Transport calculations for single molecules based on DFT

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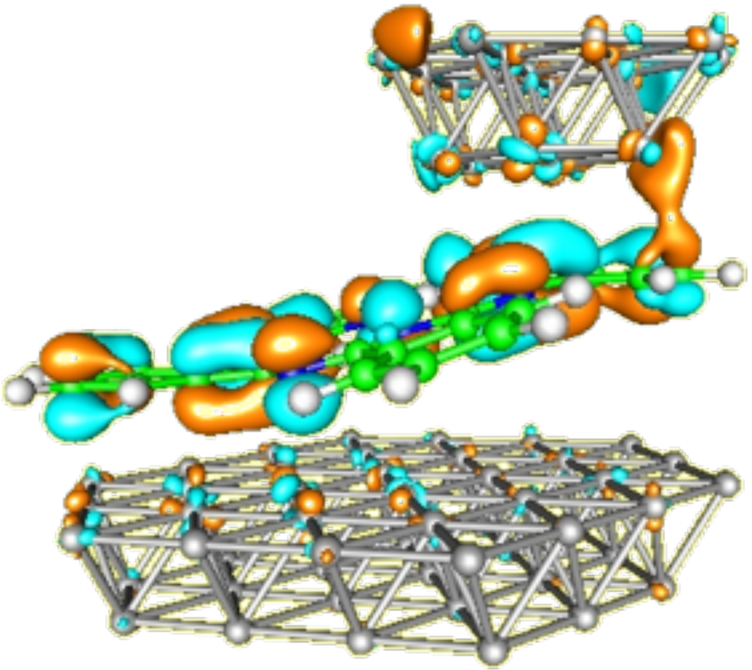
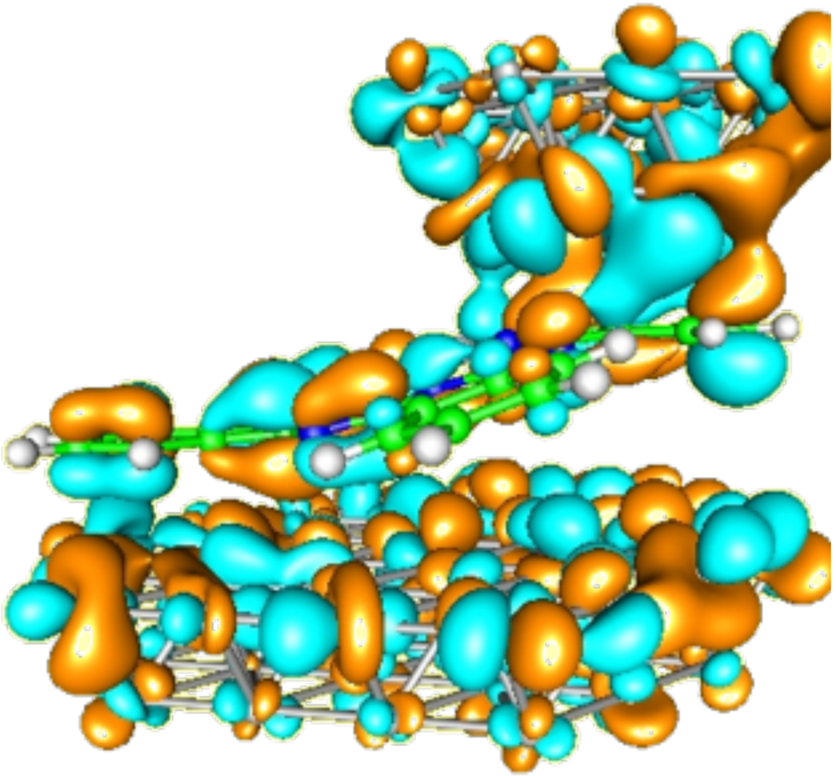
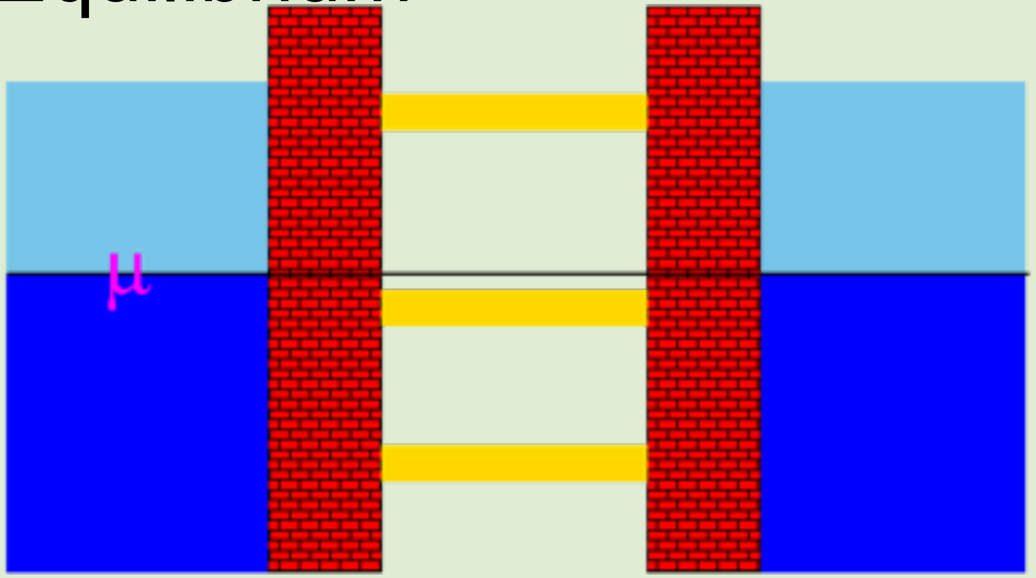
I. Pedagogical part: Basic transport theory





Transport in the scattering picture
Equilibrium vs. nonequilibrium

Equilibrium



Lumo: ε_{L}

Homo: ε_{H}

level broadening $\Gamma_{\mathrm{H,L}}$

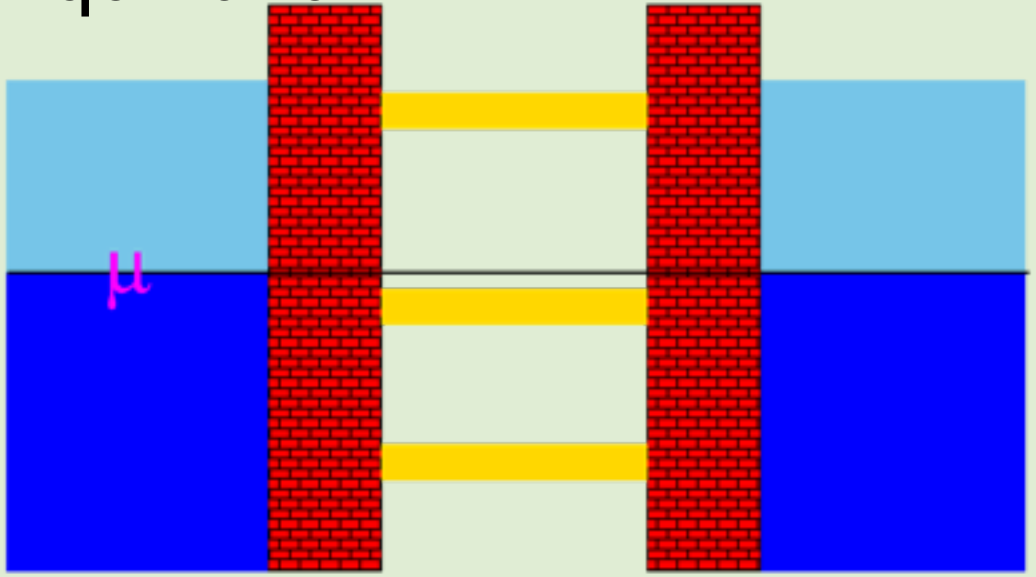
electrochemical potential: μ

temperature: T

Transport in the scattering picture

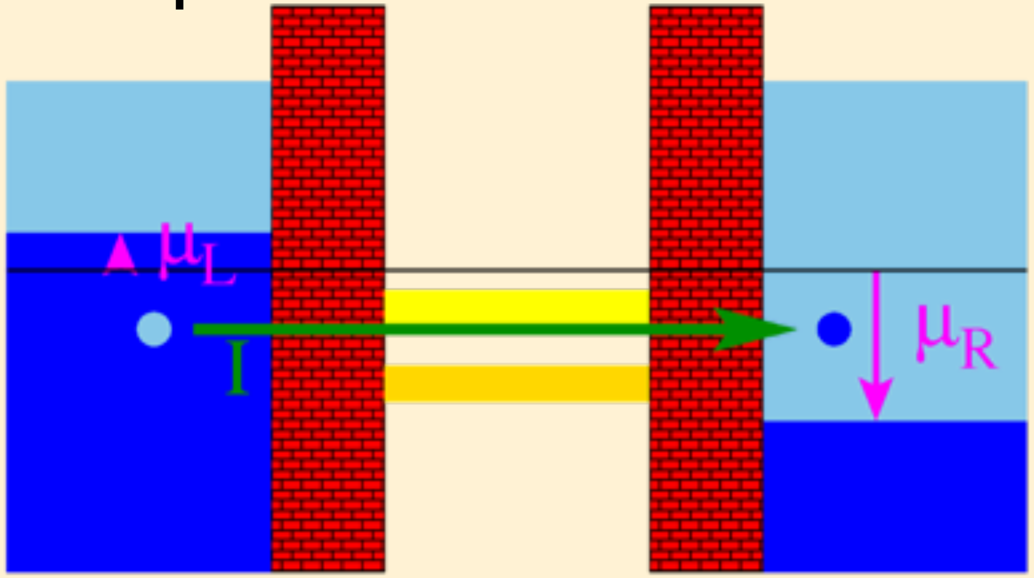
Equilibrium vs. nonequilibrium

Equilibrium



Lumo:	ε_{L}
Homo:	ε_{H}
level broadening	$\Gamma_{\mathrm{H,L}}$
electrochemical potential:	μ
temperature:	T

Non-Equilibrium



left/right electrochemical potential:	$\mu_{\mathcal{L},\mathcal{R}}$
left/right temperature:	$T_{\mathcal{L},\mathcal{R}}$

Attaching reservoirs to nanosystem

Green's function formalism

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

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

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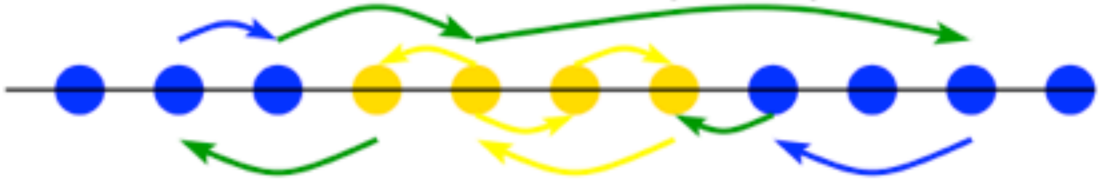
dressed Green's function (of $\mathcal{M}$):



$$G^{-1} = G^{-1}_{\mathcal{M}} - \Sigma_{\mathsf{L}} - \Sigma_{\mathsf{R}}$$

$$\Sigma_{\mathsf{X},ij} = \sum_{\mathcal{L},\nu\mu} V_{i\nu} G_{\mathsf{X},\nu\mu} V^{*}_{\mu j}$$

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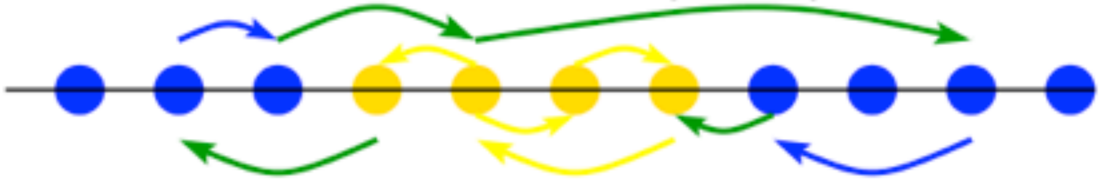

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$$H_{\text{eff}} = H_{\mathcal{M}} + \frac{1}{2}\sum_{\mathsf{X}=\mathsf{R},\mathsf{L}} (\Sigma_{\mathsf{X}} + \Sigma^{\dagger}_{\mathsf{X}})$$

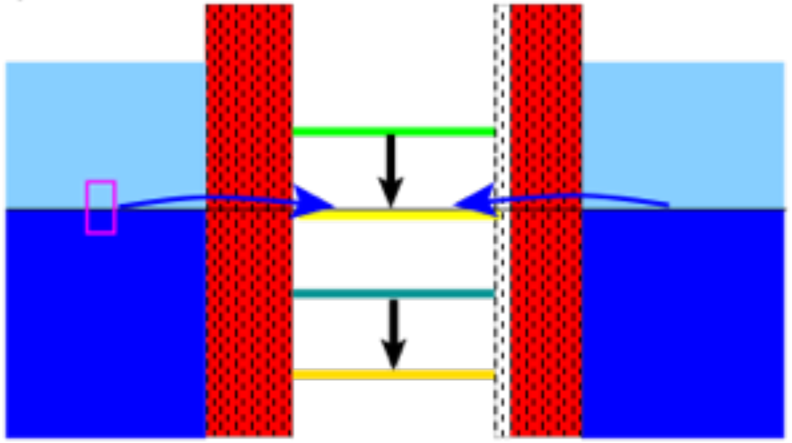
leakage rates:

$$\Gamma_{\mathsf{X}} = \frac{1}{2i}(\Sigma_{\mathsf{X}} - \Sigma^{\dagger}_{\mathsf{X}}), \qquad \mathsf{X} = \mathsf{R},\mathsf{L}$$

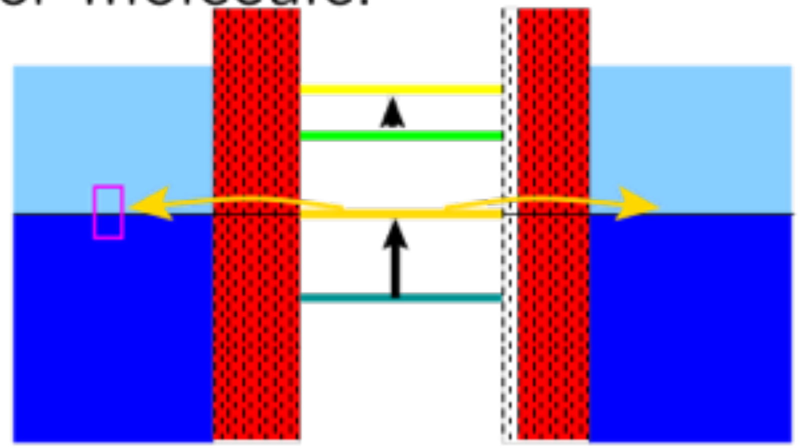
Intuitive meaning
Charge exchange and lifetime effects

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

acceptor molecule:



donor molecule:



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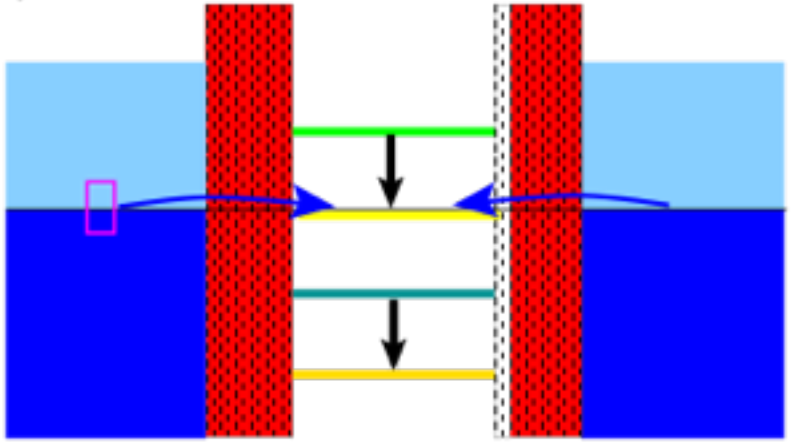

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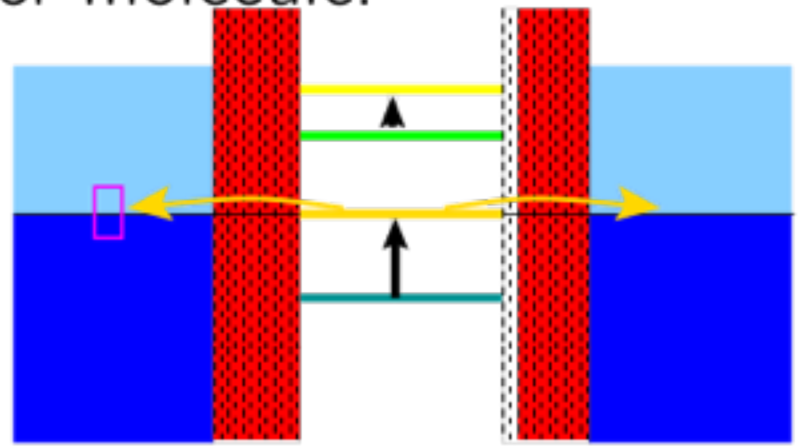
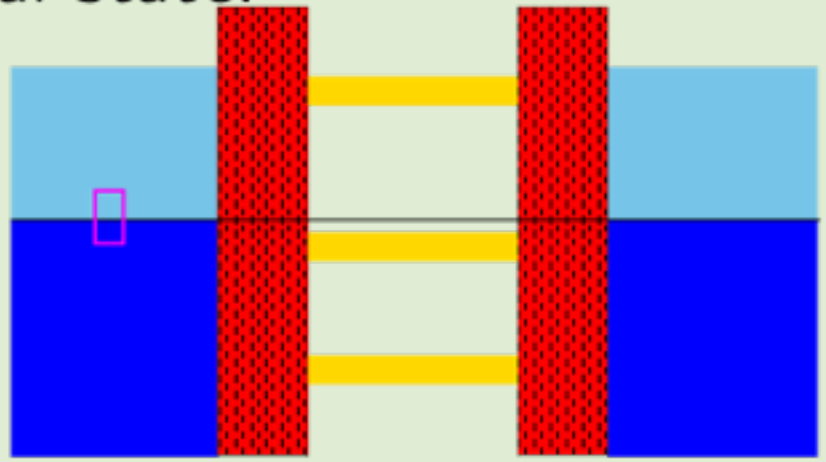
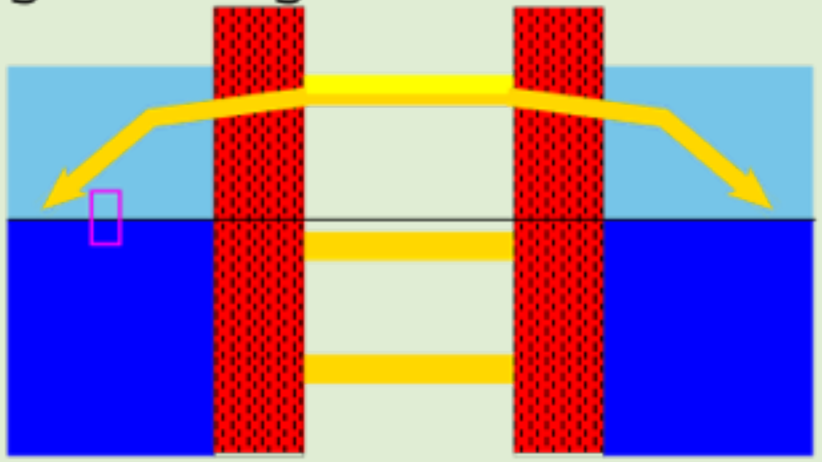


$$G^{-1} = E - H_{\text{eff}} + \frac{1}{2i}\left(\Gamma_{\text{L}} + \Gamma_{\text{R}}\right)$$

initial state:



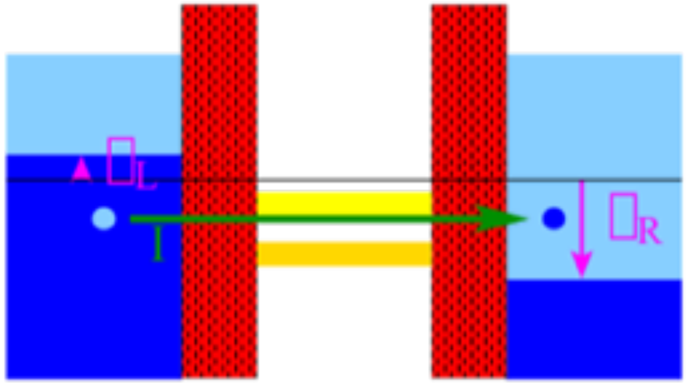
charge leakage:



Formalism with Green's function
Connecting scattering approach with NEGFs

scattering states:

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



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

$$= \int_{\mu_R}^{\mu_L} dE \ \mathrm{Tr}_{\mathcal{L}_T} \left(tt^\dagger\right)$$

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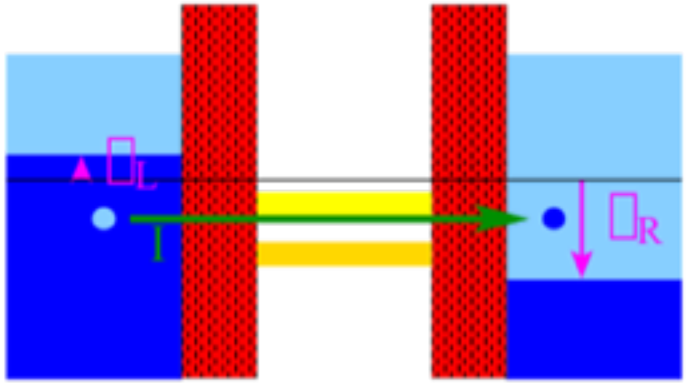

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Green's function formulation:

$$Q(E) = \int_{\mathcal{M}} d\mathbf{x} \sum_j \delta(E-\epsilon_j)\, |\psi_j(\mathbf{x})|^2 = \mathrm{Tr}_{\mathcal{M}}(G_E - G_E^\dagger)$$

leakage:

$$\partial_t Q(E) = [(1-f_R)\Gamma_R + (1-f_L)\Gamma_L]\, Q(E)$$

spectral transport current $j(E)$:

$$j(E) = \left[\frac{f_L\Gamma_L}{\Gamma_L+\Gamma_R}(1-f_R)\Gamma_R - \frac{f_R\Gamma_R}{\Gamma_L+\Gamma_R}(1-f_L)\Gamma_L\right] Q(E)$$
$$= (f_L - f_R)\frac{\Gamma_L\Gamma_R}{\Gamma_L+\Gamma_R} Q(E)$$

total current $I = \int j(E)$:

$$I = 4\int_{\mu_R}^{\mu_L} dE \;\; \mathrm{Tr}_{\mathcal{M}} \left(\Gamma_L G \Gamma_R G^\dagger\right)$$

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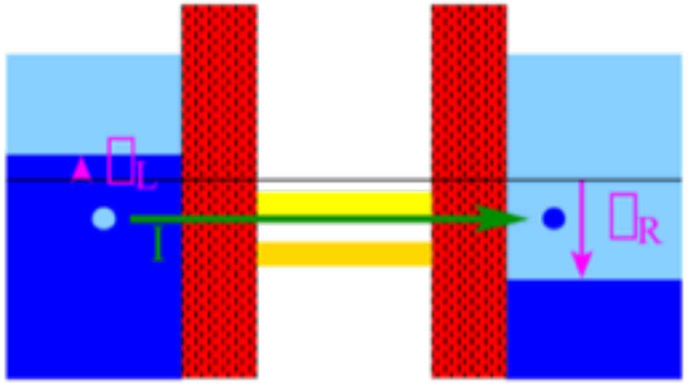

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equivalence $(E = \epsilon_\nu)$: $t_{nn'} = i\,\mathrm{Tr}_{\mathcal{L}_L}\left(\delta(\epsilon_\nu - H_{\mathcal{L}})V_R G V_L\right)$

II. Current developments

collaborations with

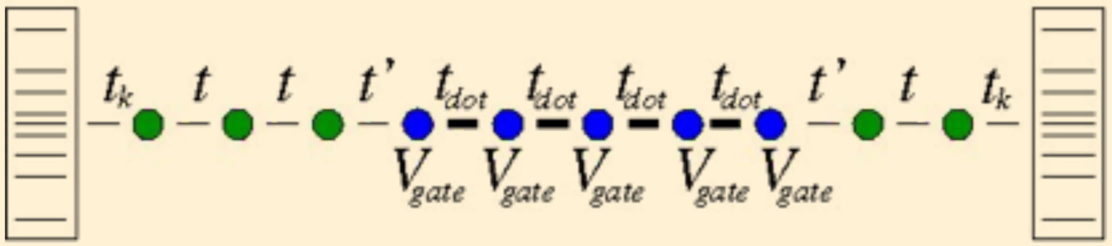
Peter Schmitteckert (INT @ KIT),

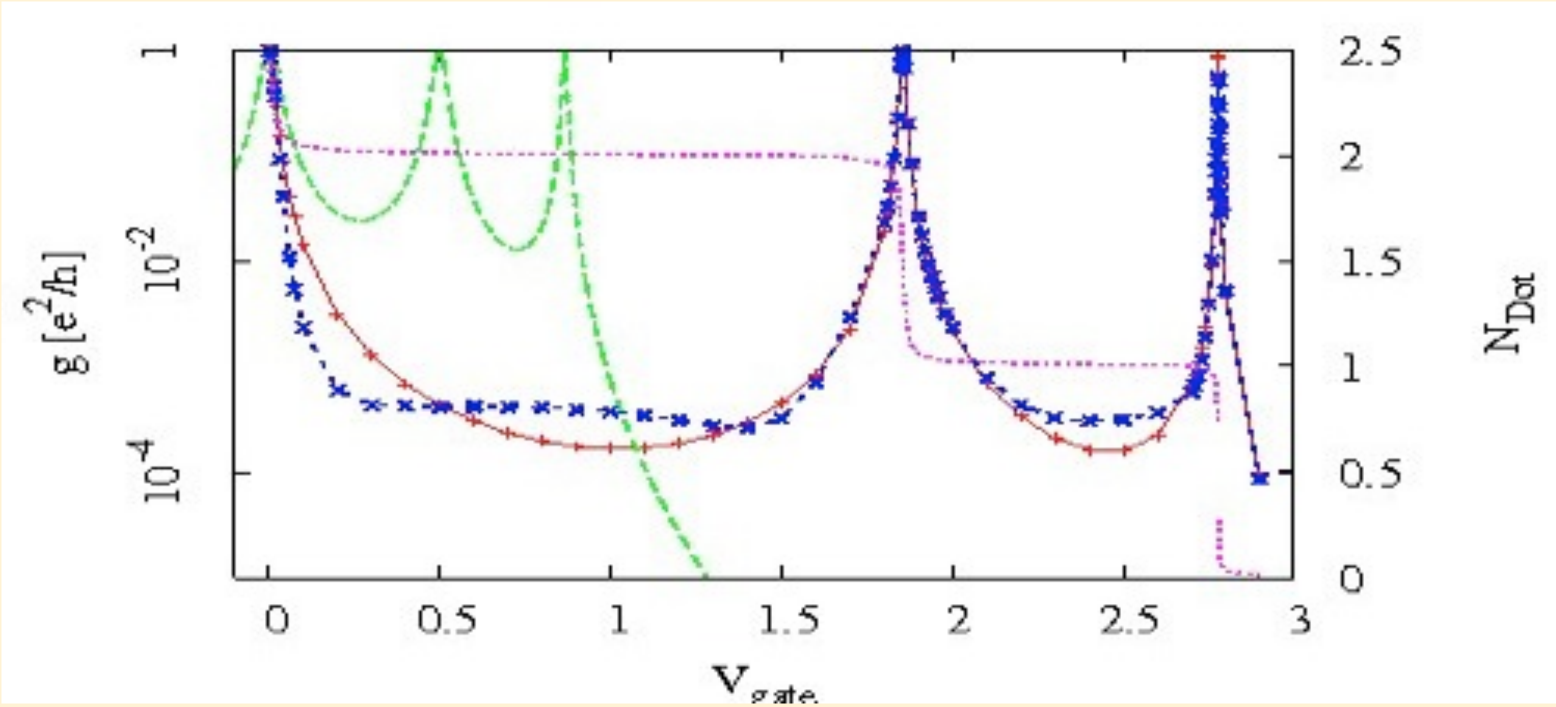
Alexei Bagrets (SCC/INT @ KIT),

Florian Weigend (INT @ KIT) & Michiel van Setten (CFN @ KIT)

Exact functionals with DMRG
Fundamental aspects of DFT based transport
(collaboration: P. Schmitteckert)

Model system:
5 site interacting
resonant levels





Comparing exact conductance (DMRG) with conductance calculated with exact XC-functional from backwards DFT

Schmitteckert & Evers, PRL 2008

Green's fcts methods in Chemistry

Karlsruhe Institute of Technology

Perturbative energy shifts with GW-approach

(collaboration: M. van Setten & F. Weigend)

Quasi particle equation with energy dependent self-energy

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V_{\rm ext} + V_{\rm H}\right\}\psi_n^{\rm qp} + \Sigma(\epsilon_n^{\rm qp})\cdot\psi_n^{\rm qp} = \epsilon_n^{\rm qp}\psi_n^{\rm qp} \qquad (1)$$

In first order the self-energy is approximated by *GW*

$$\Sigma(E) = \frac{i}{2\pi}\int e^{-i\omega 0^+} G(E-\omega)W(\omega)d\omega$$

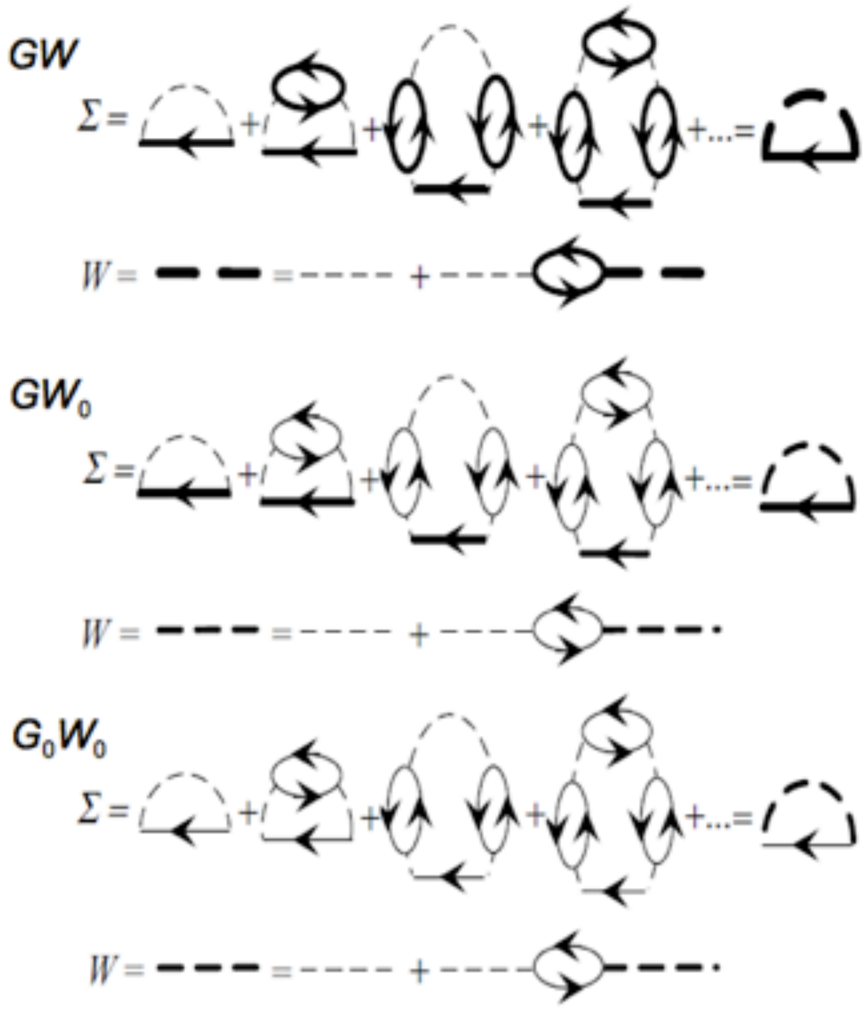
Greens and screened coulomb interaction

$$G(E) \;=\; \int_{-\infty}^{+\infty} dE' \frac{\mathrm{A}(E')}{E-E'+i\eta\,\mathrm{sgn}(E')} \qquad W(\omega) = \varepsilon^{-1}(\omega)\cdot v$$

Inverse dielectric function and polarization functions

$$\varepsilon(\omega)^{-1} = 1 + v\cdot\chi(\omega) \qquad \chi = P + P\cdot v\cdot\chi$$

$$P(\omega) = -\frac{i}{2\pi}\int_{-\infty}^{\infty} dE'\, G(E')G(E'-\omega)$$



Green's fcts methods for chemistry

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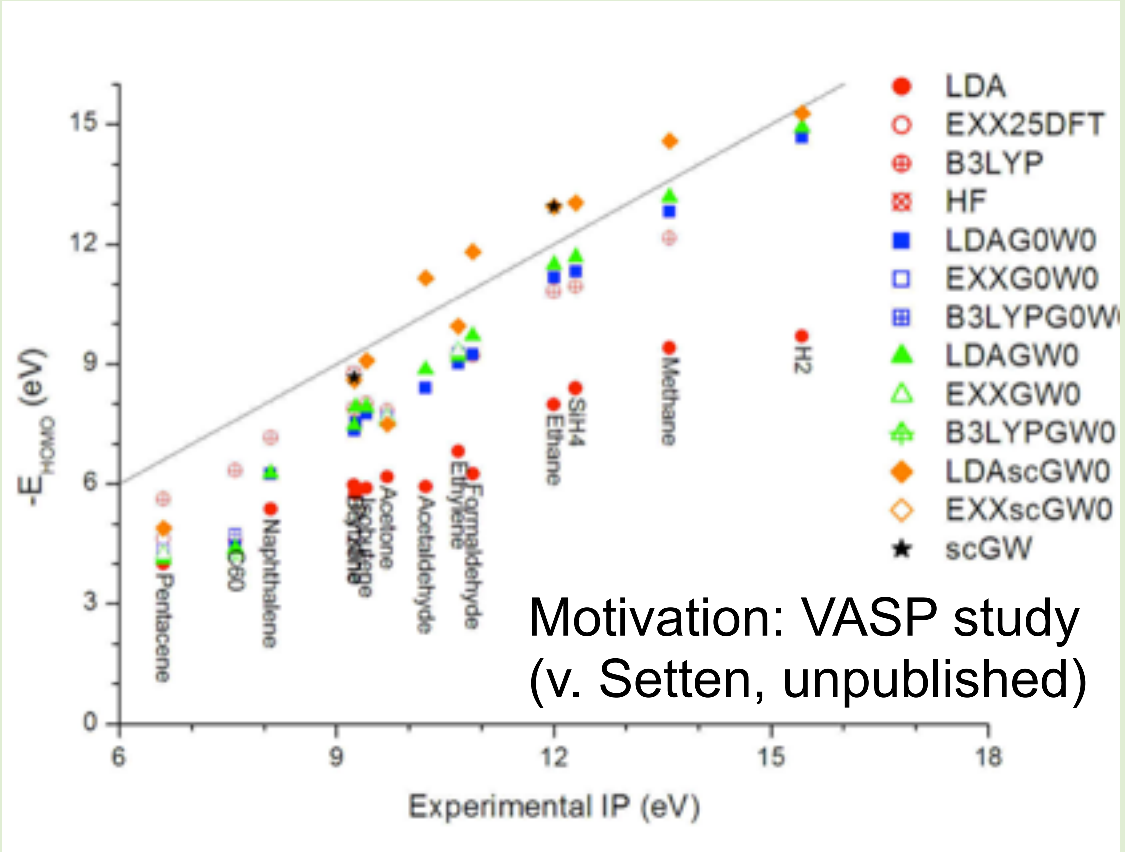
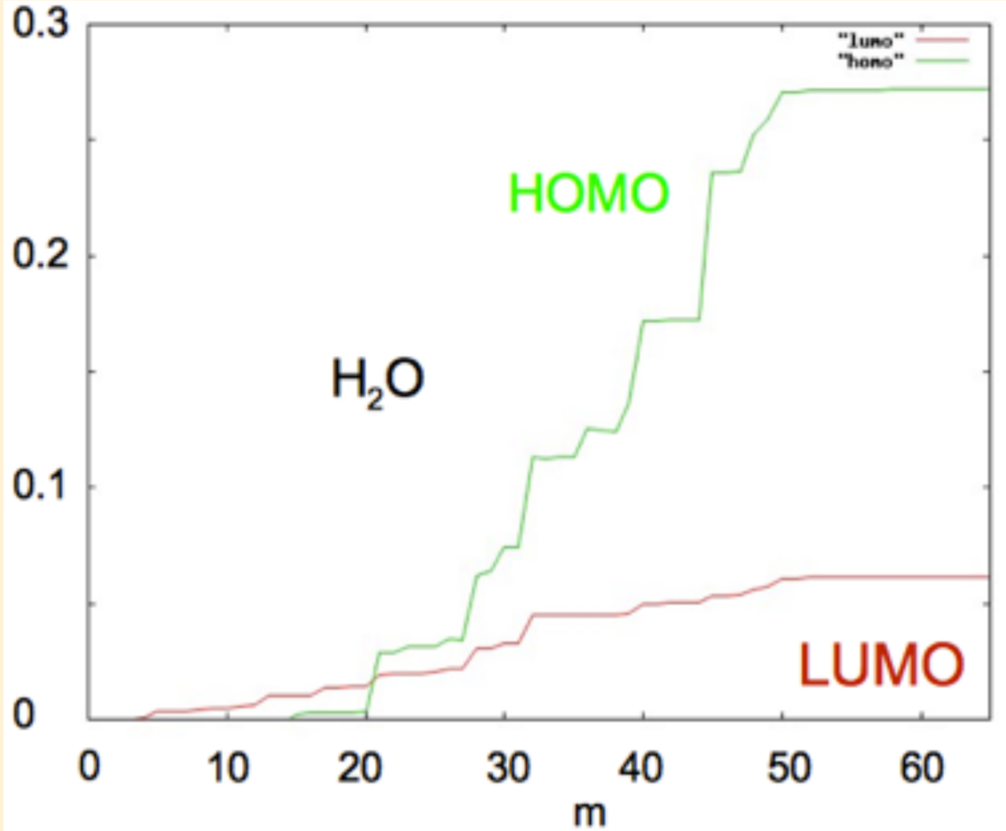


Motivation: VASP study
(v. Setten, unpublished)

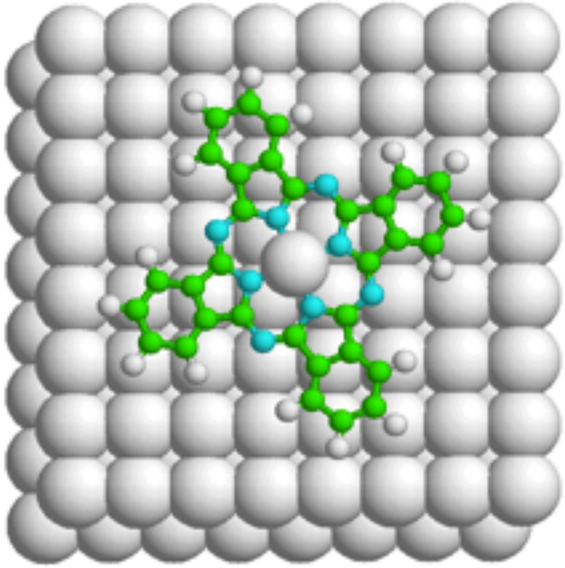


Coding: modular extension of TURBOMOLE (CFN-supported)

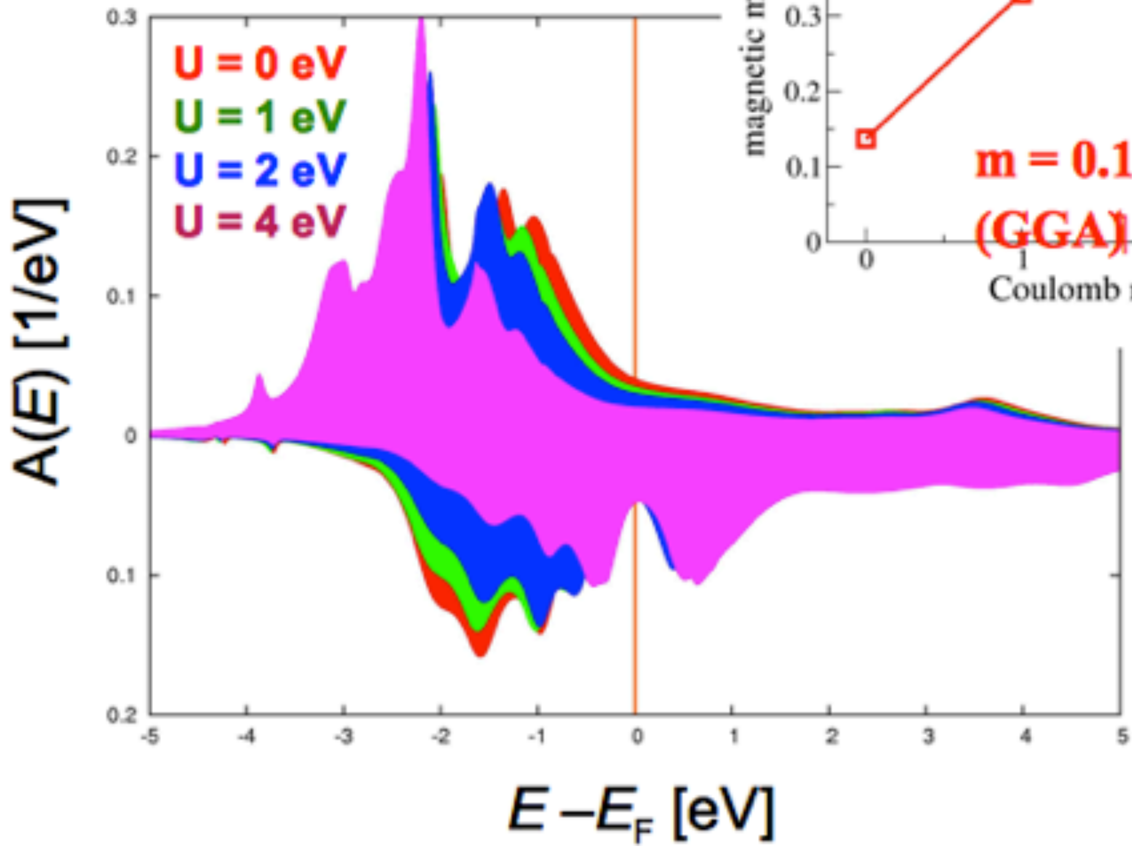
Simplified GW: LDA + U

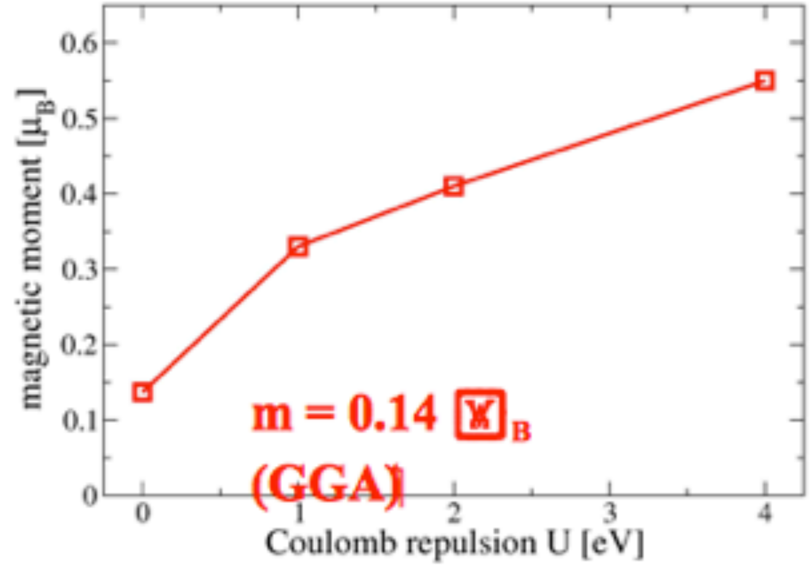
Stability of DFT against weak on-site interactions

(collaboration: A. Bagrets)



Spectral function A(*E*) projected on Co d(z^2) orbital (preliminary)





Plans

(1) implementing and testing van der Waals-functional after Langreth, Hyldgaard et al. (PRB 2004) into TURBOMOLE

(2) parallelization

(3) transport with GW-corrected Green's functions

(4) in the longer run: transport implementation also into 2d-periodic code

III. Magneto-transport through phtalocyanine (H_2Pc) molecules

collaboration with

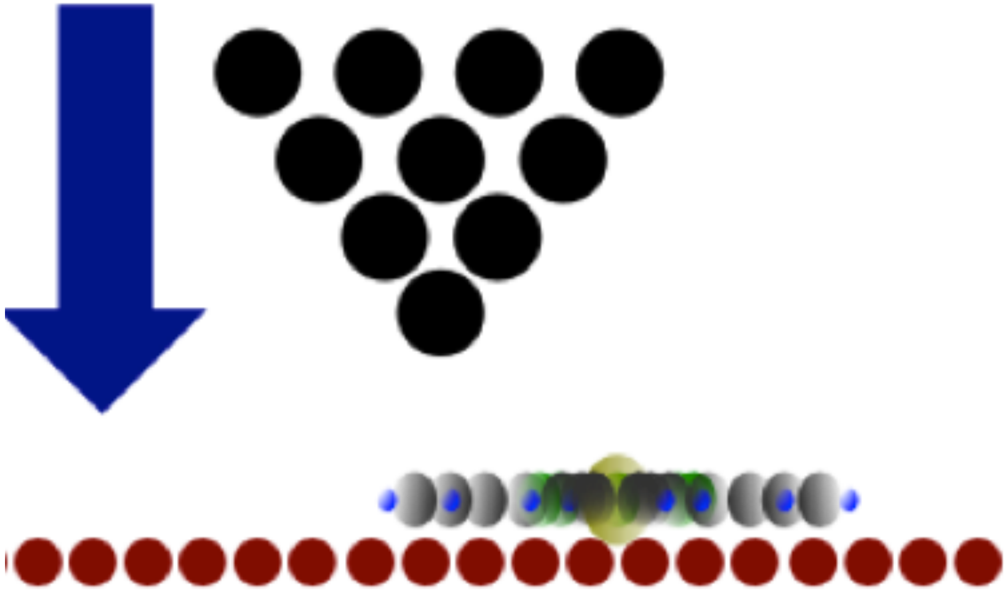
Alexei Bagrets (SCC/INT @ KIT)

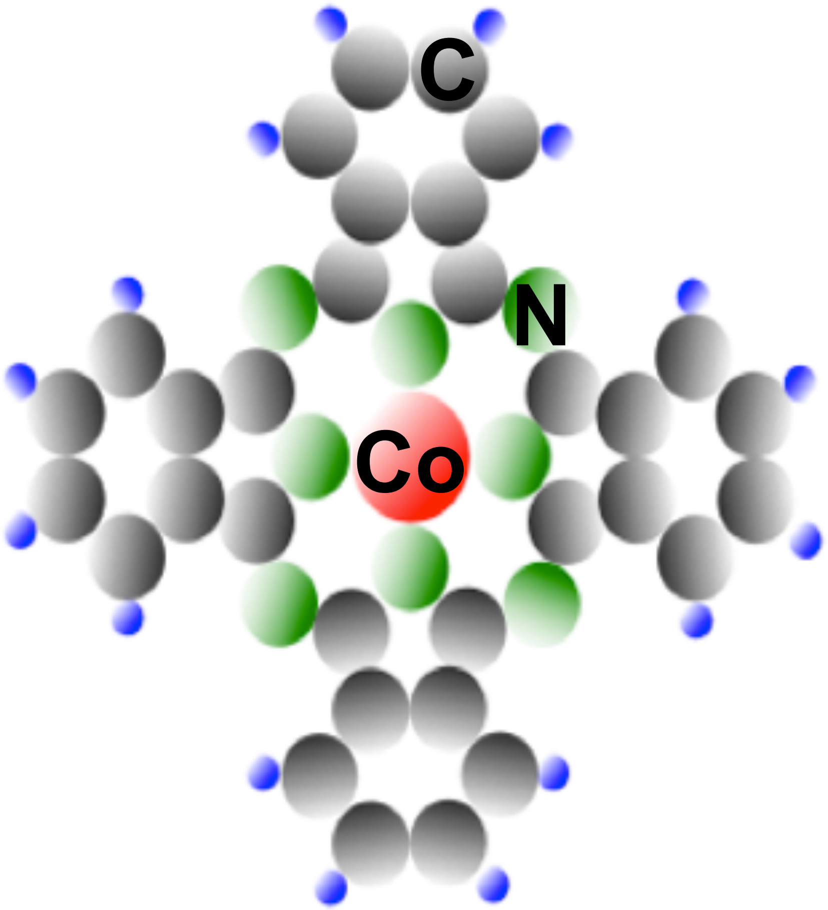
&

Stefan Schmaus and Wulf Wulfhekel (PI@KIT)

preprint submitted 2010

Phtalocyanine on Cu(111) under STM
(experiment: Schmaus & Wulfhekel, 2010)





Thursday, November 4, 2010

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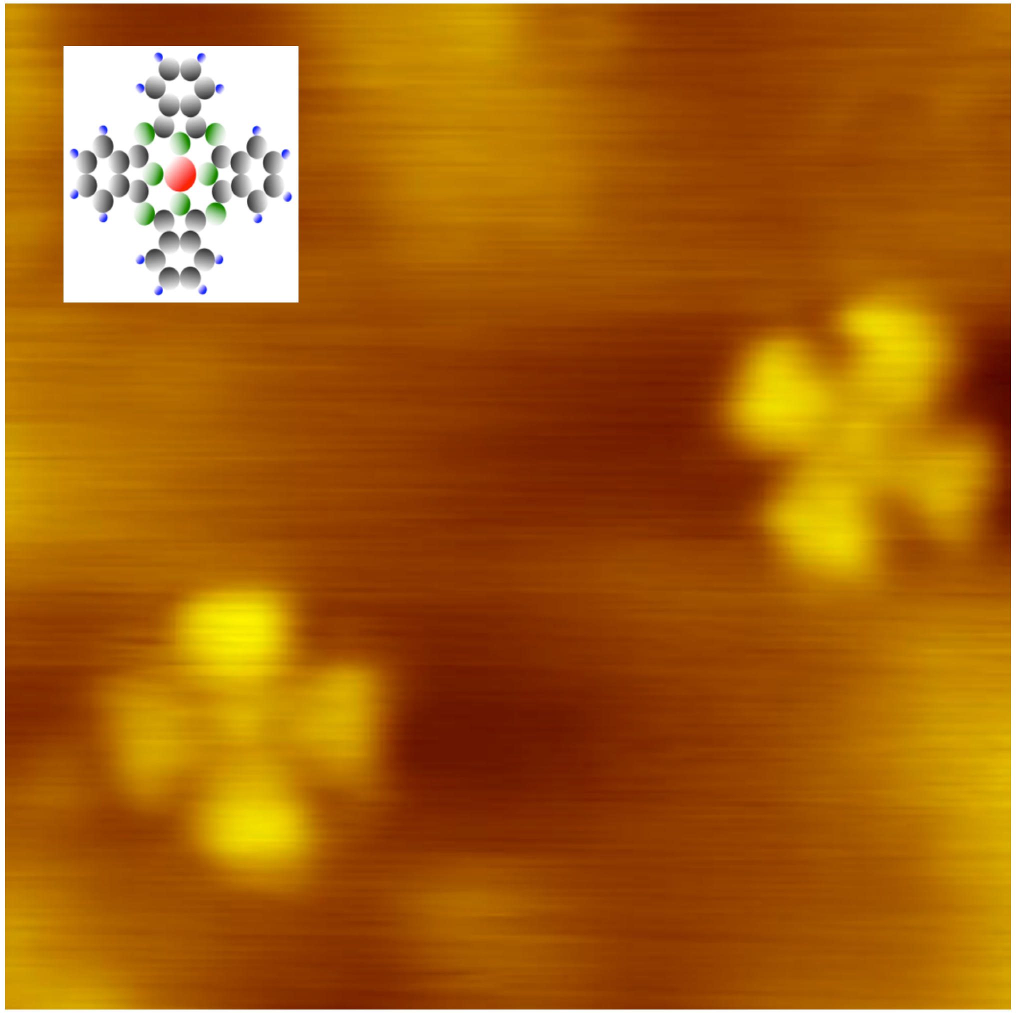

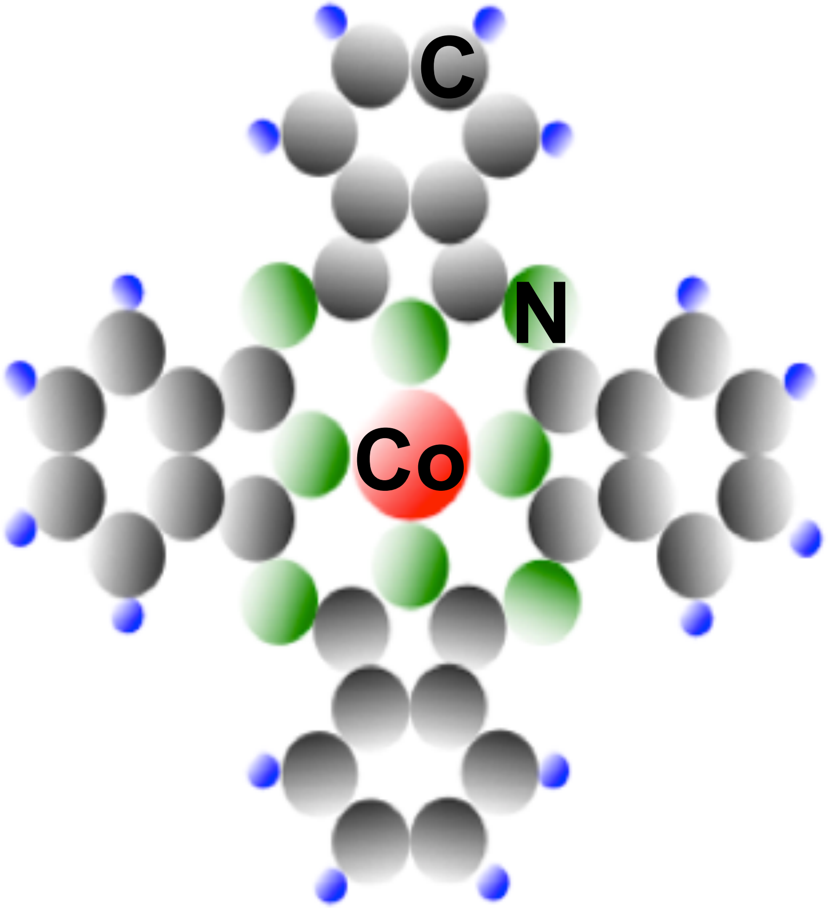

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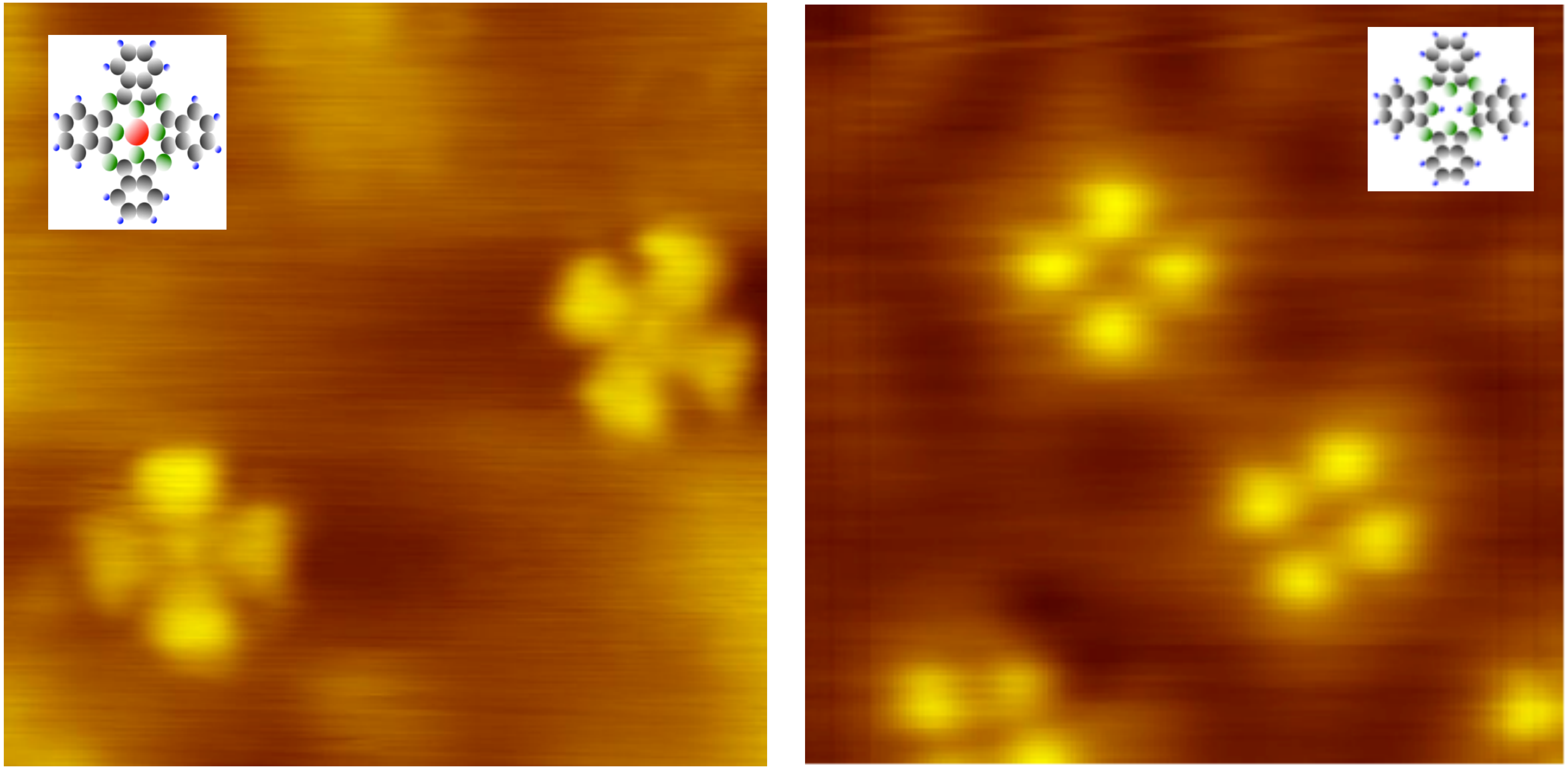
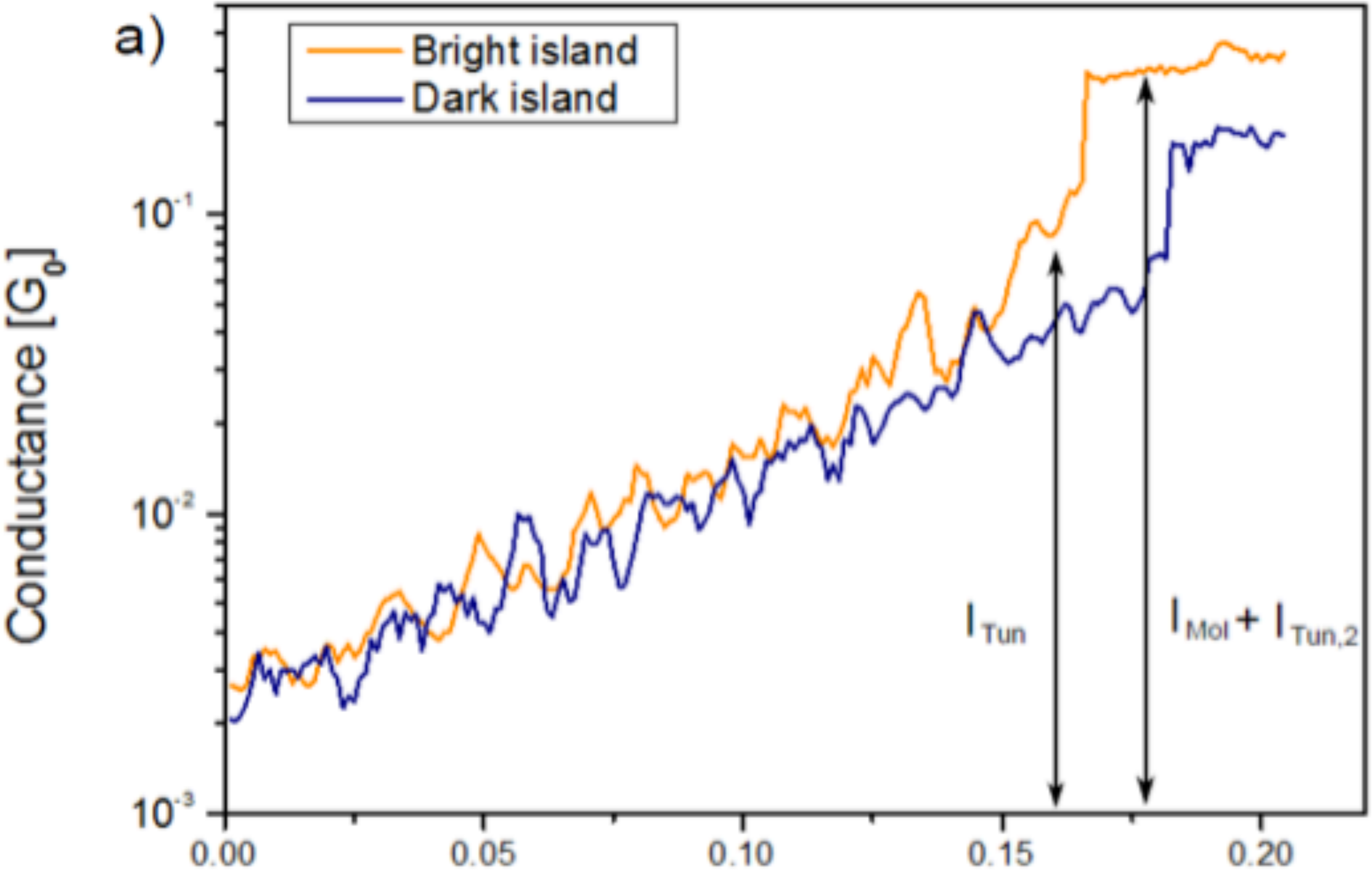


Spin-polarized low-T STM on Co(111)
(experiment: Schmaus & Wulfhekel, 2010)



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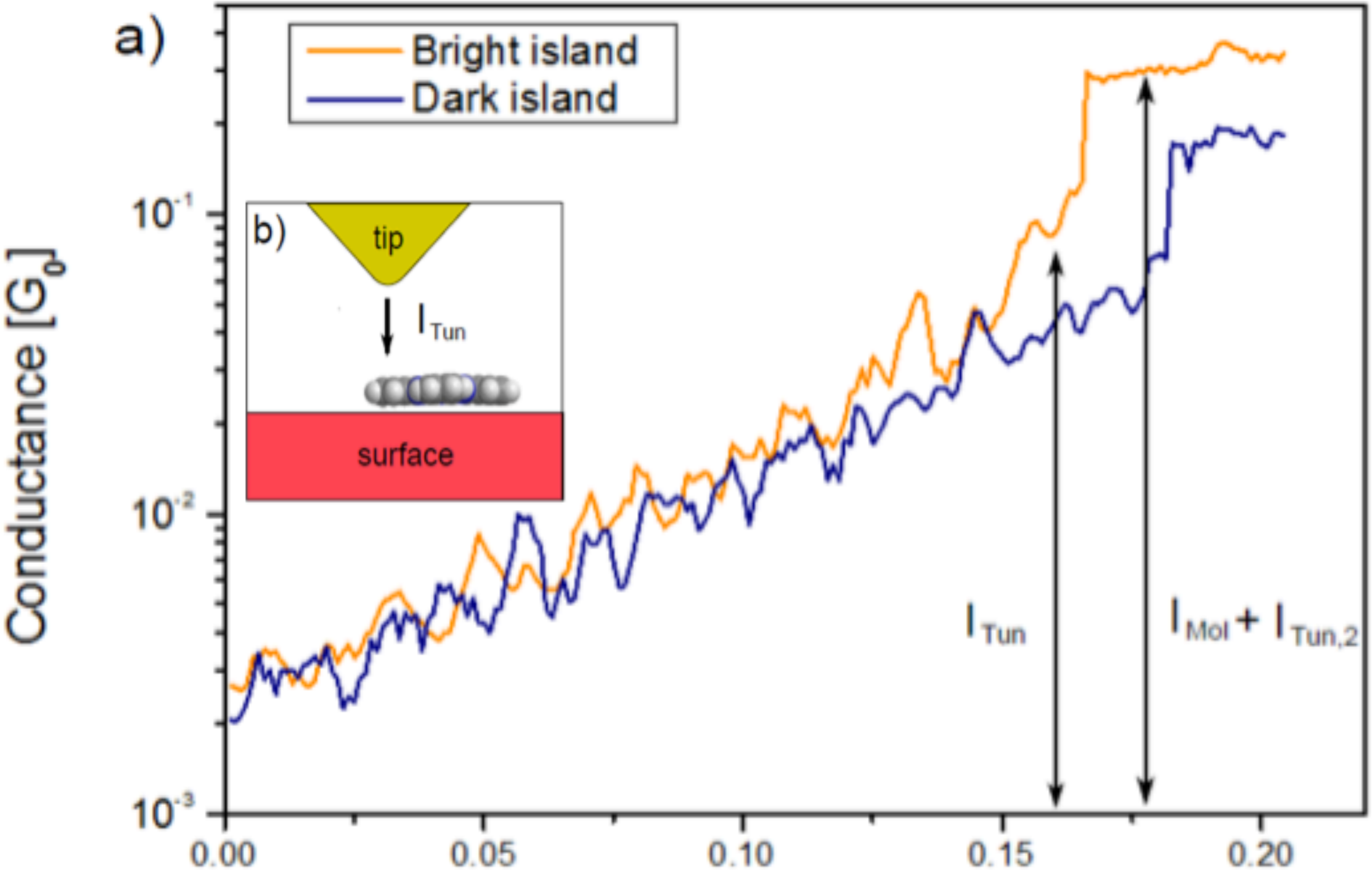

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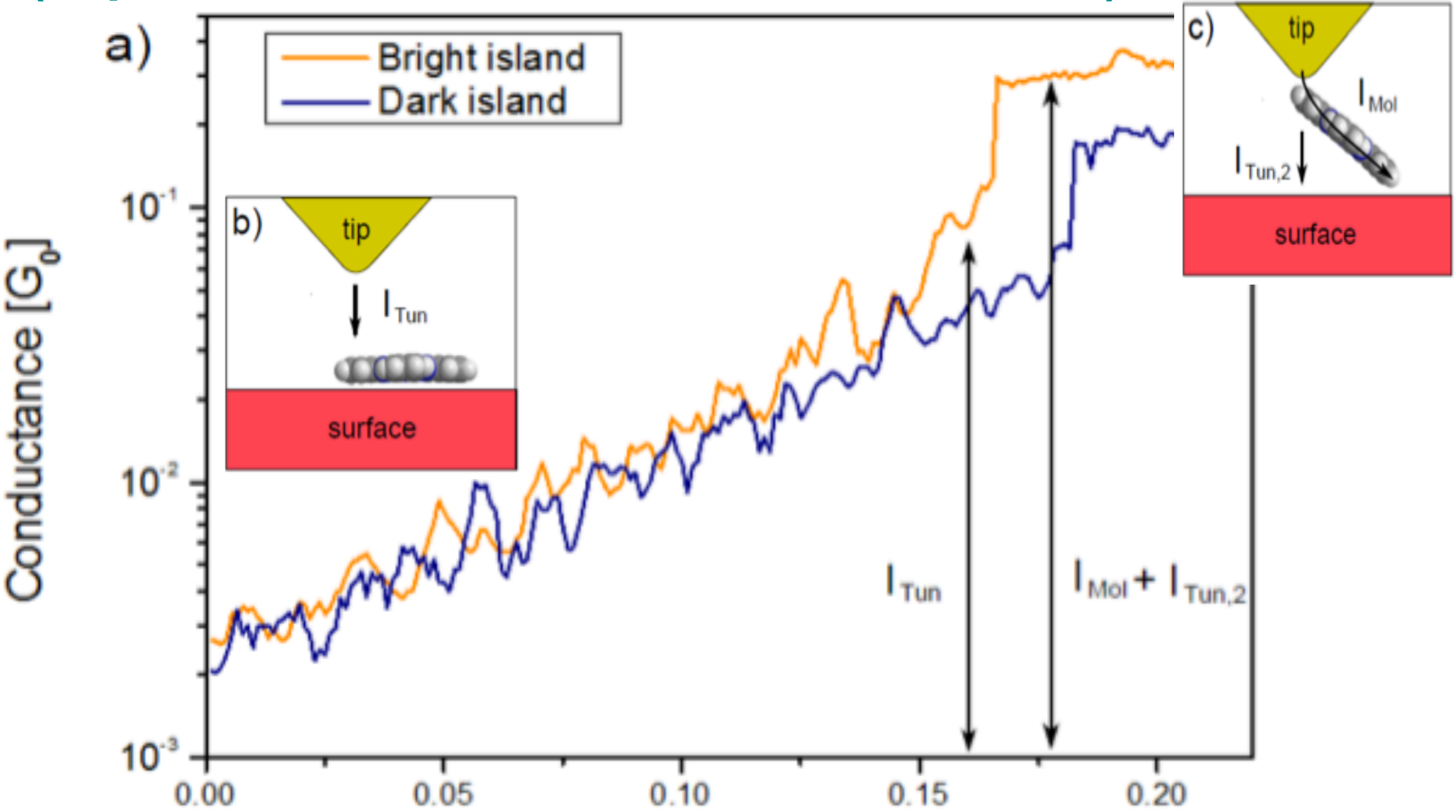

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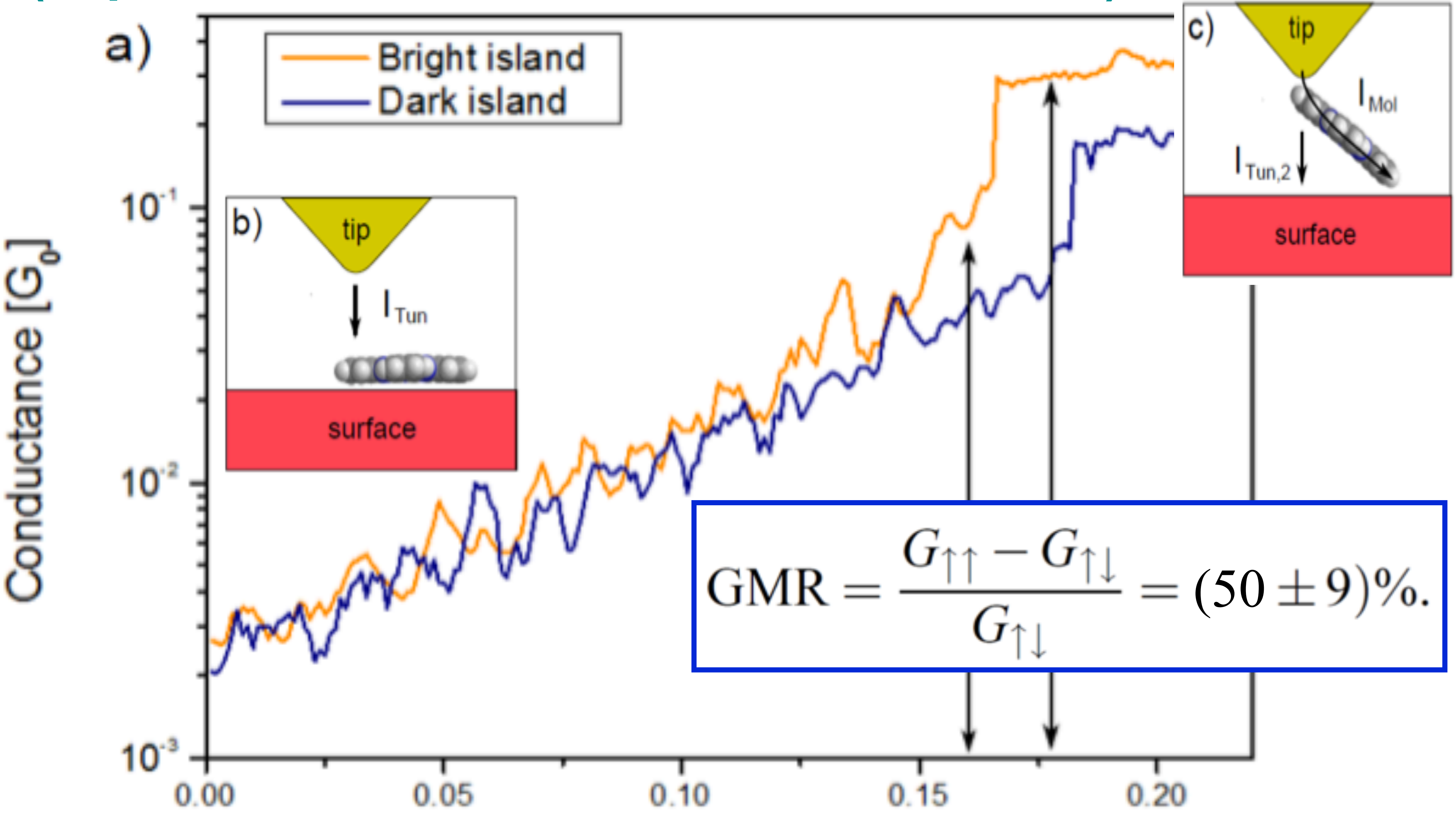
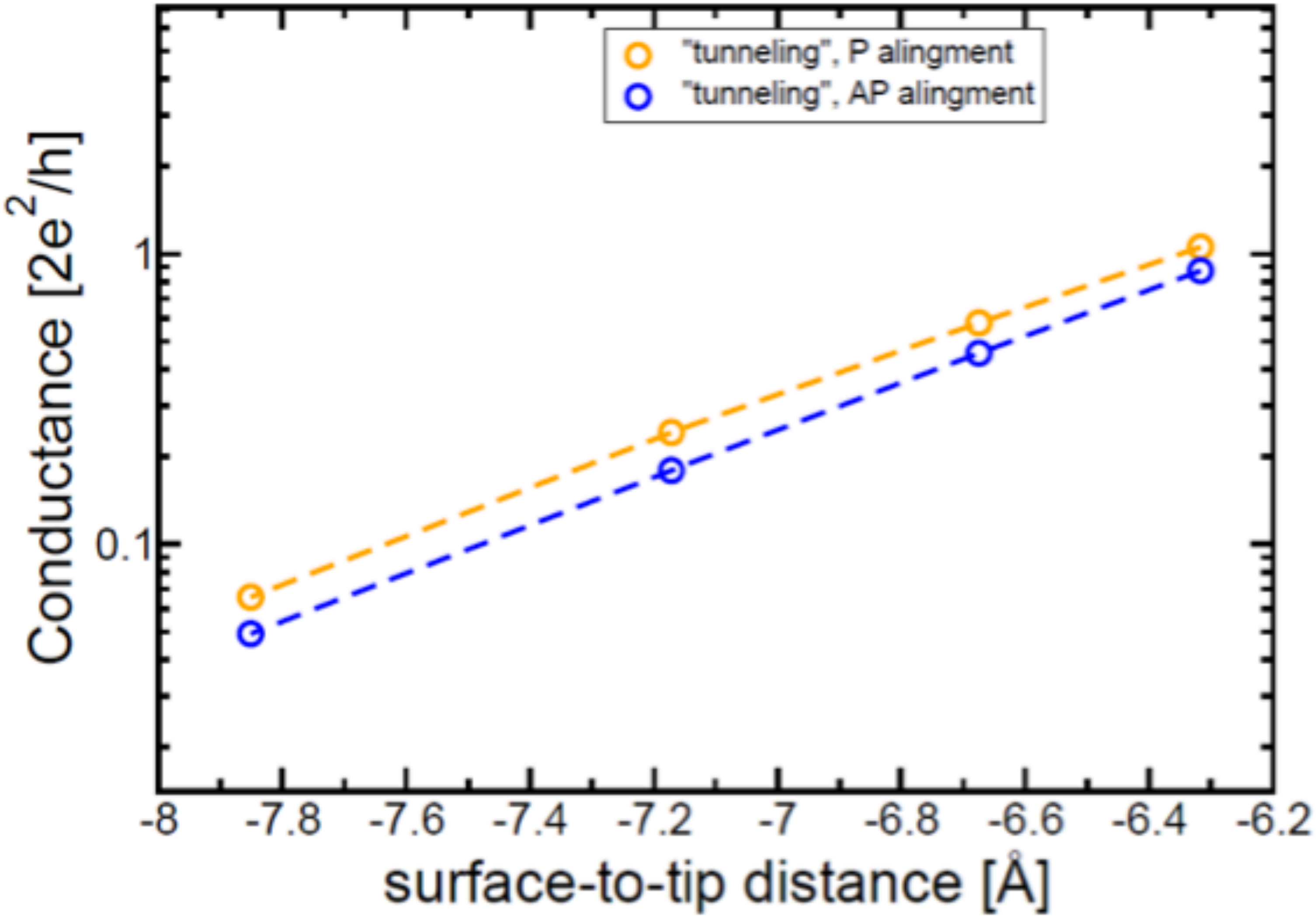
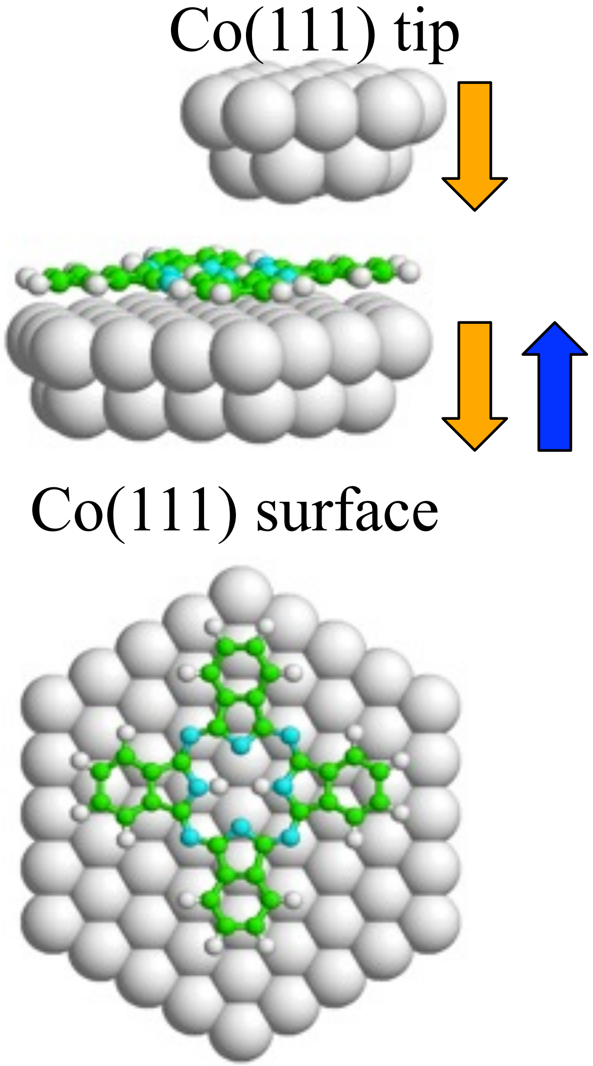


$$\mathrm{GMR} = \frac{G_{\uparrow\uparrow} - G_{\uparrow\downarrow}}{G_{\uparrow\downarrow}} = (50 \pm 9)\%.$$

Spin-polarized low-T STM on Co(111)
(SDFT-based transport theory: Bagrets & Evers, 2010)





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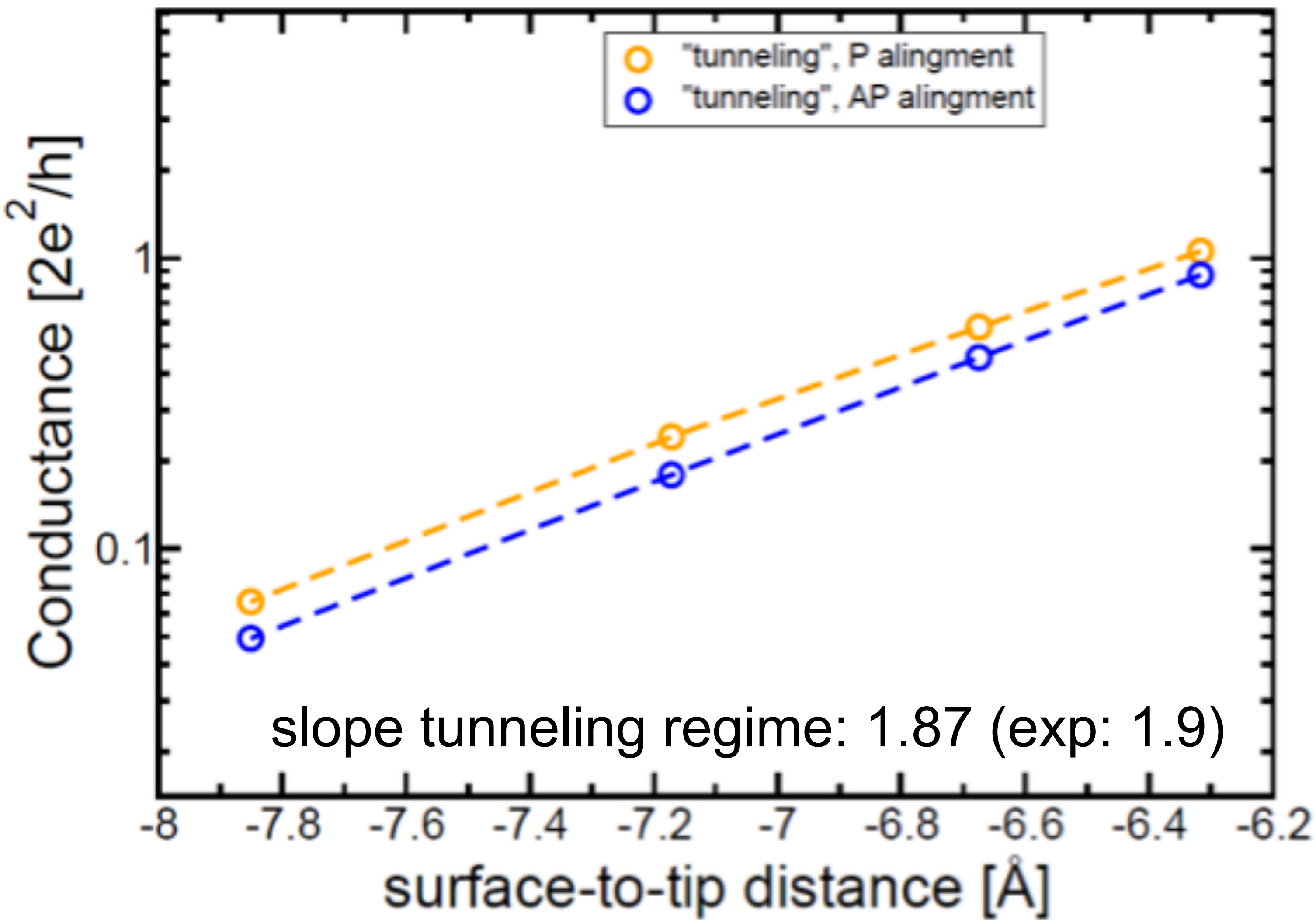
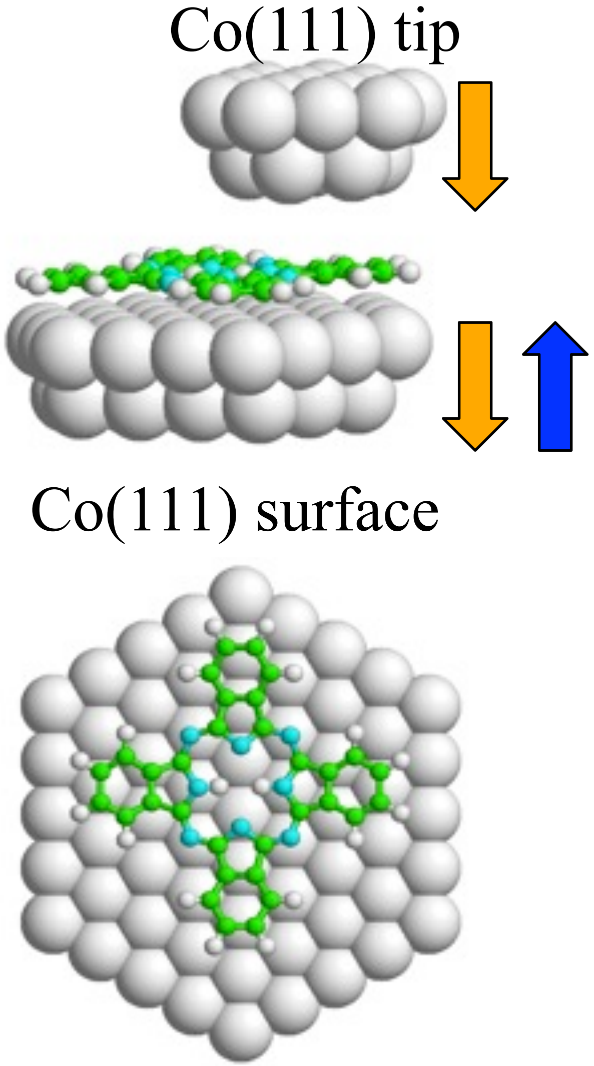


slope tunneling regime: 1.87 (exp: 1.9)



work function: W = 3.24 eV

Spin-polarized low-T STM on Co(111)
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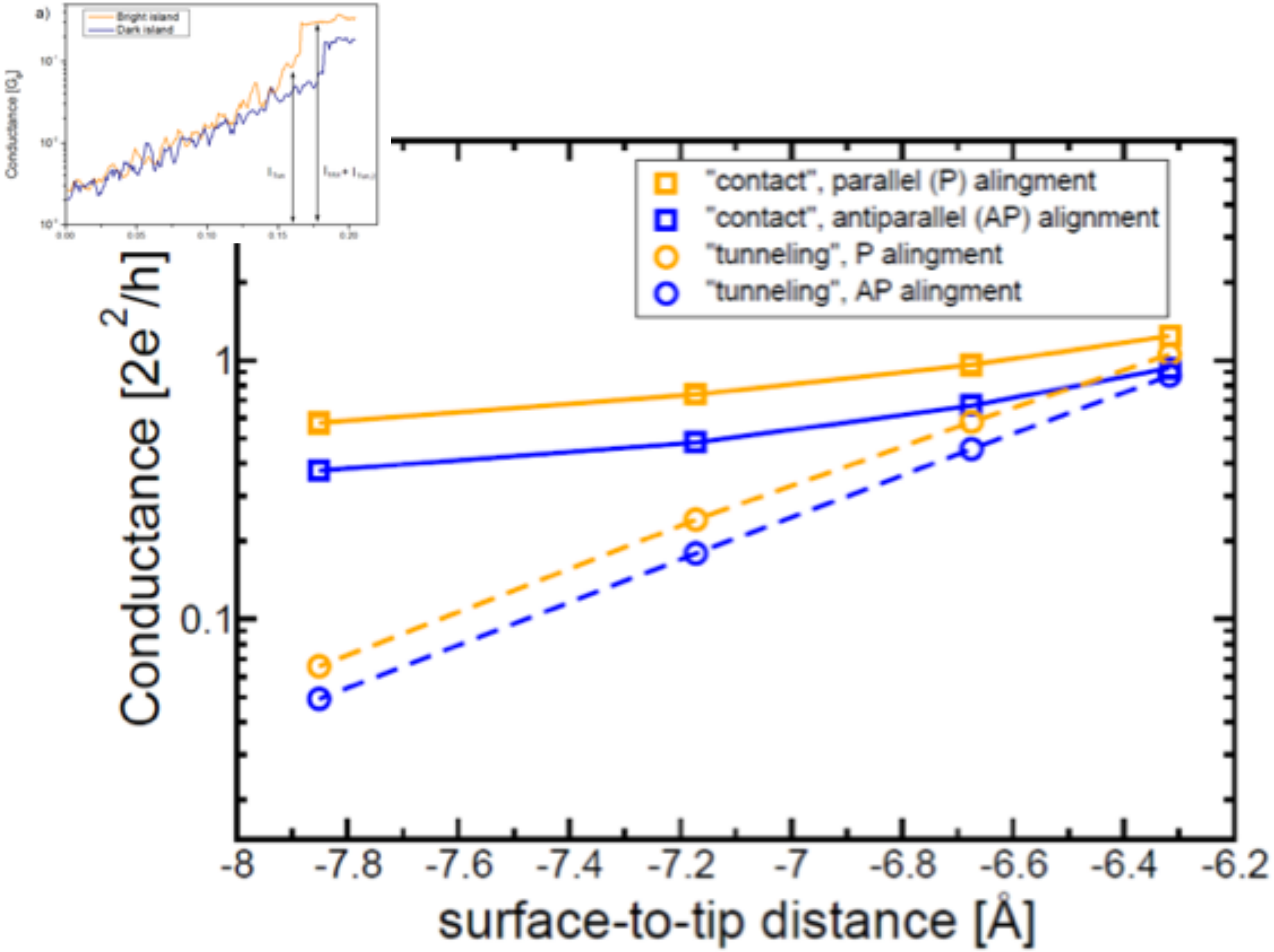

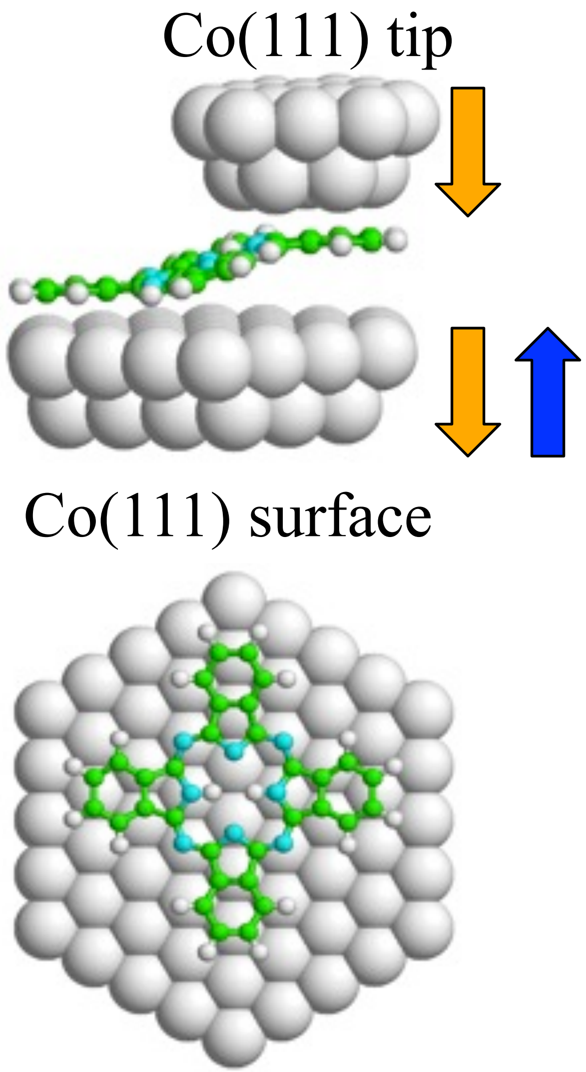

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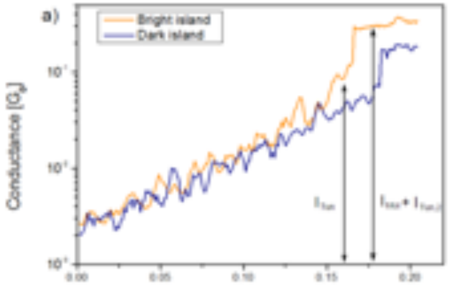
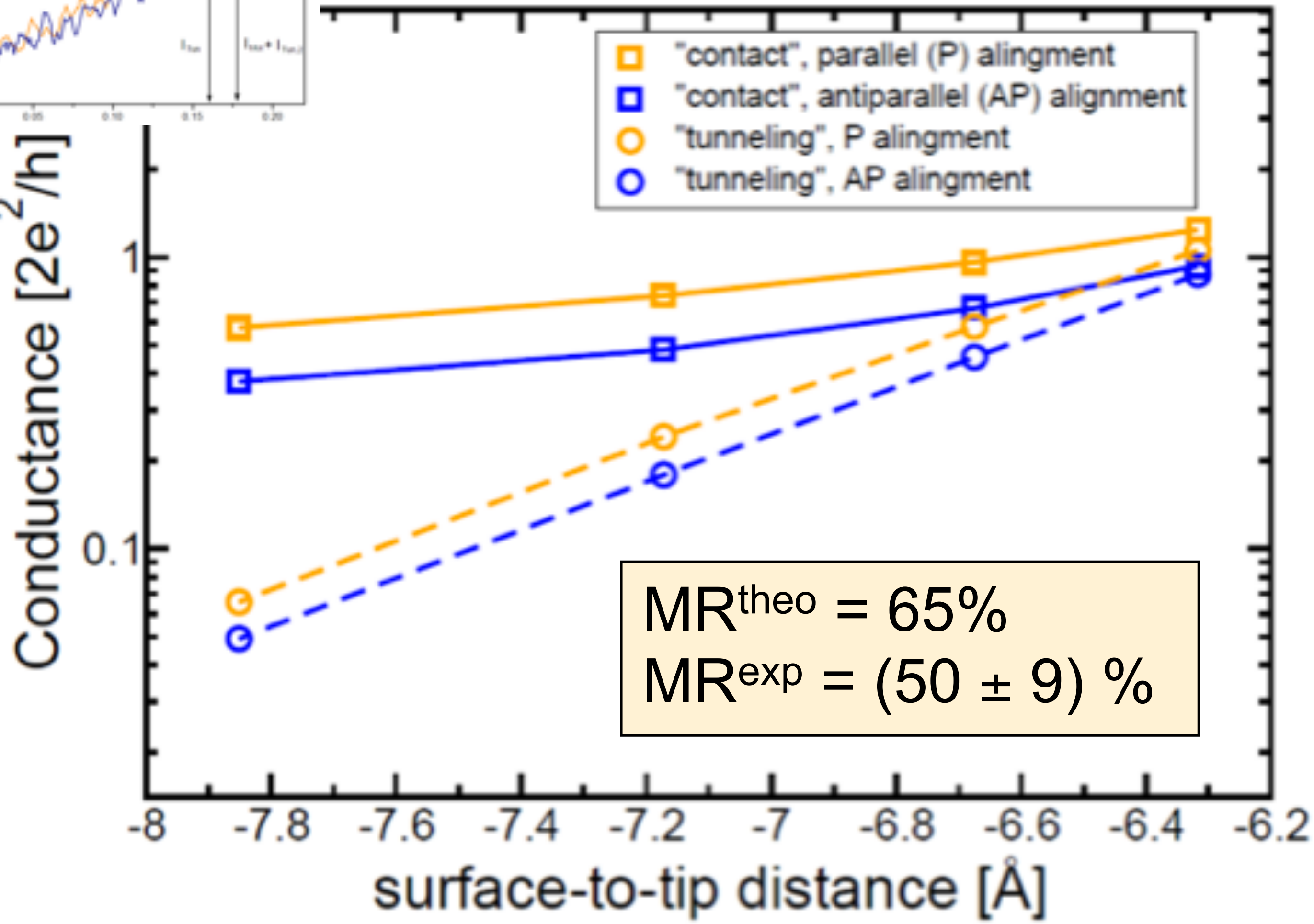
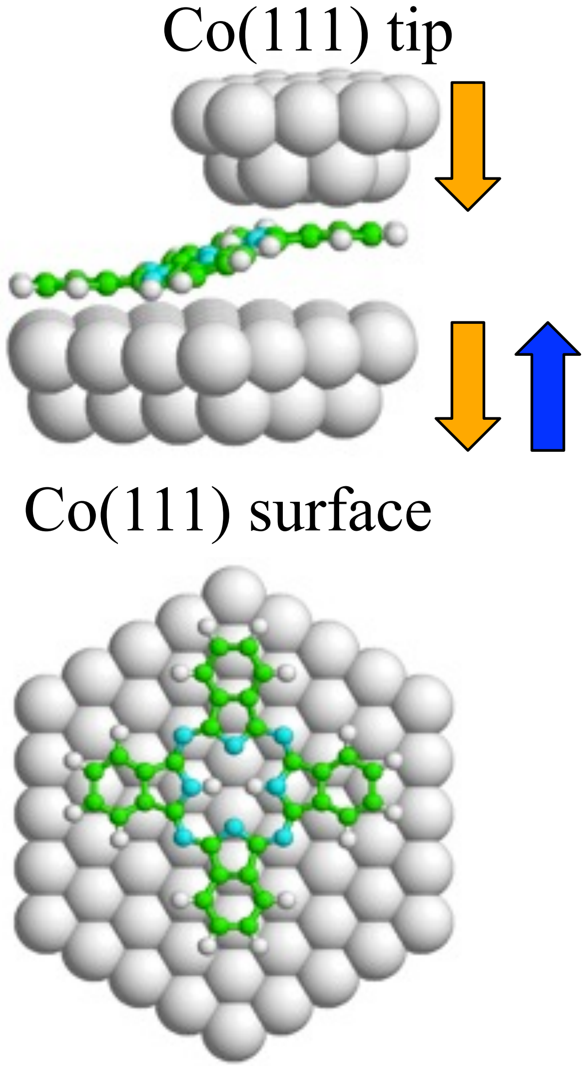
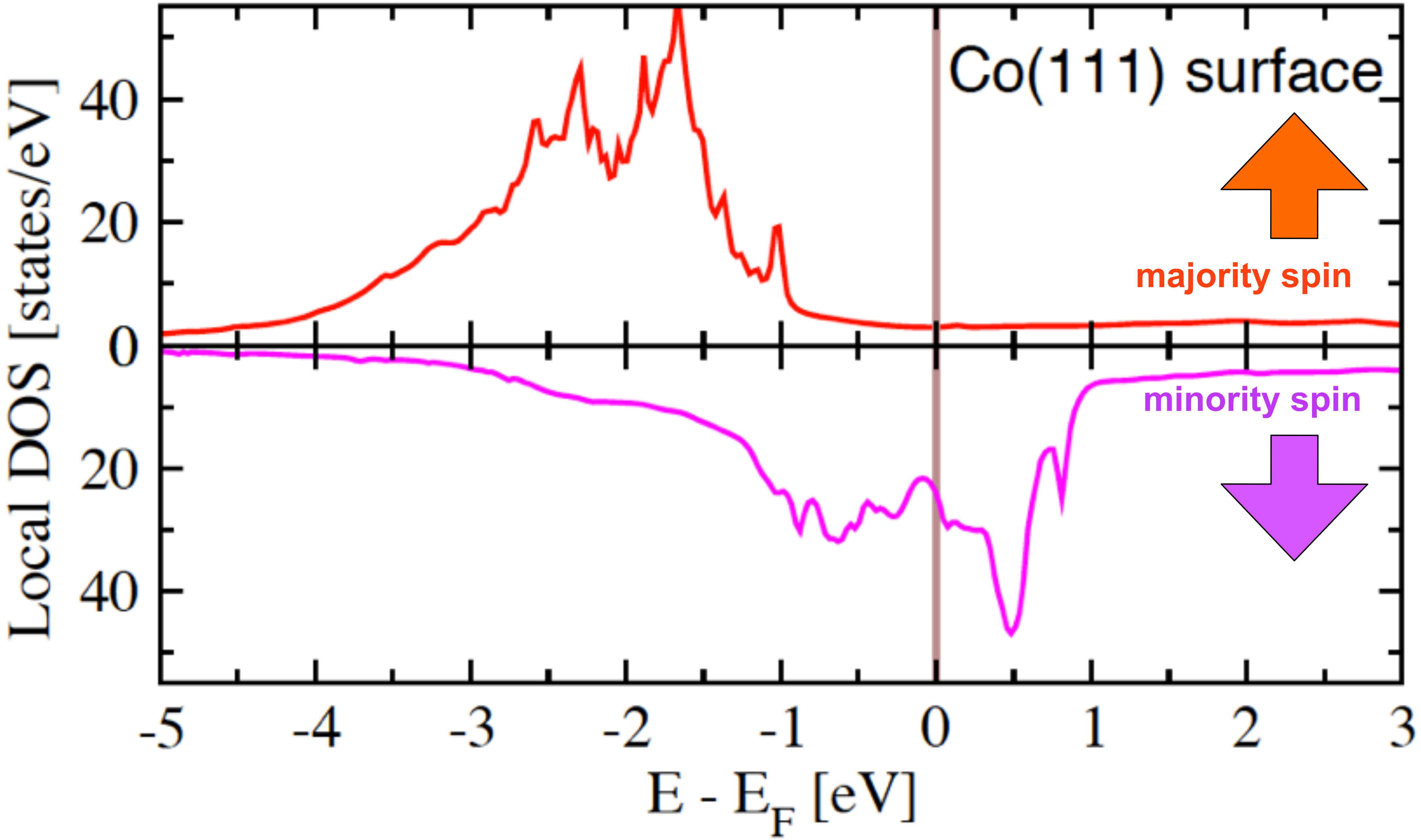






Theory: LDoS at Co-surface
(spin-DFT-transport & Turbomole: A. Bagrets & FE, 2010)



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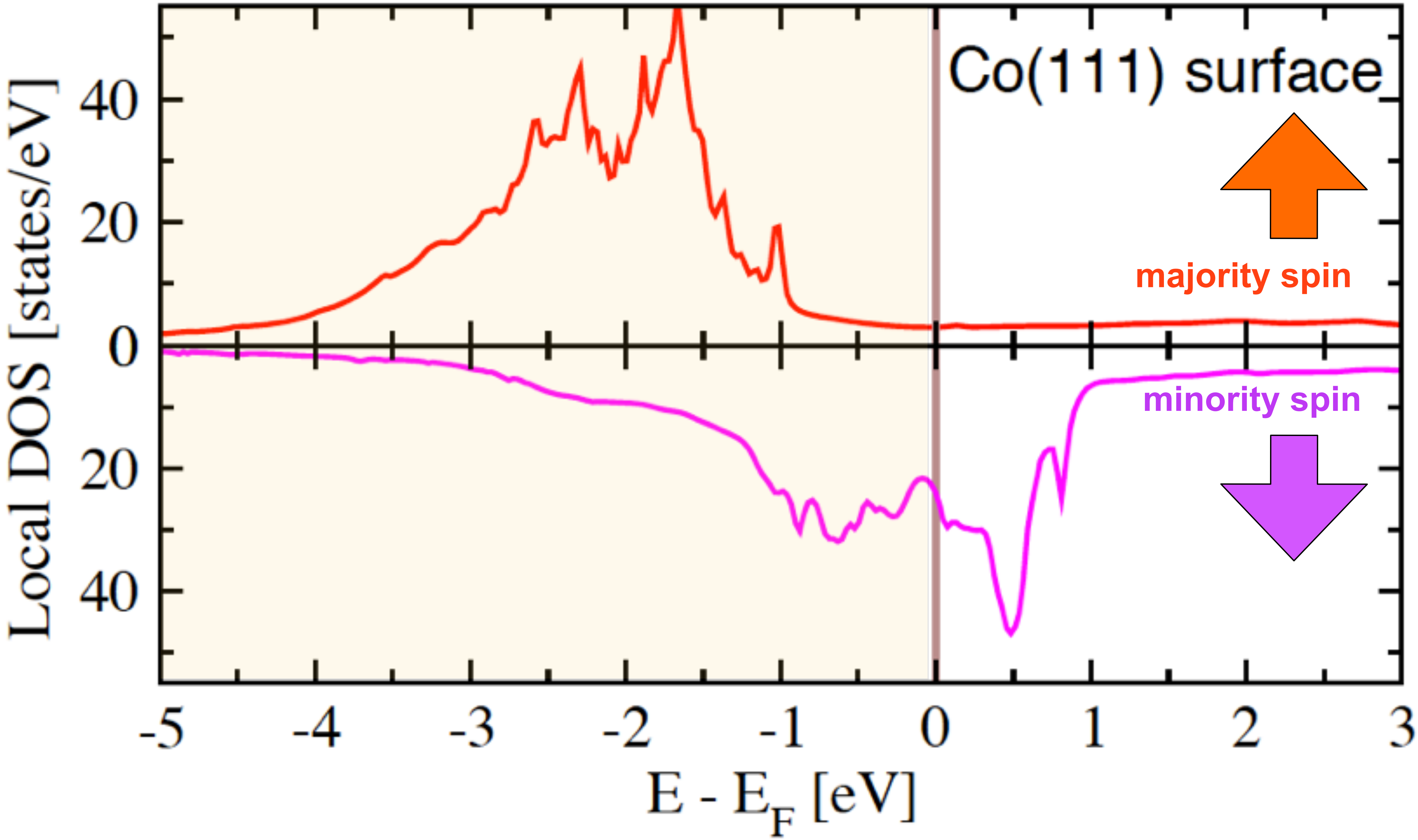

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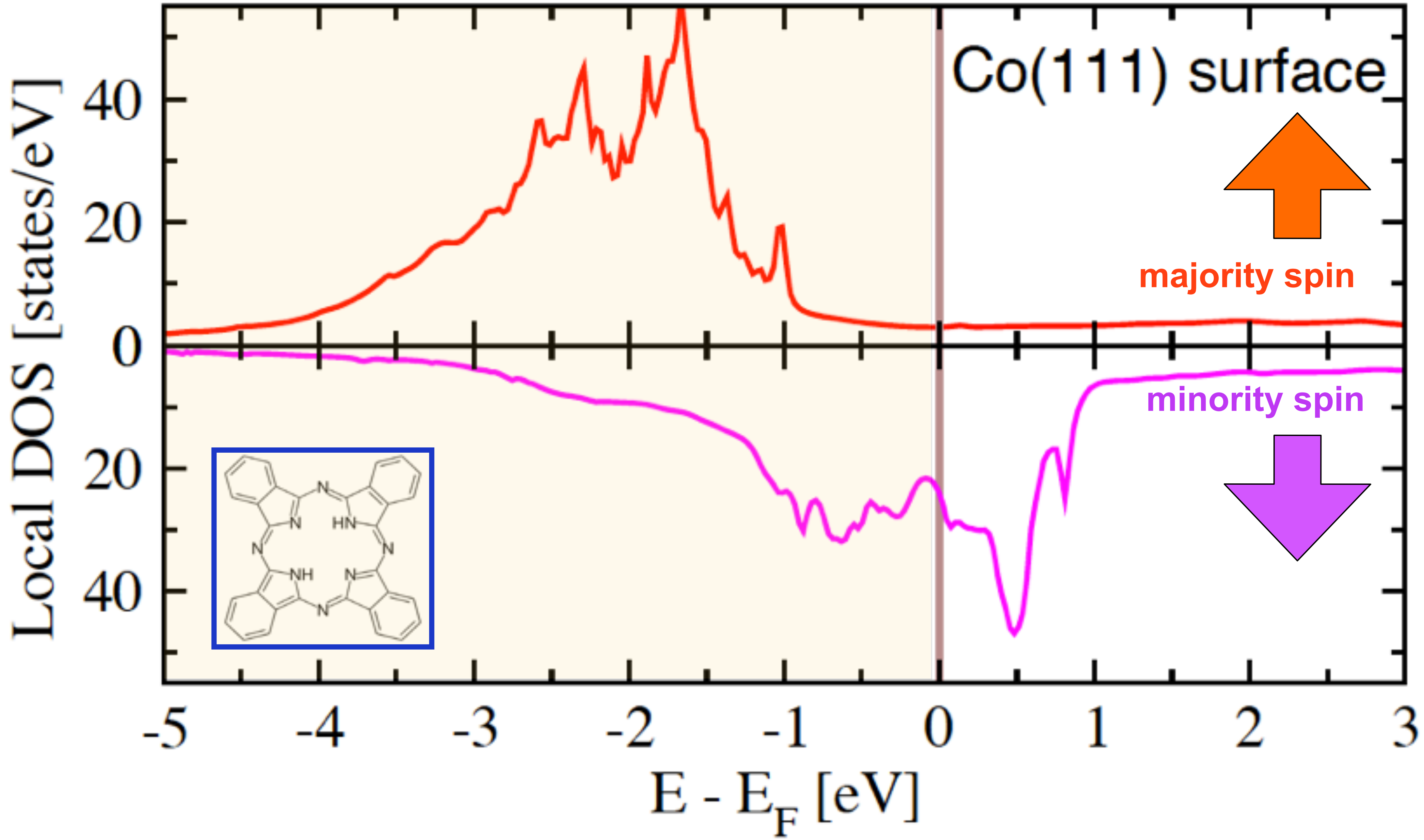

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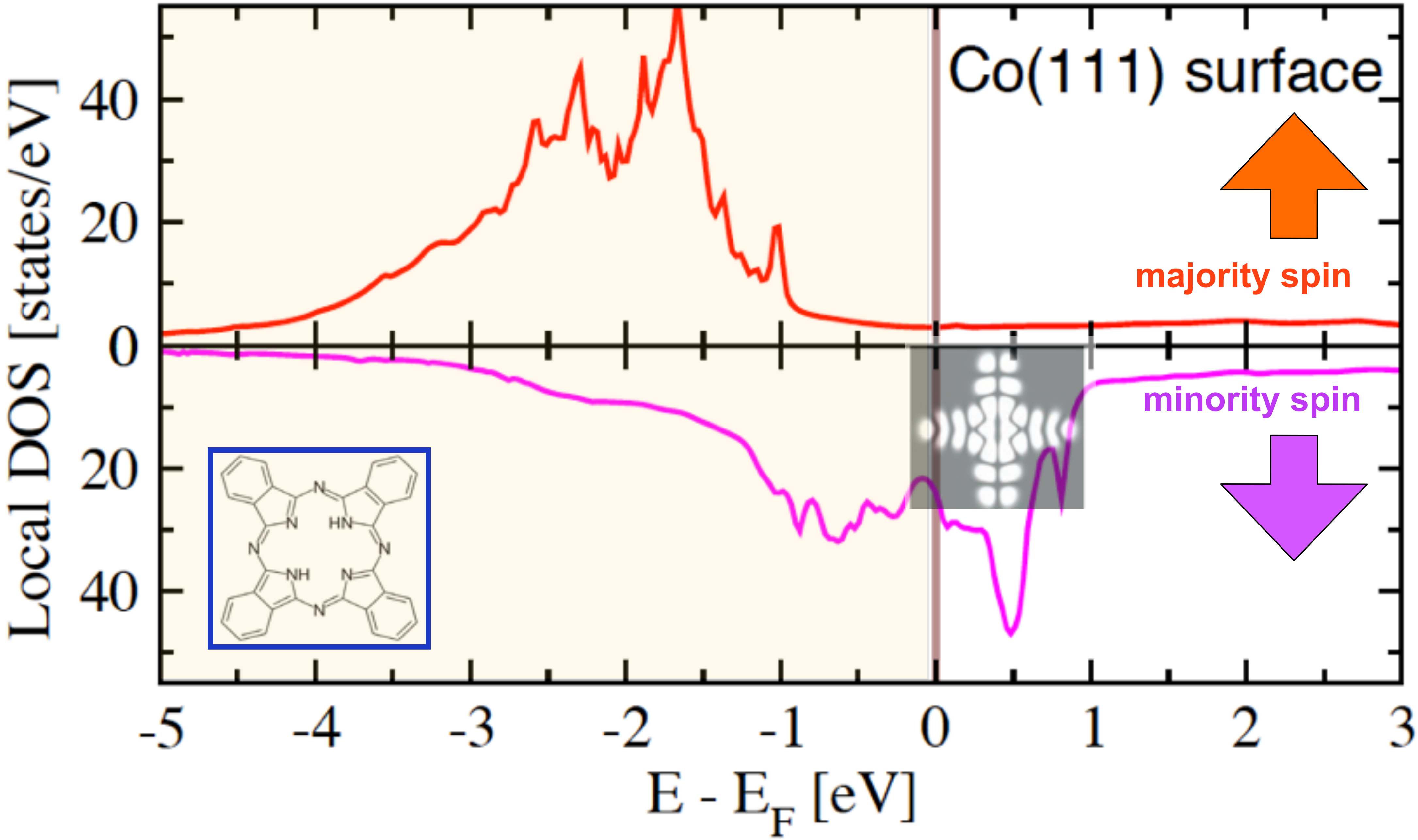
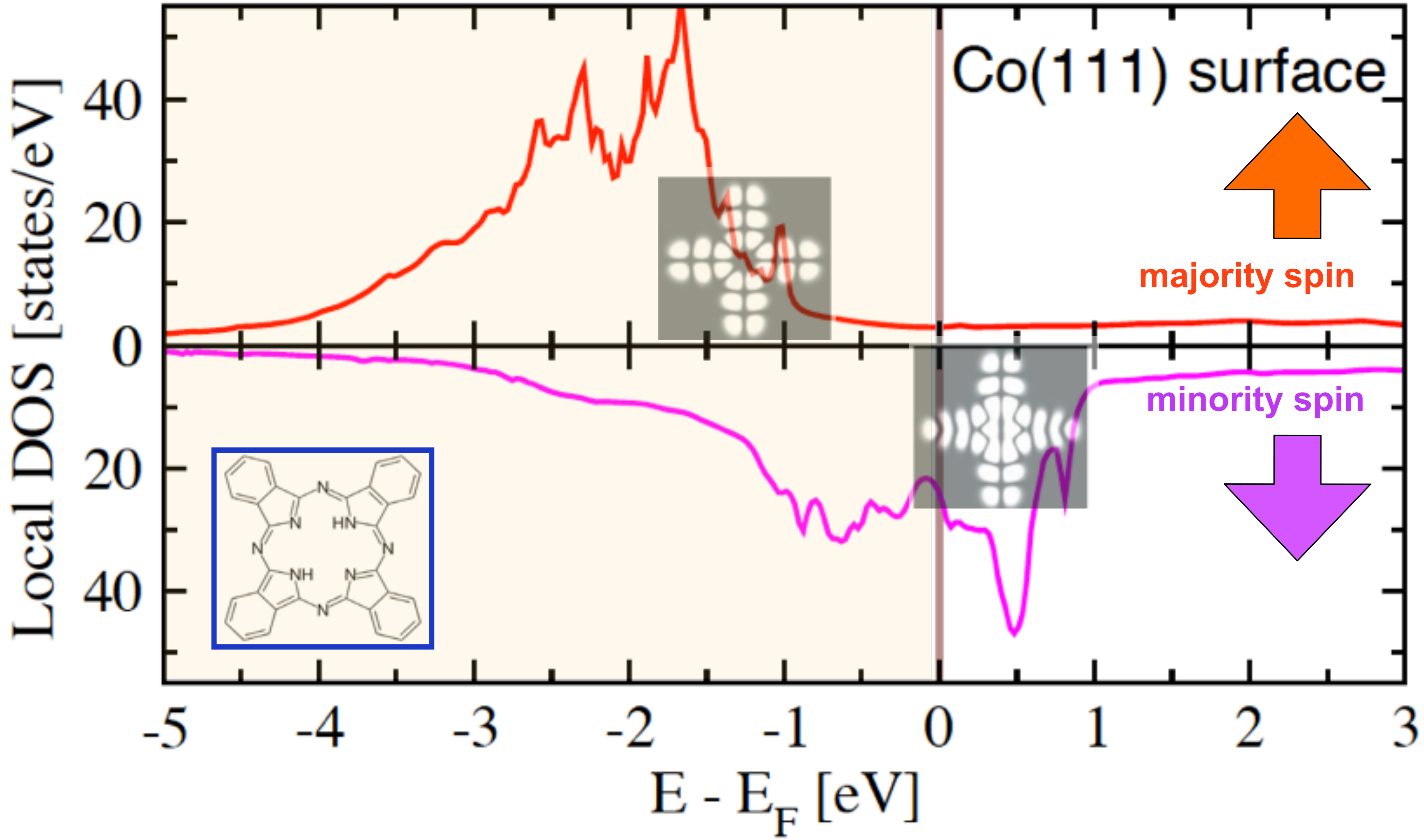
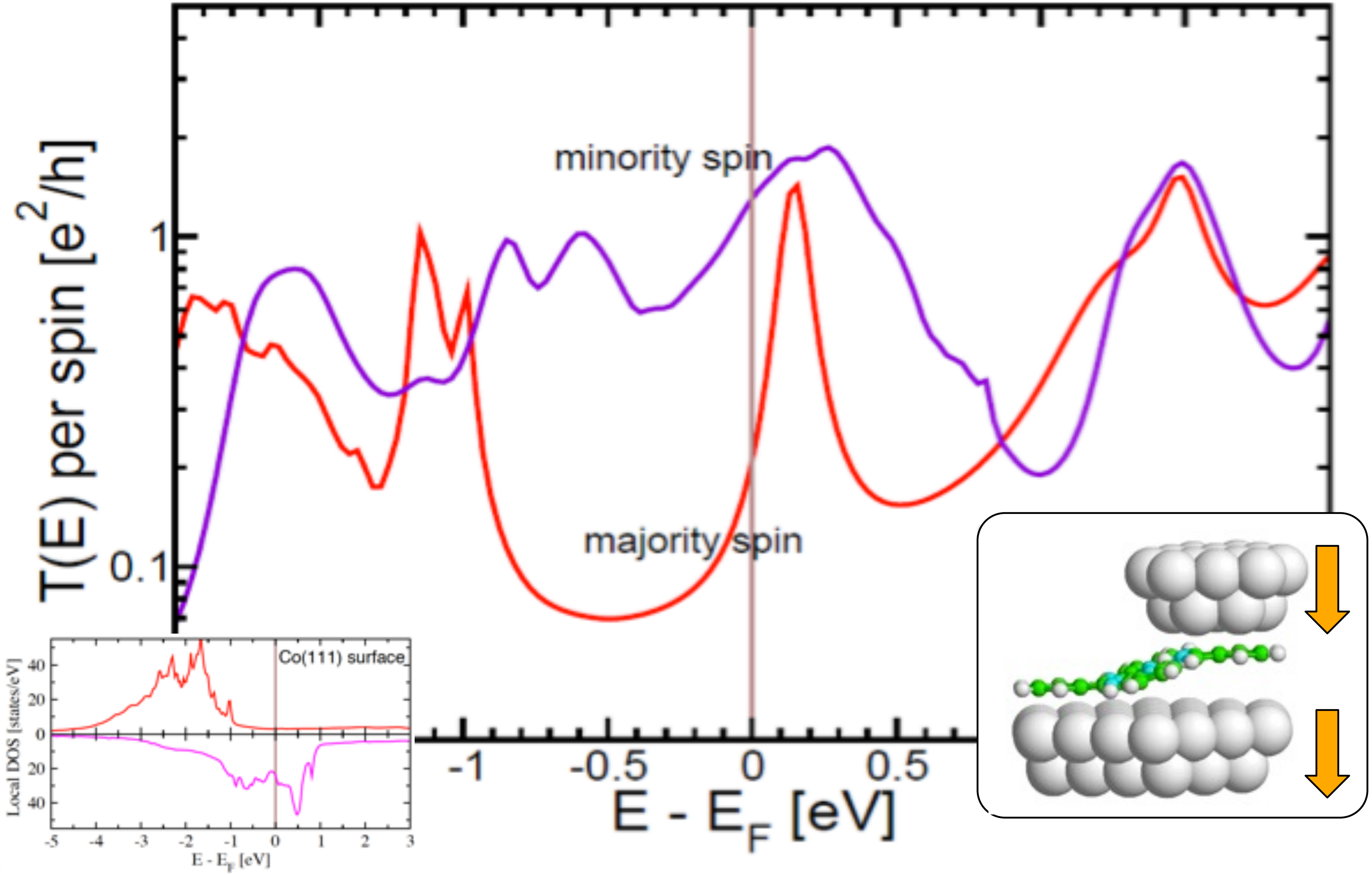


Theory: LDoS at Co-surface
(spin-DFT-transport & Turbomole: A. Bagrets & FE, 2010)



LUMO based transport resonance
(spin-DFT-transport & Turbomole: A. Bagrets & FE, 2010)



LUMO based transport resonance
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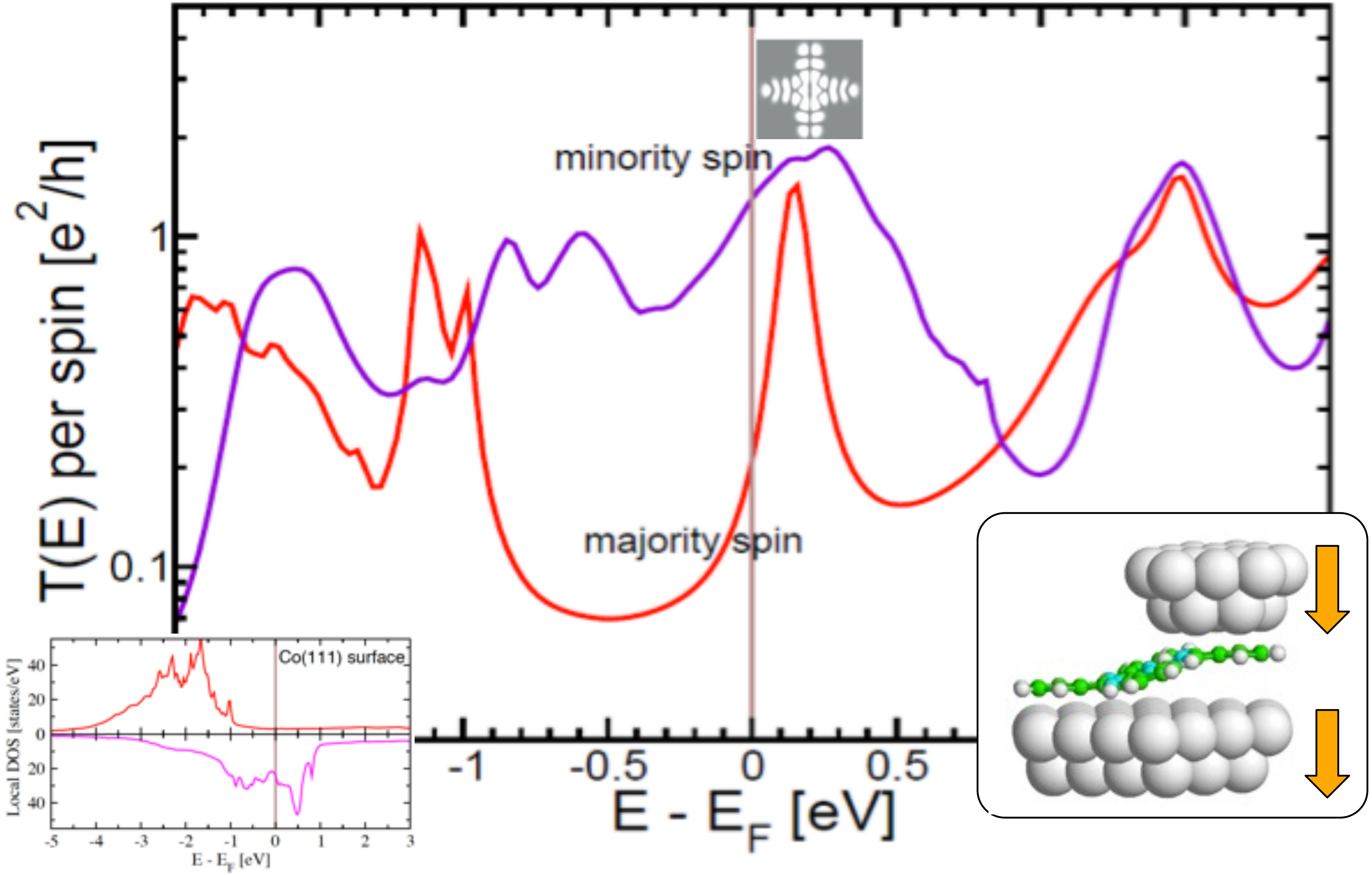

LUMO based transport resonance
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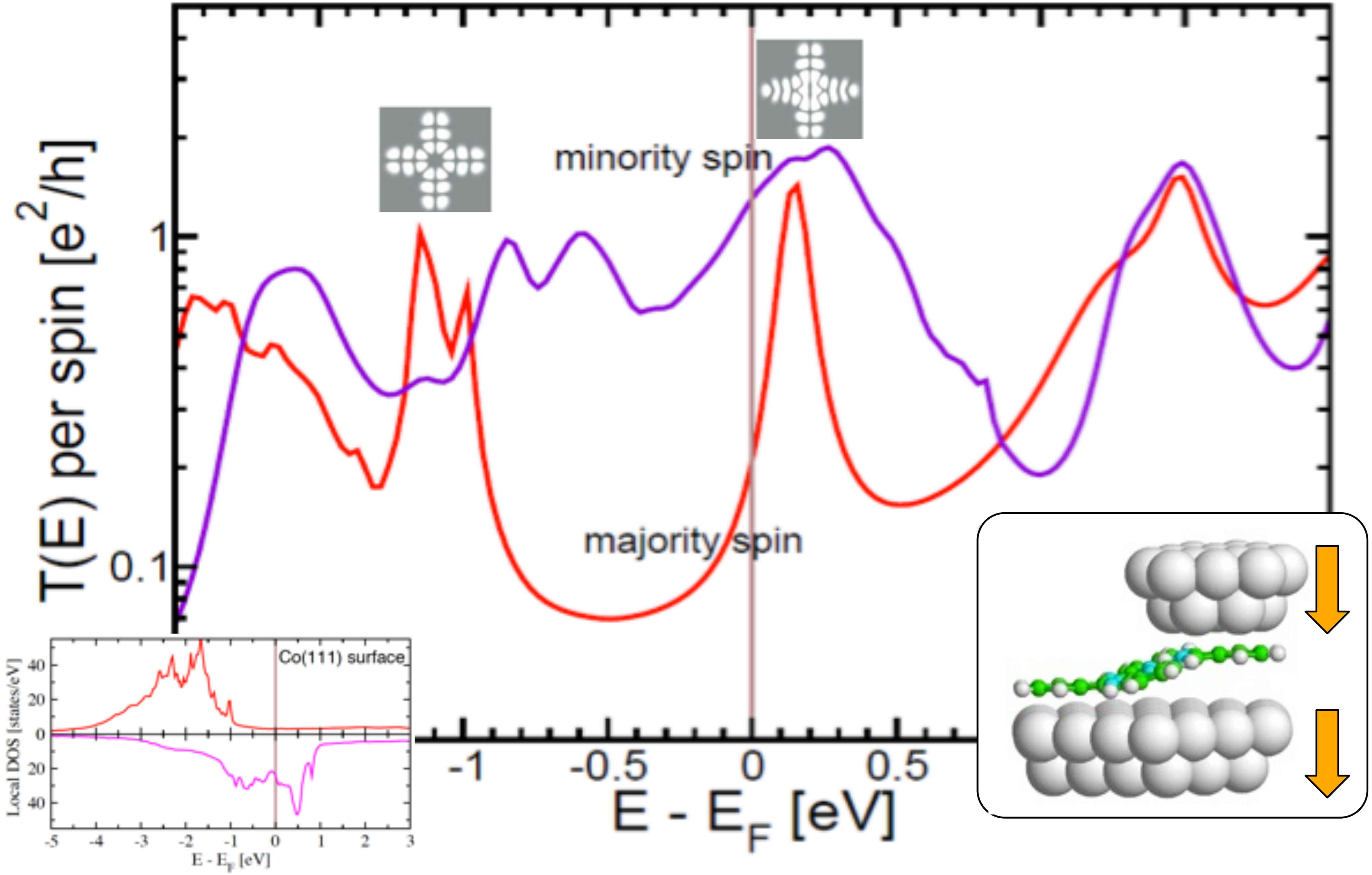

LUMO based transport resonance
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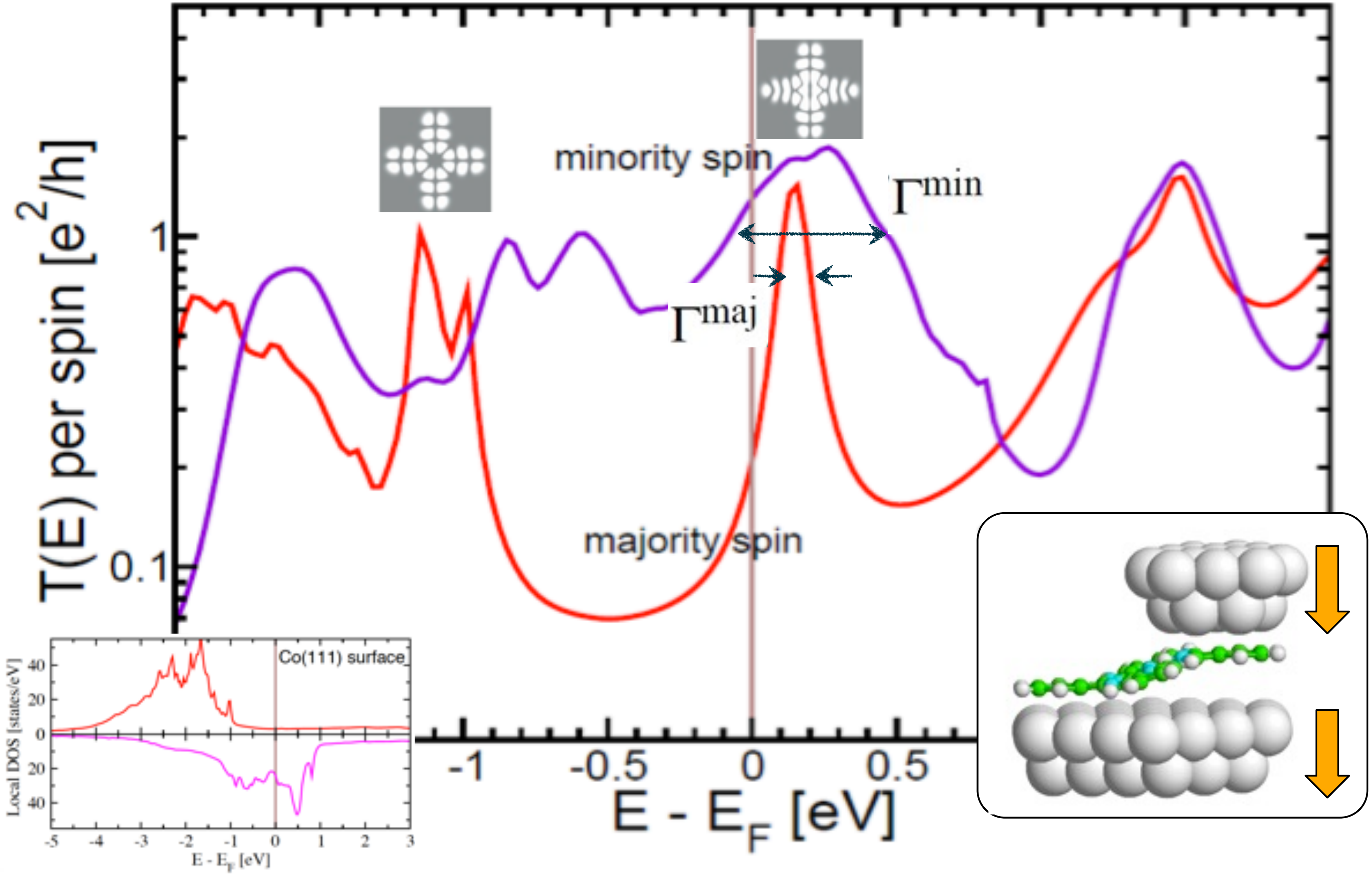
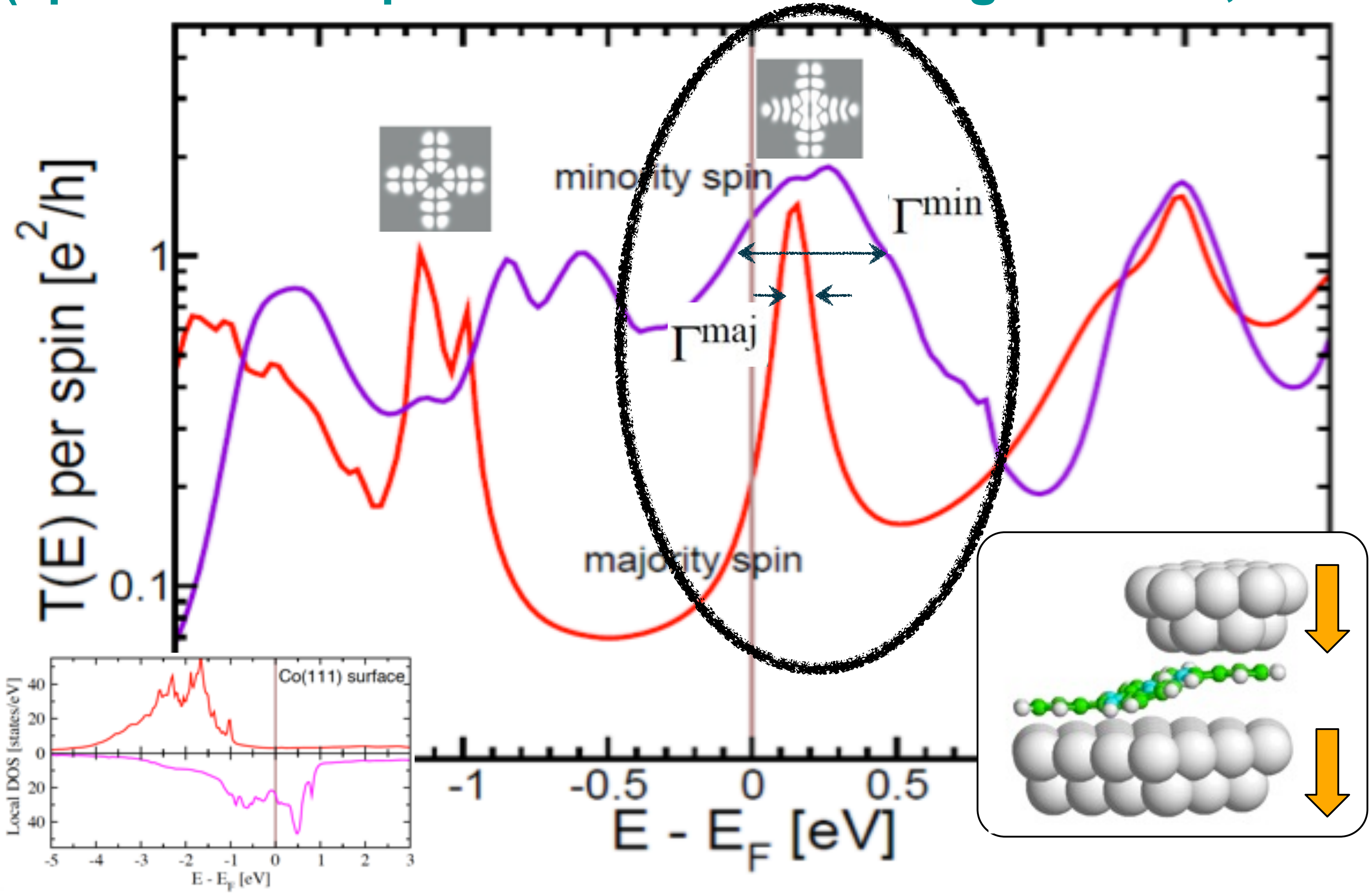
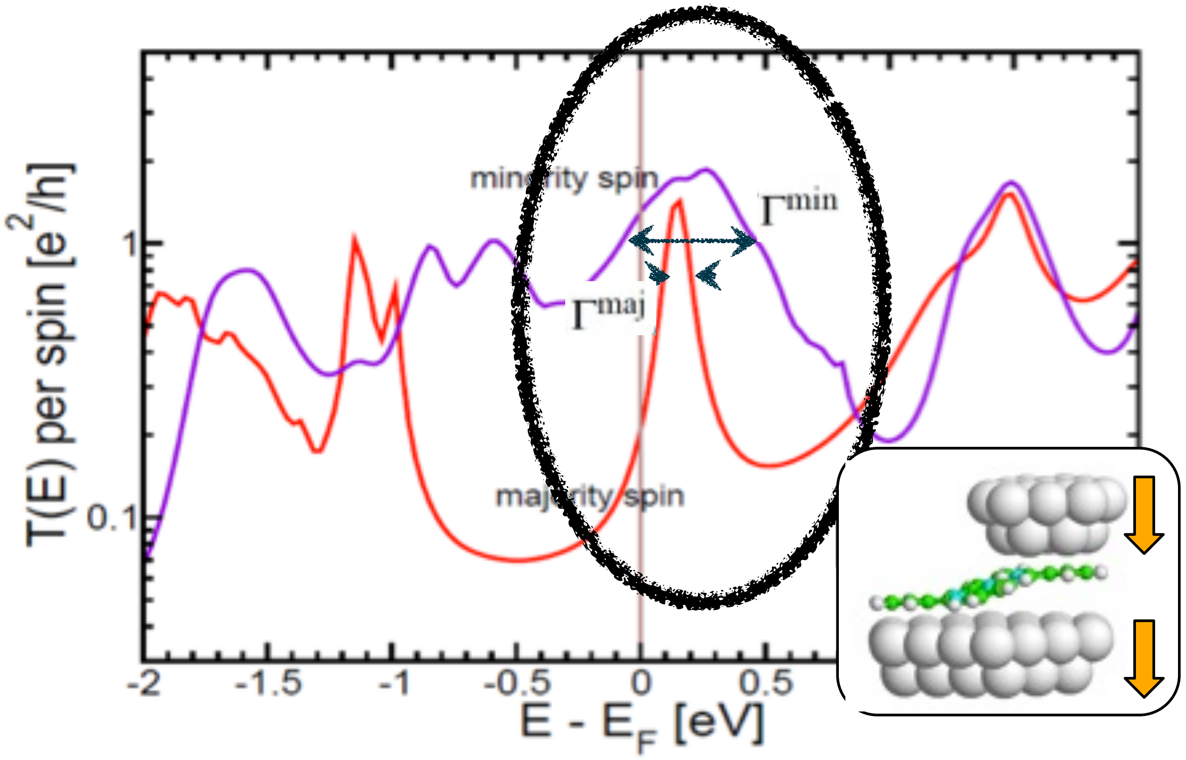


LUMO based transport resonance
(spin-DFT-transport & Turbomole: A. Bagrets & FE, 2010)

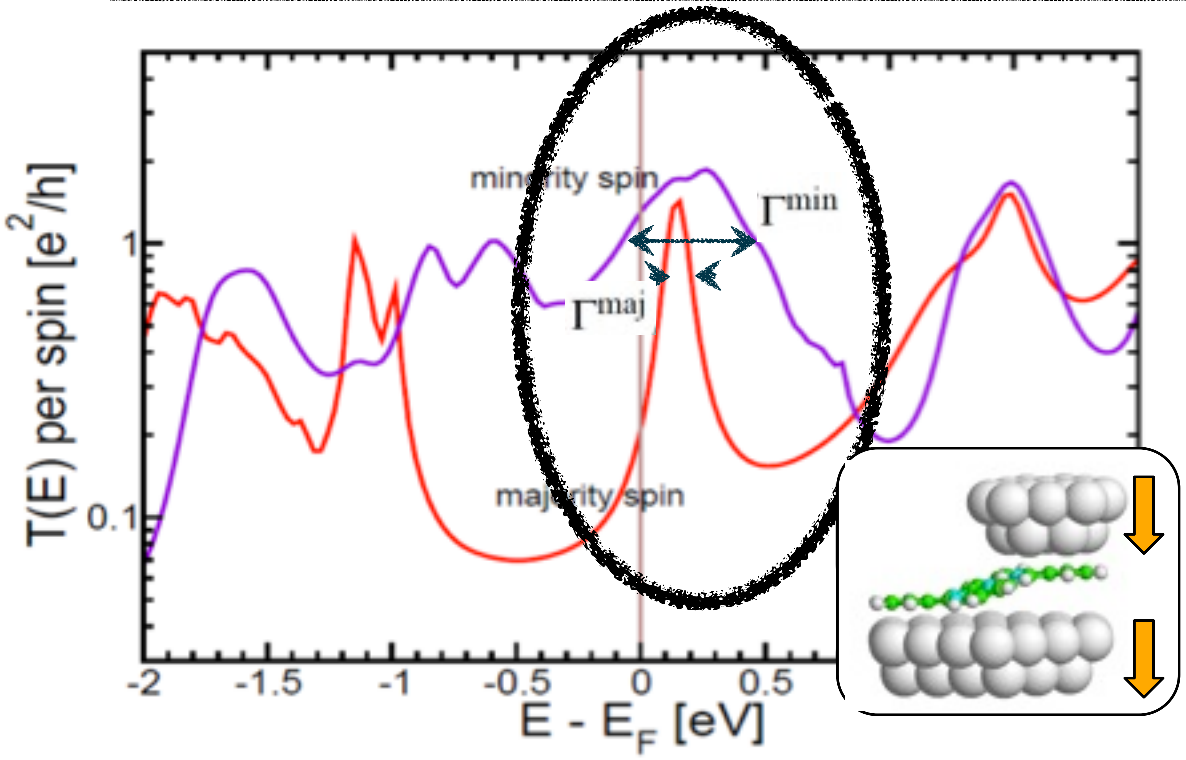


Origin of large GMR
(spin-DFT-transport & Turbomole: A. Bagrets & FE, 2010)



Origin of large GMR
(spin-DFT-transport & Turbomole: A. Bagrets & FE, 2010)

$$\boxed{T(E) = \frac{\Gamma_{\text{substrate}}\Gamma_{\text{tip}}}{(E - E_{\text{LUMO}})^2 - (\Gamma_{\text{substrate}} + \Gamma_{\text{tip}})^2/4}}$$



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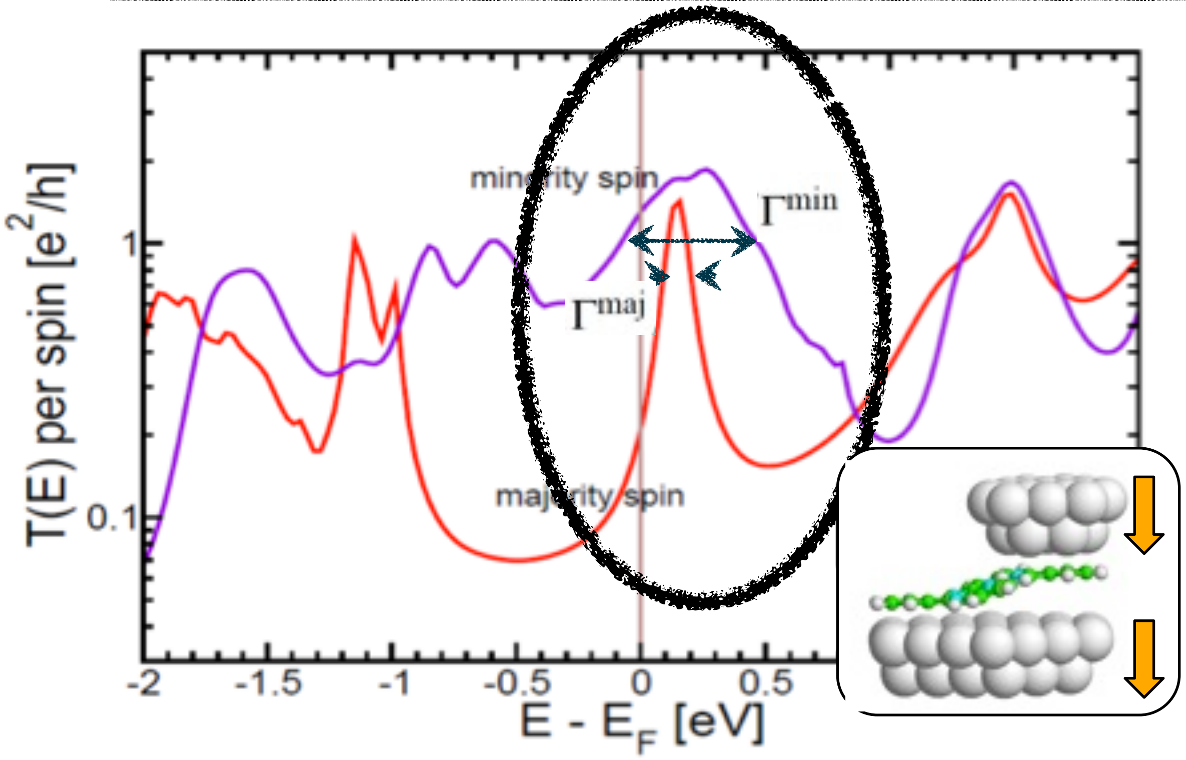
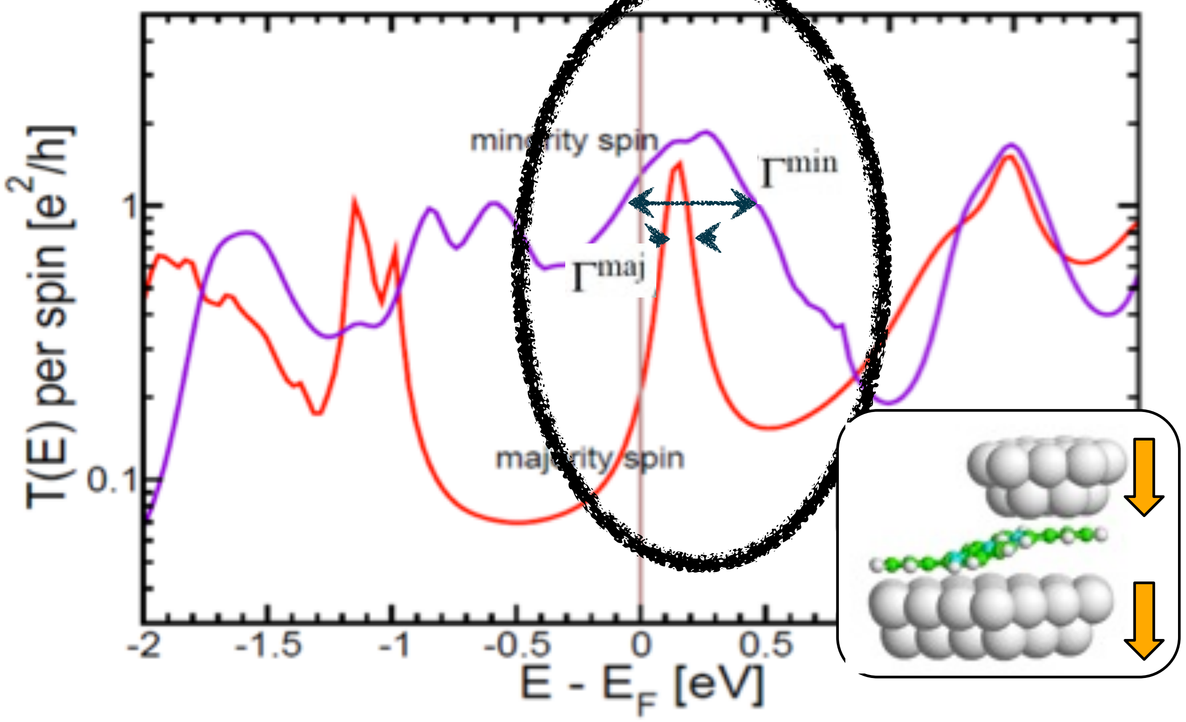
$$T(E) = \frac{\Gamma_{\text{substrate}}\Gamma_{\text{tip}}}{(E - E_{\text{LUMO}})^2 - (\Gamma_{\text{substrate}} + \Gamma_{\text{tip}})^2/4}$$



	↑↑	↓↓	↑↓	↓↑
$\Gamma_{\text{substrate}}$	Γ^{maj}	Γ^{min}	Γ^{maj}	Γ^{min}
Γ_{tip}	Γ^{maj}	Γ^{min}	Γ^{min}	Γ^{maj}

Origin of large GMR
(spin-DFT-transport & Turbomole: A. Bagrets & FE, 2010)

$$\boxed{T(E) = \frac{\Gamma_{\mathrm{substrate}}\Gamma_{\mathrm{tip}}}{(E - E_{\mathrm{LUMO}})^2 - (\Gamma_{\mathrm{substrate}} + \Gamma_{\mathrm{tip}})^2/4}}$$



	$\uparrow\uparrow$	$\downarrow\downarrow$	$\uparrow\downarrow$	$\downarrow\uparrow$
$\Gamma_{\mathrm{substrate}}$	Γ^{maj}	Γ^{min}	Γ^{maj}	Γ^{min}
Γ_{tip}	Γ^{maj}	Γ^{min}	Γ^{min}	Γ^{maj}

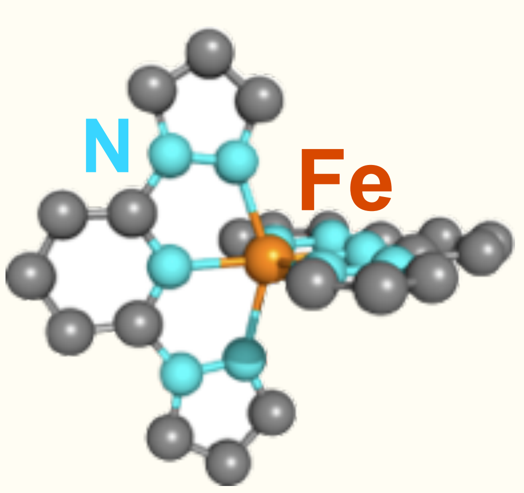
$$\mathrm{GMR} \approx \frac{(\Gamma^{\mathrm{min}} - \Gamma^{\mathrm{maj}})^2}{2\Gamma^{\mathrm{min}}\Gamma^{\mathrm{maj}}} = \frac{(1-\rho)^2}{2\rho}$$

where

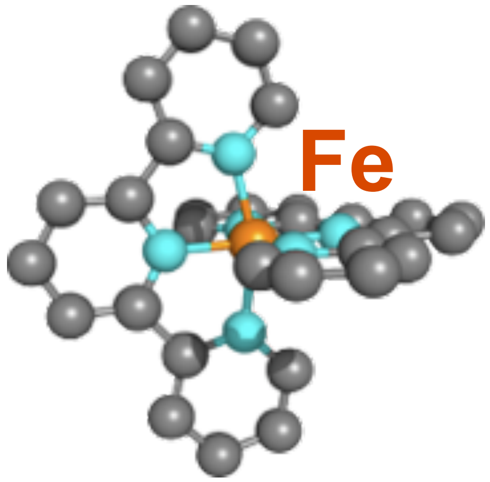
$$\rho = \Gamma^{\mathrm{maj}}/\Gamma^{\mathrm{min}} \approx \frac{|V_{\mathrm{hybrid}}|^2 \varrho^{\mathrm{maj}}_{\mathrm{LDoS}}}{|V_{\mathrm{hybrid}}|^2 \varrho^{\mathrm{min}}_{\mathrm{LDoS}}} \approx \frac{\varrho^{\mathrm{maj}}_{\mathrm{LDoS}}}{\varrho^{\mathrm{min}}_{\mathrm{LDoS}}}$$

III. Molecular Instabilities

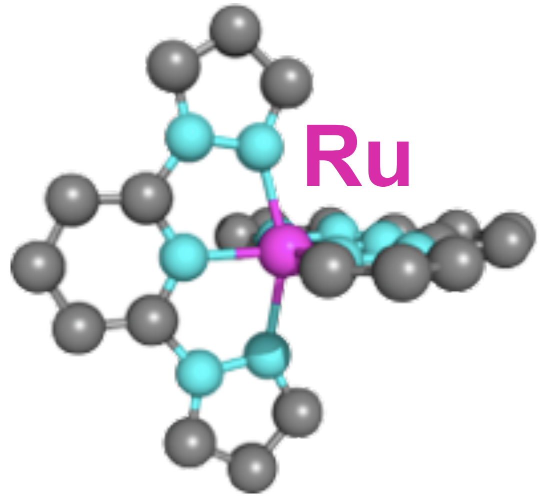
Spin transition complexes



$[Fe(bpp)_2]^{2+}$



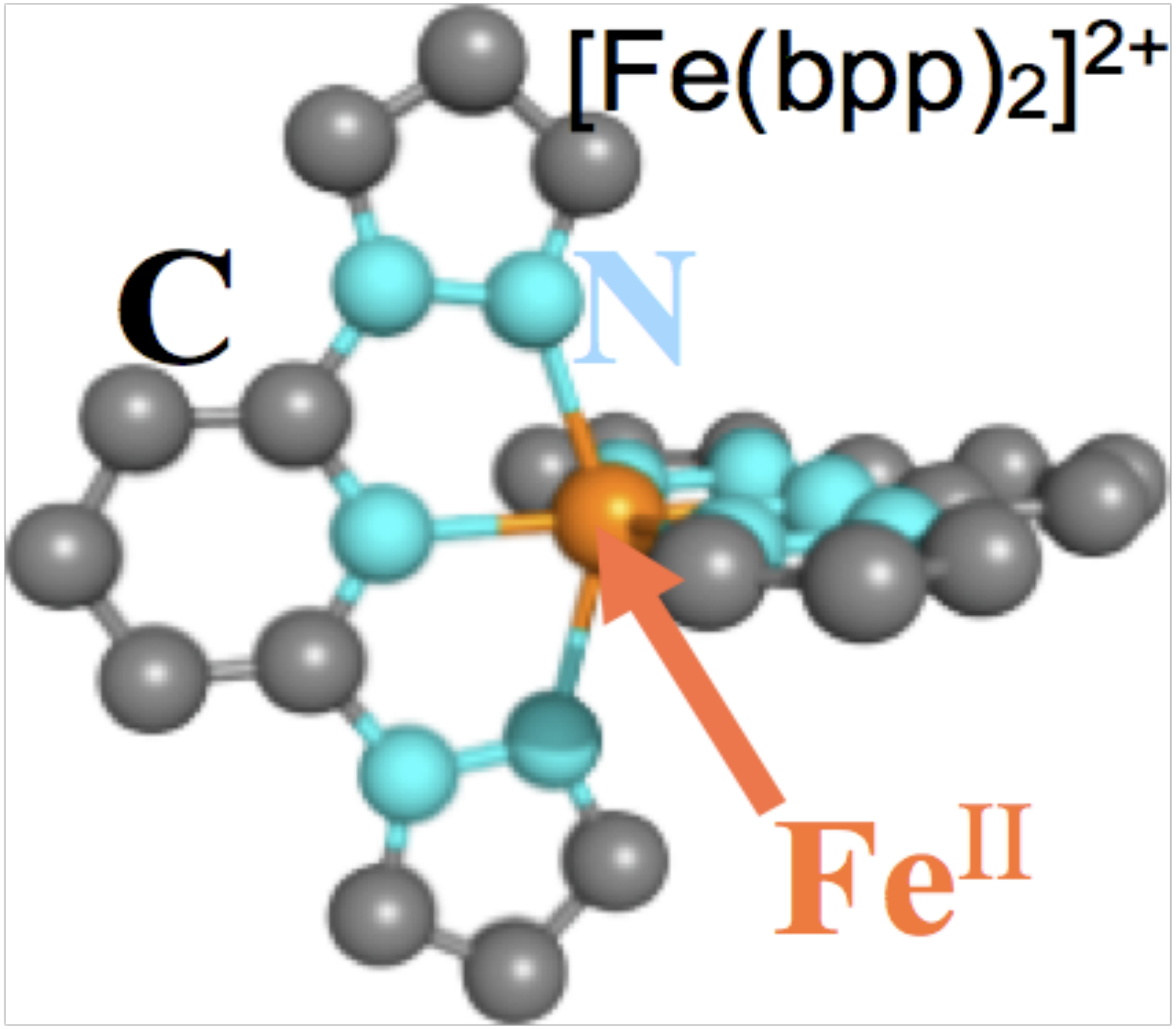
$[Fe(tpy)_2]^{2+}$



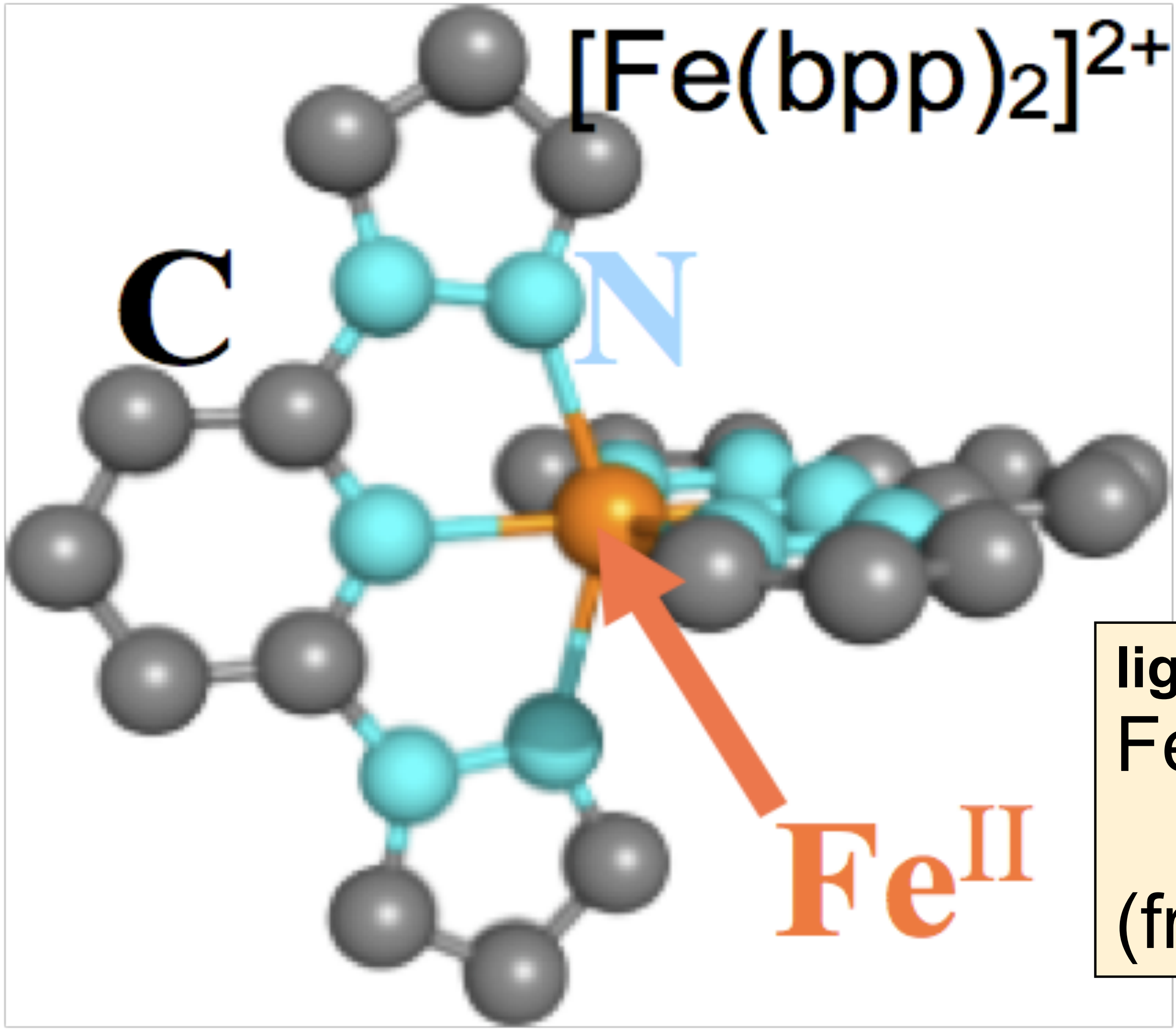
$[Ru(bpp)_2]^{2+}$

- **Transition metal (Me) : Fe or Ru (or Mn, Co, ...)**
- **Organic ligands: bpp = bispyrazol pyridine ; tpy = terpyridine**

The Protagonist of the Story



The Protagonist of the Story



ligand induced spin quenching

Fe^{II} -ion in $(bpp)_2$: $S_{Fe}=0$

(free space: $S_{Fe}=2$)

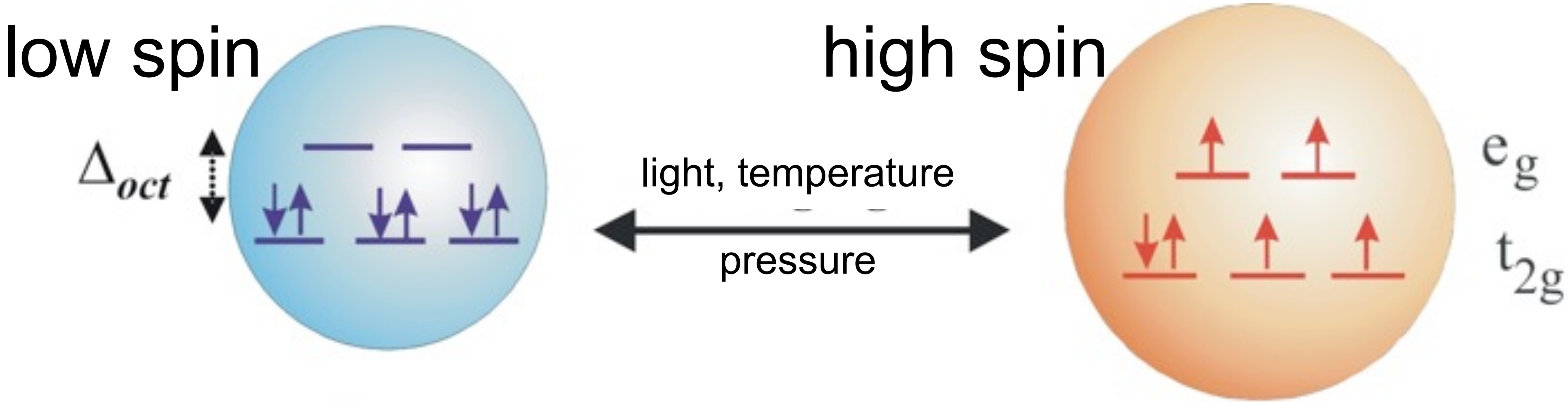
collaboration with

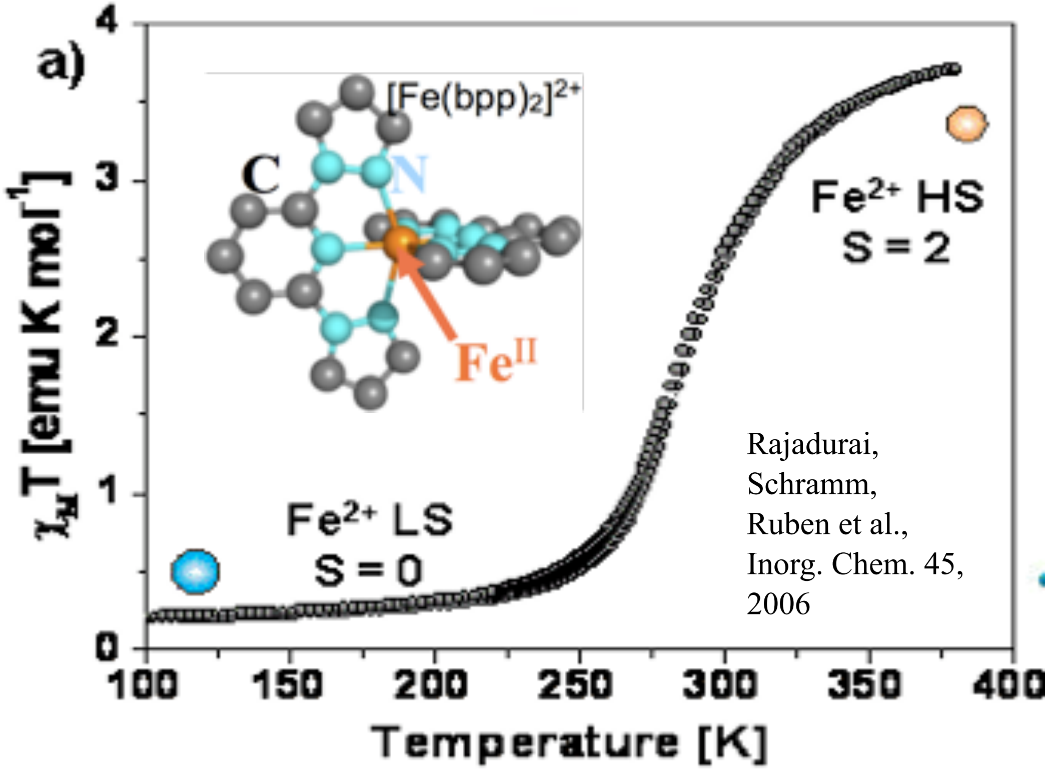
V. Meded, A. Bagrets, K. Fink, M. Ruben (INT)

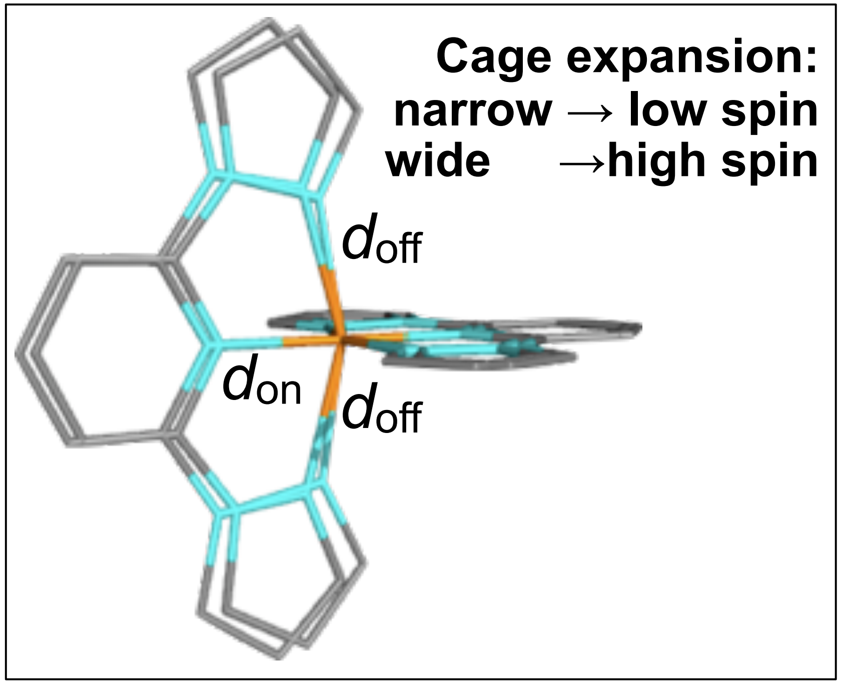
H. van der Zant , A. Bernand-Mantel (TU Delft)

(submitted 2010)

Spin transition in Me^{II}-complexes
control parameters: T, pressure, light







Thursday, November 4, 2010

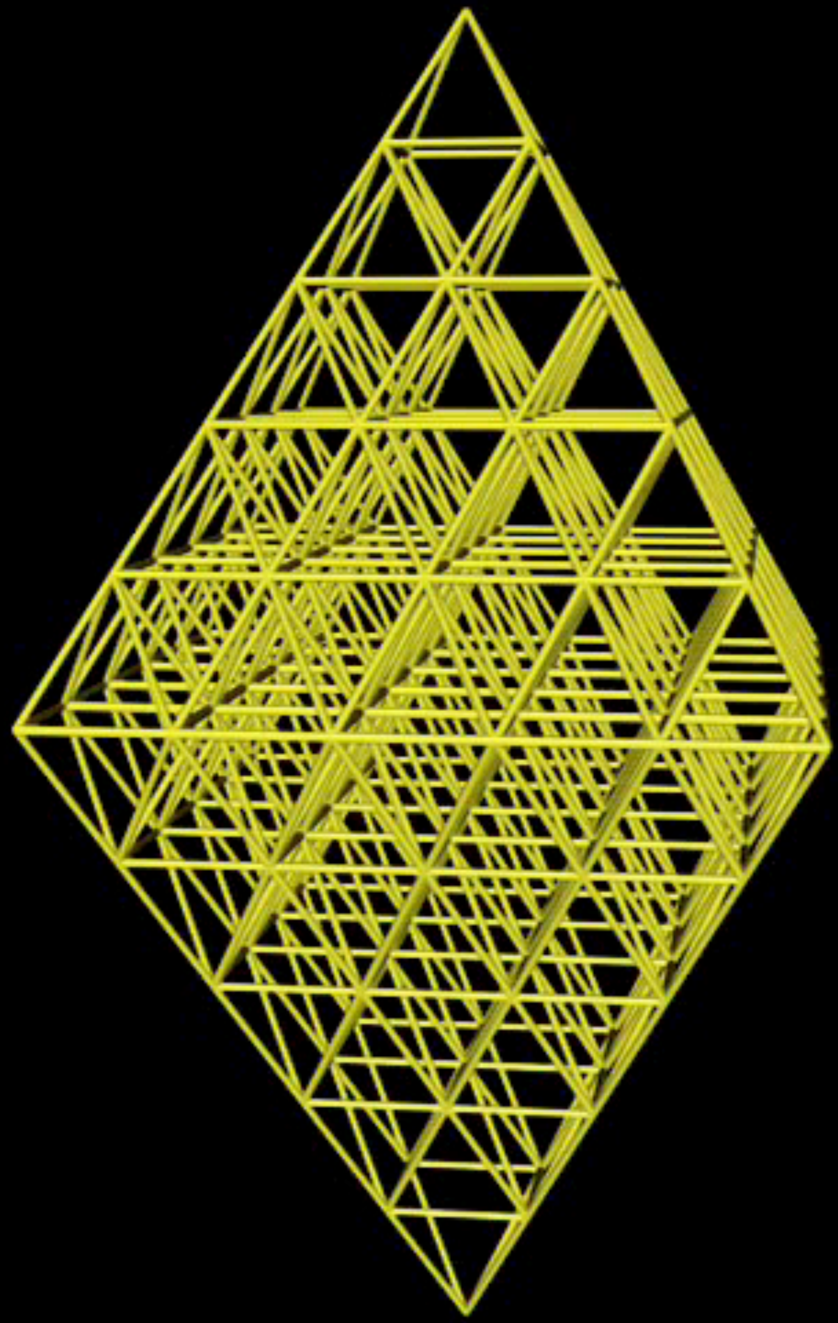
II.1 Spin transition driven by charging

Theory part

collabortion with **M. Ruben**

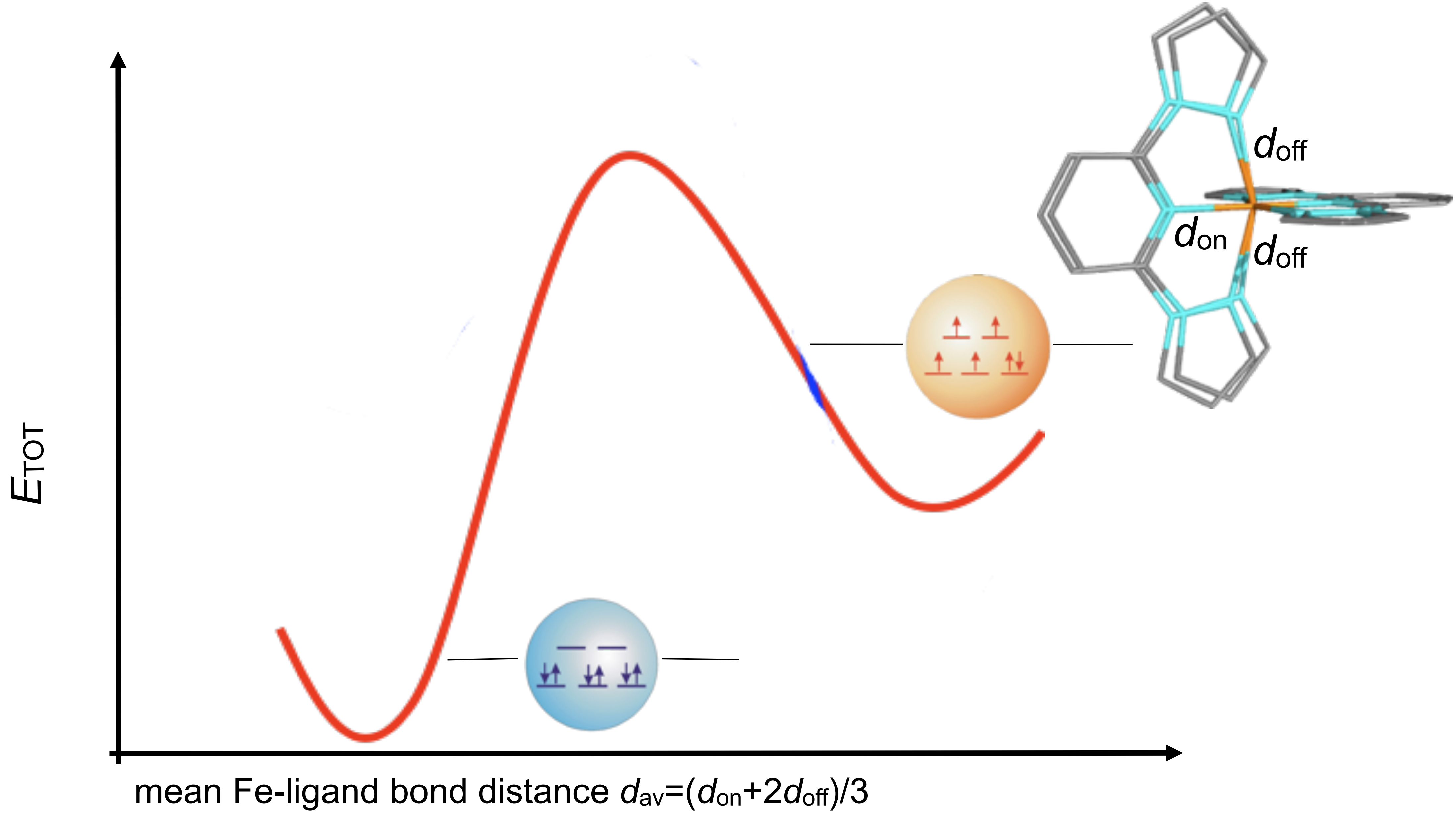
2006 - 2008

F. Weigend, FE, J. Weissmueller, SMALL 2006

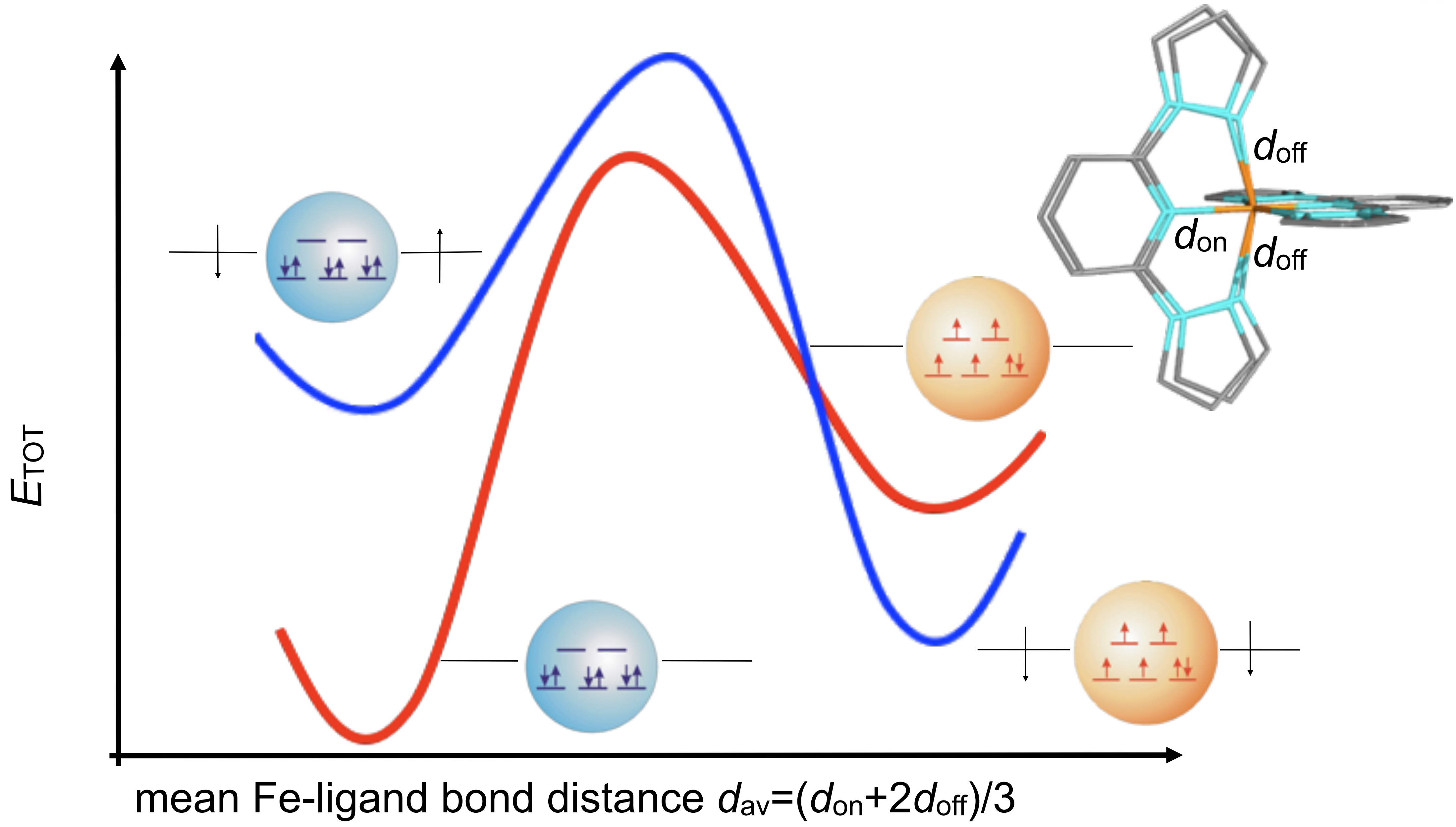


F. Weigend, FE, J. Weissmueller, SMALL 2006

Spin transition: mechanical feedback

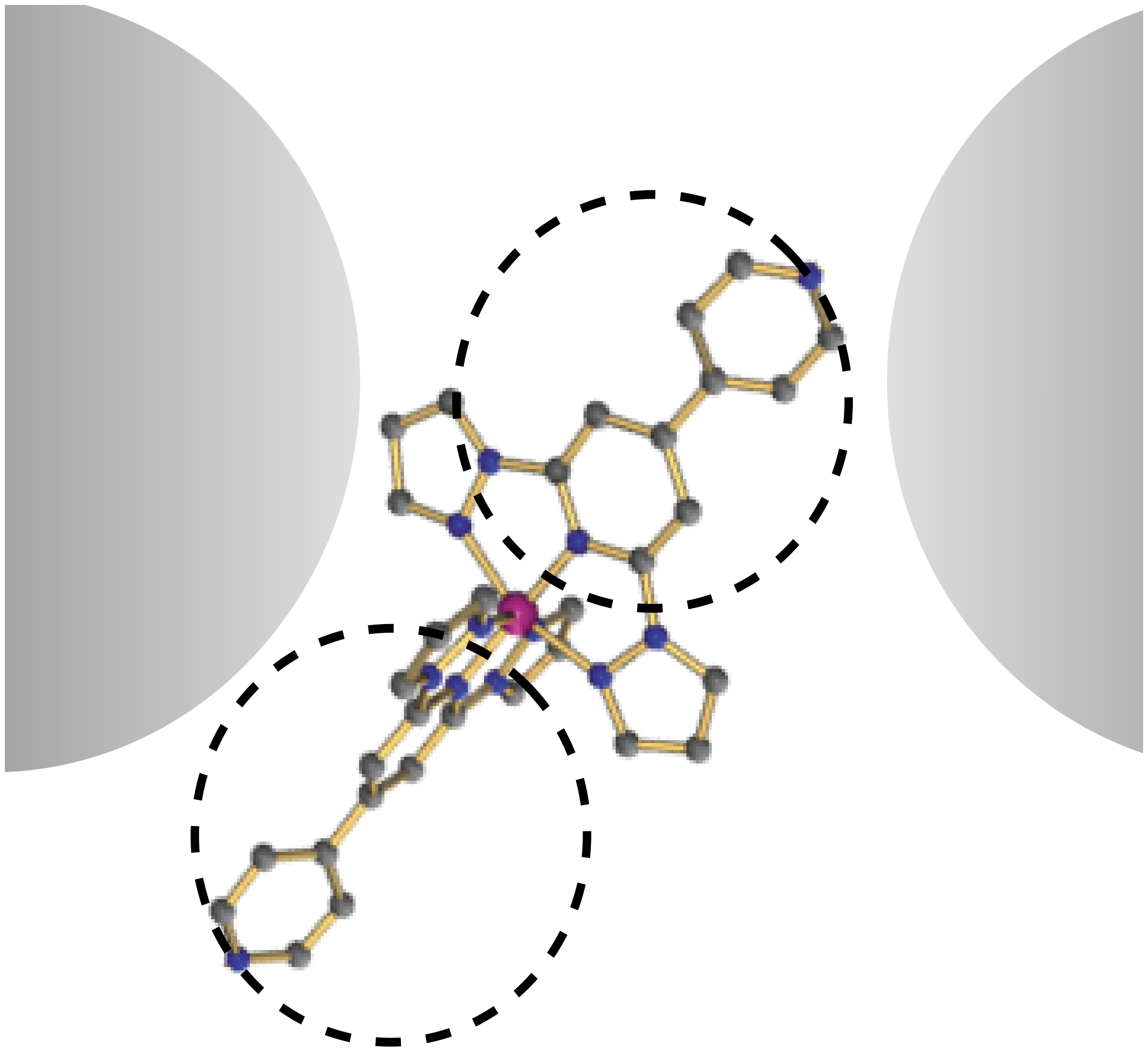


Spin transition: mechanical feedback



Method: Density functional theory (DFT) with TURBOMOLE®

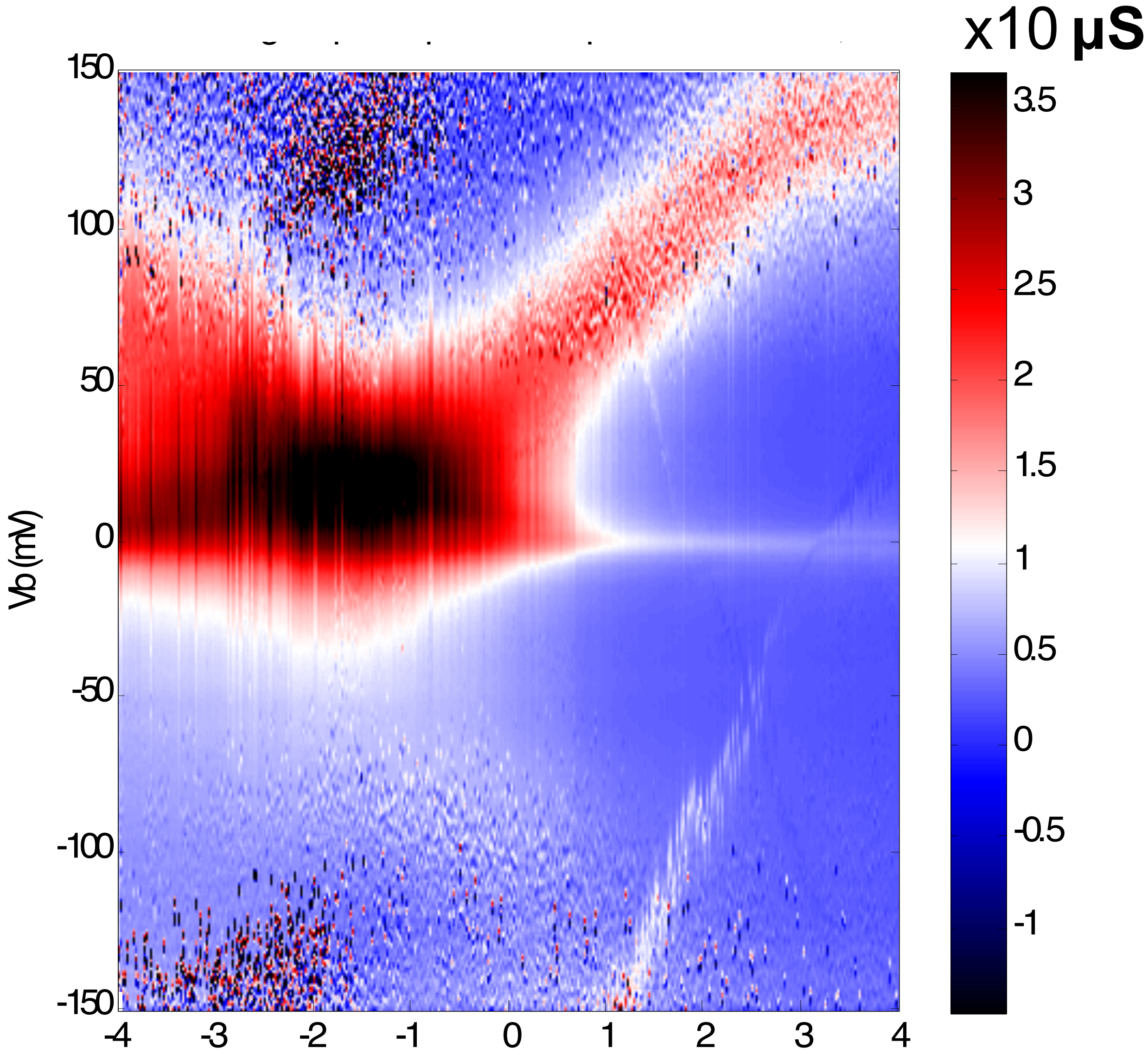
II.2 Transport experiments on spin transition complexes



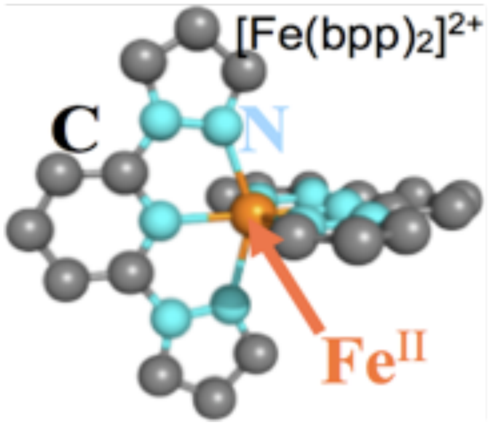
Split Kondo resonance in $[Fe(bpp)_2]^{2+}$

Control parameter: gate voltage (Delft, electro-migration method)

transport (bias) voltage

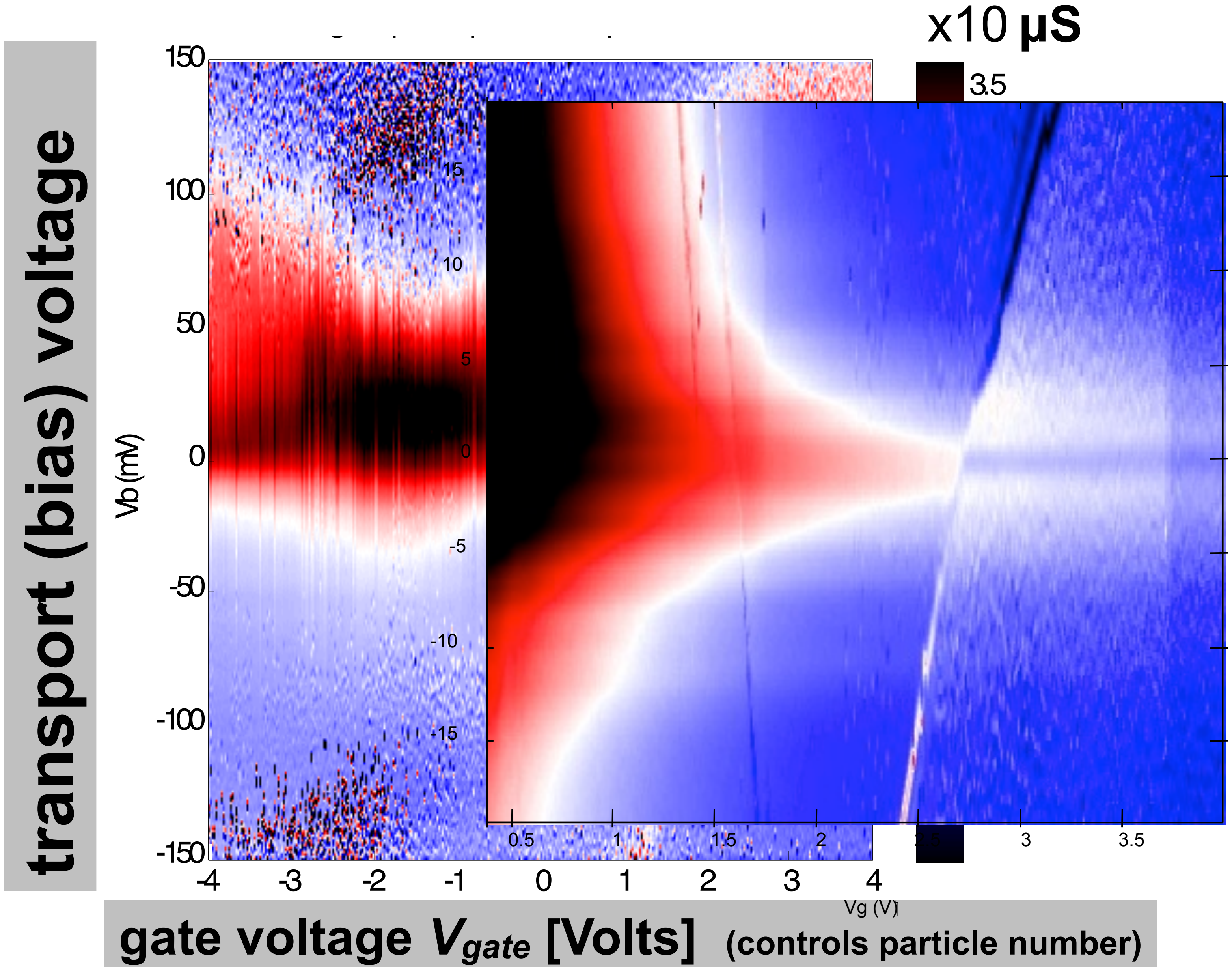


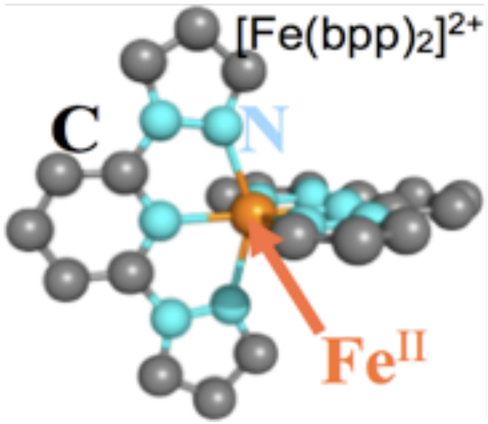
gate voltage V_{gate} [Volts] (controls particle number)



Split Kondo resonance in $[Fe(bpp)_2]^{2+}$

Control parameter: gate voltage (Delft, electro-migration method)





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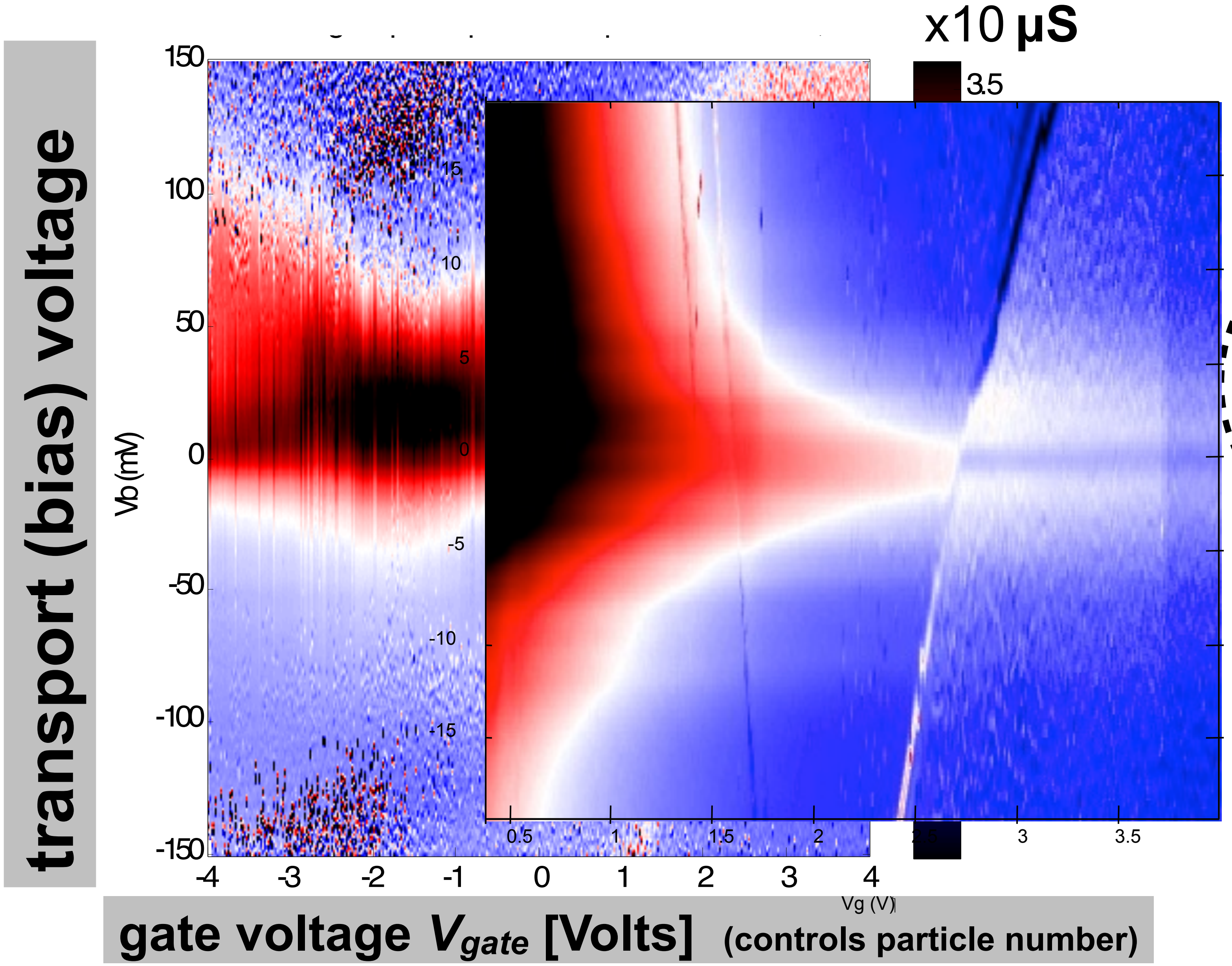

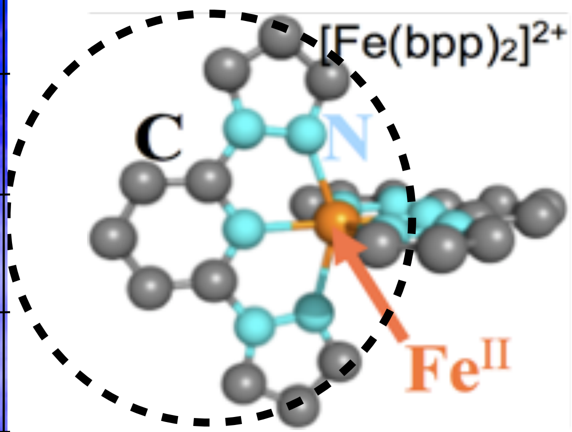

Split Kondo resonance in $[Fe(bpp)_2]^{2+}$

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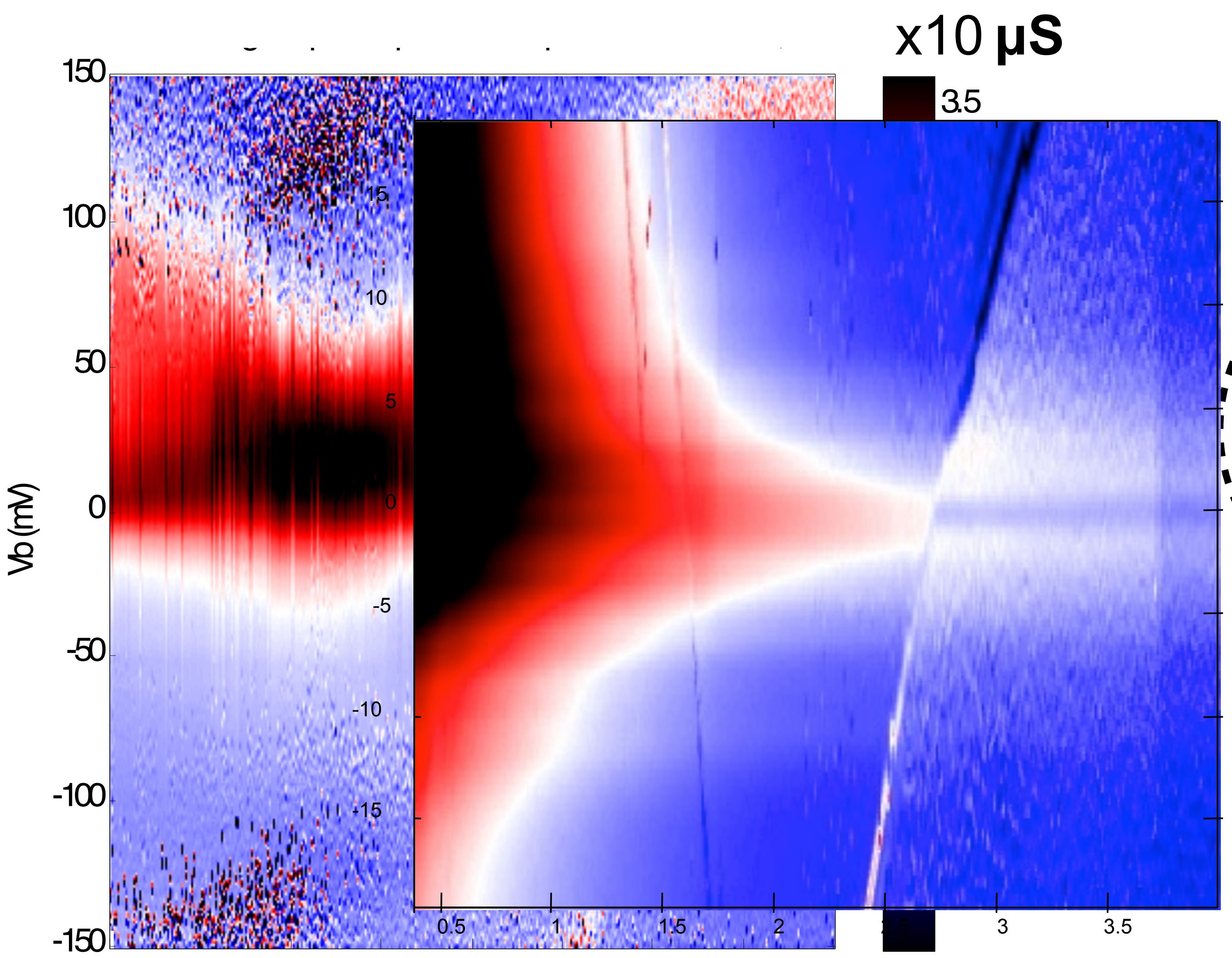
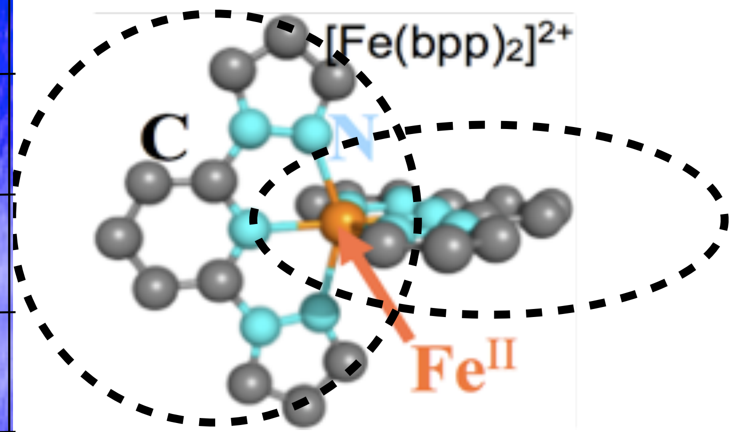


transport (bias) voltage

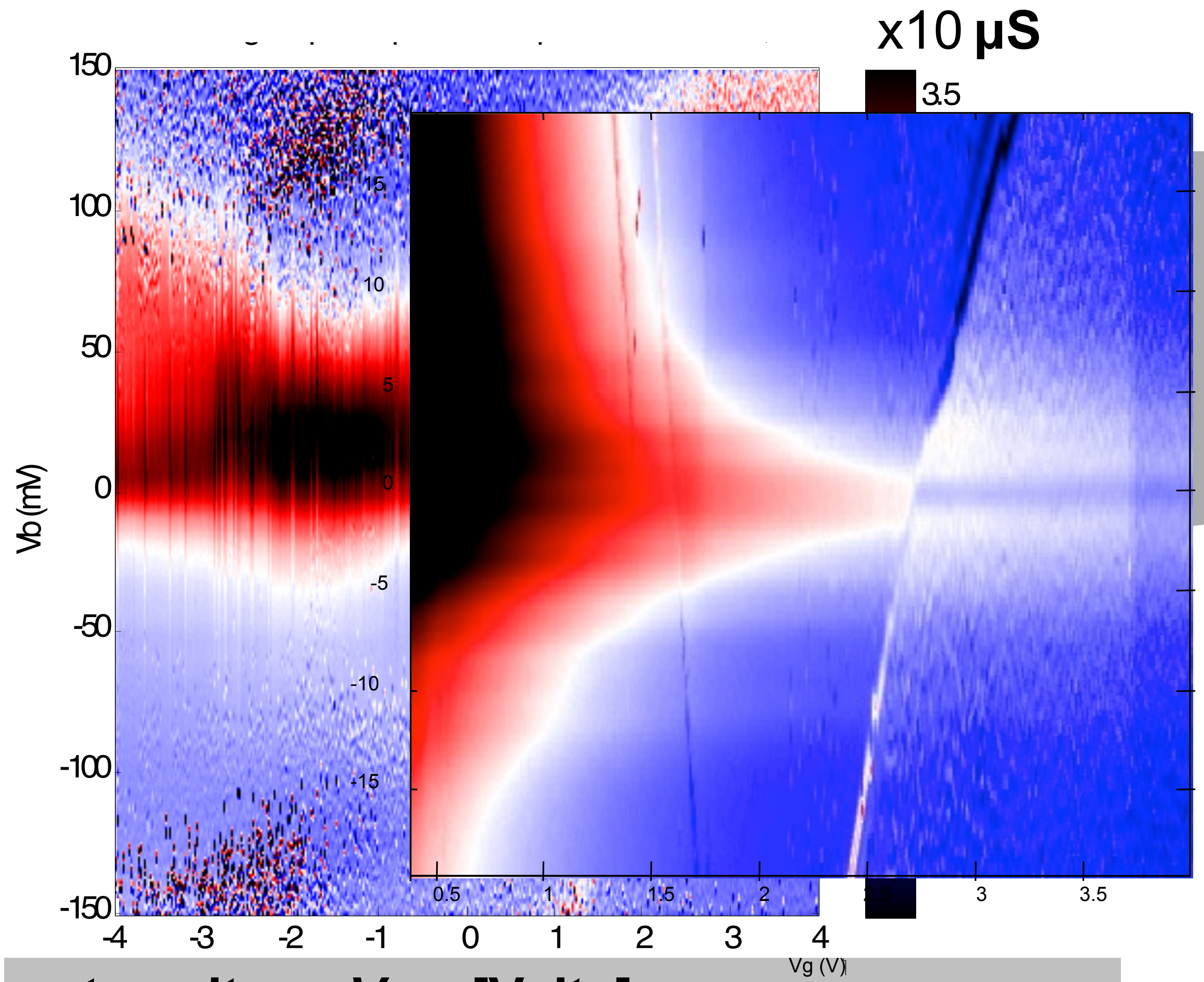
gate voltage V_{gate} [Volts] (controls particle number)



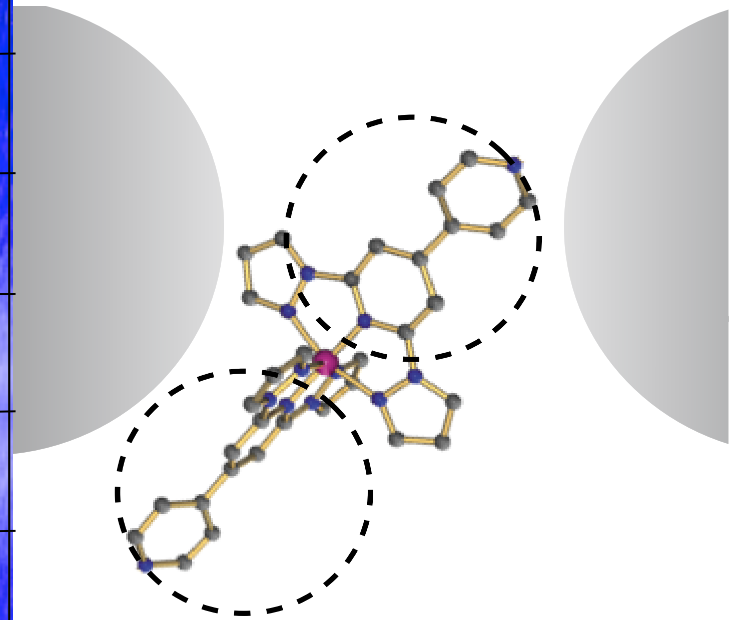
Split Kondo resonance in $[Fe(bpp)_2]^{2+}$

Control parameter: gate voltage (Delft, electro-migration method)

transport (bias) voltage

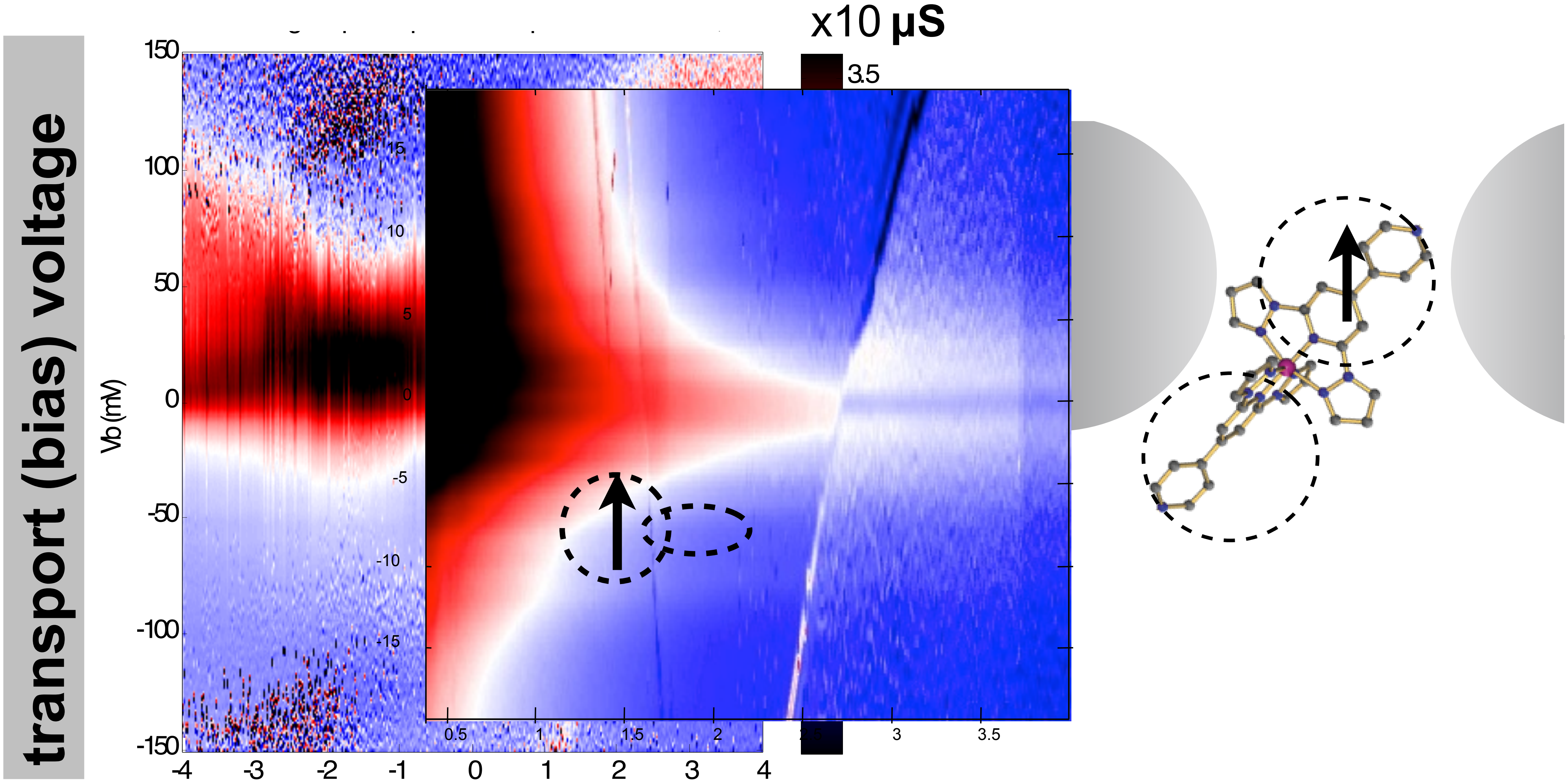


gate voltage V_{gate} [Volts] (controls particle number)



Split Kondo resonance in $[Fe(bpp)_2]^{2+}$

Control parameter: gate voltage (Delft, electro-migration method)



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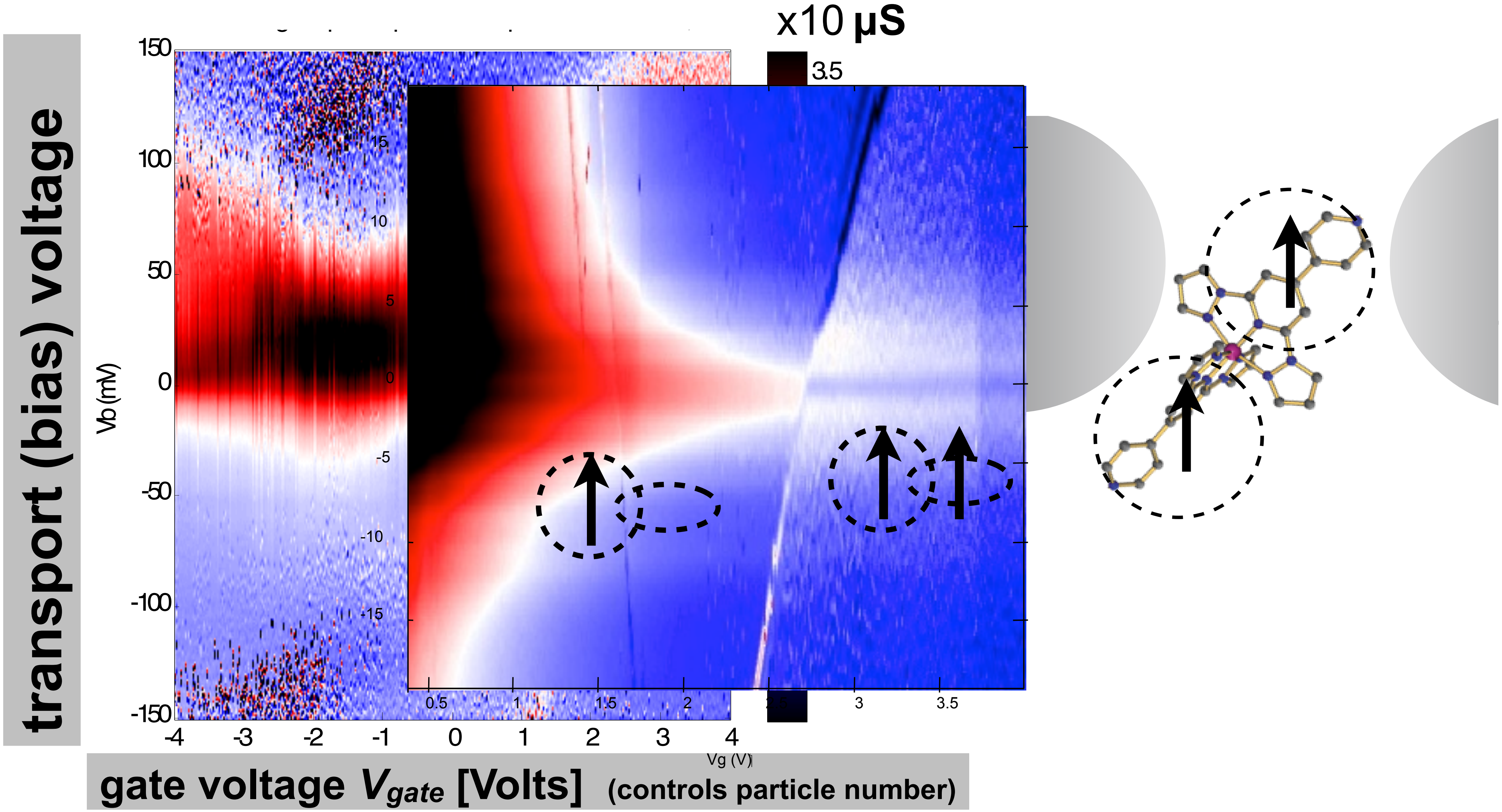
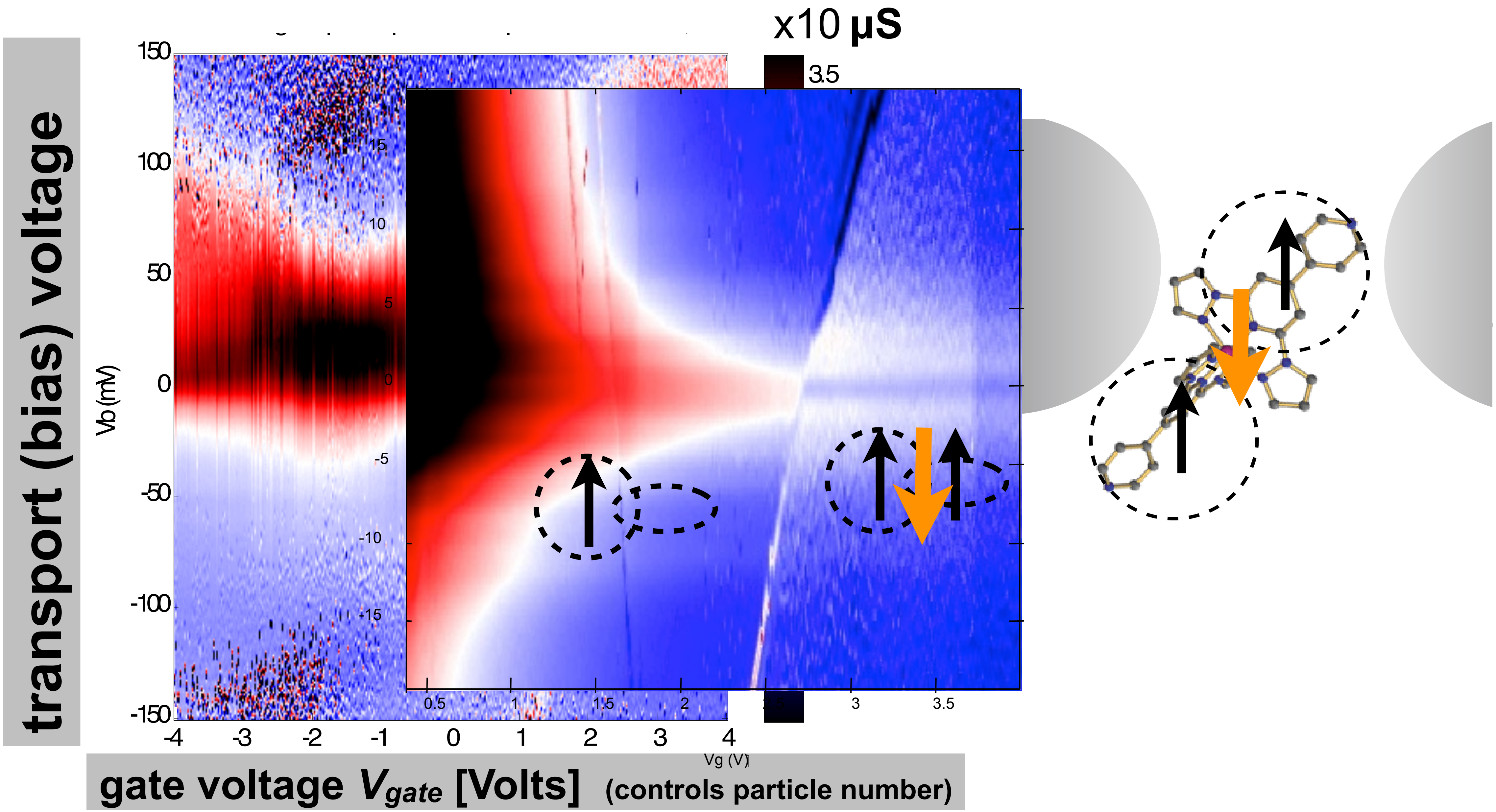


Split Kondo resonance in $[Fe(bpp)_2]^{2+}$

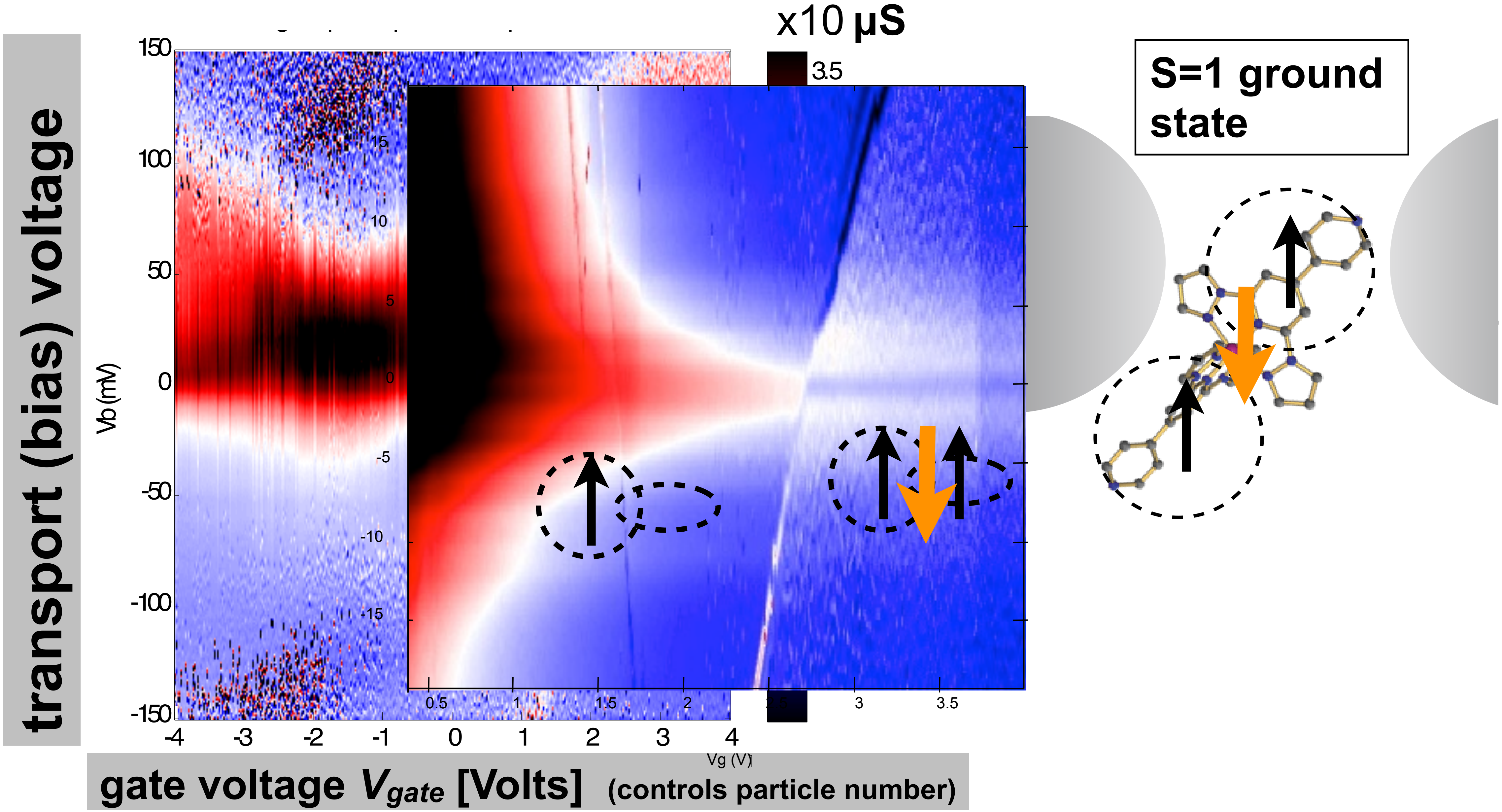
Control parameter: gate voltage (Delft, electro-migration method)



Thursday, November 4, 2010

Split Kondo resonance in $[Fe(bpp)_2]^{2+}$

Control parameter: gate voltage (Delft, electro-migration method)



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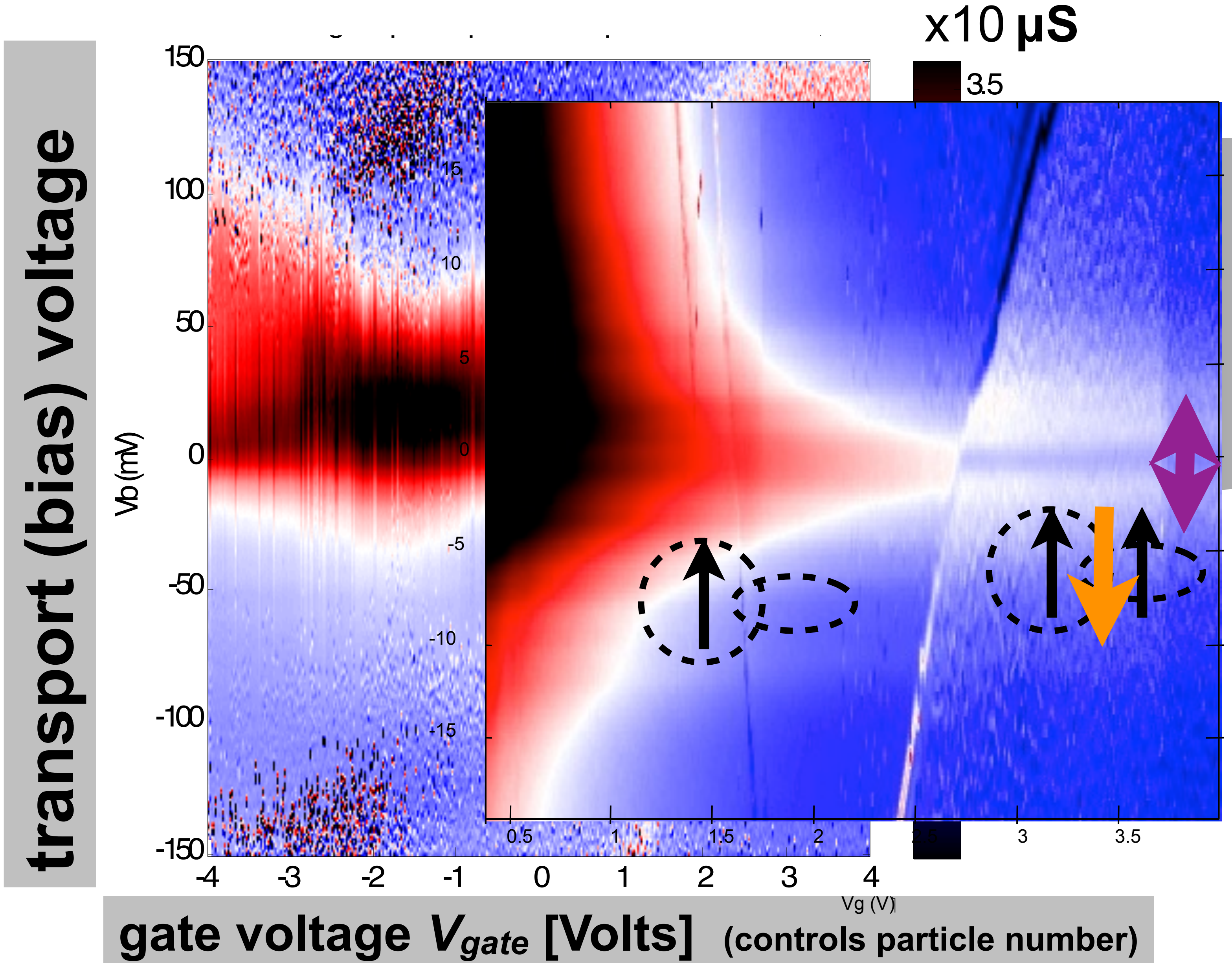
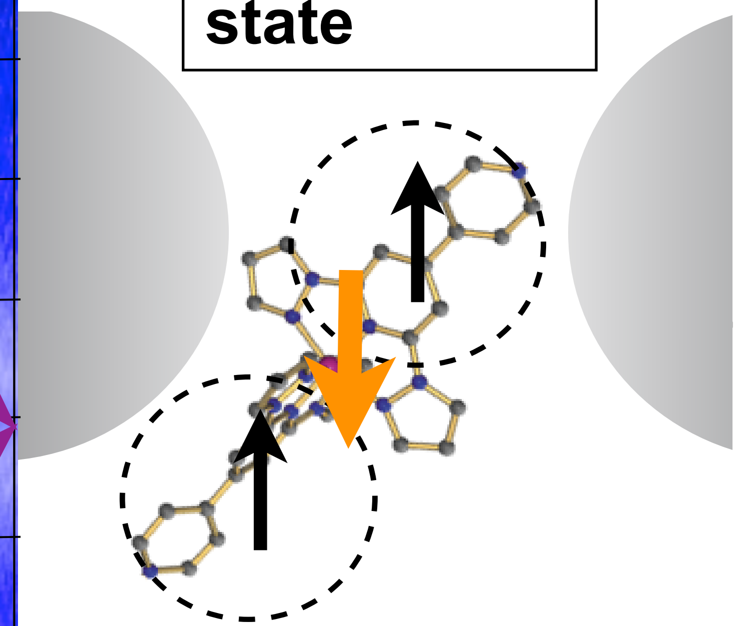
Control parameter: gate voltage (Delft, electro-migration method)



S=1 ground state

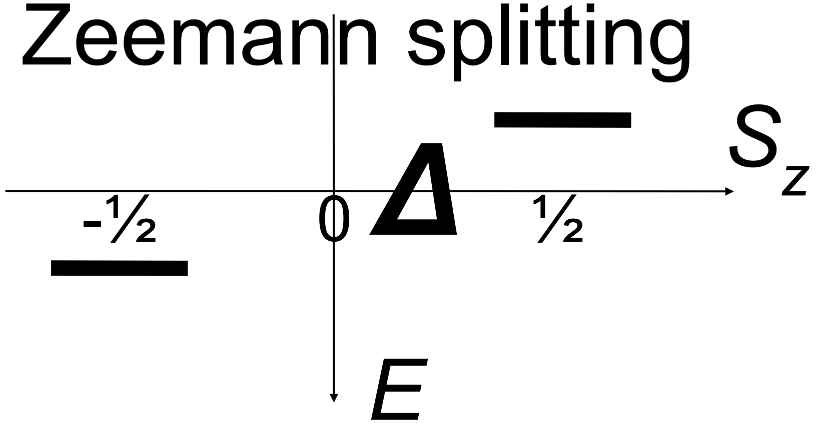


spin orbit induced splitting 1-3meV (CAS-SCF, K. Fink)

A. Bernand-Mantel et al. preprint 2010

Splitting of the Kondo resonance
Non-equilibrium Kondo Effect

S=1/2 in B-field:
Zeemann splitting



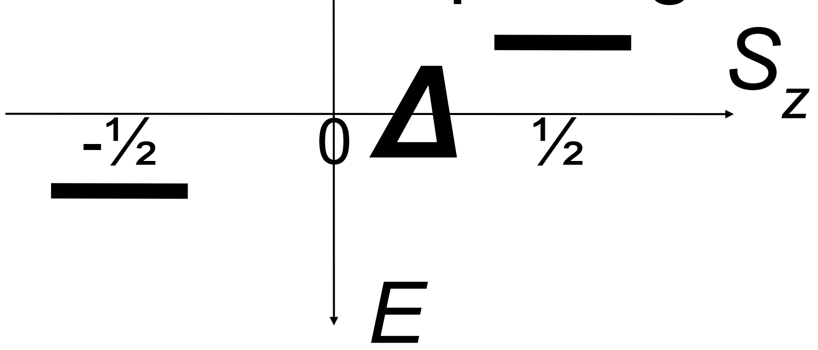
Splitting of the Kondo resonance
Non-equilibrium Kondo Effect

S=1/2 in B-field:
Zeemann splitting

$V_{bias} \ll \boldsymbol{\Delta}$: Kondo destroyed

Splitting of the Kondo resonance
Non-equilibrium Kondo Effect

S=1/2 in B-field:
Zeemann splitting



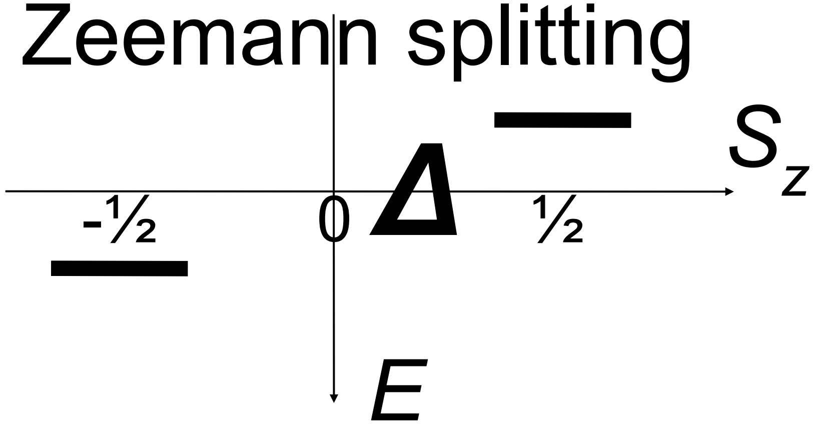
$V_{bias} \simeq \boldsymbol{\Delta} \lesssim T_K$

→ symmetry is partially restored

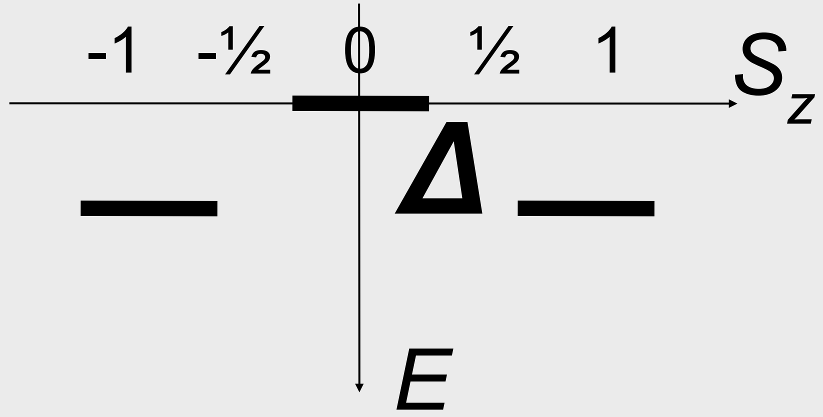
→ **Kondo resonance reappears**

Splitting of the Kondo resonance
Non-equilibrium Kondo Effect

S=1/2 in *B*-field:
Zeemann splitting



S=1 & spin orbit coupling



$V_{bias} \simeq \boldsymbol{\Delta} \lesssim T_{\mathrm{K}}$

→ symmetry is partially restored

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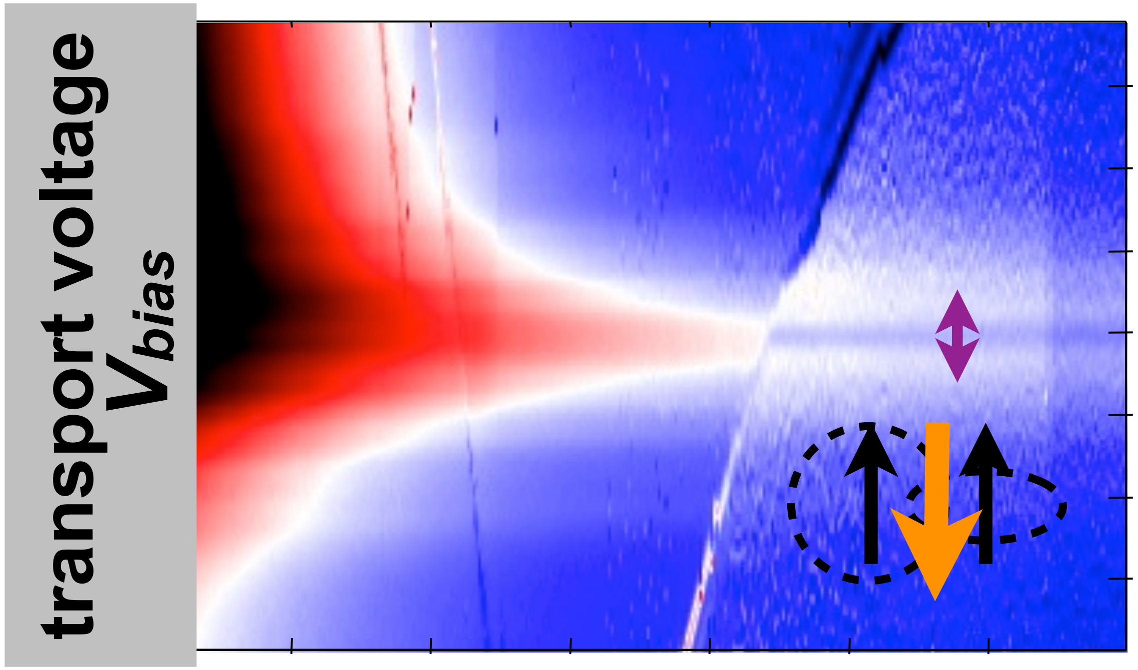
Splitting of the Kondo resonance
Non-equilibrium Kondo Effect



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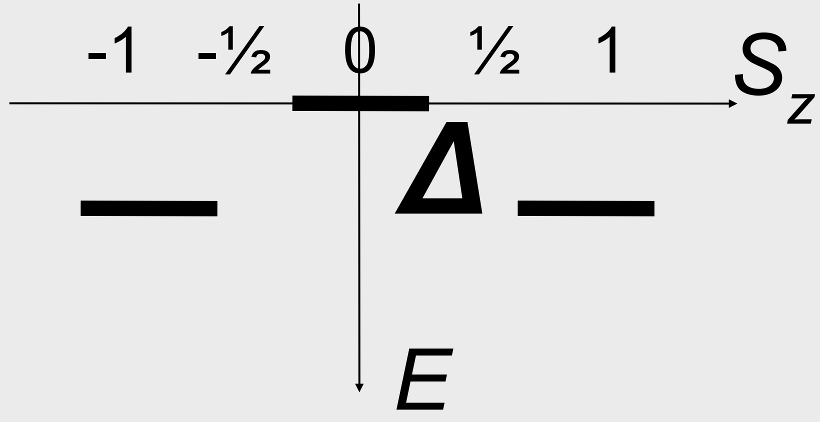

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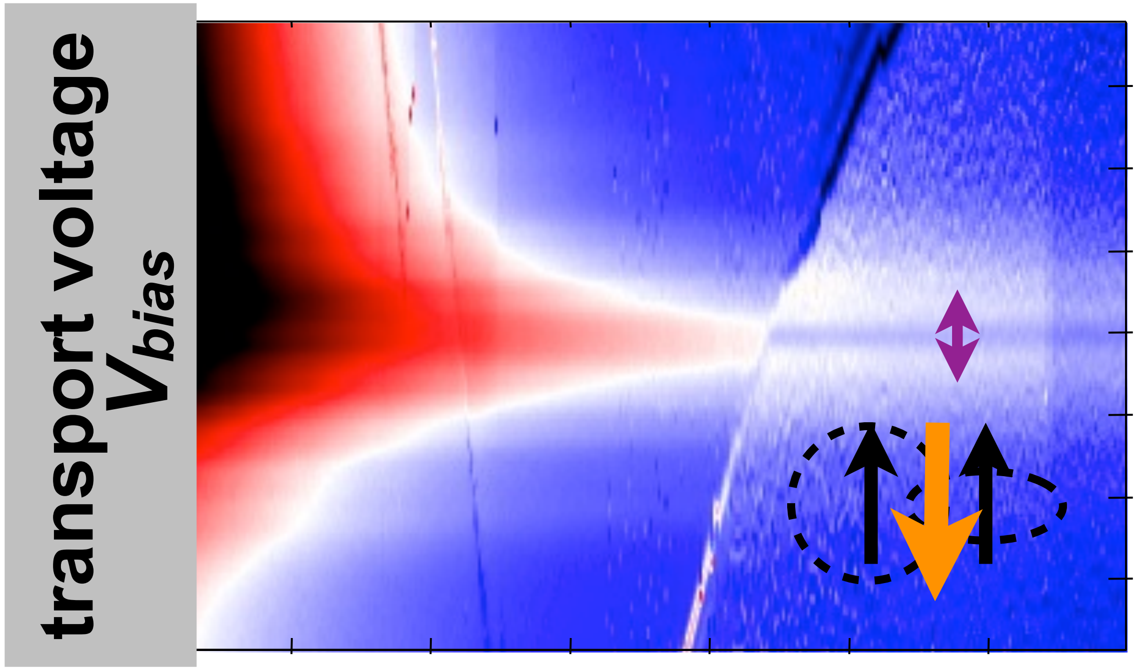
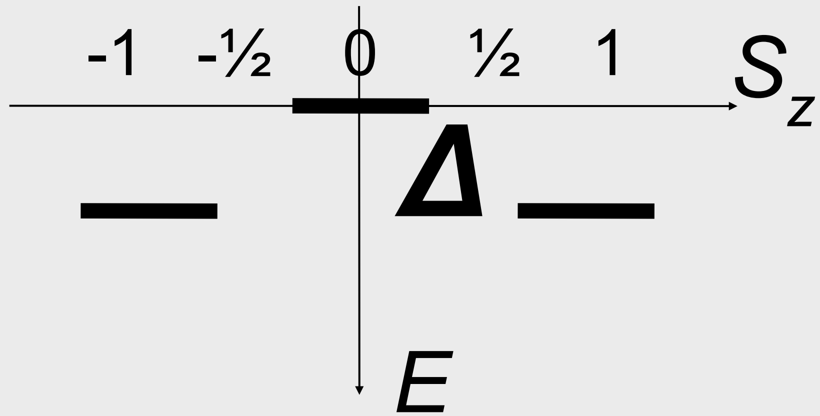
Splitting of the Kondo resonance
Non-equilibrium Kondo Effect



S=1 & spin orbit coupling



$V_{bias} \simeq \Delta \lesssim T_K$

→ symmetry is partially restored

→ **Kondo resonance reappears**

→ transport peaks at

$$V_{bias} = \Delta$$

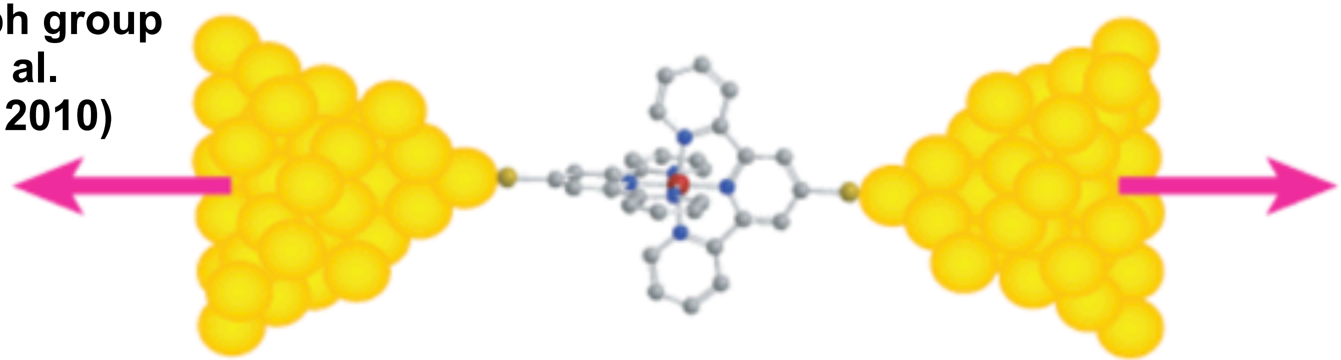
at **any** gate voltage

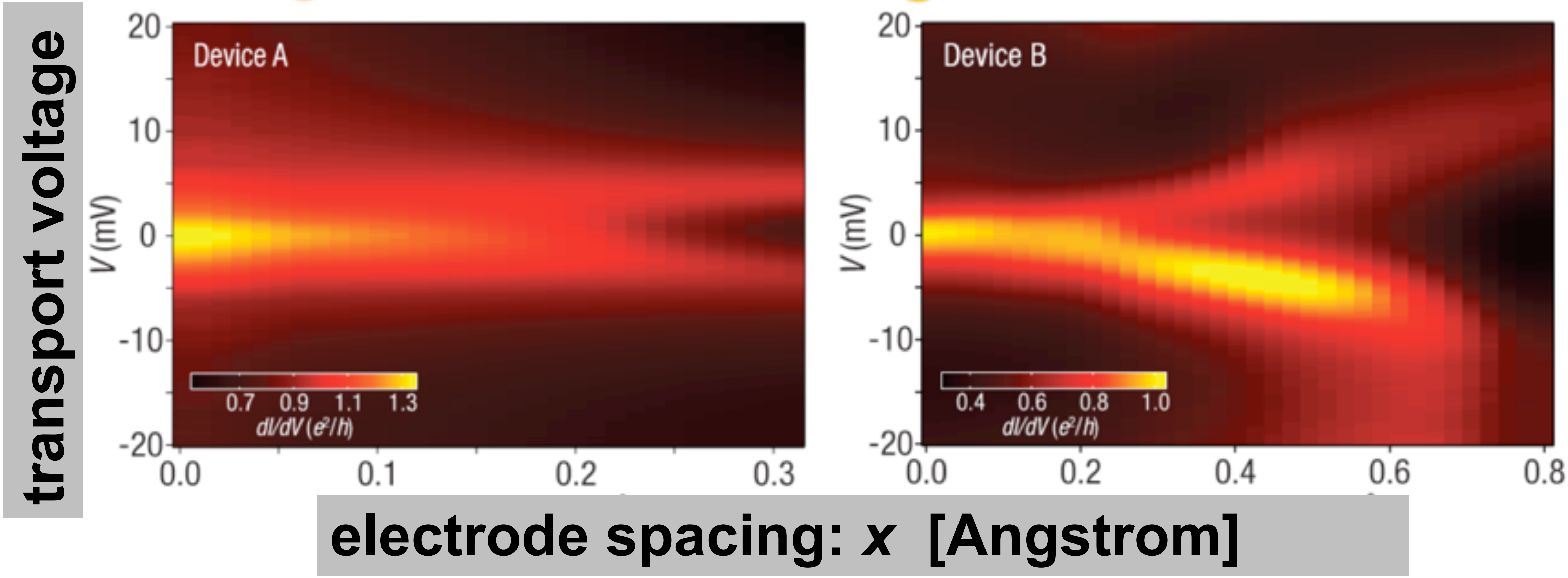
quantitative analysis: multi-determinant calculation (CAS-SCF) by K. Fink: Δ≈1-3meV

Extension: Split Kondo in $[Co(tpy)_2]$

Control parameter: strain

Dan Ralph group
(Parks et al.
Science, 2010)





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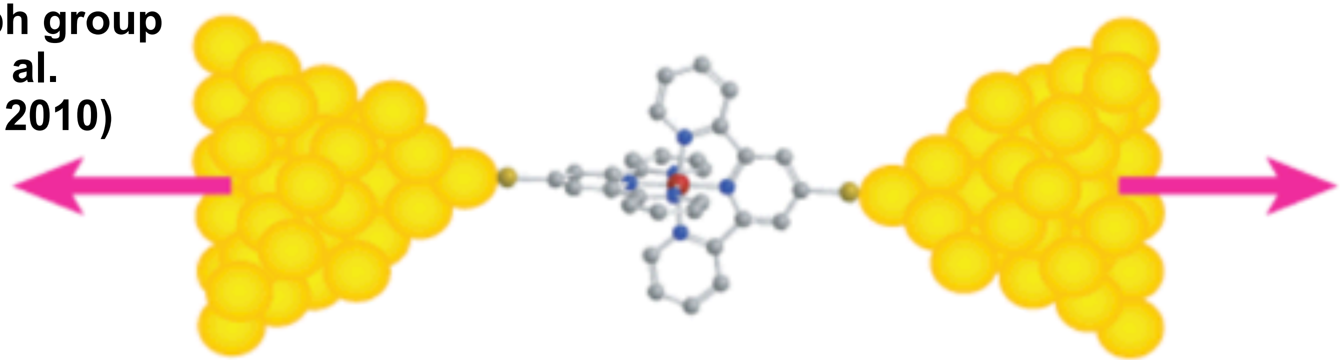
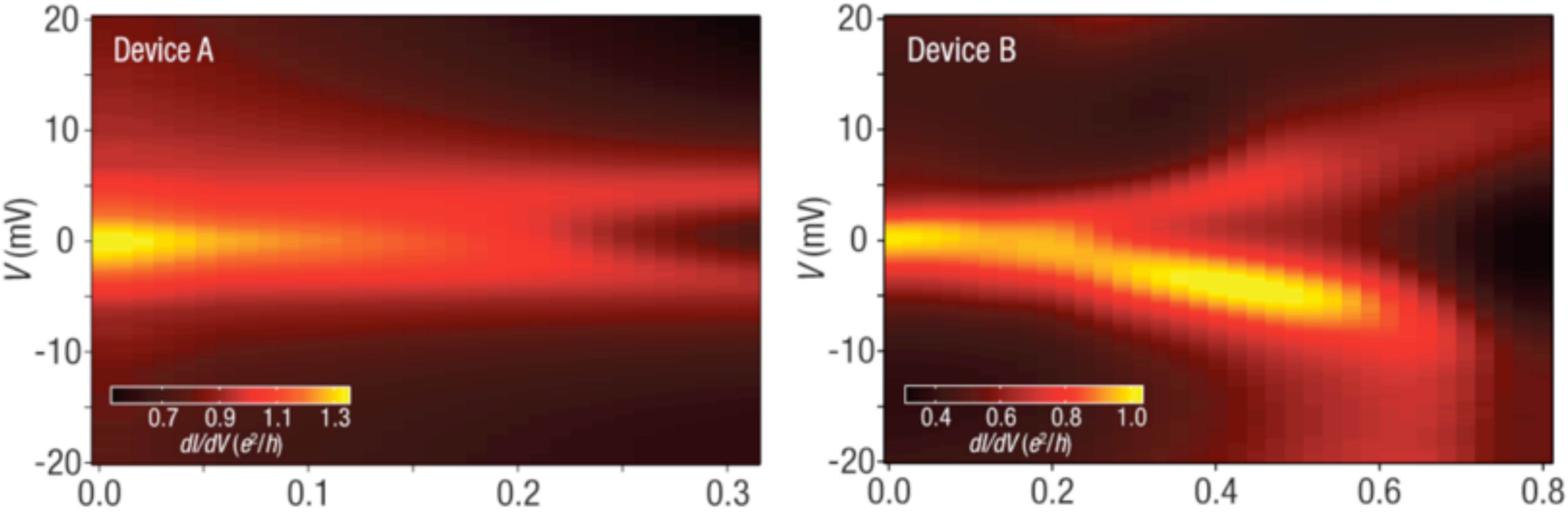


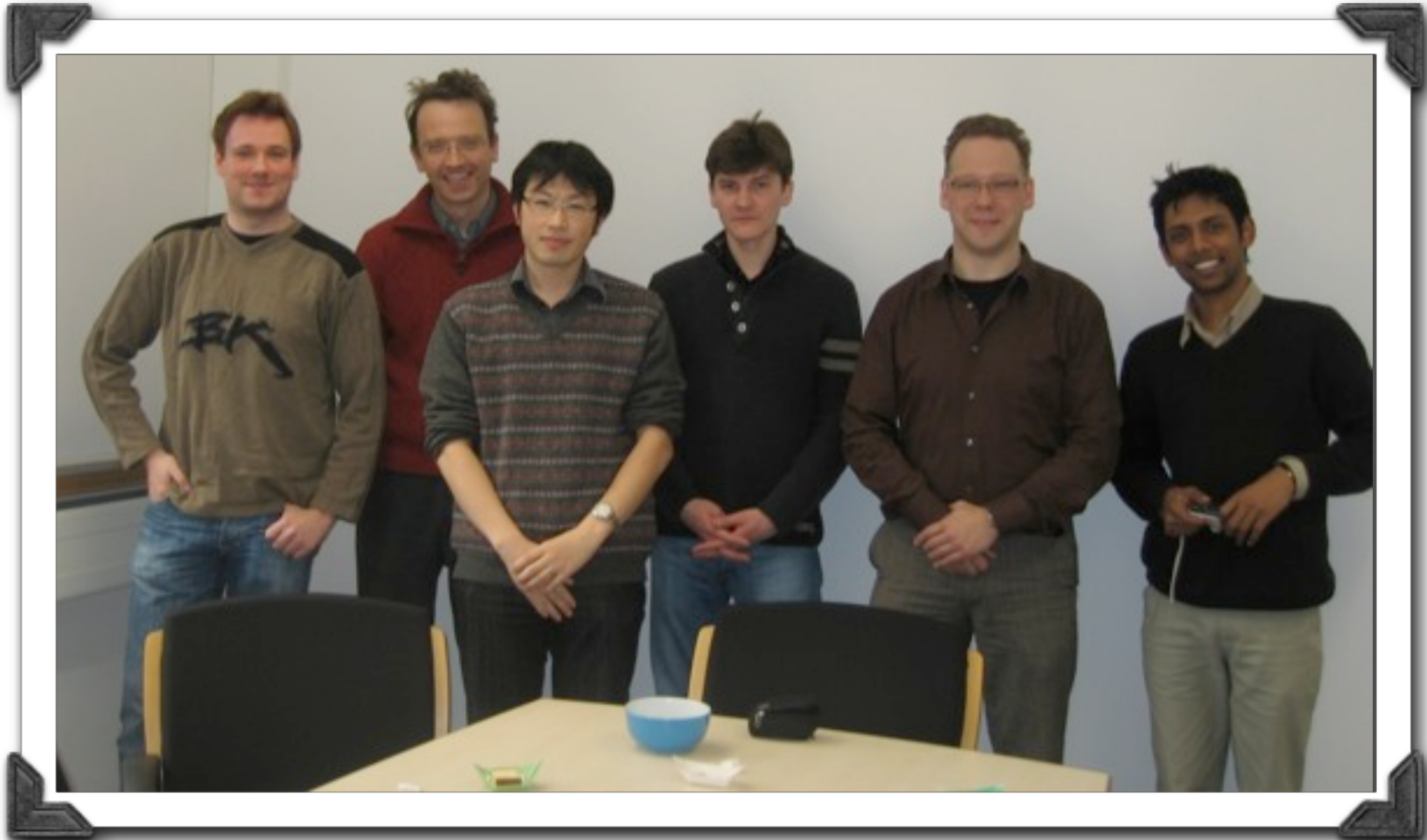
Scenario by authors:
S=1 (Co^{1+} spin triplet
ground state)
spin-orbit splitting $\Delta(x)$



transport voltage

electrode spacing: *x* [Angstrom]

Team @ KIT



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&
Velimir Meded, Arindam Dasgupta, Christian Seiler

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H. van der Zant