena





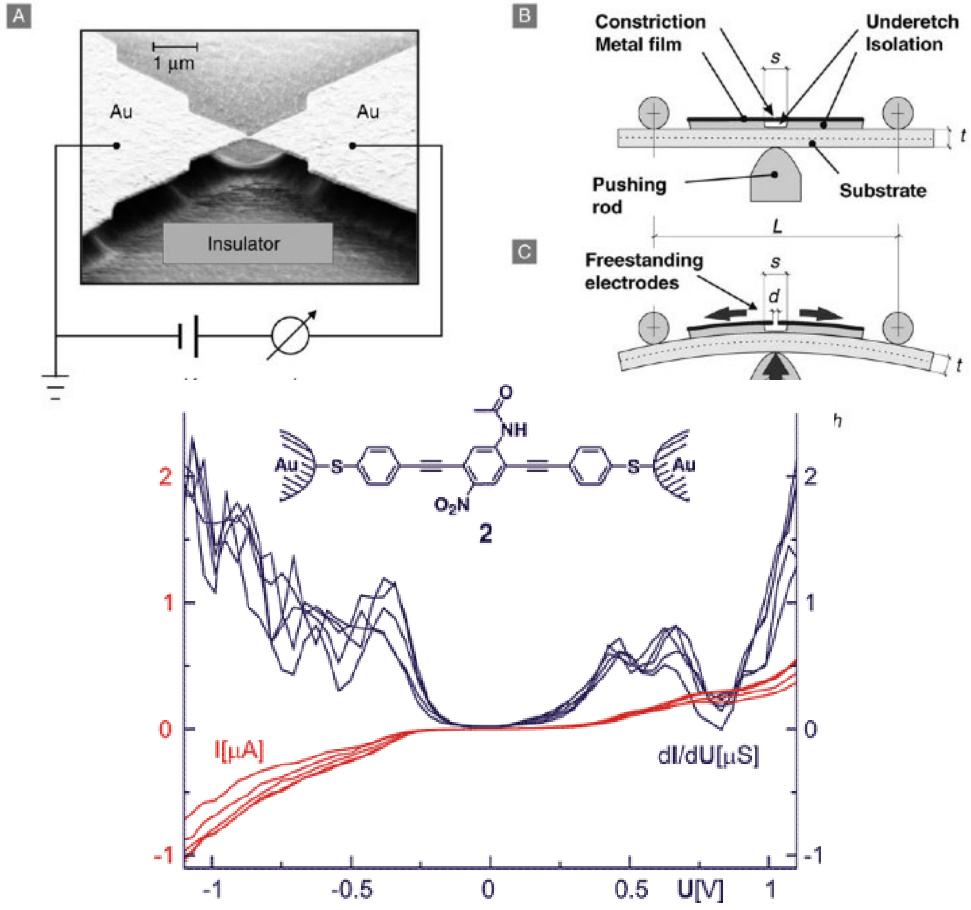
Single molecule electronics : experiments

- **STM break junctions**



Xu & Tao, *Science* '03

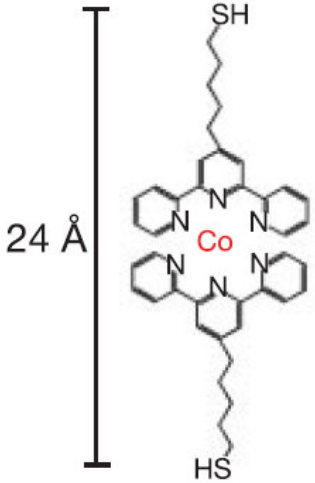
- **mechanically controlled break junctions**

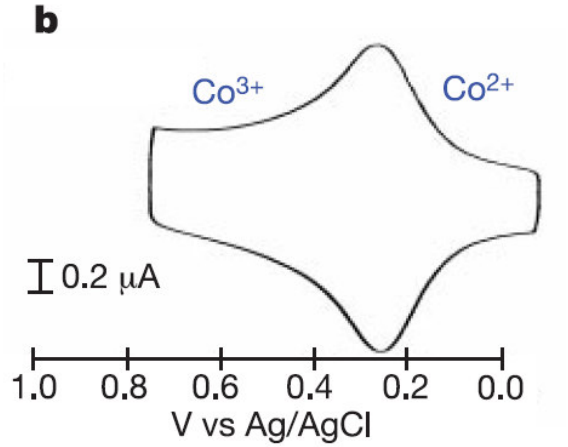


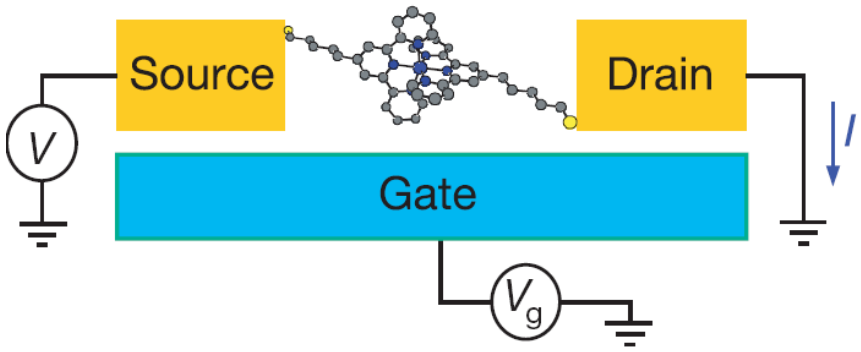
Weber, Mayor,
v. Löhneysen, *et al. PRL* '02

Single molecule electronics : experiments

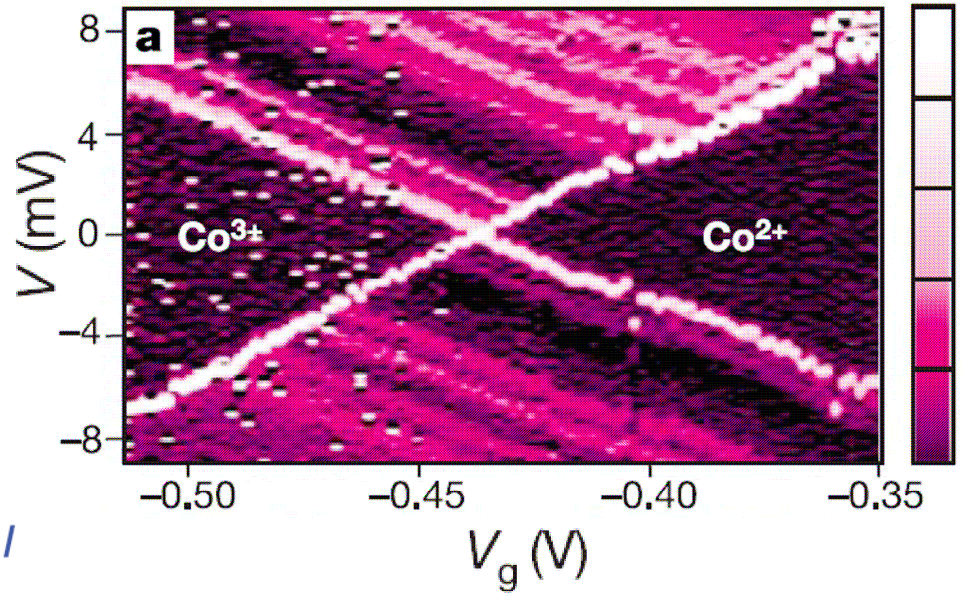
- **Electromigrated junctions: Coulomb blockade**







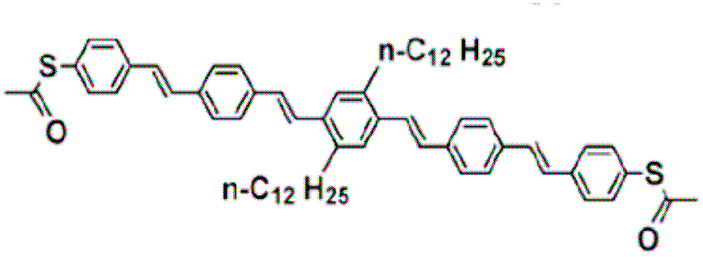
dI(V)/dV

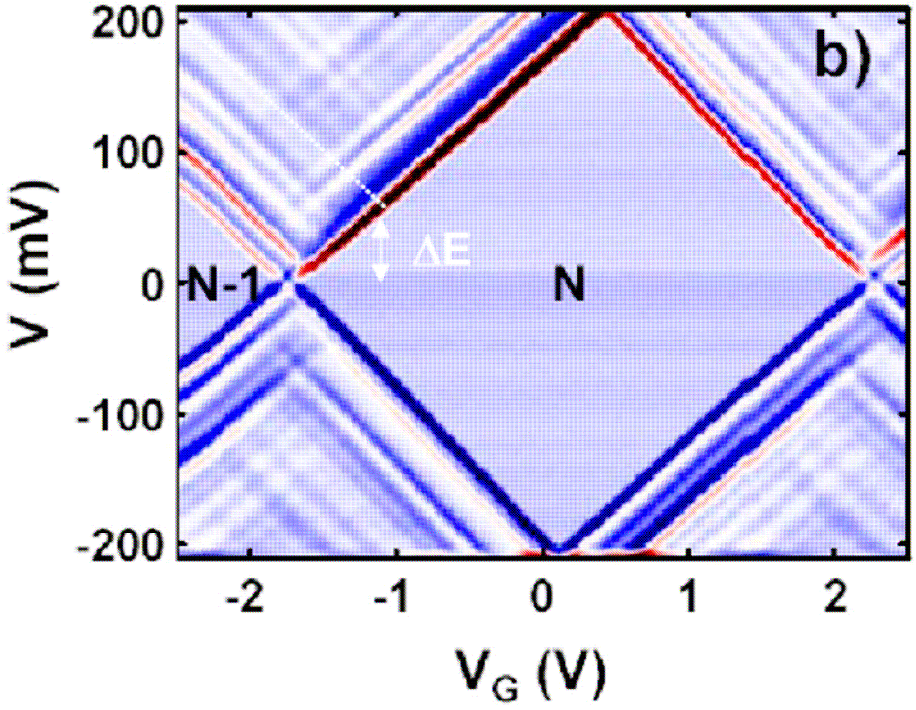


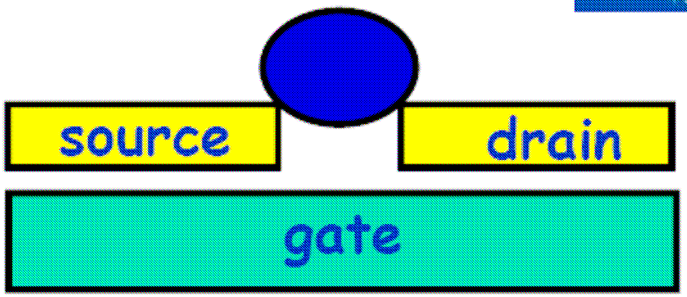
Park, McEuen, Ralph, *et al.* *Nature* '02

Single molecule electronics : experiments

- **Excitation lines: electronic fingerprints of molecular vibrations**





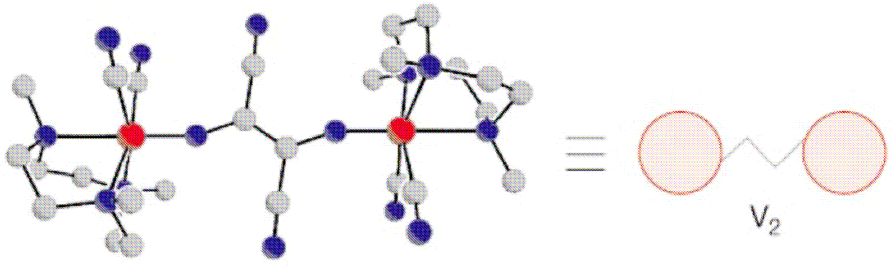


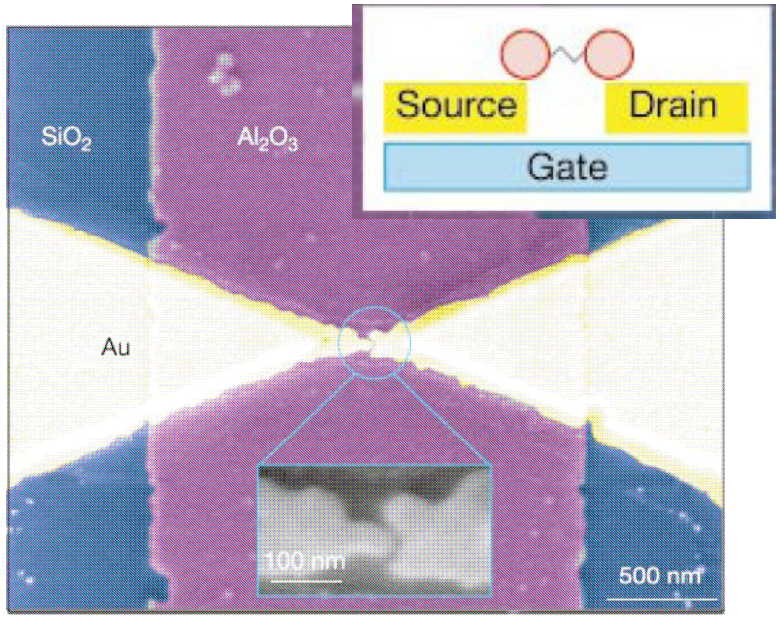
Osorio *et al.*
Adv. Materials '07

Single molecule electronics : experiments

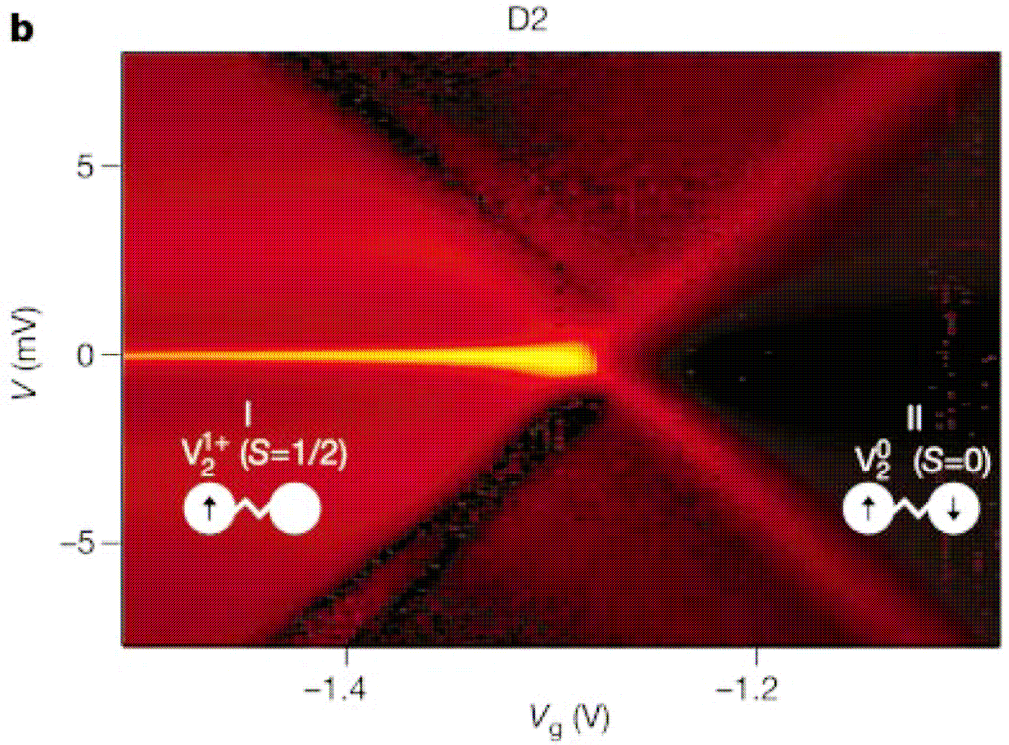
- **Electromigrated junctions: Kondo effect**

di-vanadium-complex

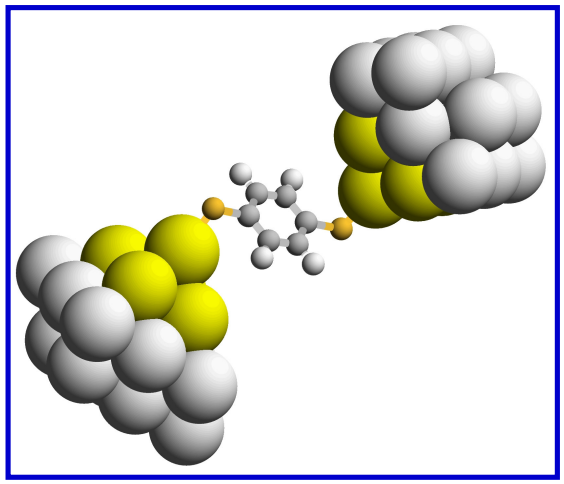


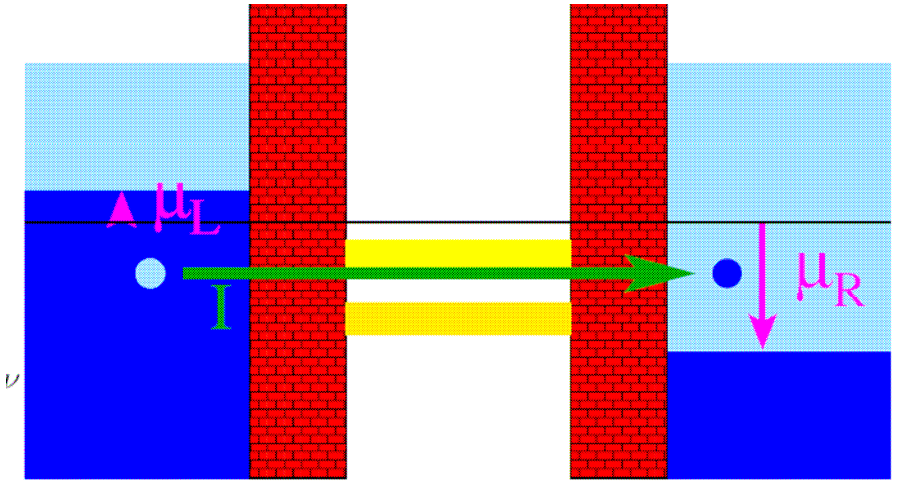


dI(V)/dV



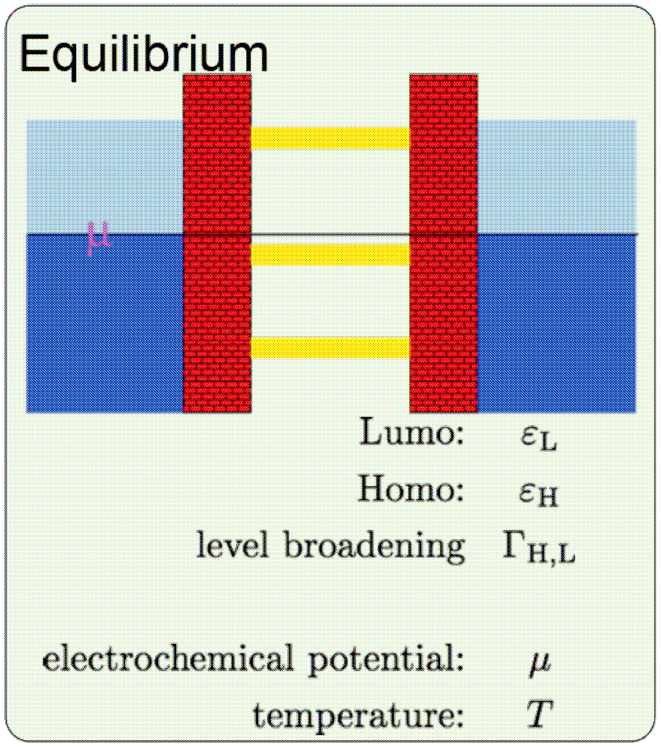
Liang *et al.*
Nature '02

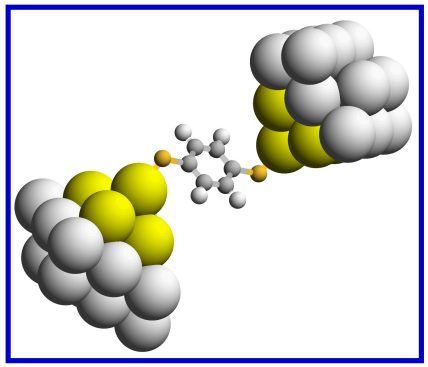


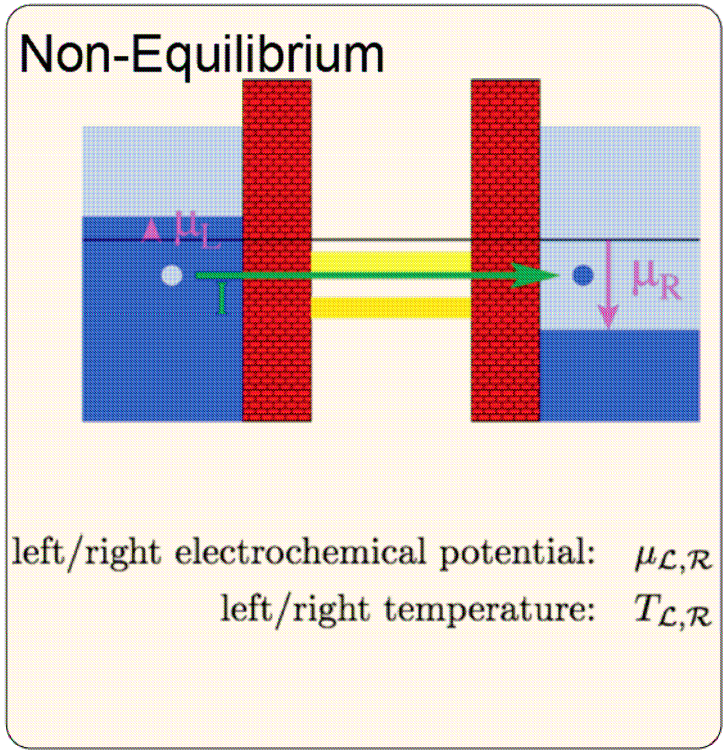


1. Essentials of *ab initio* transport simulations

Transport in the scattering picture







scattering states:

- electrode: quantum numbers $|\nu\rangle = |n, k\rangle,\ \epsilon_n(k)$

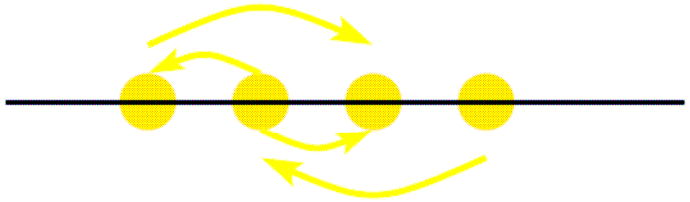
$$I = \frac{2e}{h}\int_{\mu_R}^{\mu_L} dE \sum_{nn'} |t_{nn'}(E)|^2$$

$$= \frac{2e}{h}\int_{\mu_R}^{\mu_L} dE\ \mathrm{Tr}_{\mathcal{L}_T}(tt^\dagger) = \frac{2e}{h}\int_{\mu_R}^{\mu_L} dE\ T(E)$$

Attaching reservoirs to nanosystem

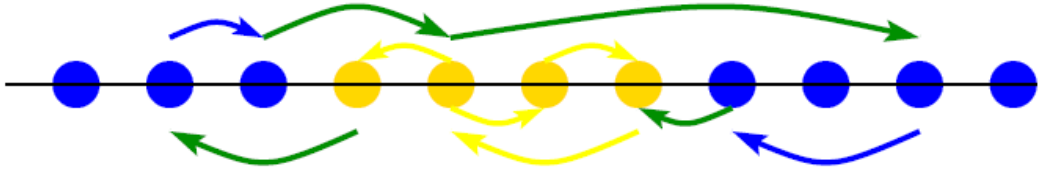
Green's function formalism

bare Green's function (of $\mathcal{M}$):



$$G(\mathbf{x},\mathbf{x}';t-t') = \langle \mathbf{x}|G(t-t')|\mathbf{x}'\rangle$$
$$G^{-1}_{\mathcal{M}}(E) = E - H_{\mathcal{M}}$$

dressed Green's function (of $\mathcal{M}$):



$$G^{-1} = G^{-1}_{\mathcal{M}} - \Sigma^{\mathcal{M}}_{\mathcal{L}} - \Sigma^{\mathcal{M}}_{\mathcal{R}}$$
$$\Sigma^{\mathcal{M}}_{\mathcal{X},ij} = \sum_{\nu\mu} V_{i\nu} G_{\mathcal{X},\nu\mu} V^*_{\mu j}, \quad \mathcal{X} = \mathcal{R},\mathcal{L}$$

$$H_{\mathcal{M}} = \sum_{ij} h_{ij} d^\dagger_i d_j$$

$$H = H_{\mathcal{M}} + H_{\mathcal{L}} + H_{\mathcal{T}}$$
$$H_{\mathcal{L}} = \sum_{\nu\mu} t_{\nu\mu}\, c^\dagger_\nu c_\mu$$
$$H_{\mathcal{T}} = \sum_{j,\nu} V_{\nu j}\, c^\dagger_\nu d_j + V^*_{j\nu}\, d^\dagger_j c_\nu$$

Attaching reservoirs to nanosystem

Green's function formalism

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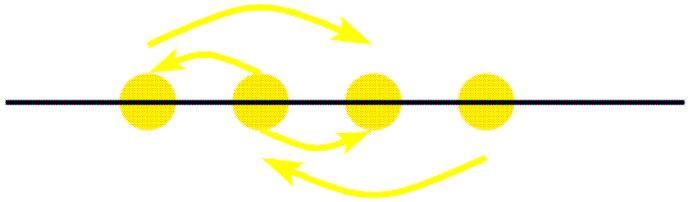

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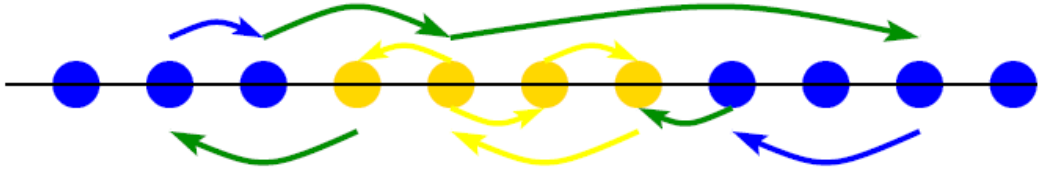

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$$\Sigma^{\mathcal{M}}_{\mathcal{X},ij} = \sum_{\nu\mu} V_{i\nu} G_{\mathcal{X},\nu\mu} V^{*}_{\mu j}, \quad \mathcal{X} = \mathcal{R},\mathcal{L}$$

effective Hamiltonian:

$$H_{\text{eff}} = H_{\mathcal{M}} + \frac{1}{2}\sum_{\mathcal{X}=\mathcal{R},\mathcal{L}} (\Sigma_{\mathcal{X}} + \Sigma^{\dagger}_{\mathcal{X}})$$

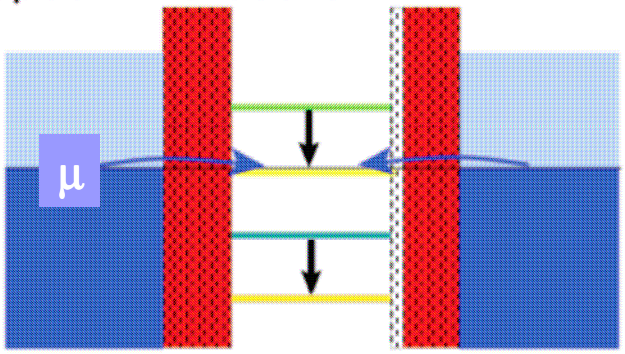
leakage rates (or level broadening / damping rate / inverse life time):

$$\Gamma_{\mathcal{X}} = \frac{1}{2i}(\Sigma^{\dagger}_{\mathcal{X}} - \Sigma_{\mathcal{X}})$$

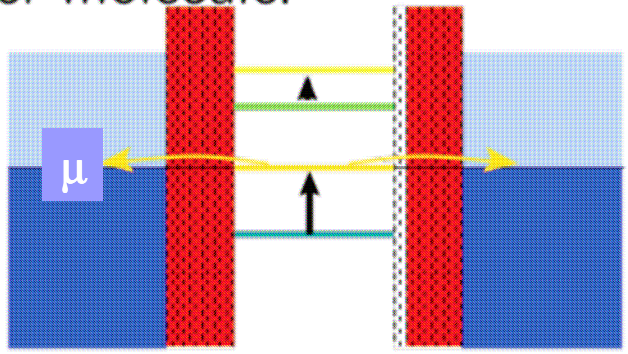
Charge exchange and life-time effects

$$H \longrightarrow H_{\text{eff}} = H + \frac{1}{2}\left(\Sigma + \Sigma^{\dagger}\right)$$

acceptor molecule:

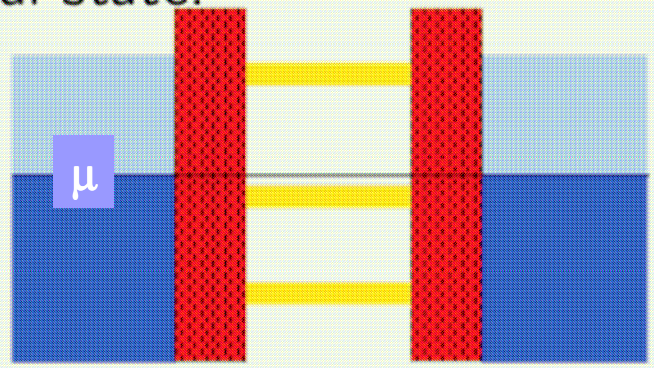


donor molecule:

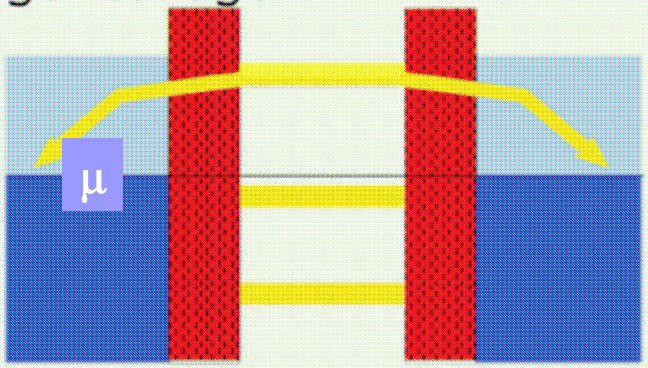


$$G^{-1} = E - H_{\text{eff}} + \frac{1}{2i}\left(\Gamma_L + \Gamma_R\right)$$

initial state:

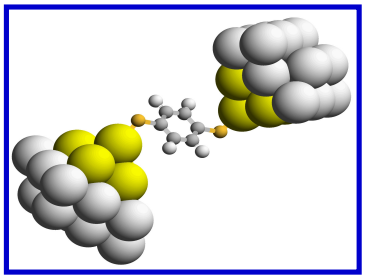


charge leakage:



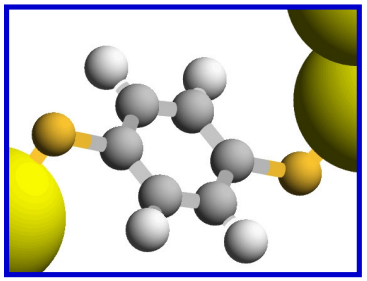
$$T(E) = \mathrm{Tr}\left[\Gamma_L G(E) \Gamma_R G^{\dagger}(E)\right]$$

Classical dilemma



level broadening level spacing

$$\delta_{\mathrm{HL}} \leq \gamma_{\mathrm{HL}} \ll \gamma_{\mathrm{hl}} \leq \delta_{\mathrm{hl}}$$



extended molecule: add lead atoms

$(\geq 100 N_e)$

effective single particle problem

$\longrightarrow$ only approximate $G^{\mathrm{ret}}_{e\mathcal{M}}$

from effective single particle SCF-theories:

- extend Hückel (tight binding)
- Hartree-Fock
- density functional theories
- ...

exact $\Sigma^{e\mathcal{M}}_{\mathrm{L,R}}$ not needed!

approximate $\Sigma^{e\mathcal{M}}_{\mathrm{L,R}}$ from

- the same theory as $G_{e\mathcal{M}}$
- construction methods

non-equilibrium readily included!

small systems: only molecule

$(\leq 100 N_e)$:

many body methods: exact $G^{\mathrm{ret}}_{\mathcal{M}}$

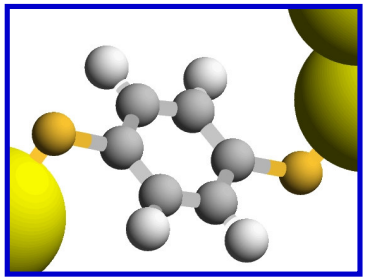
methods:

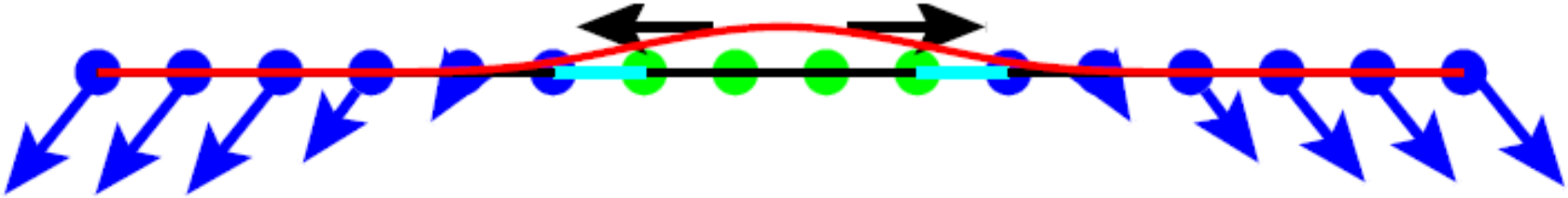
- exact diagonalization ≤ 30
- coupled cluster method
- configuration interaction
- GW-approximation
- ...

Transport needs $G^{<}$, not G^{ret} !?!

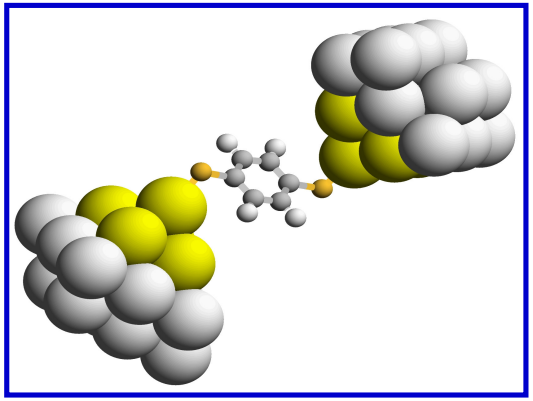
$\Sigma^{\mathcal{M}}_{\mathrm{L,R}}$ from

- ???

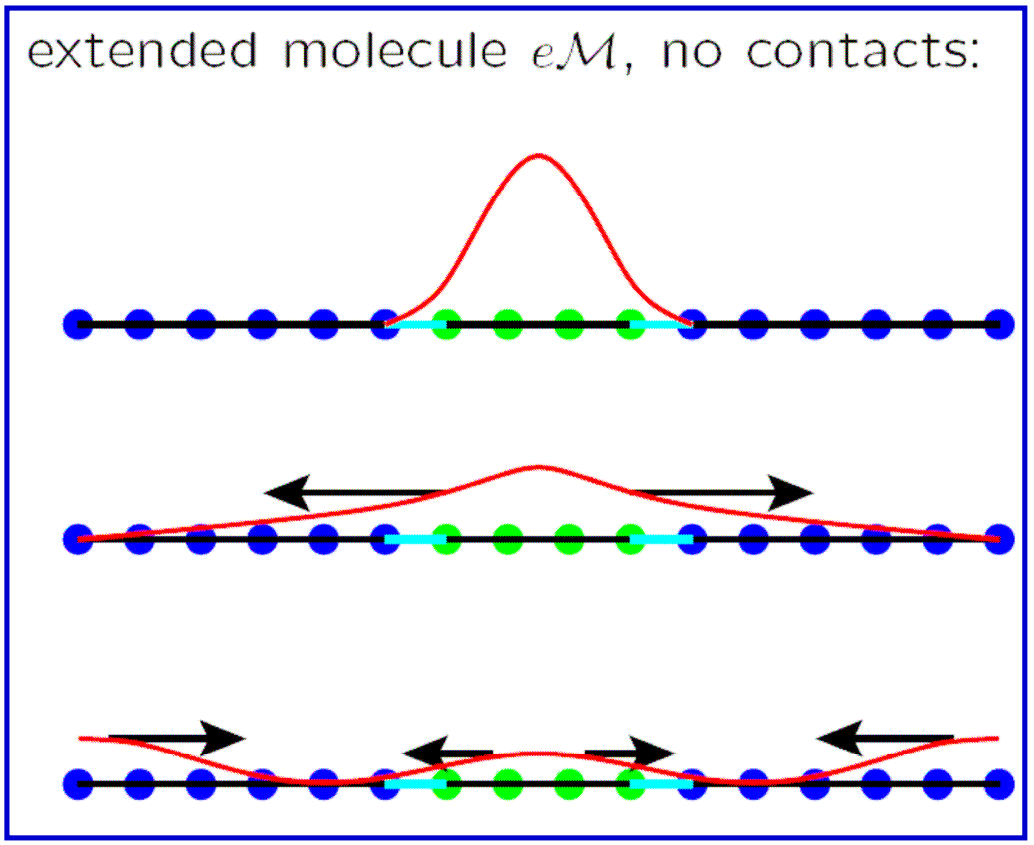




2. Self-energy as absorbing boundary condition



Gedankenexperiment: Σ_{eM} as absorb. boundary condition



Propagator:

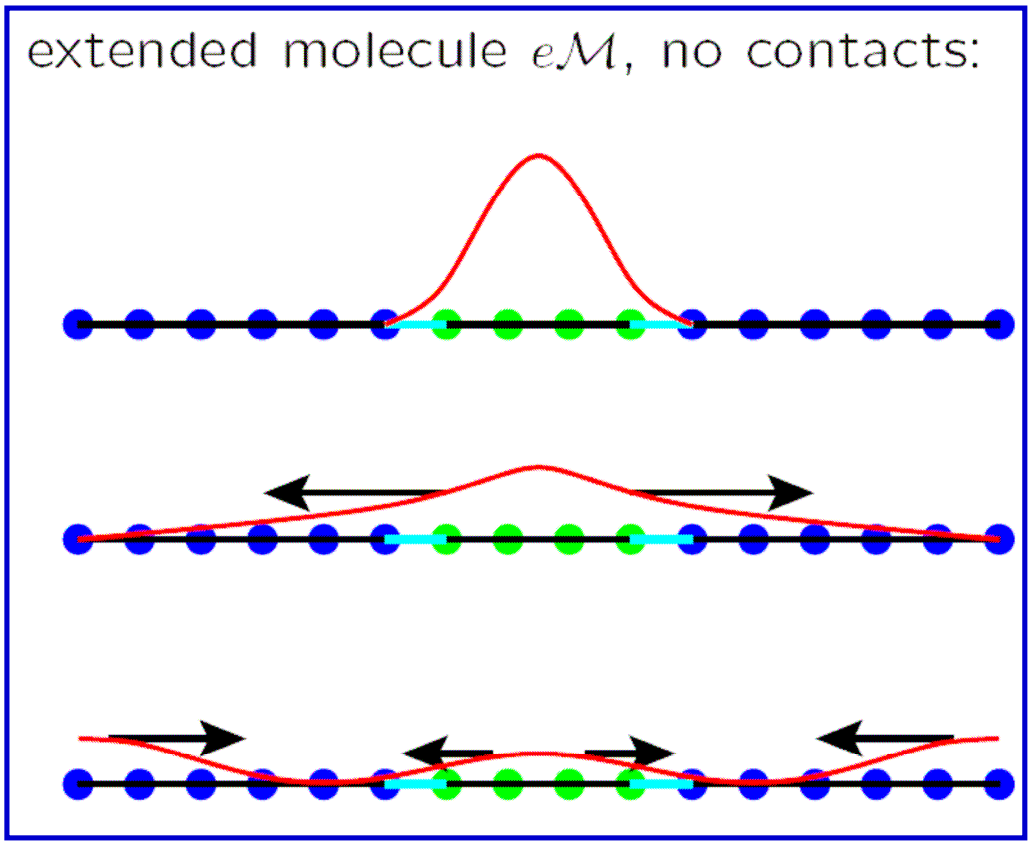
$$G(t, \mathbf{x}, \mathbf{x}') = \int dE\ G(E, \mathbf{x}, \mathbf{x}')\ e^{-iEt}$$

$$\Psi(t) = \int_{-\infty}^{t} dt' G(t - t')\Psi(t')$$

Required: $T_{\text{observation}} \geq \gamma_{hl}^{-1}$

"Dwell" time: $\tau_D \sim \delta_{HL}^{-1}$, E-resolution $\hbar/\tau_D$

Gedankenexperiment: Σ_{eM} as absorb. boundary condition



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Required: $T_{\text{observation}} \geq \gamma_{hl}^{-1}$

"Dwell" time: $\tau_D \sim \delta_{HL}^{-1}$, E-resolution $\hbar/\tau_D$

unitary time evolution:

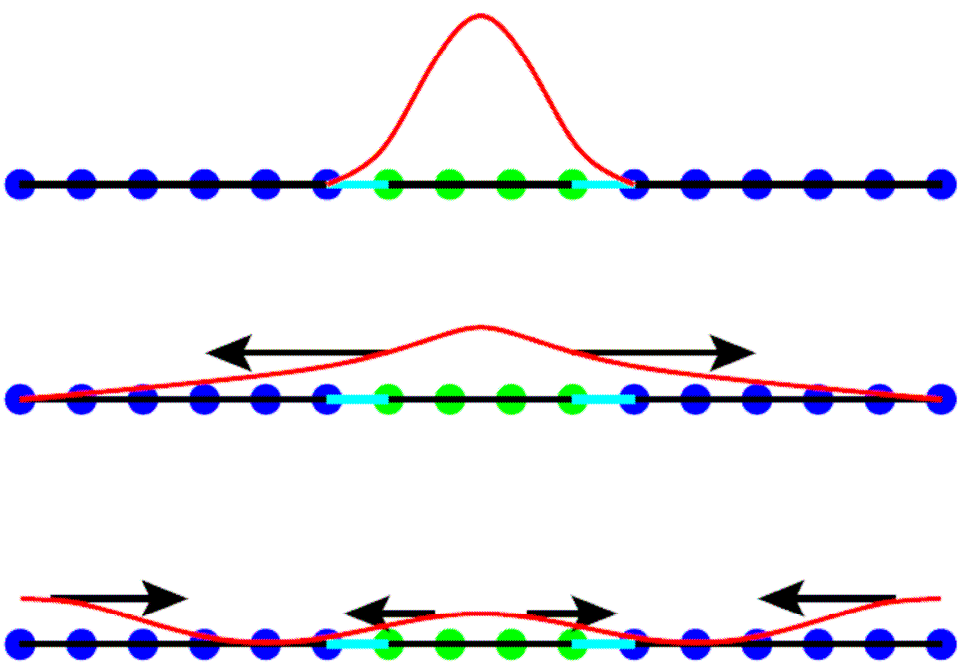
$$G_{e\mathcal{M}}^{-1} = E - H_{e\mathcal{M}} + i0$$

density of states $(T_{\text{observation}} = \infty)$:

$$\rho(E) = \sum_i \delta(E - \epsilon_i)$$

Gedankenexperiment: Σ_{eM} as absorb. boundary condition

extended molecule $e\mathcal{M}$, no contacts:



Propagator:

$$G(t, \mathrm{x}, \mathrm{x}') = \int dE\ G(E, \mathrm{x}, \mathrm{x}')\ e^{-iEt}$$

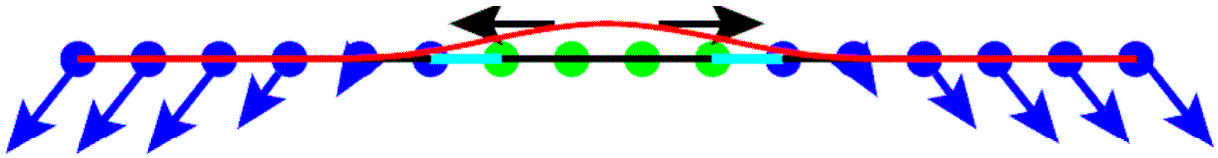
$$\Psi(t) = \int_{-\infty}^{t} dt' G(t - t')\Psi(t')$$

Required: $T_{\text{observation}} \geq \gamma_{hl}^{-1}$

"Dwell" time: $\tau_D \sim \delta_{HL}^{-1}$, E-resolution $\hbar/\tau_D$

F Evers & A Arnold, CFN Lectures on Functional Nanostructures Vol.2, Lecture Notes in Physics 820

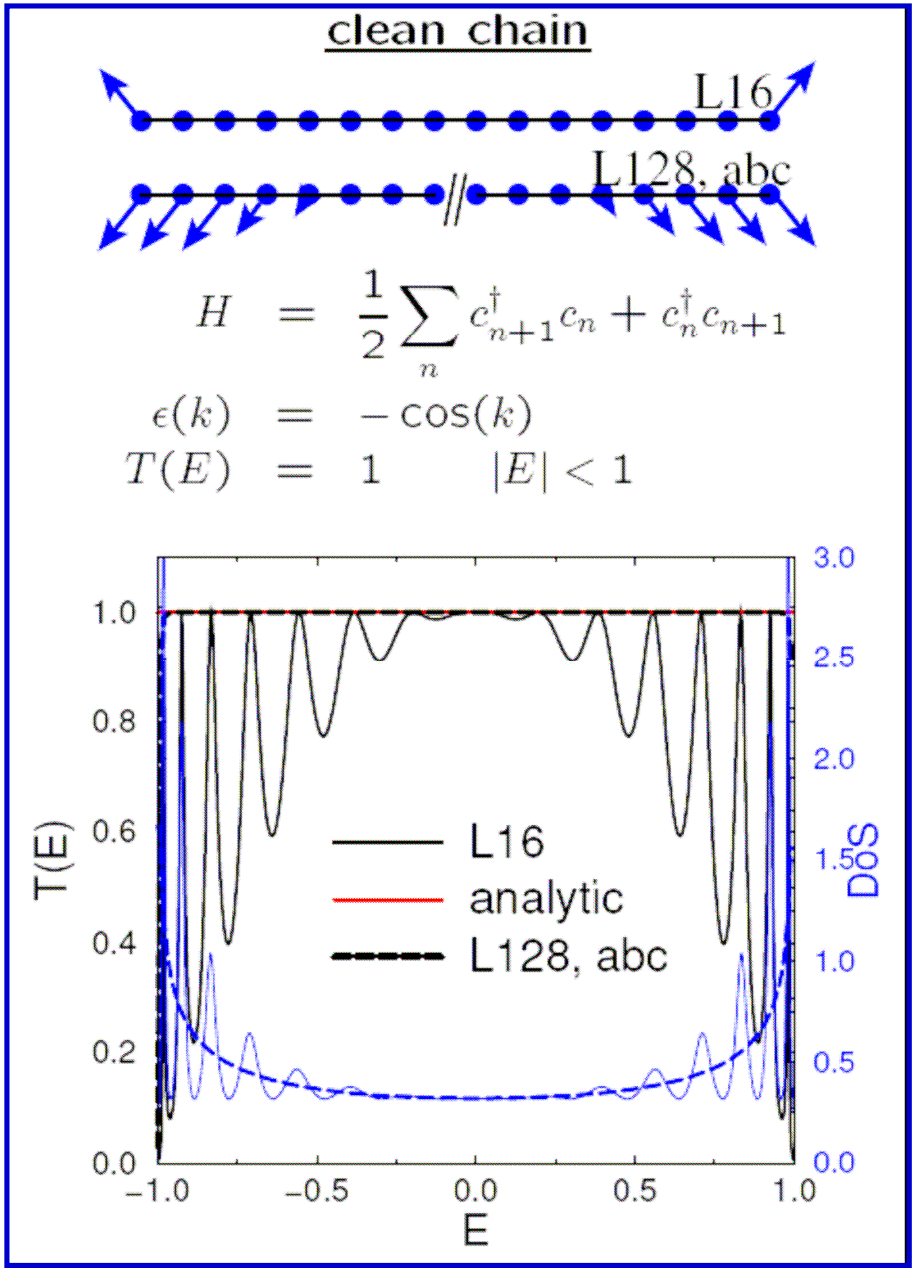
adiabatic contacts: (abc) absorbing boundary conditions, $\tau_D \gamma_{hl} \gg 1$



$$|x\rangle = |X\ell\rangle:$$

$$\langle x|\Sigma_{\mathrm{R,L}}|x'\rangle = i\eta(X)\delta_{xx'}$$

Test cases: tight-binding chain



Parameterization of the self-energy

$$\Sigma_{ij;\mathcal{L}} = i\eta_i\delta_{ij}; \quad \eta_i = \eta/(1+\exp\beta(i-i_S))$$

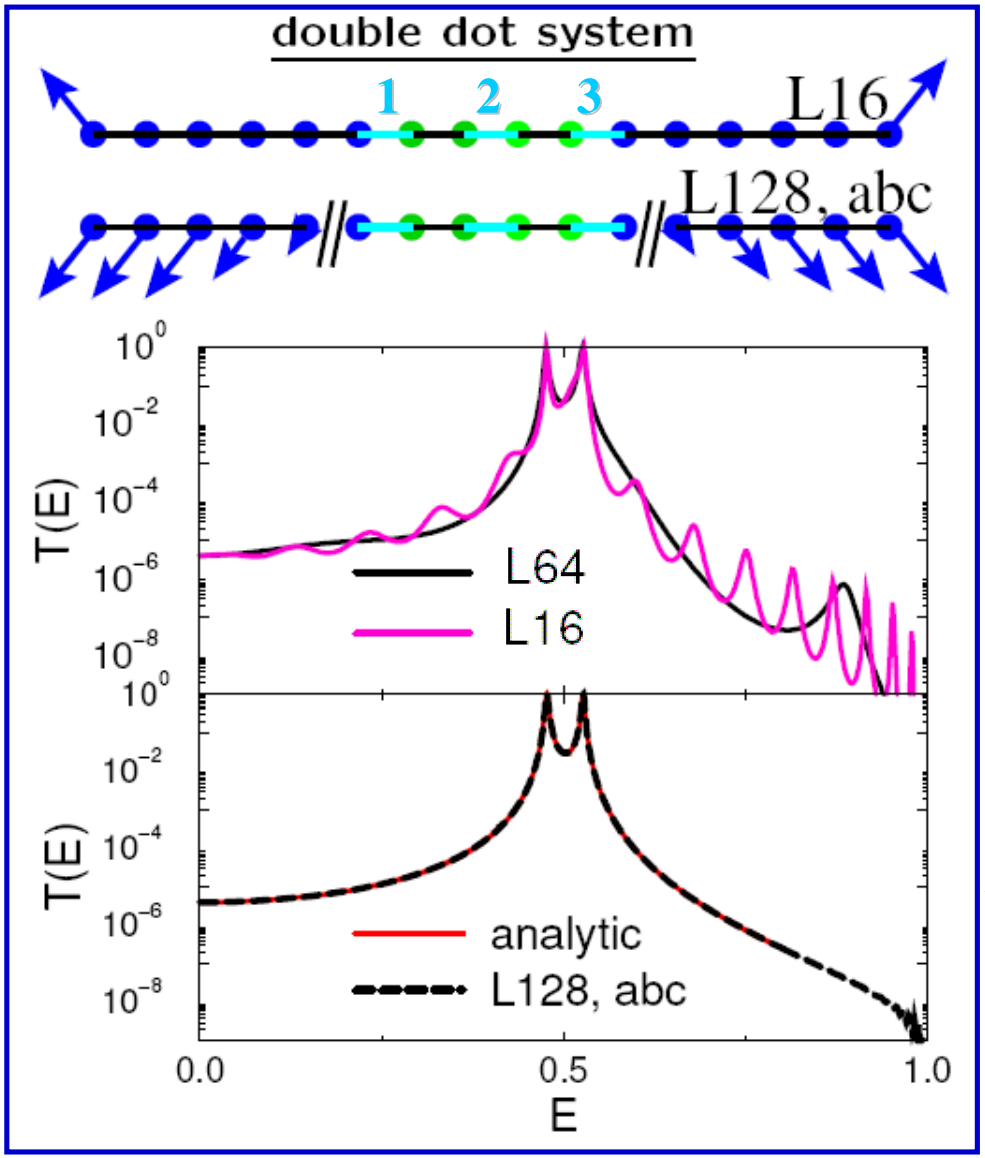
$$\Sigma_{ij;\mathcal{R}} = i\eta_i\delta_{ij}; \quad \eta_i = \eta/(1+\exp\beta(L-i-i_S))$$

$$L = 16 \quad i_S = 1,\ \beta = \infty,\ \eta = 1$$

$$L = 128 \quad i_S = 32,\ \beta = 0.3,\ \eta = 1$$

F Evers & A Arnold, CFN Lectures on Functional Nanostructures Vol.2, Lecture Notes in Physics 820

Test cases: tight-binding chain



Parameterization of the self-energy

$$\Sigma_{ij;\mathcal{L}} = i\eta_i\delta_{ij}; \quad \eta_i = \eta/(1+\exp\beta(i-i_S))$$

$$\Sigma_{ij;\mathcal{R}} = i\eta_i\delta_{ij}; \quad \eta_i = \eta/(1+\exp\beta(L-i-i_S))$$

$$L = 16 \quad i_S = 1,\ \beta = \infty,\ \eta = 1$$

$$L = 128 \quad i_S = 32,\ \beta = 0.3,\ \eta = 1$$

F Evers & A Arnold, CFN Lectures on Functional Nanostructures Vol.2, Lecture Notes in Physics 820

Recipe to perform transport calculation

- Do DFT for *eM* with a quantum chemistry package using local basis set $|\tilde{\mu}\rangle = |\mathbf{x}_n, l\rangle$
- Ask the package to provide the overlap matrix $S_{\mu\nu} = \langle\tilde{\mu}|\tilde{\nu}\rangle$
- Orthogonalize the basis set, $|\mu\rangle = \sum_\nu |\tilde{\nu}\rangle S^{-1/2}_{\nu\mu}$
- Use KS states $|p\rangle = \sum_\mu |\mu\rangle c_{\mu p}$ and energies ϵ_p to construct

$$\langle\mu|H_{eM}|\nu\rangle = \sum_p c_{\mu p}\,\epsilon_p\,c^T_{p\nu}$$

- Make the choice for the left/right local leakage function $i\eta(\mathbf{x}_n)$, construct

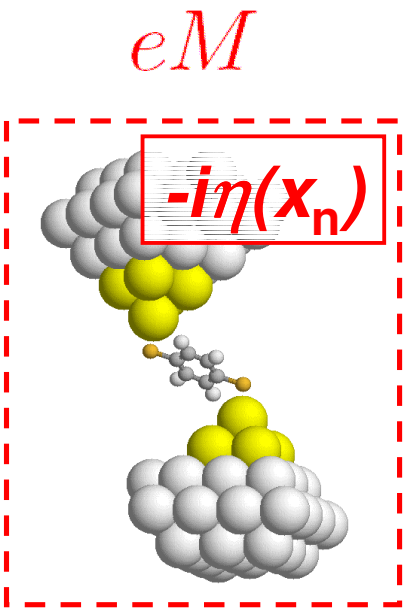
$$\langle\mu|\Sigma_{L/R}|\nu\rangle = -i\eta(\mathbf{x}_n)\delta_{\mu\nu}$$

- Build

$$\langle\mu|G(E)|\nu\rangle = \langle\mu|[E - H_{eM} - \Sigma_L - \Sigma_R]^{-1}|\nu\rangle$$

- Calculate transmission

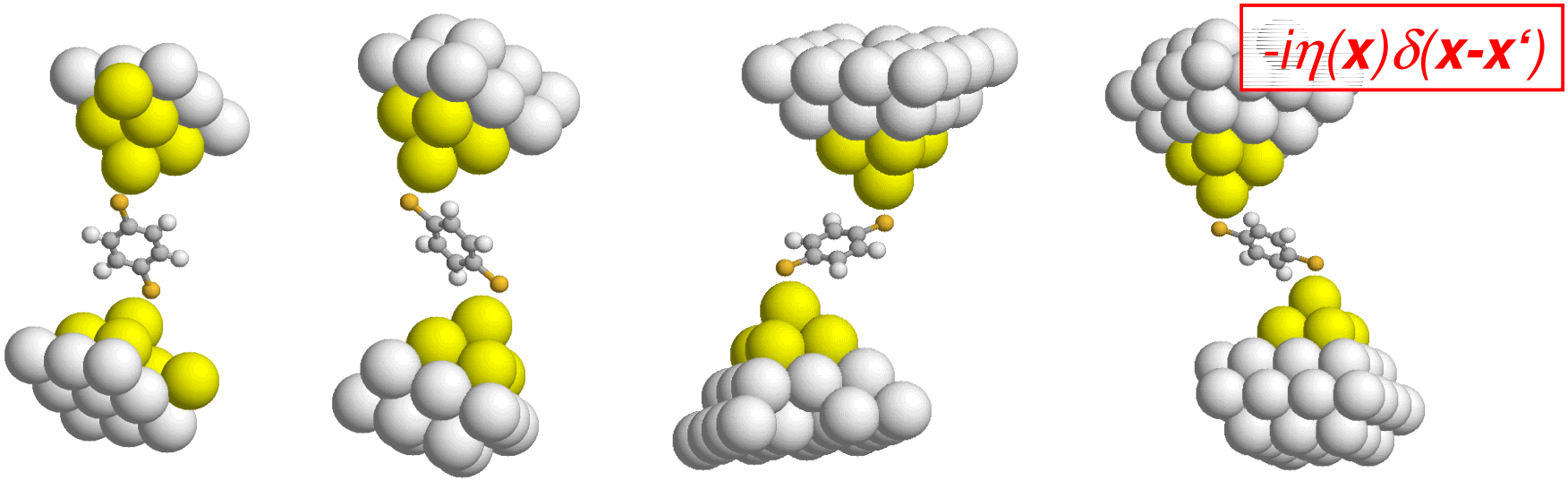
$$T(E) = \mathrm{Tr}\left[\Gamma_L G(E)\Gamma_R G^\dagger(E)\right]$$



AITRANSS module: library of electrodes

fcc Au clusters: - „chaotic“ cavities, left/right assymetric,
- gradualy increasing size,
- abc are active at „grey“ atoms, parametrized by a local leakage function

“x3”	“x3a”	“x4”	“x4a”
15 x 2	19 x 2	29 x 2	41 x 2



AITRANSS (*ab initio* transport simulations): transport module developed at Inst. of Nanotech. (INT) at KIT (by F Evers, A Arnold, F Weigend & AB)
interfaced to FHI-aims & TURBOMOLE

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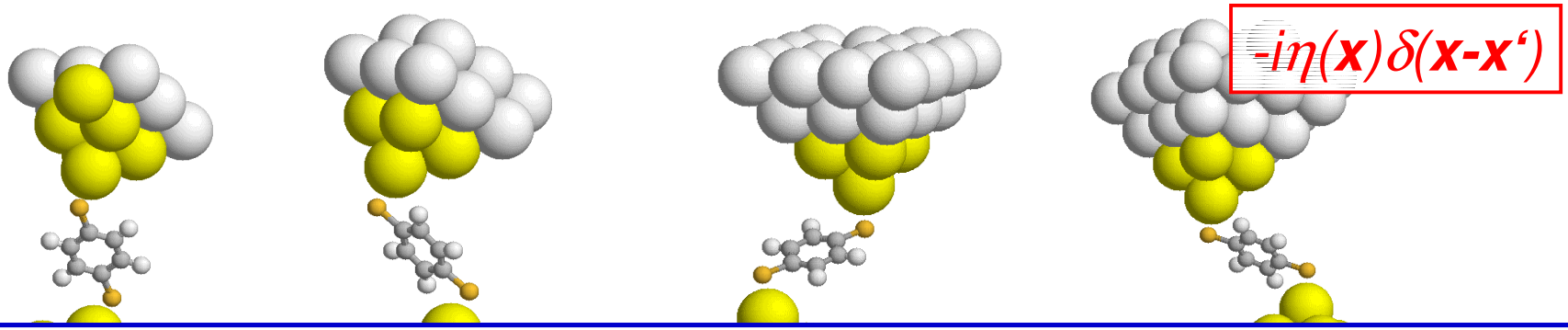

AITRANSS hands-on tutorial
Today, Wed, 29 August
14:00-16:00, Math. Instutute, Room 0.30

AITRANSS (*ab initio* transport simulations): transport module developed at Inst. of Nanotech. (INT) at KIT (by F Evers, A Arnold, F Weigend & AB)
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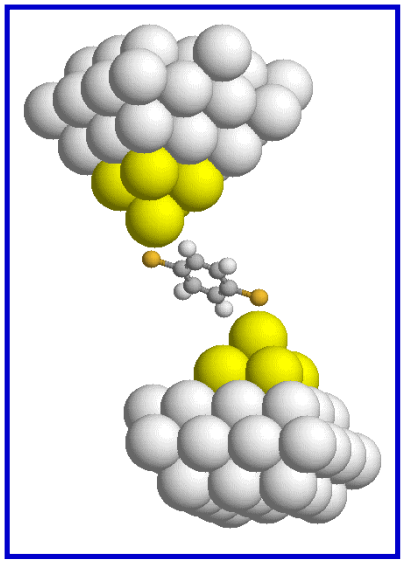
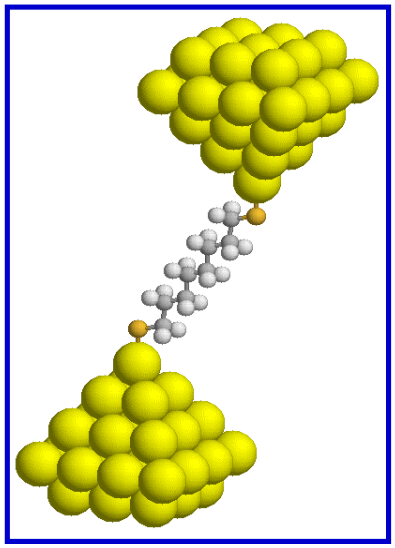
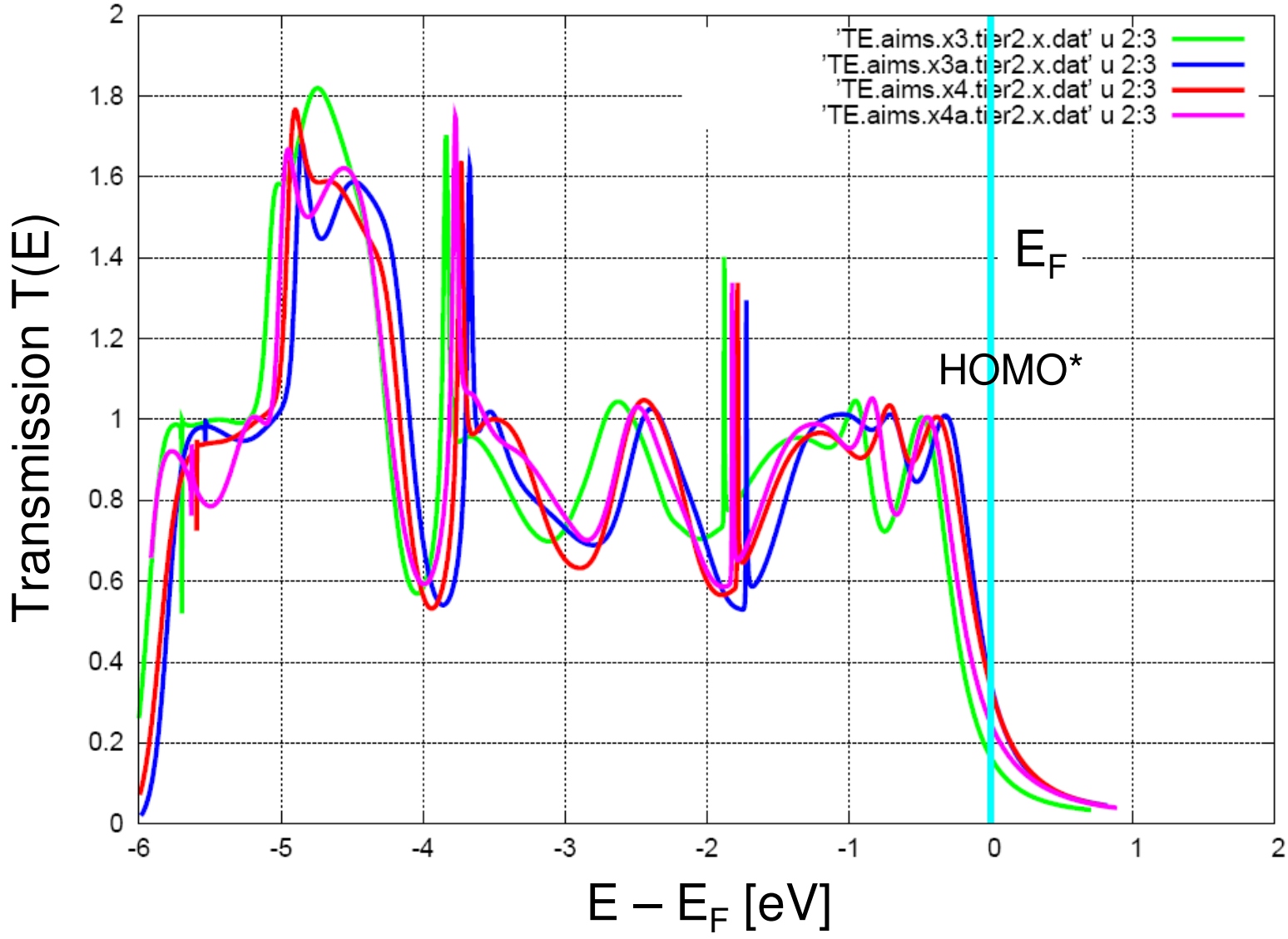




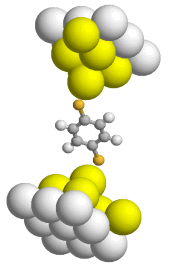
3. Paradigmatic studies: benzene-dithiol & alkyl chains

Archetypical example: transmission through BDT

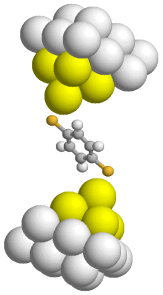
fhi-aims: “tier2”,convergence vs system size



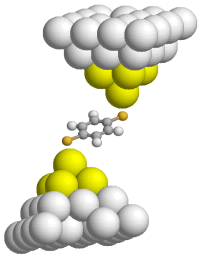
“x3”



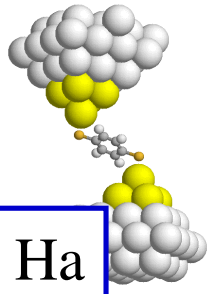
“x3a”



“x4”



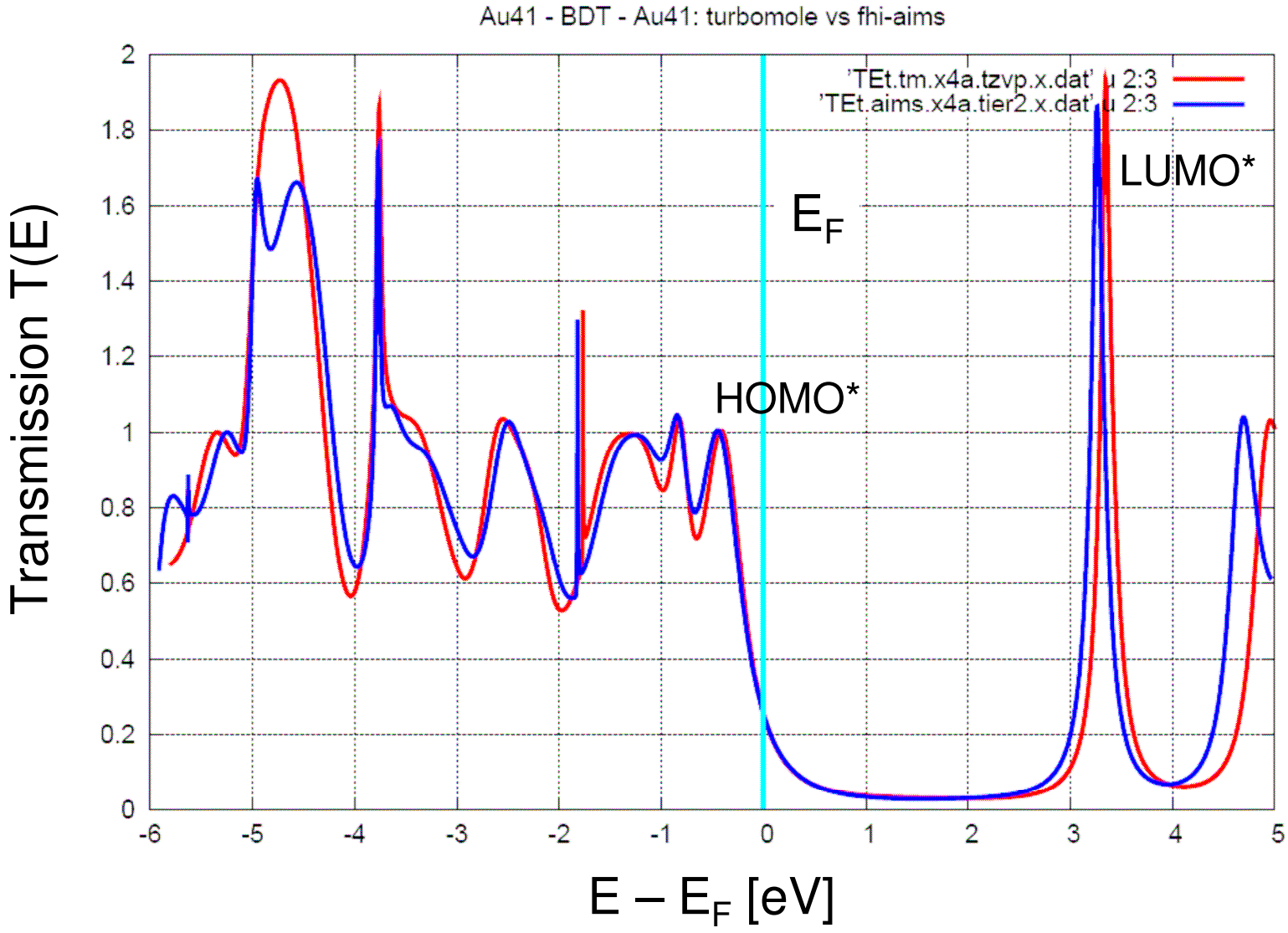
“x4a”

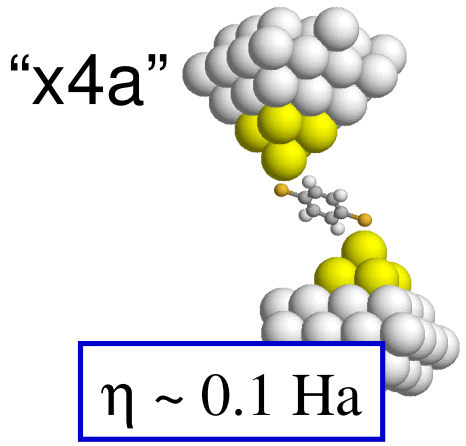


$\eta \sim 0.1$ Ha

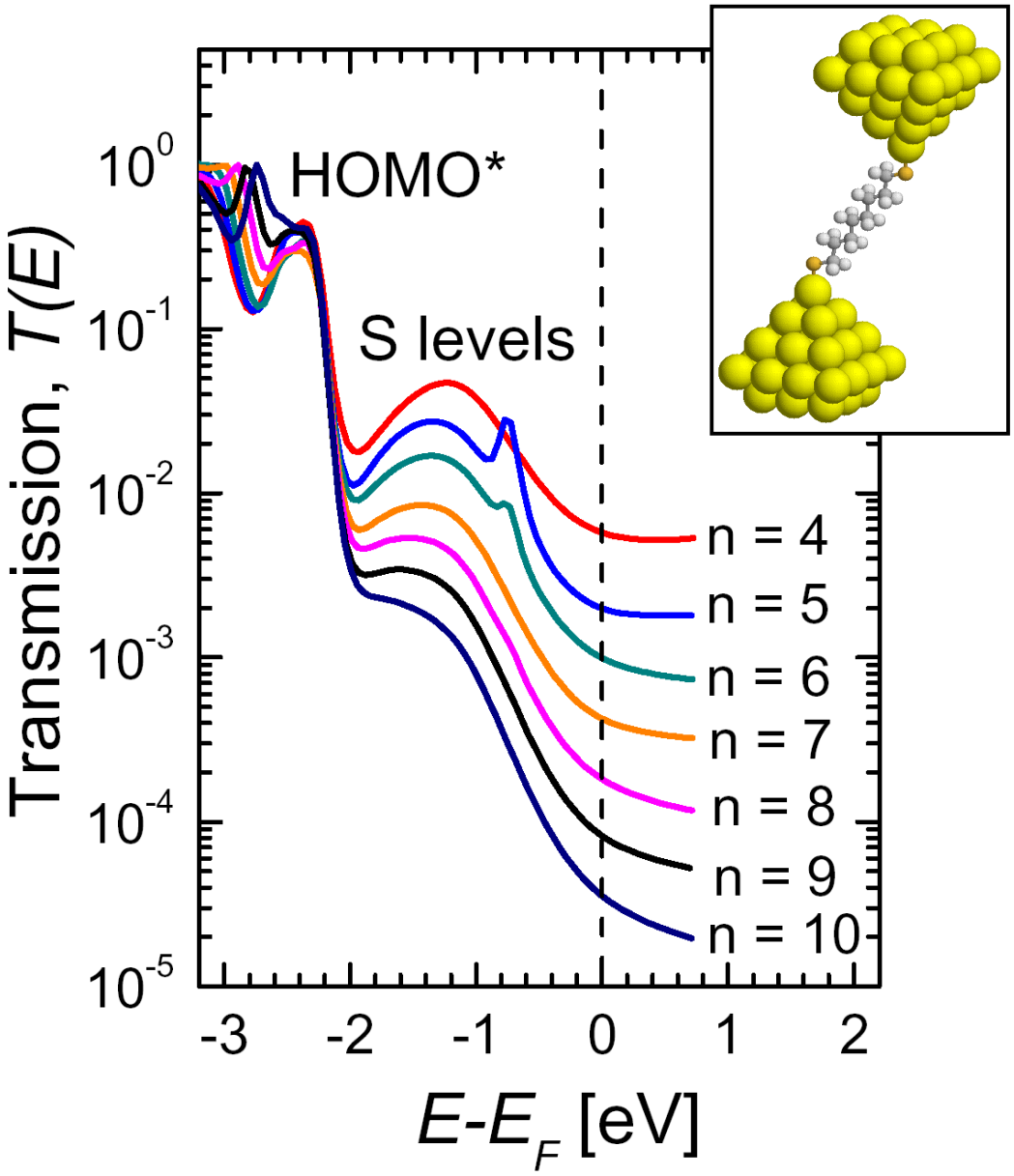
Archetypical example: transmission through BDT

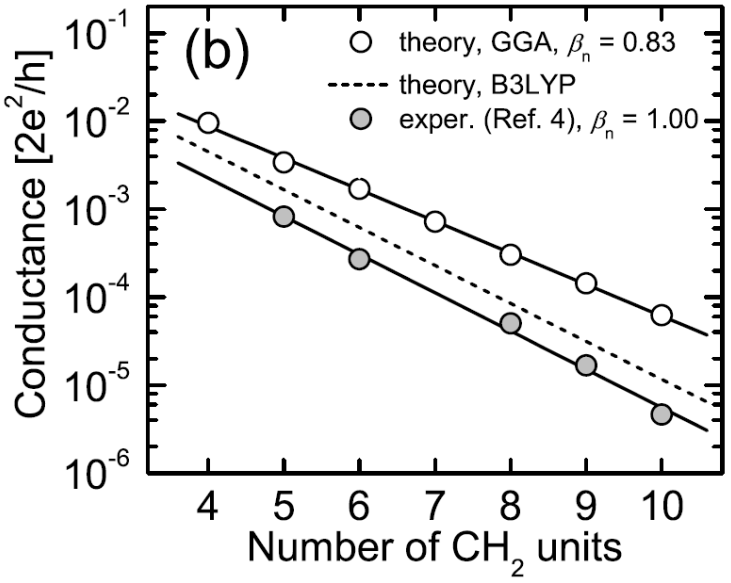
Gaussian basis sets (tzvp, TURBOMOLE)
vs numerical AOs (tier2, FHI-aims)





Alkanedithiols: wide band-gap insulators





- Conductance of *n*-alkanedithiol:

$$G(n) = \frac{2e^2}{h} T(E_F) \sim \exp[-\beta_N n]$$

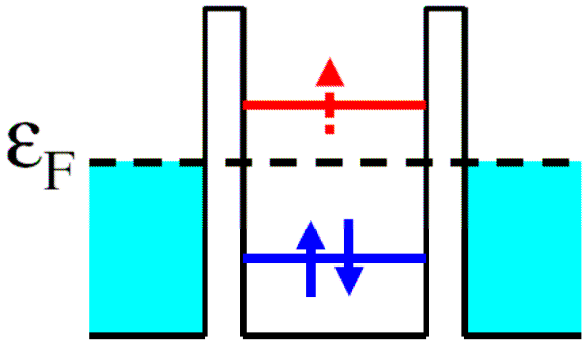
Theory: $\beta_N = 0.85$
Experiment: $\beta_N \sim 1.00$
(Jülich)

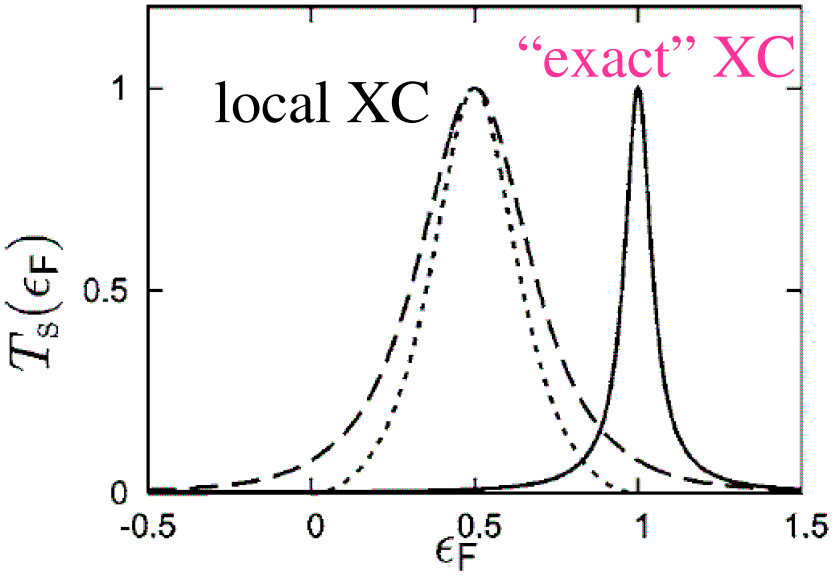
Ch Li, I Pobelov, Th Wandlowski,
AB, A Arnold & F Evers JACS **130** (2008) 318

Challenges in DFT based transport calculations

Koentopp, Burke & Evers, PRB'04

LUMO transport: missing derivative discontinuity of the local XC functional





$$T(E) = \gamma A(E)$$

$$A(E) = \frac{\gamma}{(E - \epsilon_{res}(f))^2 + \gamma^2}$$

occupation number:

$$f = \int_{-\infty}^{\epsilon_F} \frac{dE}{\pi} A(E, f)$$

$$T(\epsilon_F) = \cos^2\{\pi(f(\epsilon_f) - 1/2)\}$$

Let $\Delta\epsilon = \epsilon^{N+1}_{\text{homo}} - \epsilon^{N}_{\text{lumo}}$, then:

(i) local XC func., smooth flow of LDA-LUMO

$$\epsilon_{res} = \epsilon^{N}_{\text{lumo}} + f\,\Delta\epsilon$$

(ii) "exact" XC func. (derivative discontinuity!)

$$\epsilon_{res} = \epsilon^{N}_{\text{lumo}} + \Theta(f - \eta)\Delta\epsilon \quad (\eta \to 0^+)$$

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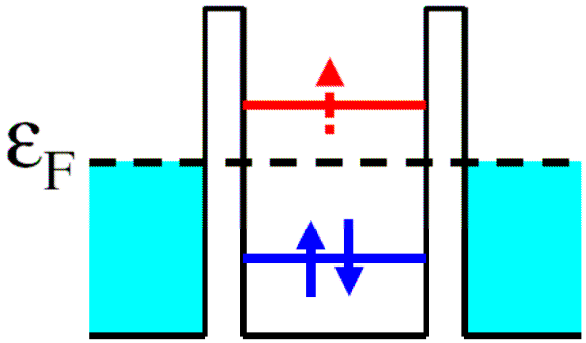

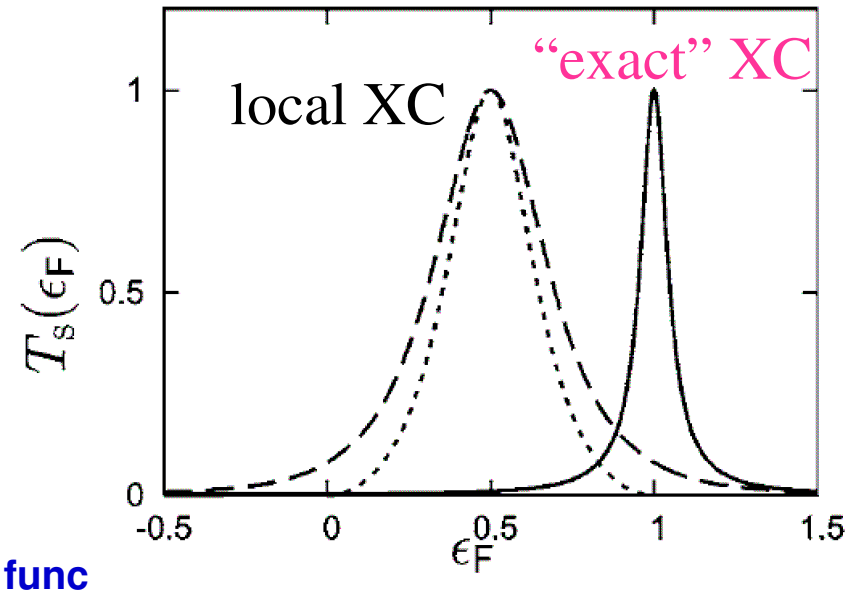

HOMO transport: spirious self-interaction of local XC func

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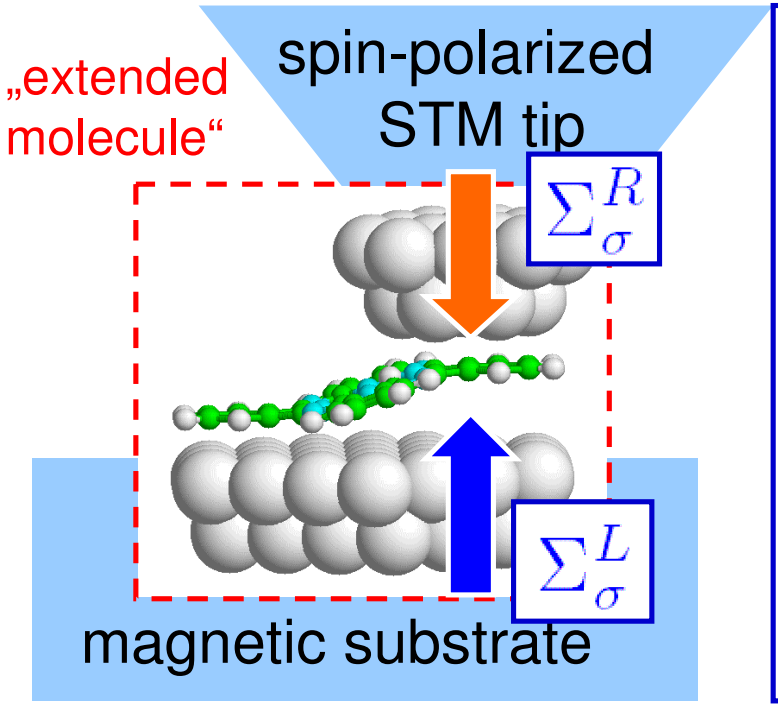
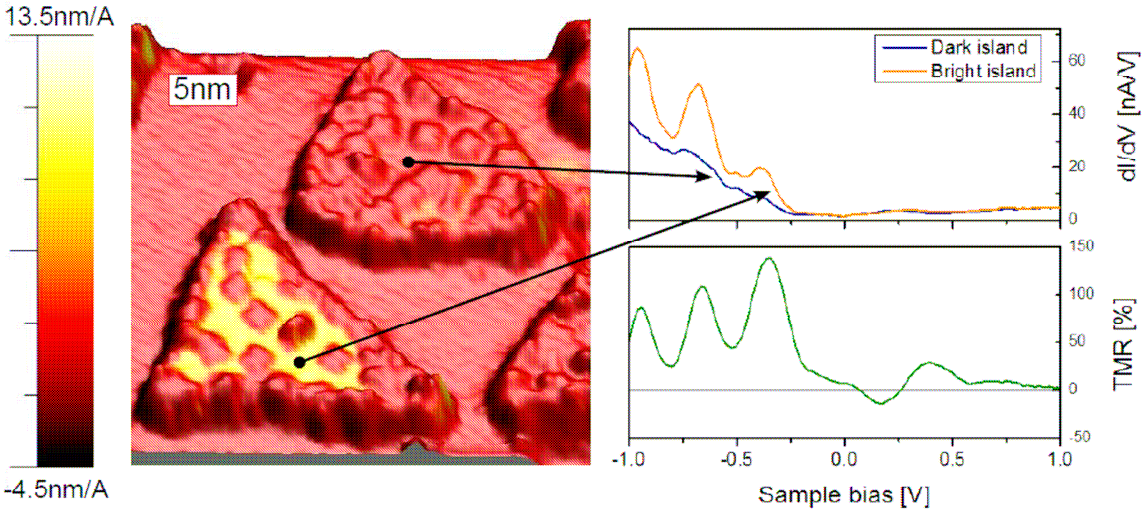
Spin transport & magnetoresistance across H_2Pc

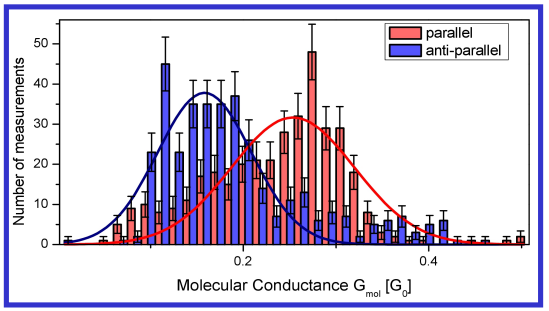


$$G_\sigma^{-1}(E) = E - H_\sigma^{\mathrm{KS}} - \Sigma_\sigma^L - \Sigma_\sigma^R$$

$$\Sigma_\sigma^{L/R} \simeq \delta(\mathbf{x}-\mathbf{x}')\left[\delta\epsilon + \frac{\sigma}{2}\Delta_{\mathrm{ex}}^{L/R} - i\eta\right]$$

$$\hat{n}_\sigma = \int_{-\infty}^{+\infty} \frac{dE}{2\pi}\, G_\sigma \left[f_L\Gamma^L + f_R\Gamma^R\right] G_\sigma^\dagger$$

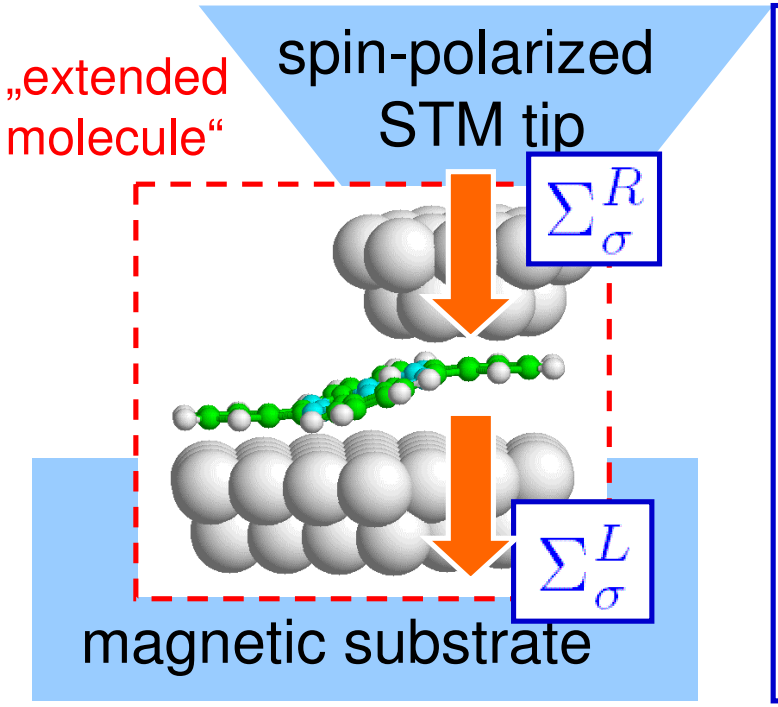




Key observation:
magnetoresistance ~ 60% through H_2Pc in STM setup

Nature Nano **6**, 185 (2011)
by S.Schmaus, AB, Y.Nahas, *et al.*

Spin transport & magnetoresistance across H_2Pc



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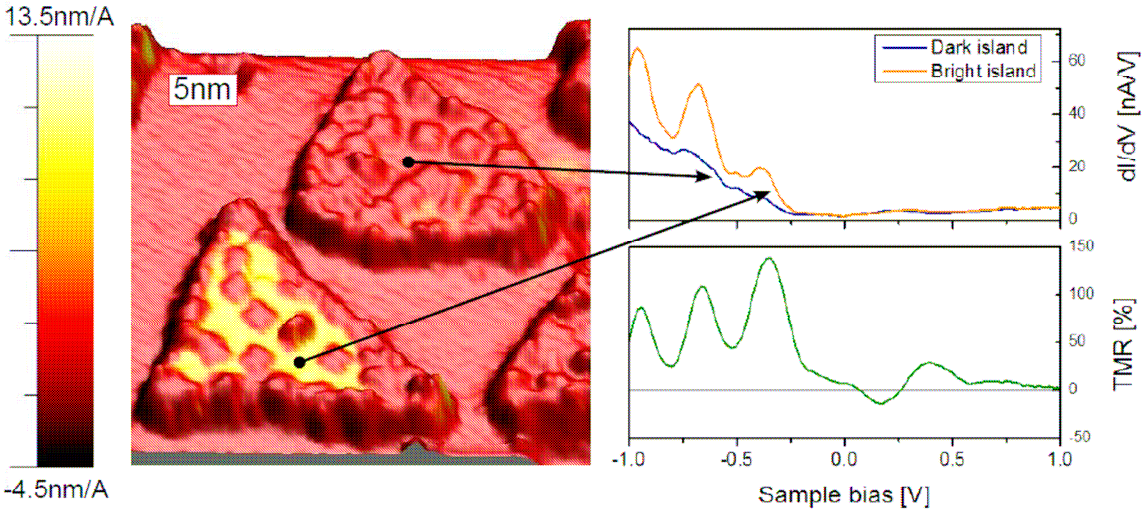

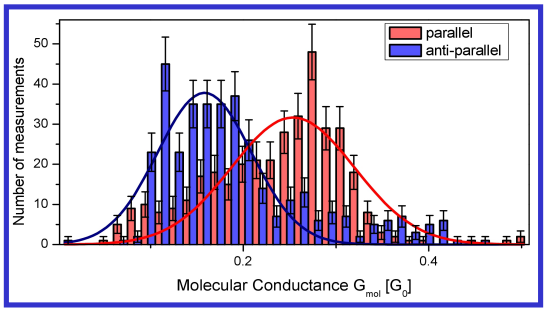

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Thanks to ...

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Ferdinand Evers

Michiel van Setten

Funding:
DFG Center for Functional Nanostructures (CFN)
SPP1243 “Quantum transport at the molecular scale”
DFG BA4265 “Electron transport & magnetism in single molecules”

Thank you for your kind attention!

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