First-principles material design

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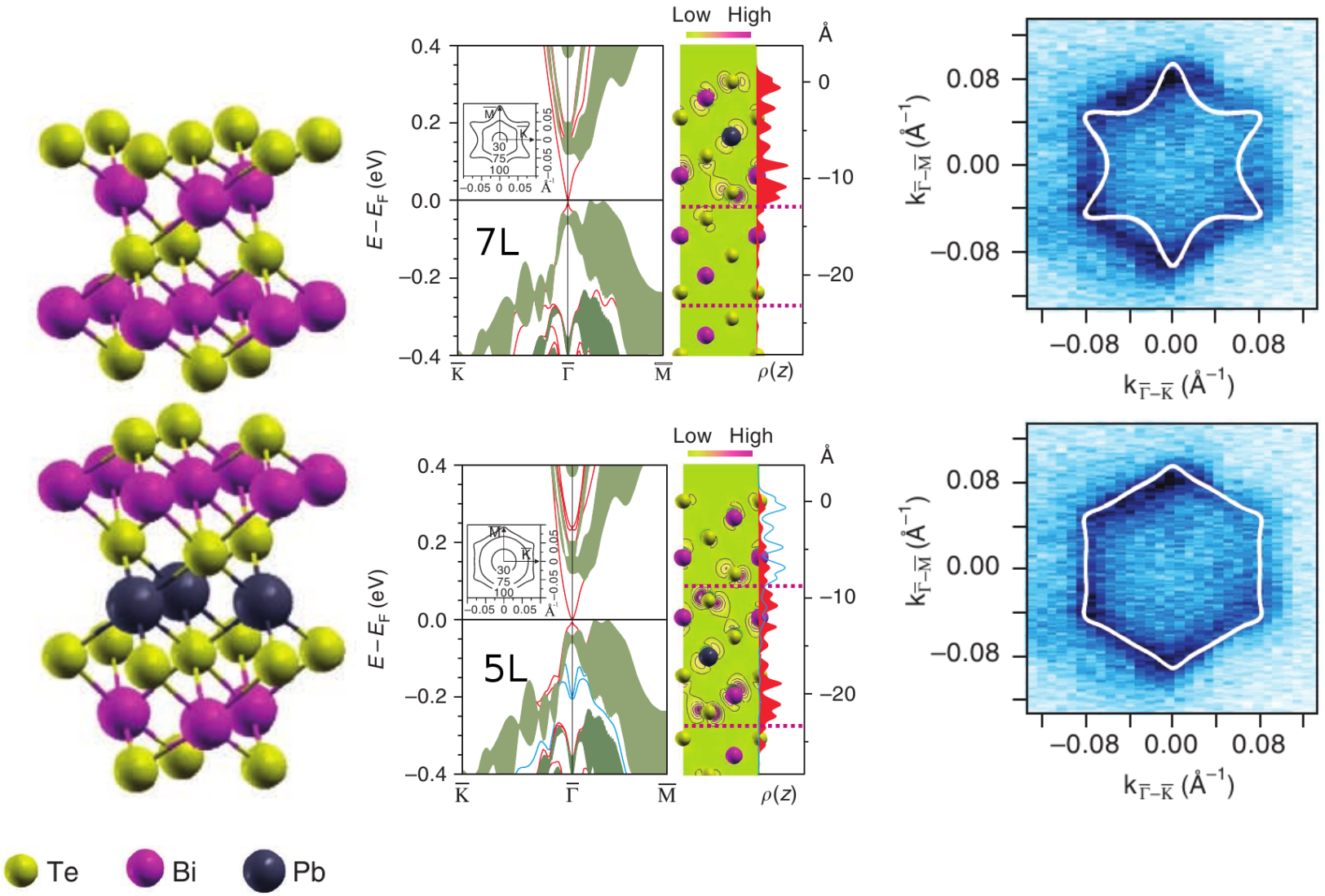
Challenges for computational solid state physics

New material design: topological insulators

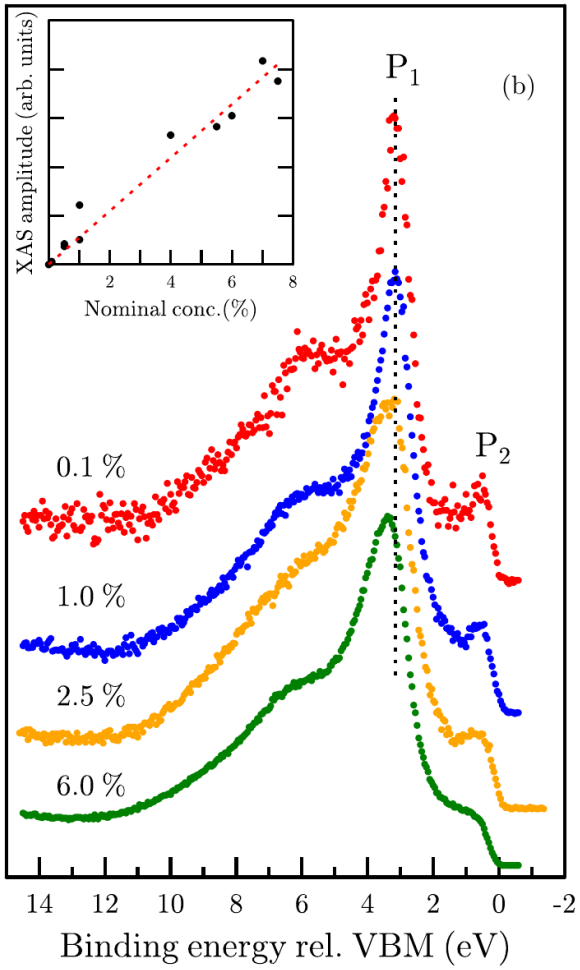
Theory suggests: $PbBi_4Te_7$

ARPES measurements

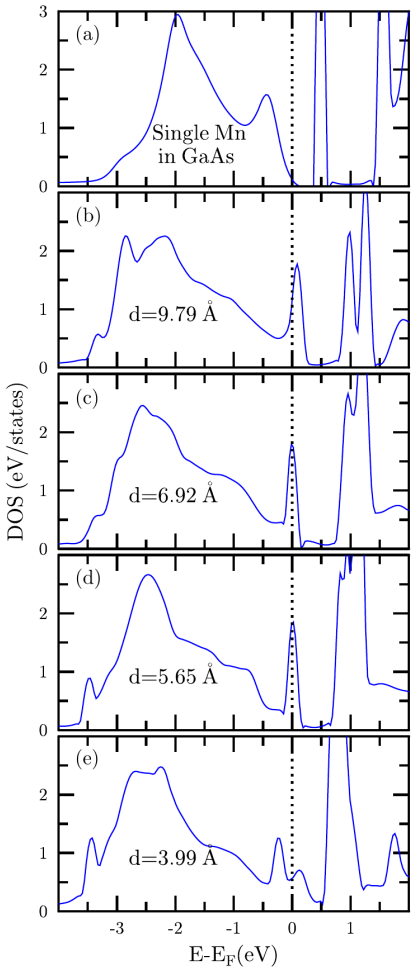


Supporting experiments: GaMnAs

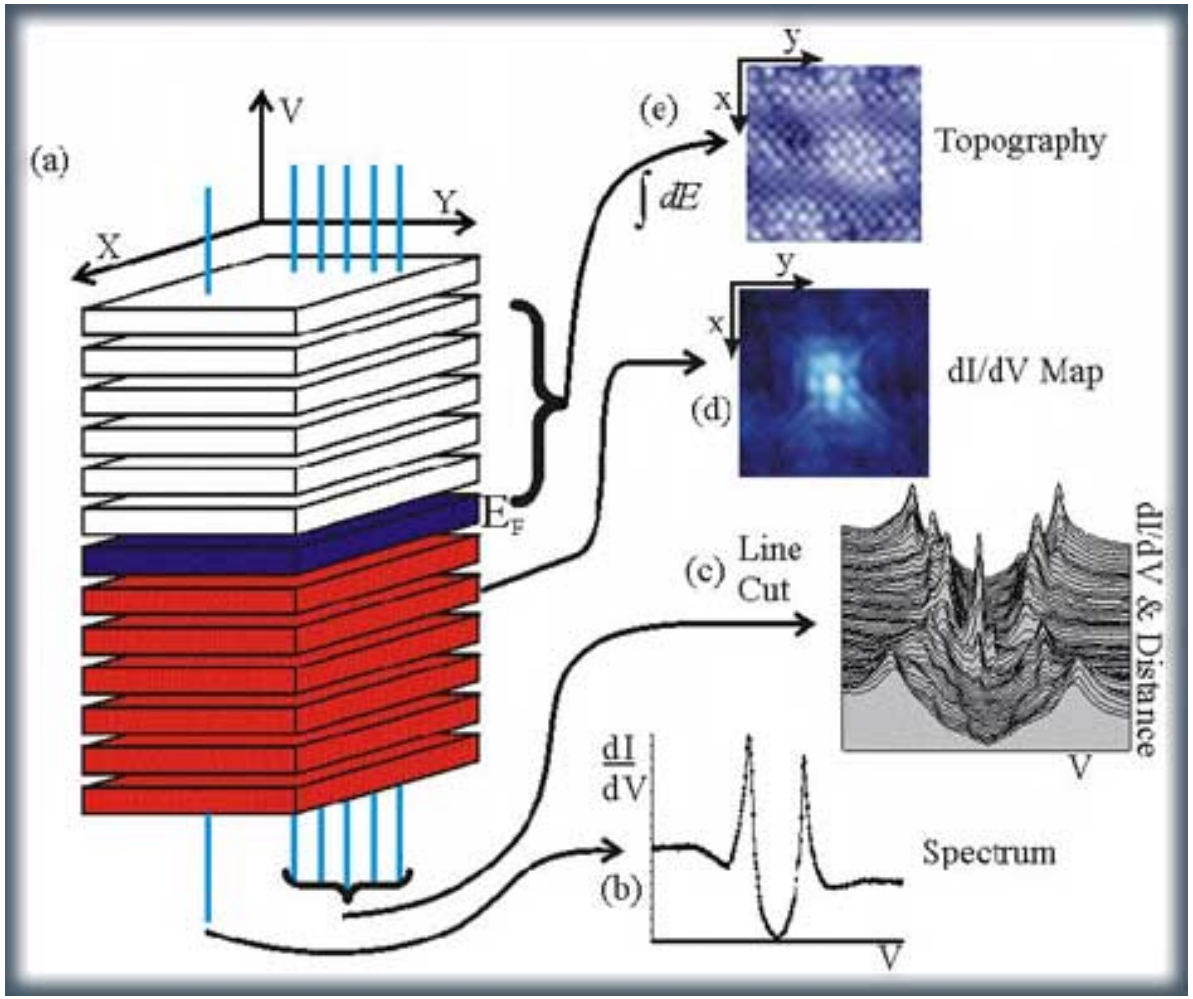
ARPES measurements



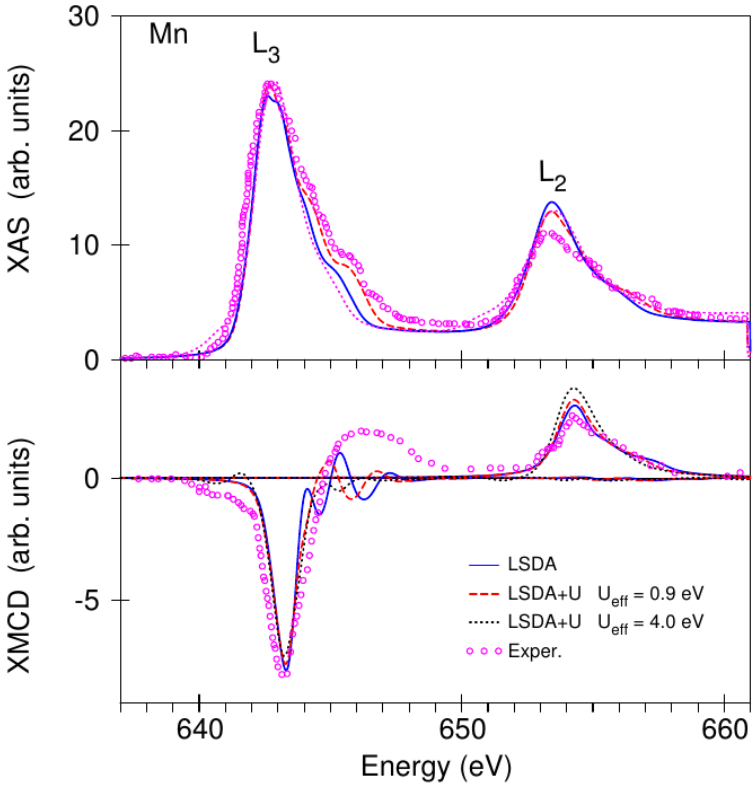
Theory

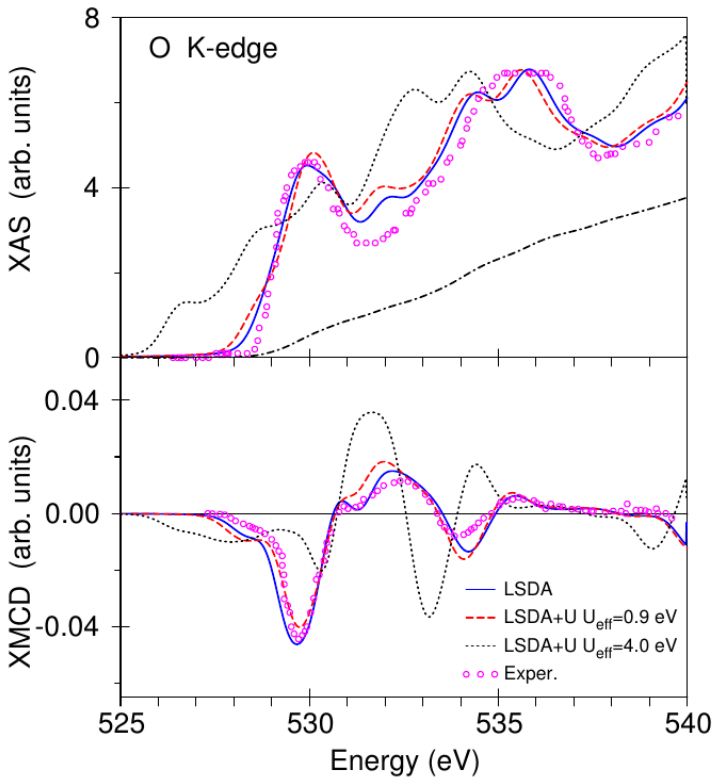


Supporting experiments: STM



Simulating experiments: XMCD in $La_{2/3}Sr_{1/3}MnO_3$





Topics

First-principles material design

I. **First-principle approach**
- Many-body problem
- *Ab-initio* molecular dynamics
- Density functional theory
  a) Kohn-Sham equation
  b) Approximations for exchange-correlation energy
  c) Solving the Kohn-Sham equation
  d) Linear response theory within the DFT
- Beyond the DFT

II. **Real systems from first-principles**
- Fe islands on Cu(111)
- Ho atoms on Pt(111)
- Magnetic oxides

III. **Summary**

I. First-principle approach

I. First-principles approach

Hamiltonian of a many-body system:

$$\hat{H} = -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 + \sum_{i<j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{I,i} \frac{e^2 Z_I}{|\mathbf{R}_i - \mathbf{r}_i|} + \sum_{I<J} \frac{e^2 Z_I Z_J}{|\mathbf{R}_i \mathbf{R}_J|}$$

$$= -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 - \sum_i \frac{\hbar^2}{2m_i}\nabla_i^2 + V_e(\{\mathbf{r}_i\}, \{\mathbf{R}_i\})$$

$$= -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \hat{H}_e(\{\mathbf{r}_i\}, \{\mathbf{R}_i\})$$

$\mathbf{r}_i$, $\mathbf{R}_I$: electronic & nuclear degrees of freedom

$\hat{H}_e(\{\mathbf{r}_i\}, \{\mathbf{R}_i\})$: electronic Hamiltonian

Time-dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}; t) = \hat{H}\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}; t)$$

I. First-principles approach

Hamiltonian of a many-body system:

$$\hat{H} = \underbrace{-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2}_{T_K} \underbrace{-\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2}_{T_e} + \underbrace{\sum_{i<j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}}_{V_{ee}} \underbrace{-\sum_{I,i} \frac{e^2 Z_I}{|\mathbf{R}_i - \mathbf{r}_i|}}_{V_{eK}} \underbrace{+\sum_{I<J} \frac{e^2 Z_I Z_J}{|\mathbf{R}_i \mathbf{R}_J|}}_{V_{KK}}$$

$$= -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 - \sum_i \frac{\hbar^2}{2m_i}\nabla_i^2 + V_e(\{\mathbf{r}_i\},\{\mathbf{R}_i\})$$

$$= -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \hat{H}_e(\{\mathbf{r}_i\},\{\mathbf{R}_i\})$$

$\mathbf{r}_i$, $\mathbf{R}_I$: electronic & nuclear degrees of freedom

$\hat{H}_e(\{\mathbf{r}_i\},\{\mathbf{R}_i\})$: electronic Hamiltonian

Time-dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\Phi(\{\mathbf{r}_i\},\{\mathbf{R}_i\};t) = \hat{H}\Phi(\{\mathbf{r}_i\},\{\mathbf{R}_i\};t)$$

I. First-principles approach

Separation of nuclear & electron contributions: Single configuration ansatz

$$\Phi(\{\mathbf{r}_i\},\{\mathbf{R}_i\};t) \approx \Psi(\{\mathbf{r}_i\};t)\chi(\{\mathbf{R}_I\};t)\exp\left[\frac{i}{\hbar}\int_{t_0}^{t} d\,t'\,\tilde{E}_e(t')\right]$$

with

$$\tilde{E}_e = \int d\,\mathbf{r}d\,\mathbf{R}\,\Psi^*(\{\mathbf{r}_i\};t)\chi^*(\{\mathbf{R}_I\};t)\hat{H}_e\Psi(\{\mathbf{r}_i\};t)\chi(\{\mathbf{R}_I\};t)$$

Time-dependent self-consistent field approach: Dirac (1930)

$$\begin{aligned} i\hbar\frac{\partial\Psi}{\partial t} &= -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2\Psi + \left\{\int d\mathbf{R}\,\chi^* V_e\chi\right\}\Psi \\ i\hbar\frac{\partial\chi}{\partial t} &= -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2\chi + \left\{\int d\,\mathbf{r}\,\Psi^*\hat{H}_e\Psi\right\}\chi \end{aligned}$$

I. First-principles approach

Nuclear as a classical particle:

$$\chi(\{\mathbf{R}_I\};t) \approx A(\{\mathbf{R}_I\};t)\exp\left[\frac{i}{\hbar}S(\{\mathbf{R}_I\};t)\right]$$

with an real amplitude $A(\{\mathbf{R}_I\};t)$ and a phase factor $S(\{\mathbf{R}_I\};t)$

$$\frac{\partial S}{\partial t} + \sum_I \frac{1}{2M_I}\left(\nabla_I S\right)^2 + \int d\,\mathbf{r}\Psi^*\hat{H}_e\Psi = \hbar^2\sum_I \frac{1}{2M_I}\frac{\nabla_I^2 A}{A}$$

$$\frac{\partial A}{\partial t} + \sum_I \frac{1}{M_I}\left(\nabla_I A\right)\left(\nabla_I S\right) + \sum_I \frac{1}{2M_I}A\left(\nabla^2 S\right) = 0$$

Classical limit: $\hbar \to 0$

$$\frac{\partial S}{\partial t} + \sum_I \frac{1}{2M_I}\left(\nabla_I S\right)^2 + \int d\,\mathbf{r}\Psi^*\hat{H}_e\Psi = 0$$

I. First-principles approach

Hamilton-Jacobi form:

$$\frac{\partial S}{\partial t} + H(\{\mathbf{R}_I\}, \{\nabla_I S\}) = 0$$

with

$$H(\{\mathbf{R}_I\}, \{\mathbf{P}_I\}) = T(\{\mathbf{P}_I\}) + V(\{\mathbf{R}_I\}) \text{ and } \mathbf{P}_I = \nabla_I S$$

Thus, we have

$$\begin{aligned} \frac{d\,\mathbf{P}_I}{d\,t} &= -\nabla_I \int d\,\mathbf{r}\,\Psi^* \hat{H}_e \Psi \quad \text{or} \\ M_I \ddot{\mathbf{R}}_I(t) &= -\nabla_I \int d\,\mathbf{r}\,\Psi^* \hat{H}_e \Psi = -\nabla_I V_e^E(\{\mathbf{R}_i(t)\}) \end{aligned}$$

Further approximation: $\hbar \to 0 \Rightarrow |\chi(\{\mathbf{R}_I\})| \approx \prod_I \delta(\mathbf{R}_I - \mathbf{R}_I(t))$

$$i\hbar \frac{\partial \Psi}{\partial t} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \Psi + V_e \Psi$$

I. First-principles approach

***Ab-initio* self-consistent set of molecular dynamics equations:**

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}_e(\{\mathbf{r}_i,\},\{\mathbf{R}_I,\})\Psi$$

$$M_I\ddot{\mathbf{R}}_I(t) = -\nabla_I V_e^E(\{\mathbf{R}_I(t)\})$$

with

$$\hat{H}_e(\{\mathbf{r}_i,\},\{\mathbf{R}_I,\}) = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 + V_e(\{\mathbf{r}_i,\},\{\mathbf{R}_I,\})$$

Classical molecular dynamics equation:

$$M_I\ddot{\mathbf{R}}_I(t) = -\nabla_I V_e^{cl}(\{\mathbf{R}_I(t)\})$$

with

$$V_e^{cl}(\{\mathbf{R}_I(t)\}) = \sum_I v_1(\mathbf{R}_I) + \sum_{I<J} v_2(\mathbf{R}_I,\mathbf{R}_J) + \sum_{I<J<K} v_3(\mathbf{R}_I,\mathbf{R}_J,\mathbf{R}_K) + ...$$

I. First-principles approach

Electronic system:

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}_e(\{\mathbf{r}_i,\},\{\mathbf{R}_I,\})\Psi \text{ with } \hat{H}_e = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eK} + \hat{V}_{KK}$$

Ansatz for time independent Hamiltonian

$$\Psi(\mathbf{r},\mathbf{R};t) = \psi(\mathbf{r},\mathbf{R})\cdot f(t) \quad \Rightarrow \begin{cases} \hat{H}_e\psi = E\psi \\ i\hbar\dfrac{1}{f(t)}\dfrac{d\,f(t)}{d\,t} = E \end{cases}$$

Density matrix: density instead the wave function

$$\hat{\gamma}_N = |\psi_N\rangle\langle\psi_N| \quad \Rightarrow i\hbar\frac{\partial}{\partial t}\hat{\gamma}_N = \left[\hat{H}_e,\hat{\gamma}_N\right] = \left[\hat{\gamma}_N,\hat{H}_e\right]$$

Advantages:

- unique for a state
- Hermitian
- Observable $\langle\hat{A}\rangle = \mathrm{Tr}\left(\hat{\gamma}_N\hat{A}\right) = \mathrm{Tr}\left(\hat{A}\hat{\gamma}_N\right)$

I. First-principles approach

Reduced density matrix for fermions: $\psi_N(\mathbf{x}_1, ..., \mathbf{x}_N)$ is antisymmetric

$$\hat{\gamma}_1(\mathbf{x}_1{}', \mathbf{x}_1) = N \int d\mathbf{x}_2 ... d\mathbf{x}_N \psi_N^*(\mathbf{x}_1{}', \mathbf{x}_2, ...\mathbf{x}_N)\psi_N(\mathbf{x}_1, \mathbf{x}_2, ...\mathbf{x}_N)$$

$$\hat{\gamma}_2(\mathbf{x}_1{}'\mathbf{x}_2{}', \mathbf{x}_1\mathbf{x}_2) =$$

$$= \frac{N(N-1)}{2} \int d\mathbf{x}_3 ... d\mathbf{x}_N \psi_N^*(\mathbf{x}_1{}', \mathbf{x}_2{}', ...\mathbf{x}_N)\psi_N(\mathbf{x}_1, \mathbf{x}_2, ...\mathbf{x}_N)$$

Expectation value of the electronic Hamiltonian (in atomic units):

$$E = \mathrm{Tr}\left(\hat{H}_e \hat{\gamma}_N\right) = \int d\mathbf{x}_1 \left[\left(-\frac{1}{2}\nabla_1^2 + v(\mathbf{r}_1)\right)\gamma_1(\mathbf{x}_1{}', \mathbf{x}_1)\right]_{\mathbf{x}_1{}'=\mathbf{x}_1}$$

$$+ \iint d\mathbf{x}_1 d\mathbf{x}_2 \frac{1}{r_{12}} \gamma_2(\mathbf{x}_1{}'\mathbf{x}_2{}', \mathbf{x}_1\mathbf{x}_2)$$

I. First-principles approach

Spinless density matrices:

$$\rho_1\left(\mathbf{r}_1{}', \mathbf{r}_1\right) = \int ds_1 \gamma_1\left(\mathbf{r}_1{}' s_1, \mathbf{r}_1 s_1\right)$$

$$\rho_2\left(\mathbf{r}_1{}'\mathbf{r}_2{}', \mathbf{r}_1\mathbf{r}_2\right) = \iint ds_1 ds_2 \gamma_2\left(\mathbf{r}_1{}' s_1 \mathbf{r}_2{}' s_2, \mathbf{r}_1 s_1 \mathbf{r}_2 s_2\right)$$

Hartree term:

$$J[\rho] = \frac{1}{2}\iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{r_{12}} \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)$$

Pair correlation function:

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\left[1 + h(\mathbf{r}_1, \mathbf{r}_2)\right]$$

Pair correlation function:

$$\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1) h(\mathbf{r}_1, \mathbf{r}_2)$$

Electron-repulsion term:

$$V_{ee} = \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{r_{12}} \rho_2(\mathbf{r}_1, \mathbf{r}_2) = J[\rho] + \frac{1}{2}\iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{r_{12}} \rho(\mathbf{r}_1)\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2)$$

I. First-principles approach

Energy functional of an external potential $v(\mathbf{r})$:

$$E_v = T[\rho] + v[\rho] + V_{ee}[\rho] = T[\rho] + v[\rho] + J[\rho] + [V_{ee}[\rho] - J[\rho]]$$

First Hohenberg-Kohn theorem:

The external potential $v(\mathbf{r})$ is determined, within a trivial additive constant, the electron density $\rho(\mathbf{r})$. $\rho(\mathbf{r})$ determines the ground state and all other electronic properties of the system.

Second Hohenberg-Kohn theorem:

For a trial density $\tilde{\rho}(\mathbf{r})$ such that $\tilde{\rho}(\mathbf{r}) \geq 0$ and $\int d\mathbf{r}\tilde{\rho}(\mathbf{r}) = N$,

$$E_0 \leq E_v[\tilde{\rho}]$$

Levi constrained-search formulation:

$$E_0 = \underset{\rho}{\mathrm{Min}} \left\{ \underset{\psi \to \rho}{\mathrm{Min}} \left[\langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle + \int d\mathbf{r} v(\mathbf{r}) \rho(\mathbf{r}) \right] \right\}$$

I. First-principles approach

Total energy functional:

$$E_v[\rho] = T[\rho] + v[\rho] + J[\rho] + [V_{ee}[\rho] - J[\rho]] = F[\rho] + v[\rho]$$

Two main problems:

- Kinetic energy of interacting particles $T[\rho]$
- Electron-electron interaction $[V_{ee}[\rho] - J[\rho]]$

Kohn-Sham approach:

$$E_v[\rho] = T_s[\rho] + v[\rho] + J[\rho] + E_{xc}[\rho]$$

with the kinetic energy of non-interacting particles $T_s[\rho]$ and the exchange-correlation functional

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho]$$

$E_{xc}[\rho]$ should be approximated

I. First-principles approach

Kohn-Sham non-interaction equation:

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r})\right]\psi_i = \varepsilon_i\psi_i$$

with

$$\rho(\mathbf{r}) = \sum_i^N \sum_s |\psi_i(\mathbf{r}, s)|^2$$

and

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \frac{\delta J[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})} = v(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}(\mathbf{r})$$

Local density approximation:

$$E_{xc}^{LDA}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\varepsilon_{xc}(\rho)$$

$\varepsilon_{xc}(\rho)$: the exchange-correlation energy of a uniform electron gas

$$v_{xc}^{LDA}(\mathbf{r}) = \varepsilon_{xc}(\rho(\mathbf{r})) + \rho(\mathbf{r})\frac{\delta\varepsilon_{xc}(\rho)}{\delta\rho}$$

Generalized gradient approximation (GGA):

$$E_{xc}^{GGA}[\rho^{\uparrow},\rho^{\downarrow}] = \int d\mathbf{r} f\left(\rho^{\uparrow},\rho^{\downarrow},\nabla\rho^{\uparrow},\nabla\rho^{\downarrow}\right)$$

Hybrid functionals: B3LYP (Becke, three-parameter, Lee-Yang-Parr)

$$E_{xc}^{B3LYP} = E_x^{LDA} + a_0\left(E_x^{HF} - E_x^{LDA}\right) + a_x\left(E_x^{GGA} - E_x^{LDA}\right)$$
$$+ \quad E_c^{LDA} + a_c\left(E_c^{GGA} - E_c^{LDA}\right)$$

Exact exchange method: Only exchange, no correlations

$$E_x[\rho] = -\frac{1}{2}\sum_{i,j}^{occ}\iint d\mathbf{r}d\mathbf{r}'\frac{\psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_j(\mathbf{r})\psi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

with the exchange potential

$$v_x(\mathbf{r}) = \frac{\delta E_x[\rho]}{\delta\rho}$$

Correlation part of E_{xc} can be calculated with another (e.g. LDA, GGA) approach

One electron system:

$$J[\rho] \neq 0\,, \;\; V_{ee}[\rho] = 0$$

It is not the case for many functionals such as LSDA, GGA etc

Necessary requirement:

$$J[\rho_i^\sigma, 0] + E_{xc}[\rho_i^\sigma, 0] = 0$$

Self-interaction correction: Perdew, Zunger (1981)

$$E_{xc}^{SIC}[\rho^\uparrow, \rho^\downarrow] = E_{xc}^{LSDA}[\rho^\uparrow, \rho^\downarrow] - \sum_{i\sigma} \left(J[\rho_i^\sigma] + E_{xc}^{LSDA}[\rho_i^\sigma, 0] \right)$$

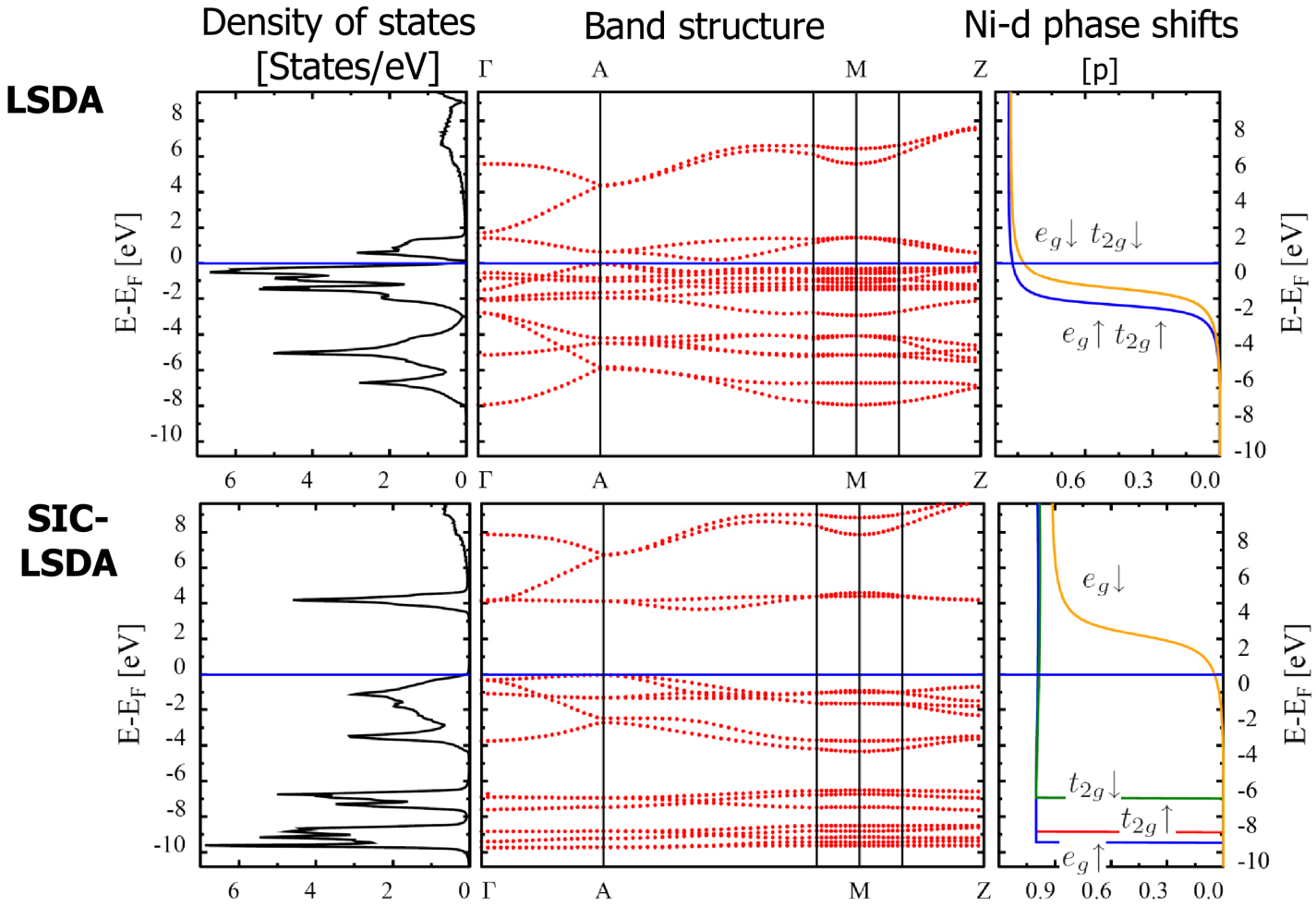
SIC Kohn-Sham equation:

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}^{LSDA}(\mathbf{r}) + v_{i\sigma}^{SIC}(\mathbf{r}) \right] \psi_i^{SIC}(\mathbf{r}) = \varepsilon_i \psi_i^{SIC}(\mathbf{r})$$

with

$$v_{i\sigma}^{SIC}(\mathbf{r}) = -\int d\mathbf{r}' \, \frac{\rho_i^\sigma(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \frac{\delta E_{xc}[\rho_i^\sigma, 0]}{\delta \rho_i^\sigma(\mathbf{r})}$$

Example: NiO



M. Däne, M. Lüders, A. Ernst, D. Ködderitzsch, W. M. Temmerman, Z. Szotek, and W. Hergert, J. Phys.: Condens. Matter (2009)

Exactly solvable two electron models: Harmonian (Taut 1993)

$$\hat{H} = -\frac{1}{2}\nabla_1^2 + \frac{1}{2}\omega^2\mathbf{r}_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{2}\omega^2\mathbf{r}_2^2 + \frac{1}{|\mathbf{r}-\mathbf{r}'|}$$

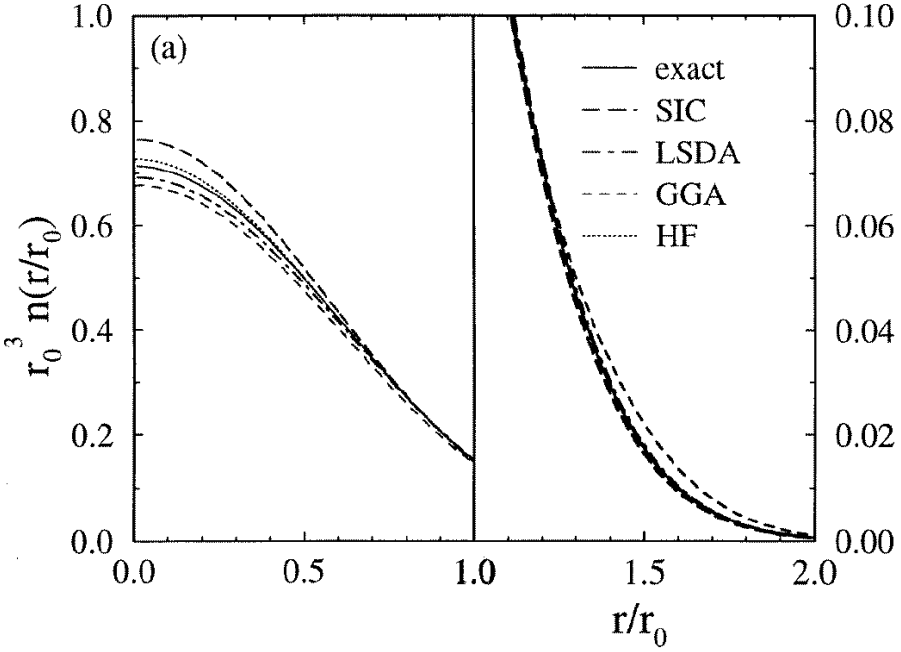
ω is a degree of correlations:

strong ($\omega \ll 1$), middle ($\omega \approx 1$), weak ($\omega \gg 1$)

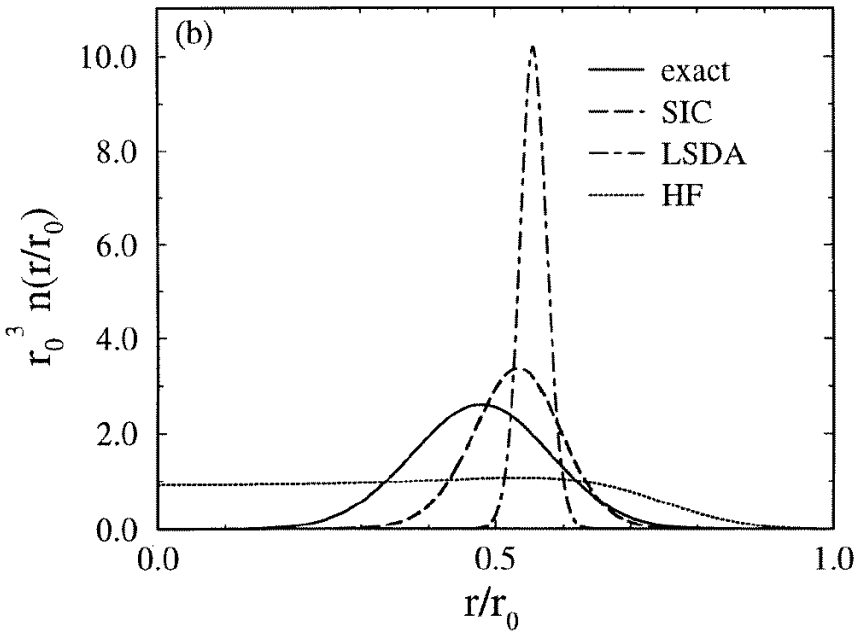
Idea: solve the problem with first-principles approaches and compare with the exact solution

Comparison of charge densities

$\omega = 1/2$



$\omega = 6.48771 \times 10^{-5}$



M. Taut, A. Ernst, and H. Eschrig, J. Phys. B: (1998)

Time dependent Kohn-Sham equation: Runge & Gross (1984)

$$\left(-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r},t)\right)\psi_i(\mathbf{r},t) = -i\frac{\partial}{\partial t}\psi_i(\mathbf{r},t), \;\; \psi_i(\mathbf{r},0) = \psi_i(\mathbf{r})$$

with the time dependent density

$$\rho(,t) = \sum_i^N \mid \psi_i(\mathbf{r},t) \mid^2$$

Linear response theory:

$$\hat{H}'_{KS}[\rho](t) = \hat{H}_{KS}[\rho](t) + \delta V_H[\rho](t) + \delta V_{xc}[\rho](t) + \delta V^{ext}(t)$$

Charge density response:

$$\delta\rho(\mathbf{r},t) = \chi_{KS}(\mathbf{r},t;\mathbf{r}',t')\left(\delta V_H[\rho](t) + \delta V_{xc}[\rho](t) + \delta V^{ext}(t)\right)$$

The Dyson equation of the TDDFT:

$$\begin{aligned}\chi(\mathbf{r}_1,t_1;\mathbf{r}_2,t_2) &= \chi_{KS}(\mathbf{r}_1,t_1;\mathbf{r}_2,t_2) \\ &+ \quad \chi_{KS}(\mathbf{r}_1,t_1;\mathbf{r}'_2,t'_2)\left(\frac{1}{|\mathbf{r}'_2-\mathbf{r}'_1|} + f_{xc}(\mathbf{r}'_2,t'_2;\mathbf{r}'_1,t'_1)\right)\chi(\mathbf{r}'_1,t'_1;\mathbf{r}_2,t_2)\end{aligned}$$

Wave function equation

$$\left[\varepsilon + \frac{\hbar^2}{2m}\nabla^2 - V_{eff}(\mathbf{r})\right]\Psi(\mathbf{r};\varepsilon) = 0$$

Green function equation

$$\left[\varepsilon + \frac{\hbar^2}{2m}\nabla^2 - V_{eff}(\mathbf{r})\right]G(\mathbf{r},\mathbf{r}';\varepsilon) = \delta(\mathbf{r}-\mathbf{r}')$$

Korringa (1947), Kohn & Rostoker (1954)

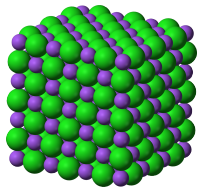
Dyson equation

$$G = G_0 + G_0 \Delta V_{eff} G$$
$$\Delta V_{eff} = V_{eff} - V_{eff}^0$$

I. First-principles approach
Green function method

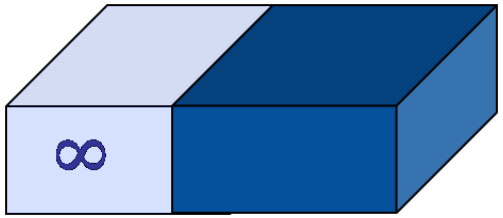
- **Bulk**

$$G_{bulk} = G_{free} + G_{free} V_{eff} G_{bulk}$$



- **Surfaces & interfaces**

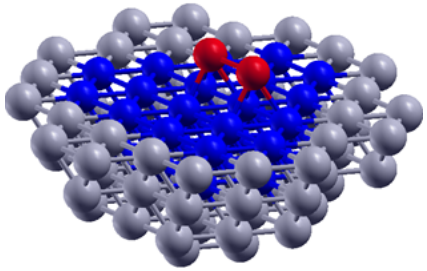
$$G_{surf} = G_{bulk} + G_{bulk} \Delta V_{eff} G_{surf}$$



Wildberger et al. (1997), Uiberacker et al. (1998)

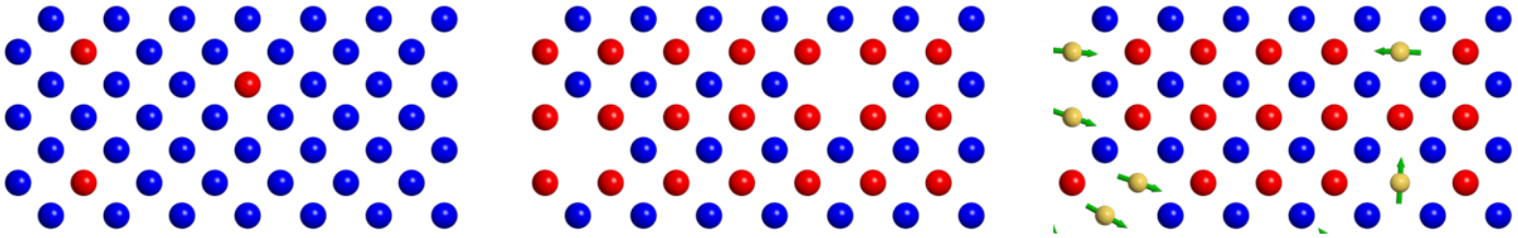
- **Defects in bulk & surfaces**

$$G_{cluster} = G_{host} + G_{host} \Delta V_{eff} G_{cluster}$$



Zeller & Dederichs (1979)

Alloys and pseudo-alloys

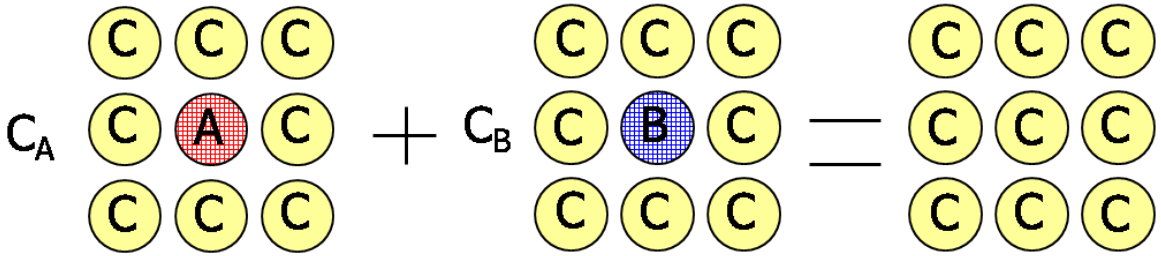


doping/alloys vacancies magnetic impurities

Coherent potential approximation

Soven (1967), Györffy (1972)

CPA equation for a binary alloy: $c_A G_A + c_B G_B = G_C$



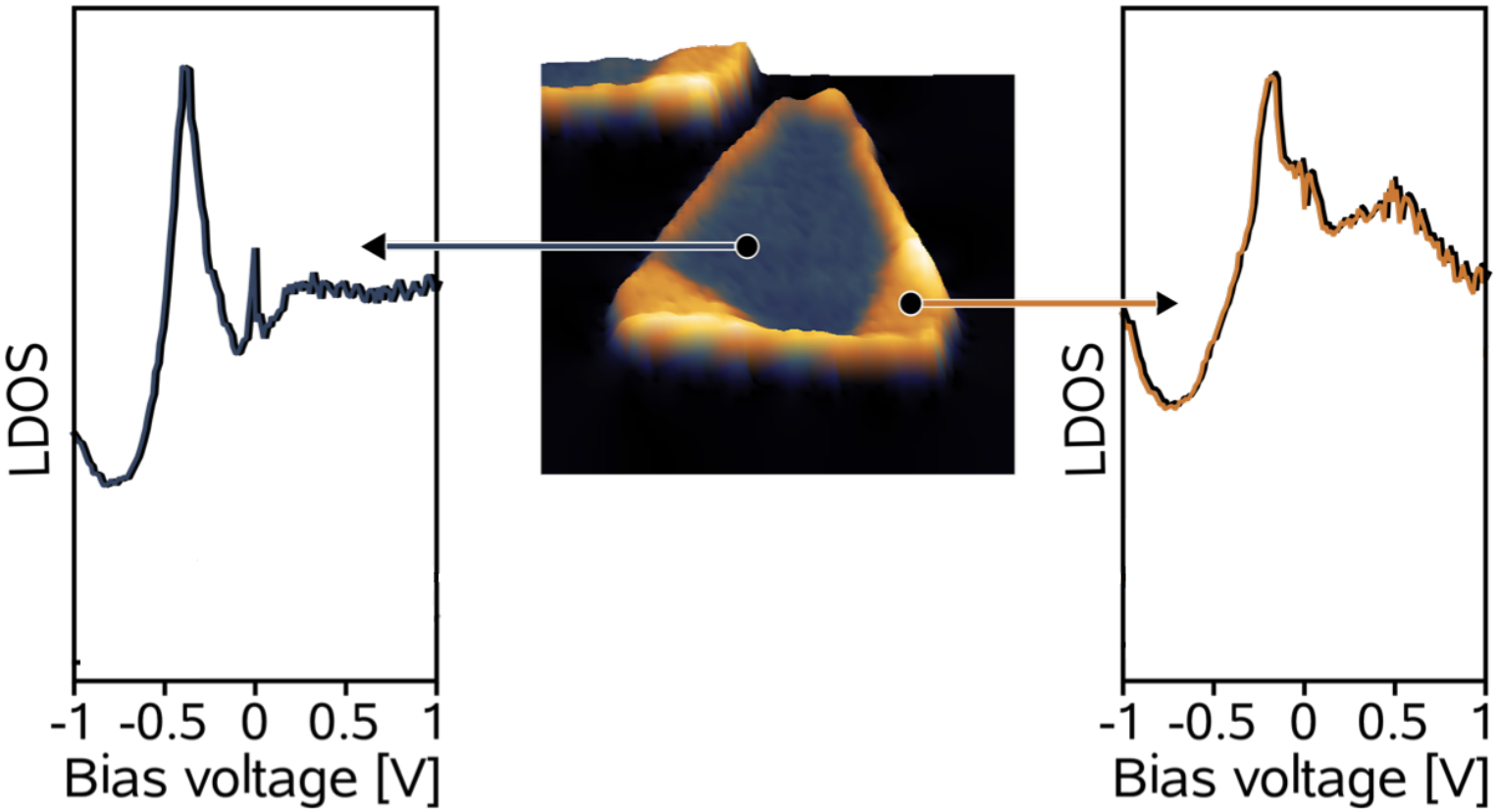
Nonlocal CPA: Charge and Spin-Fluctuations

D. A. Rowlands, A. Ernst, J. B. Staunton, B. L. Györffy, PRB 73, 165122 (2006)

I. First-principles approach
Green function method: short summary

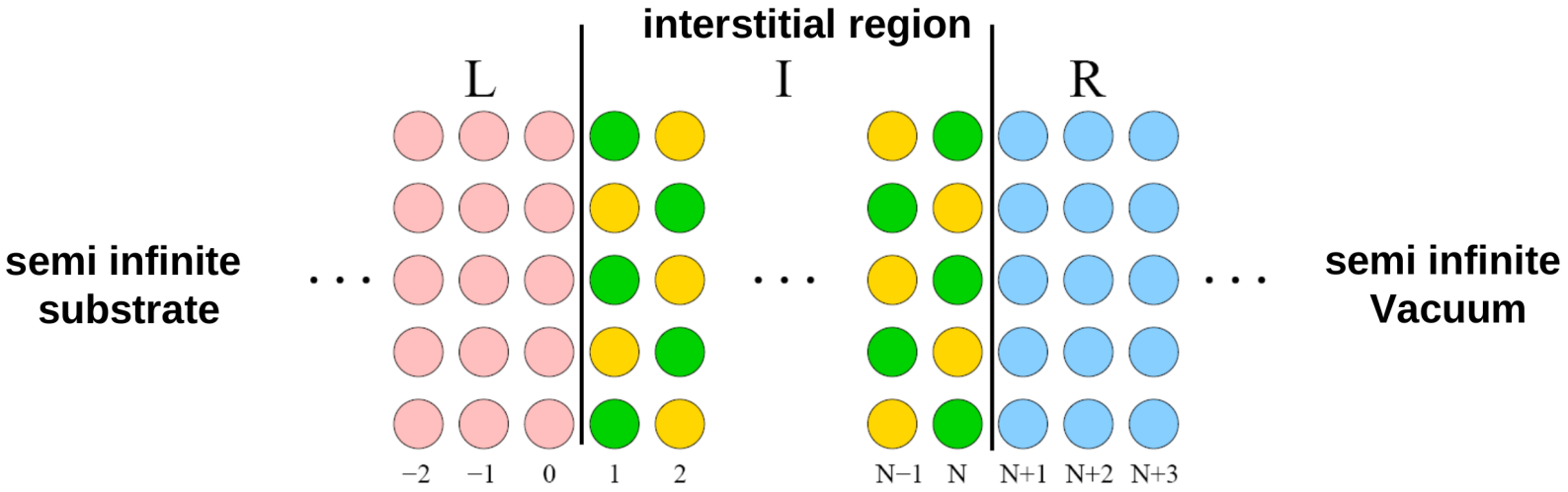
- Explicit Green Function
- Dimensions: 1D, 2D, 3D & Cluster
- $\mathcal{O}(N)$ method
- CPA for disordered alloys
- *multi-code approach*: crystalline structure from VASP or experiments

STM experiment by Wulfhekel *et al*: 2 ML Fe on Cu(111)



Challenge for theory: How to explain different STS spectra?

Method: Green function for semi-infinite systems



STS spectra: Tersoff-Hamann approach (1983)

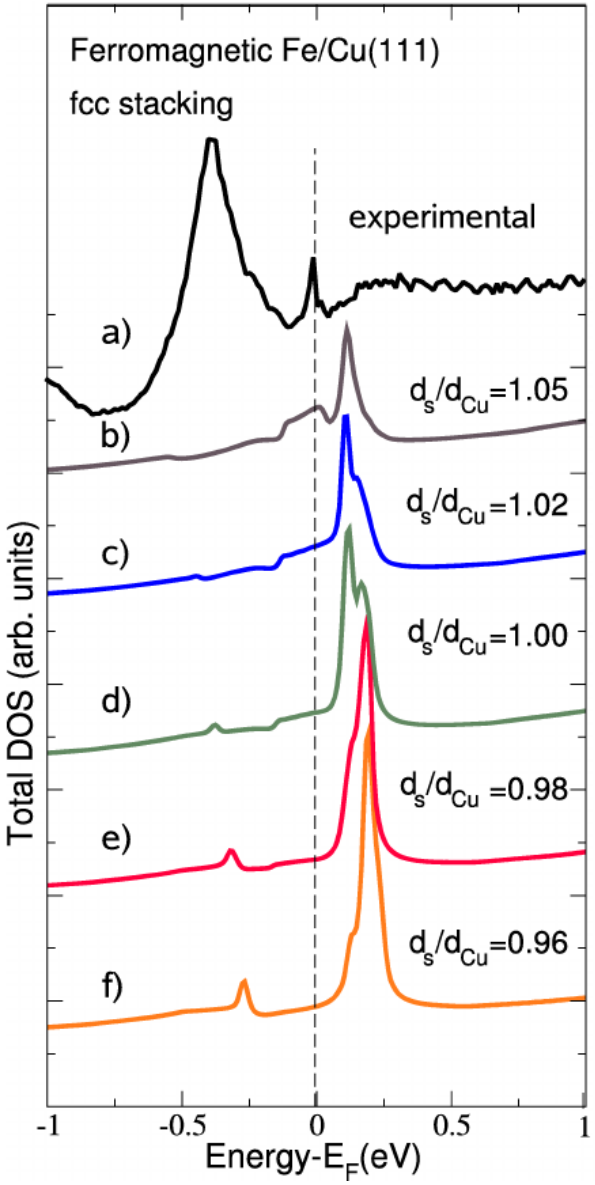
$$dI/dV \sim LDOS$$

Atomic relaxations: VASP code

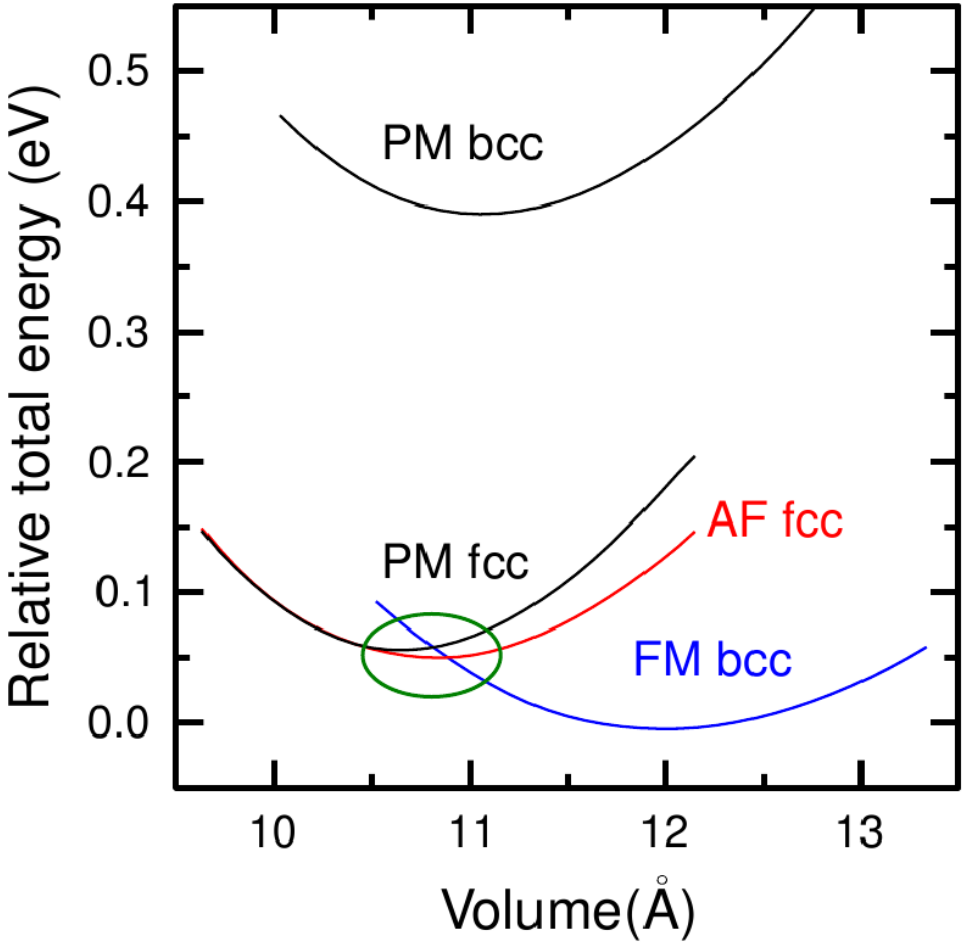
II. Real systems from first-principles
Fe islands on Cu(111)

Island size $\approx 20 \times 20$ **nm**^{2}

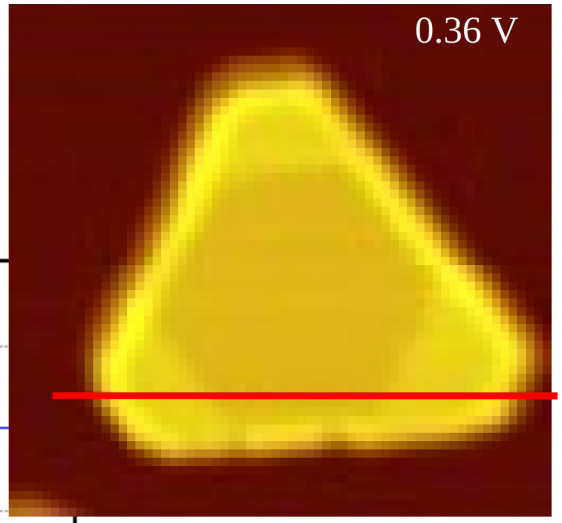
- Islands approximated by 2 Fe ML
- Variational parameters: interlayer spacing, stacking and magnetic order
- Assumption: 2 Fe ML are ferromagnetic (fcc)
- Result: LDOS does not fit experimental STS



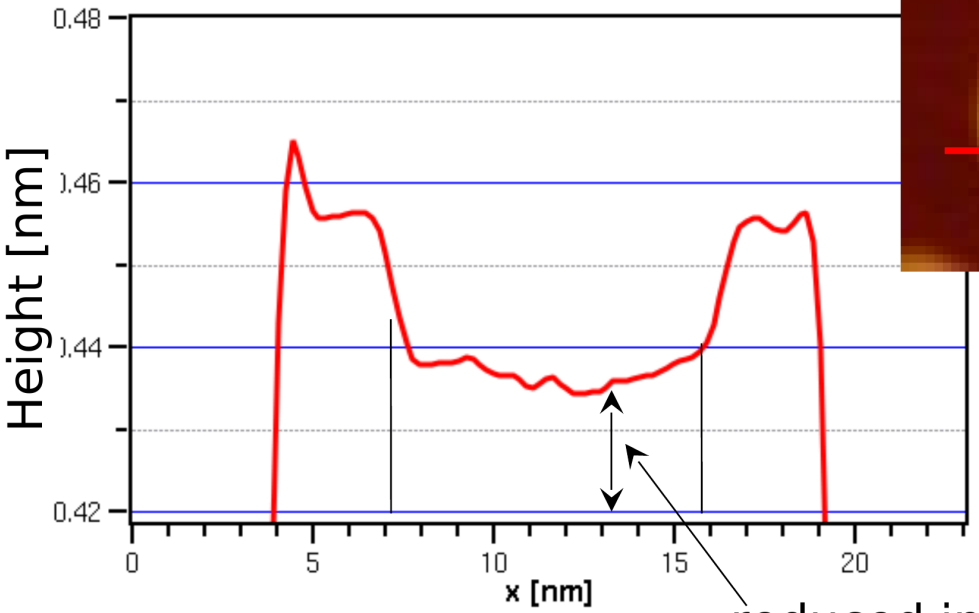
Phase diagram for Fe bulk



Topology of Fe islands



Island cross section



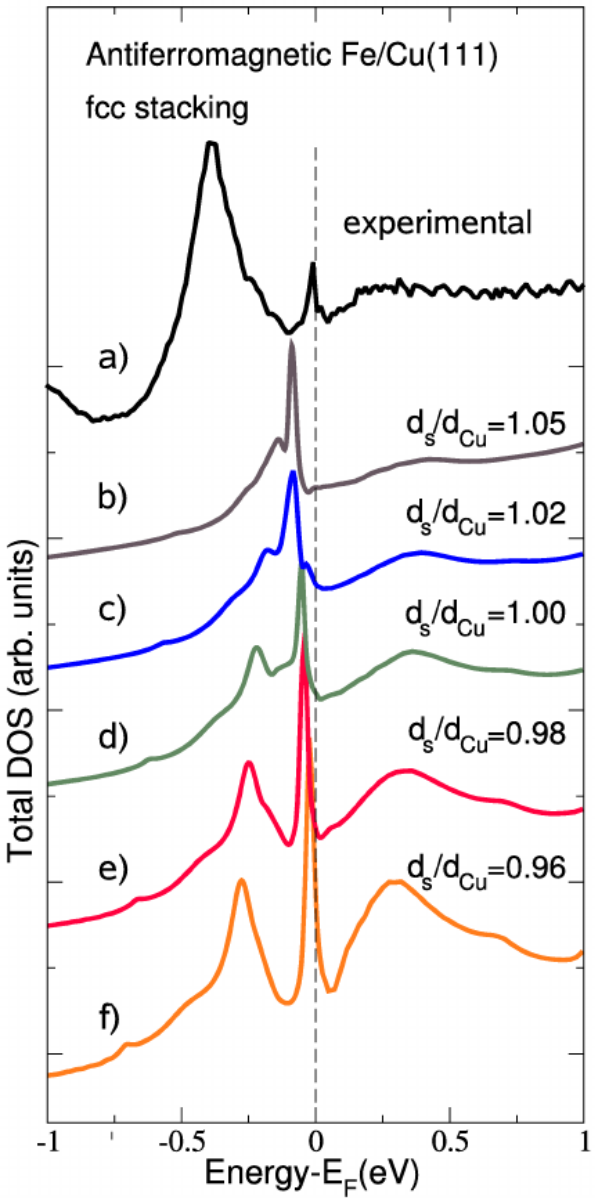
reduced interlayer distance in fcc phase: antiferromagnetism is possible

II. Real systems from first-principles
Fe islands on Cu(111)

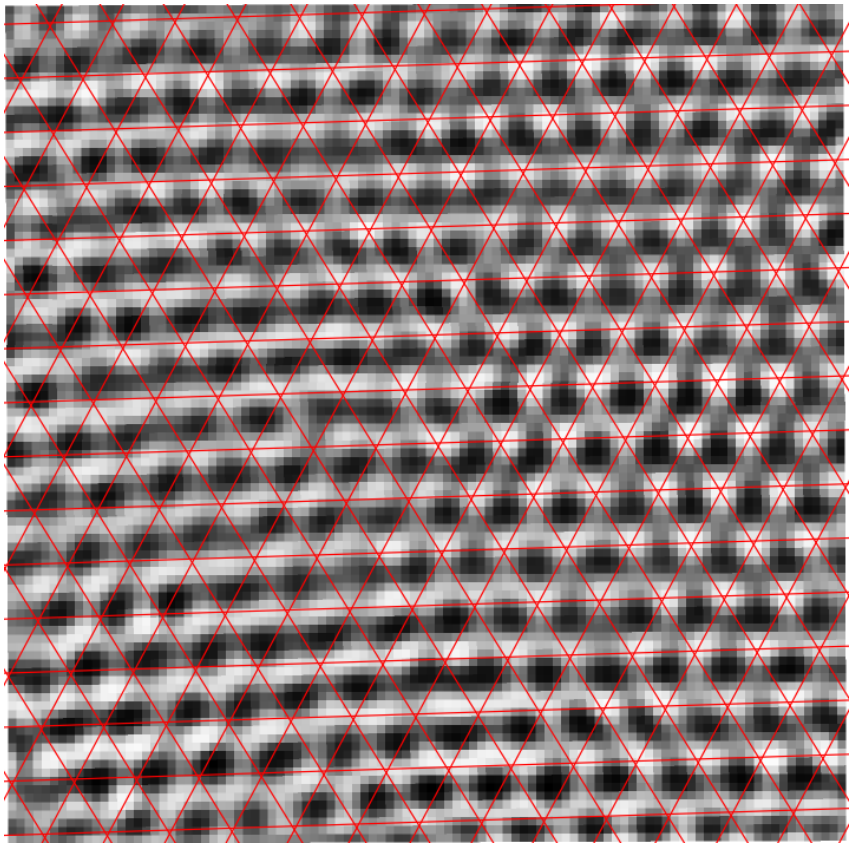
Island size $\approx 20 \times 20$ nm^2

- Islands approximated by 2 Fe ML
- Variational parameters: interlayer spacing, stacking and magnetic order
- Assumption: 2 Fe ML are layerwise antiferromagnetic (fcc)
- Result: LDOS for $d_s/d_{Cu} < 0.98$ fit experimental spectra obtained for the center of Fe islands

How to explain the spectra for the rim?

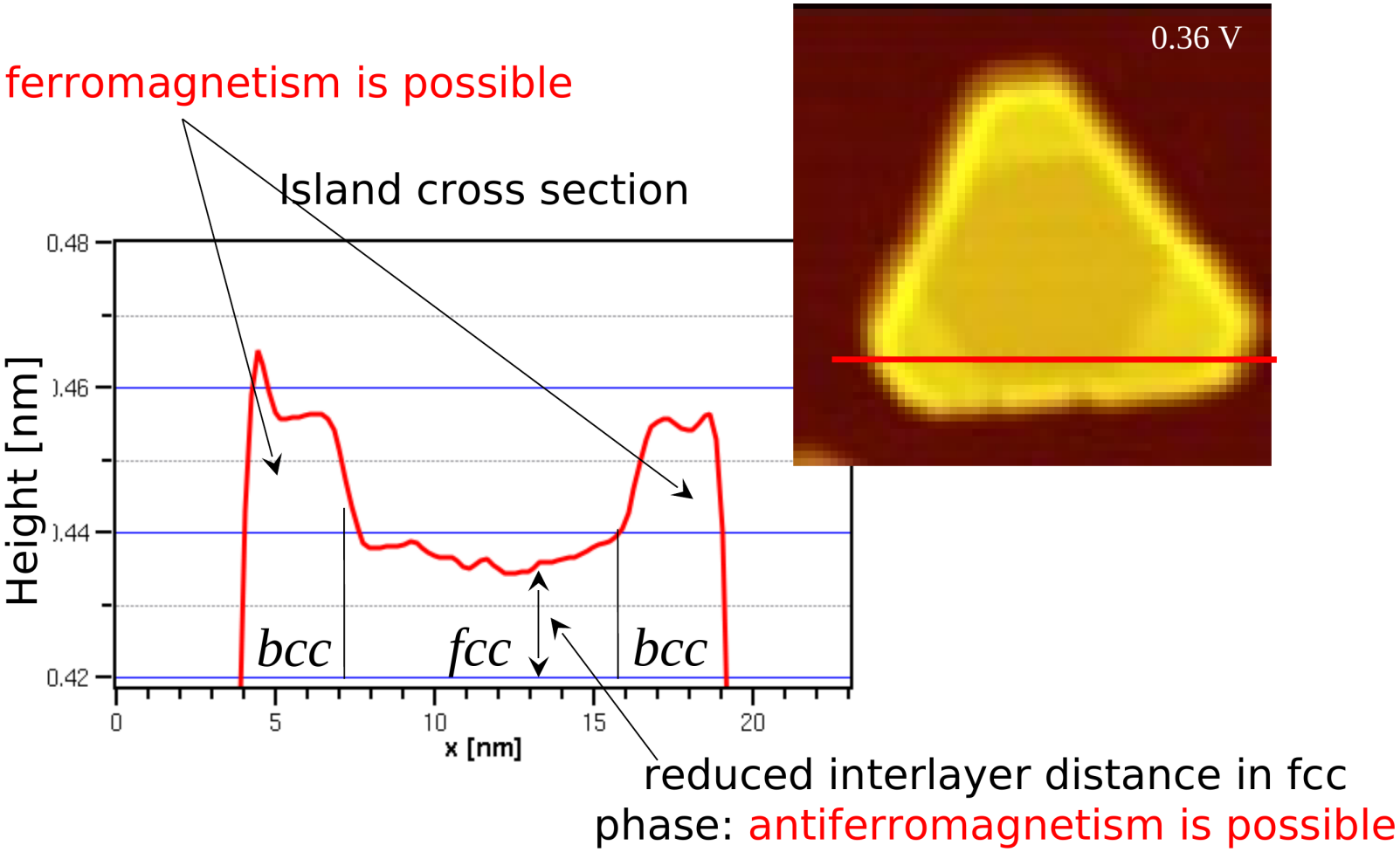


Island topology of Fe islands: coexistence of bcc & fcc phases



A. Biedermann et al, PRB 73, 165418 (2006)

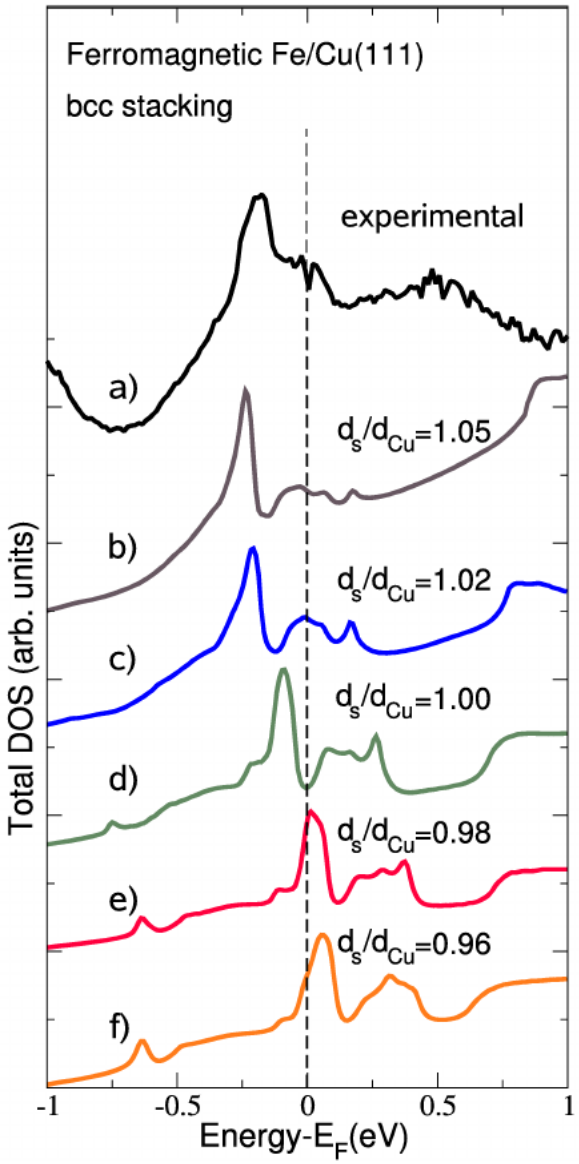
Topology of Fe islands



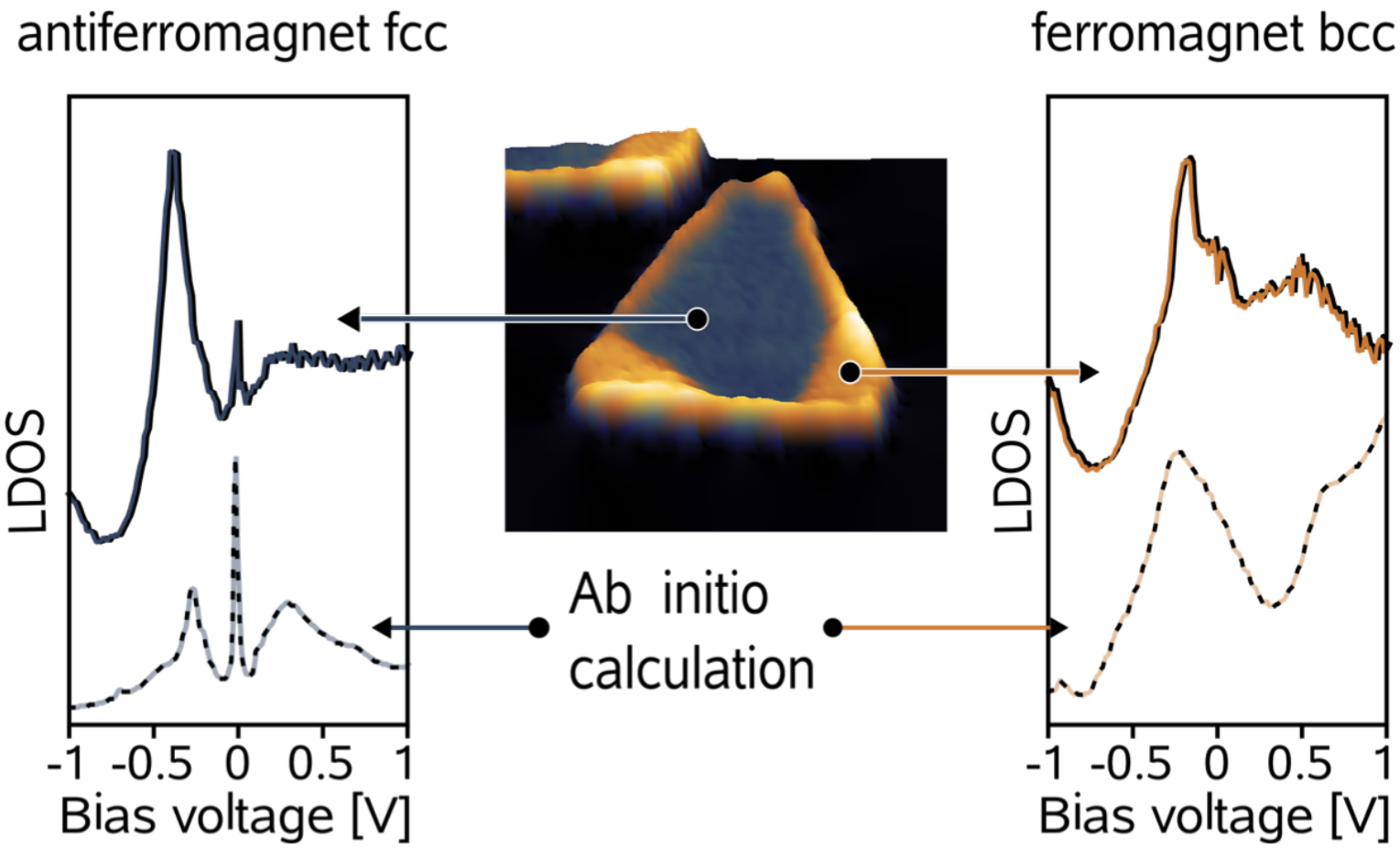
II. Real systems from first-principles
Fe islands on Cu(111)

Island size $\approx 20 \times 20$ nm^2

- Islands approximated by 2 Fe ML
- Variational parameters: interlayer spacing, stacking and magnetic order
- Assumption: 2 Fe ML are ferromagnetic (bcc)
- Result: LDOS for $d_s/d_{Cu} > 1.02$ fit experimental spectra obtained for the rim of Fe islands

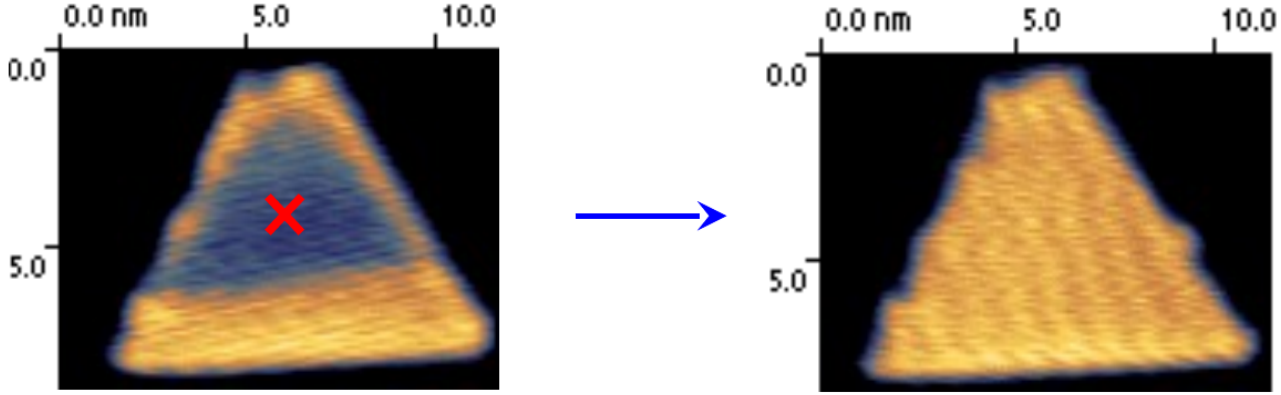


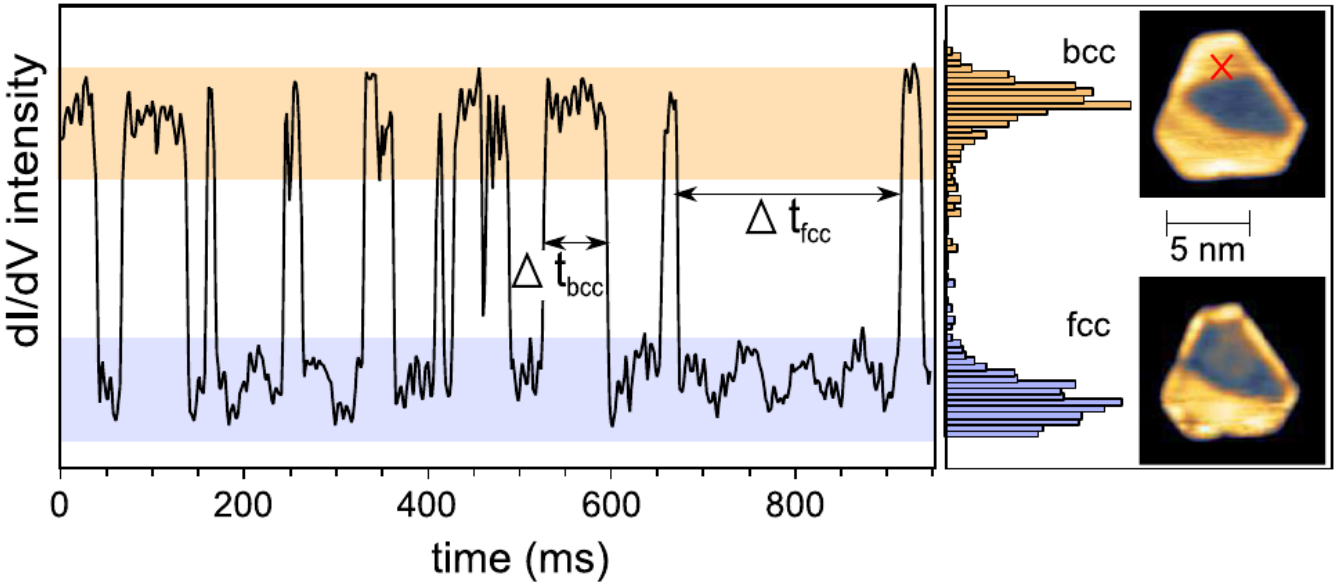
STM experiment by Wulfhekel *et al*: 2 ML Fe on Cu(111)



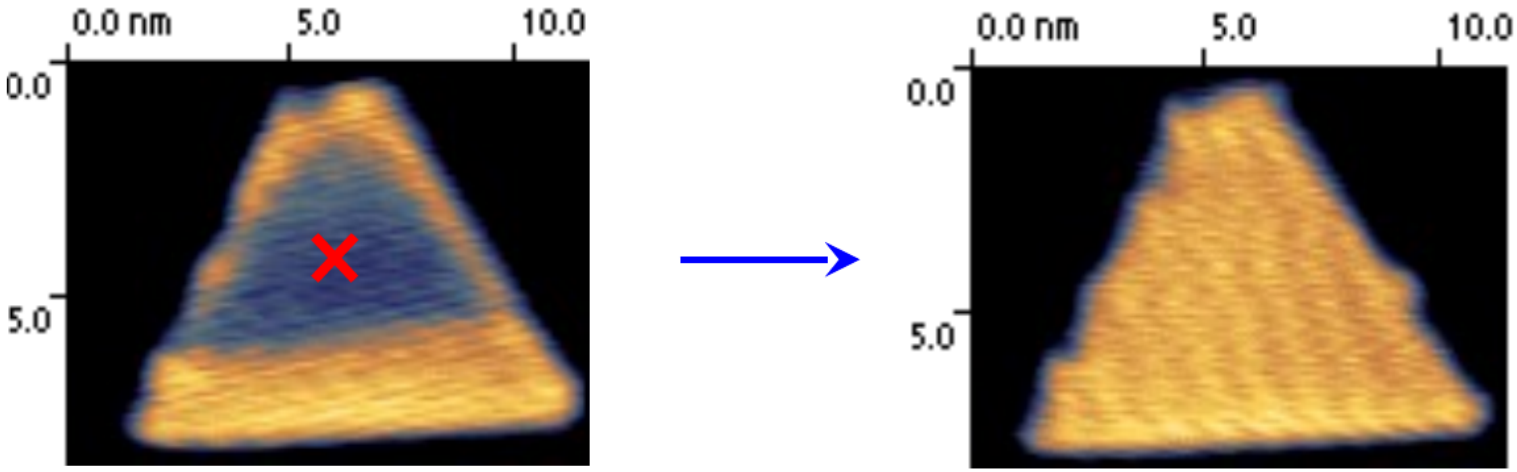
STS spectra with Tersoff-Hamann approach: $dI/dV \sim$ **LDOS**

Topology of Fe islands can modified by an electric field

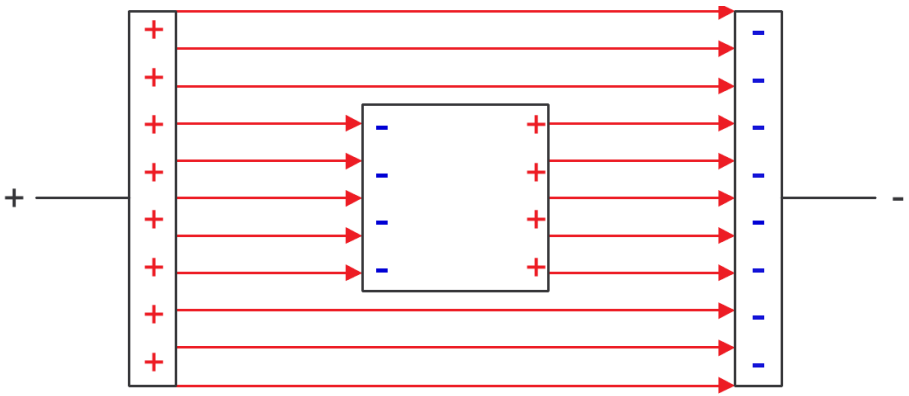




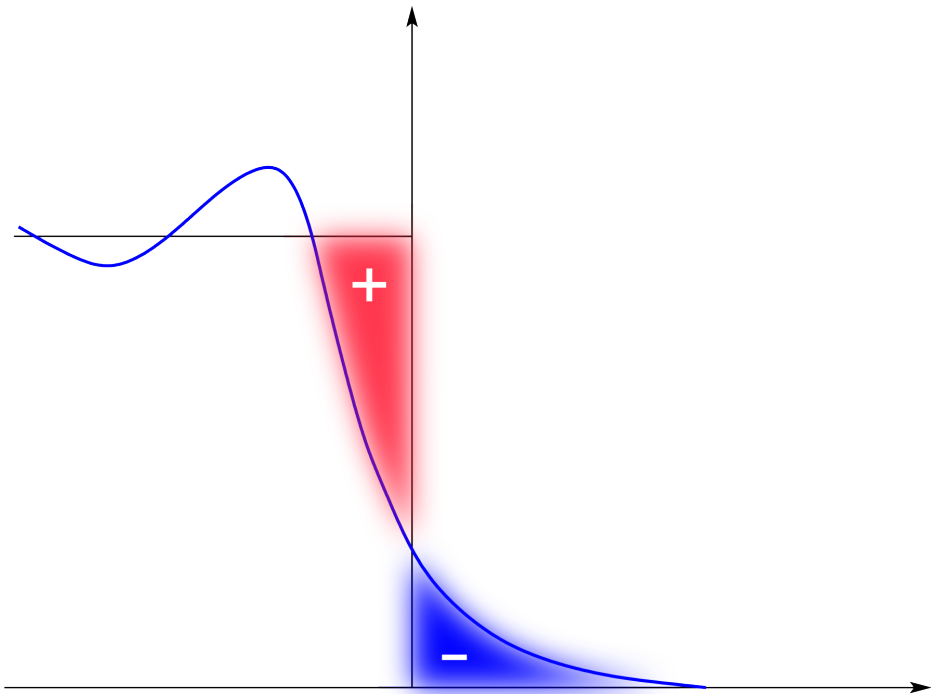
Experiment: Topology of Fe islands can modified by an electric field



Electric field in metals is screened at the surface by free charge carrier

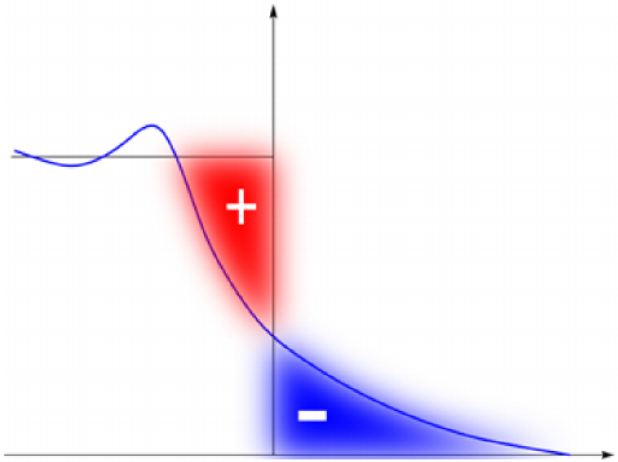


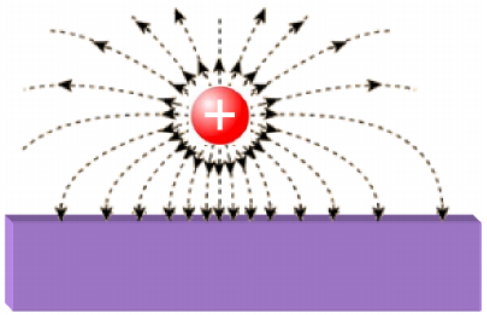
Charge density in vicinity of a surface (Lang & Kohn 1971)



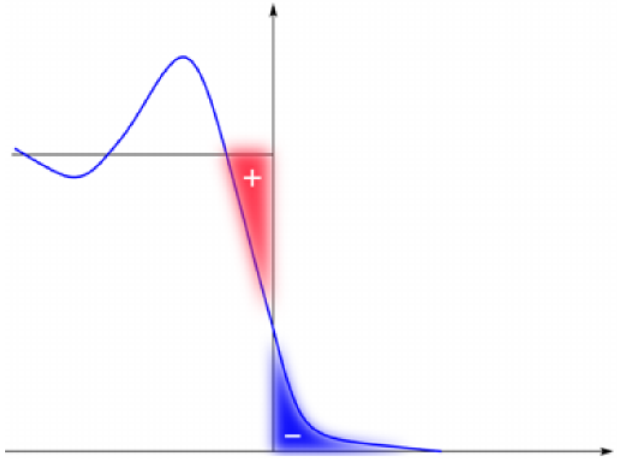
Formation of a surface dipole

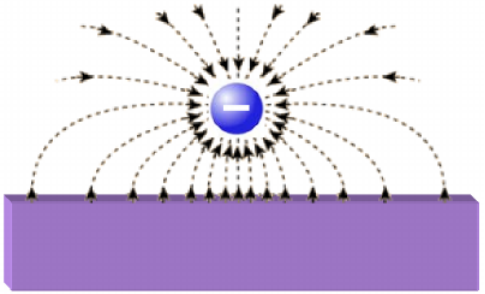
Metallic surface under an applied electric field



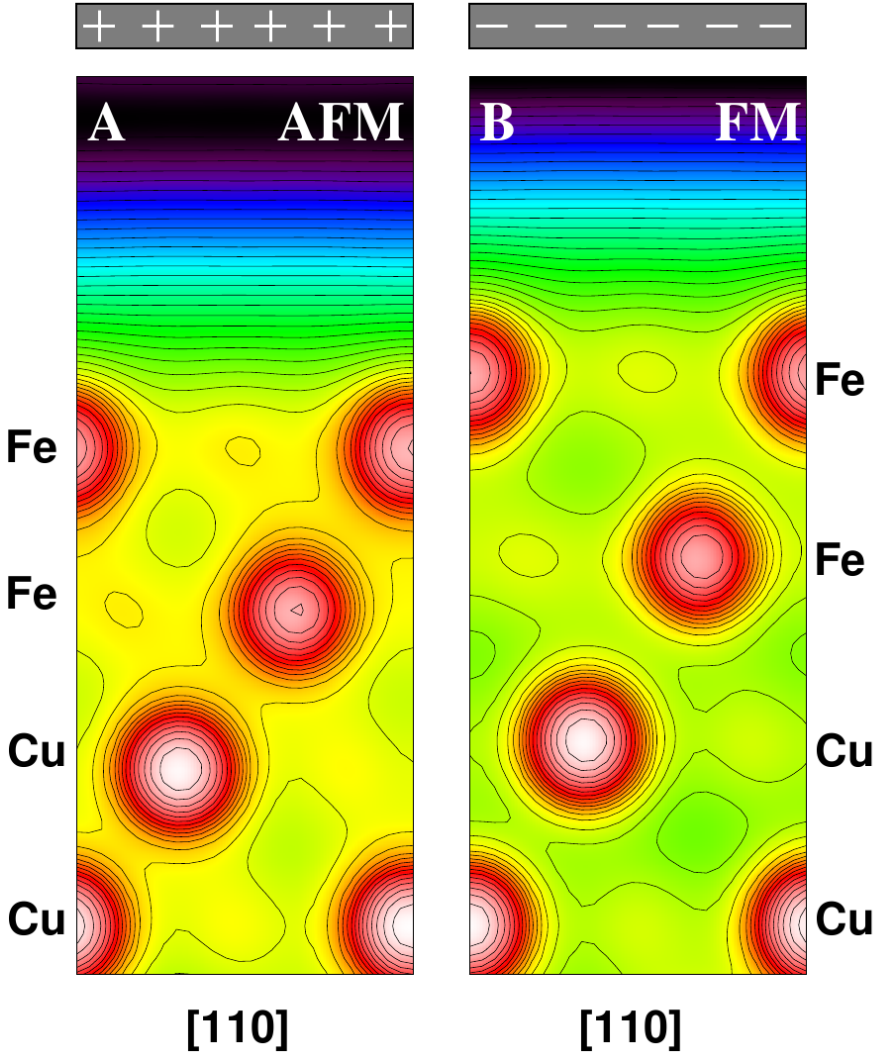


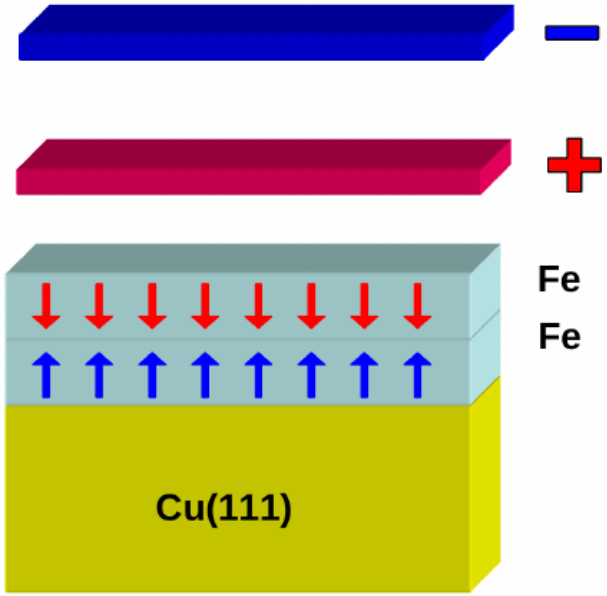
Change of the dipole barrier induces atomic relaxations in the vicinity of the surface





Layer relaxations under an applied electric field



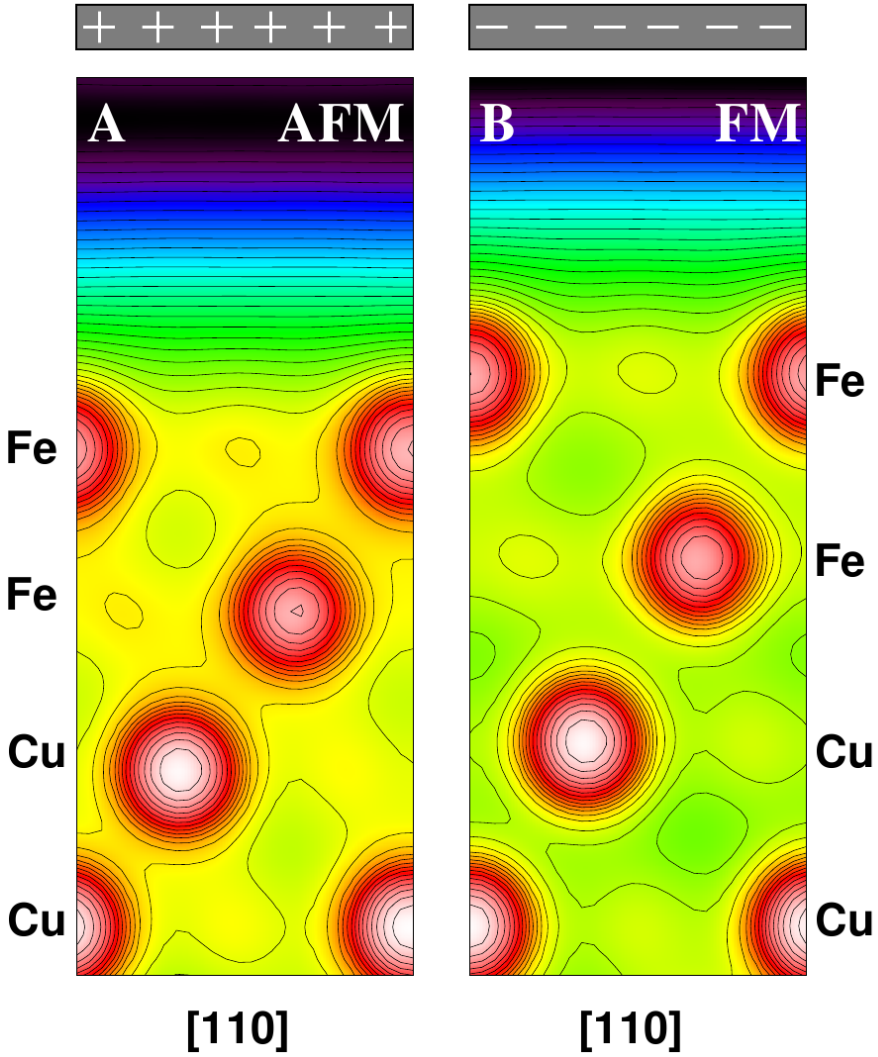


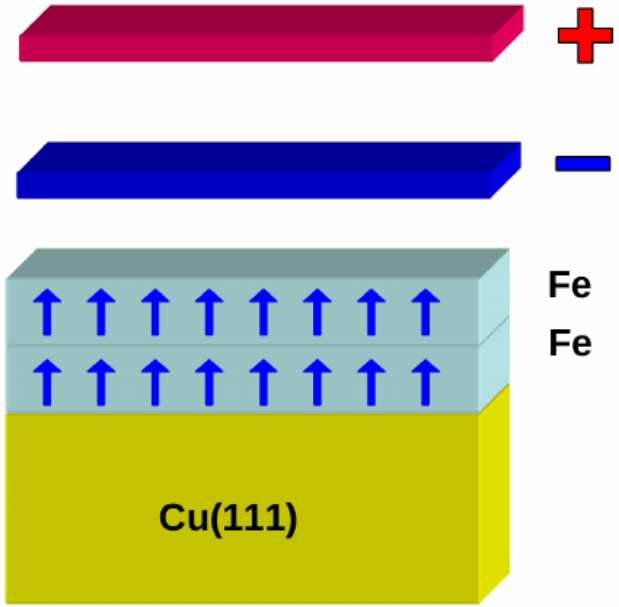
Only vertical displacements

$$d_{Fe_2-Fe_1} < d_{12}^{Cu}$$

Antiferromagnetic order

Layer relaxations under an applied electric field



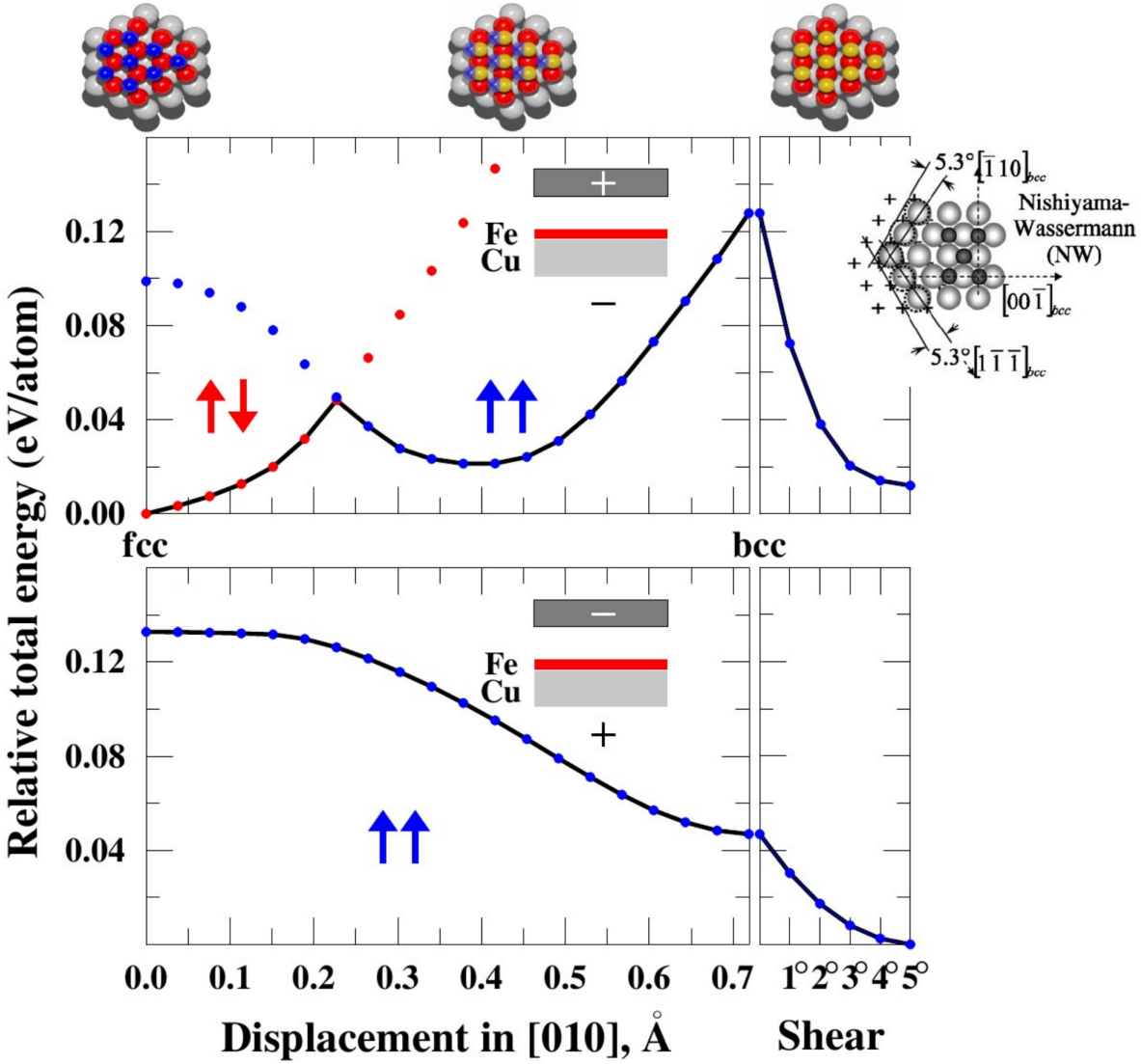


Only vertical displacements

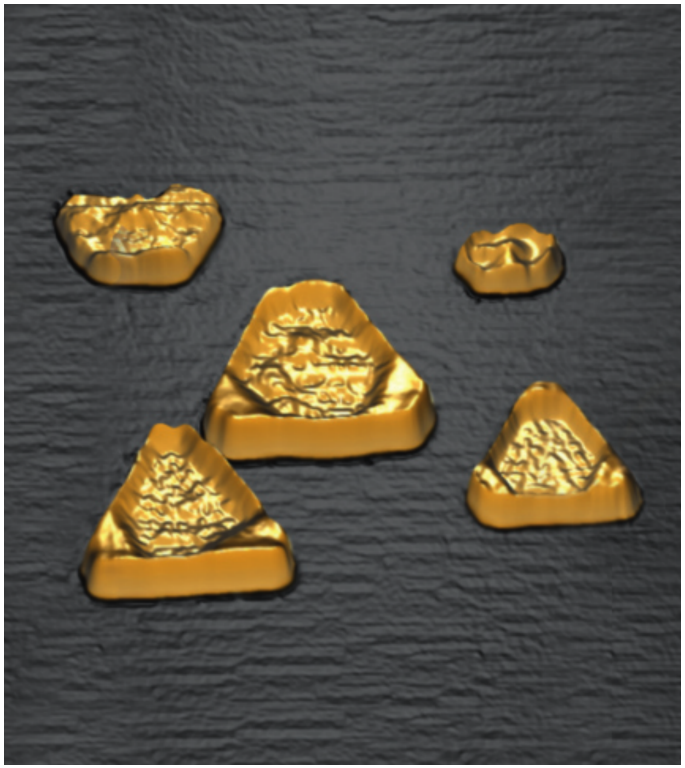
$$d_{Fe_2-Fe_1} > d_{12}^{Cu}$$

Ferromagnetic order

Martensitic transformation under an applied electric field



Fe islands as a memory device switchable by an electric field

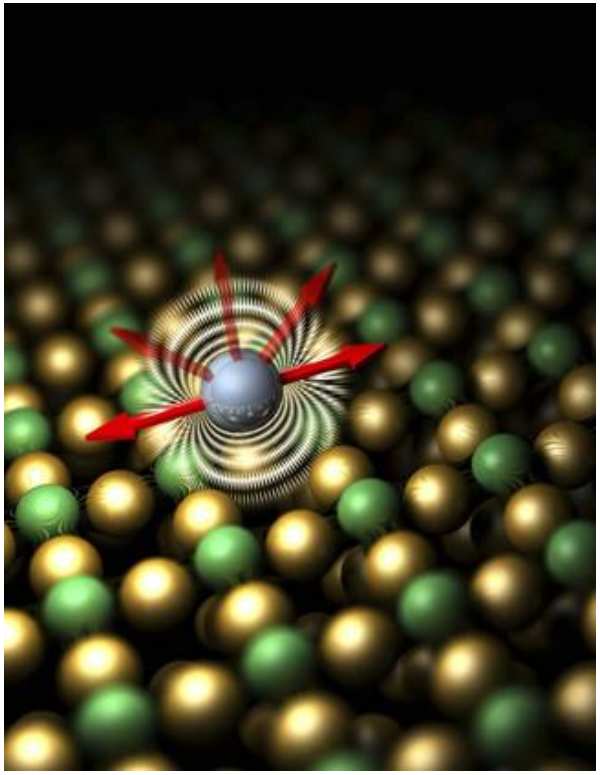


Capacity: 400-600 larger then in conventional memory devices

L. Gerhard, T. K. Yamada, T. Balashov, A. F. Takacs, R. J. H. Wesselink, M. Däne, M. Fechner, S. Ostanin, A. Ernst, I. Mertig and W. Wulfhekel

Nature Nanotechnology (2010)

Single atoms on metallic surfaces

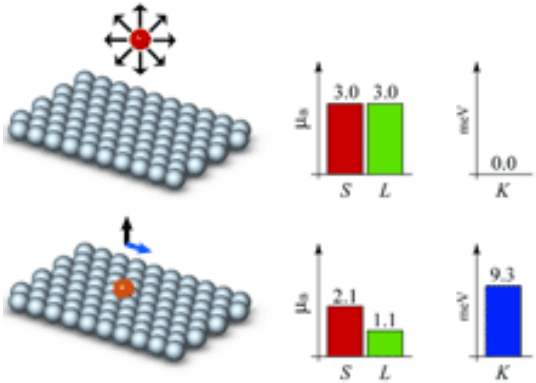


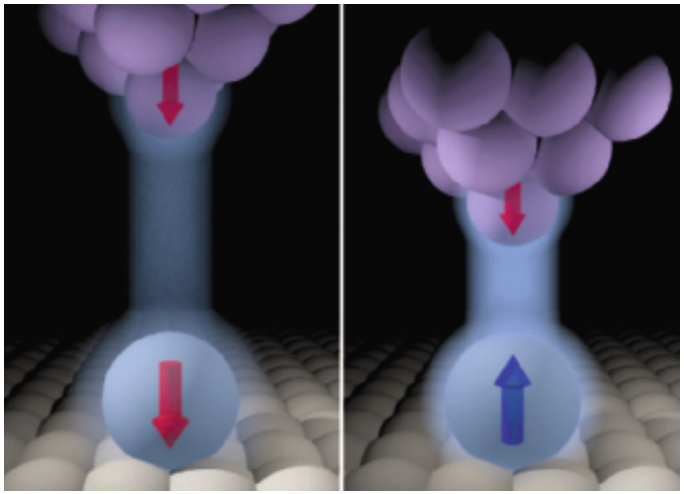
A singe atom on a metallic surface

- The smallest magnetic memory
- The moment direction as a bit
- Conducting surface as an electrode

II. Real systems from first-principles

Fe Ho atoms on Pt(111) surface





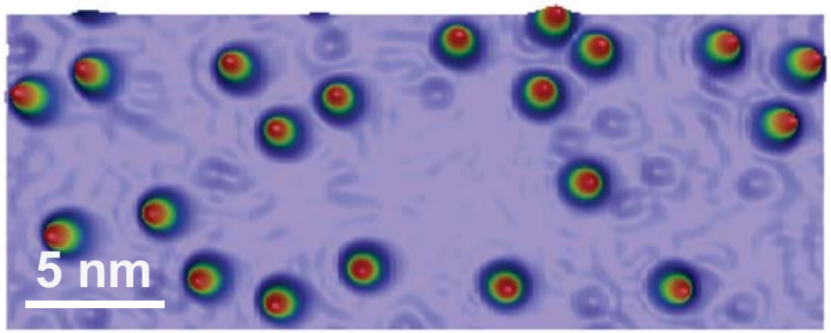
- First experiments

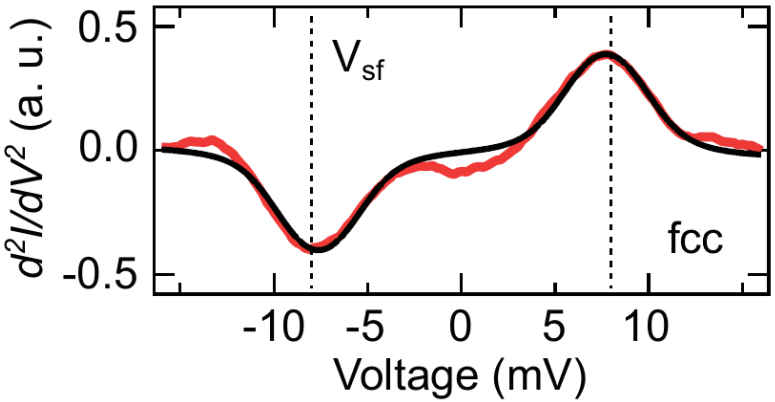
  Co on Pt(111): Gambardella (2003)

  Co & Fe on Pt(111): Balashov (2009)
- STM as a spin-flip switcher
- Problem

  Short lifetime: $10^{-12} - 10^{-6}$ s

STM-Experiment of W. Wulfhekel: Ho-Atoms on Pt(111)





Topology

Excitations

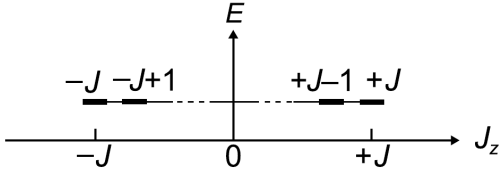
Magnetic moments can be switched by the voltage change

Very long lifetime: 381 ± 49 **s**

T. Miyamachi, T. Schuh, T. Miärkl,i C. Bresch, T. Balashov, A. Stöhr, C. Karlewski, S. André, M. Marthaler, M. Hoffmann, M. Geilhufe, S. Ostanin, W. Hergert, I. Mertig, G. Schön, A. Ernst & Wulf Wulfhekel

Nature (2013)

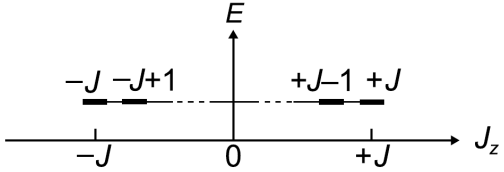
Free atoms:



II. Real systems from first-principles

Fe Ho atoms on Pt(111) surface

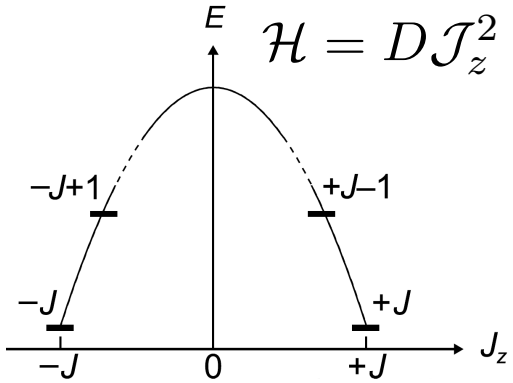
Free atoms:



On a substrate:

Uniaxial magnetic anisotropy

Broken inverse symmetry



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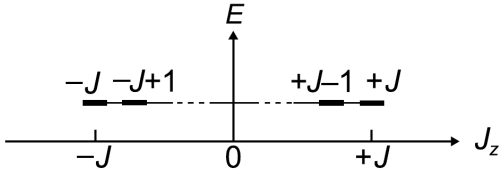

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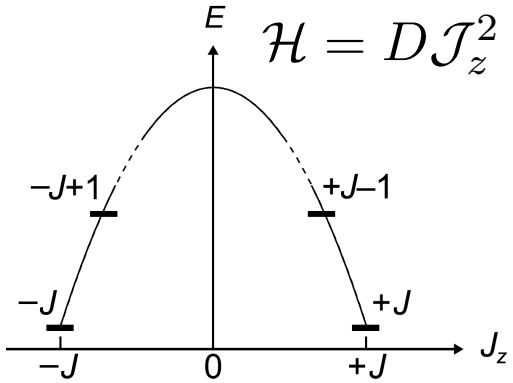
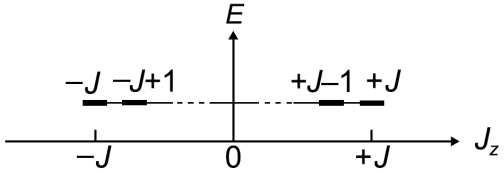


→ Crystal field Hamiltonian:

II. Real systems from first-principles

Fe Ho atoms on Pt(111) surface

Free atoms:



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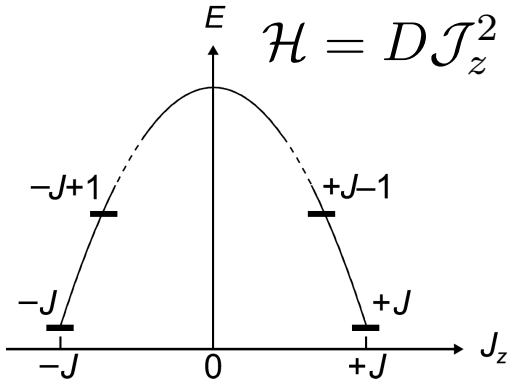


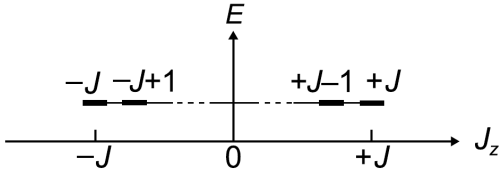
→ Crystal field Hamiltonian:

$$\mathcal{H}_{\mathrm{CF}} = \sum_{n=0}^{\infty} \sum_{m=0}^{n} B_n^m \mathcal{O}_n^m$$

B_n^m Anisotropy constants

$\mathcal{O}_n^m$ Crystal field or Stevens operators

Free atoms:



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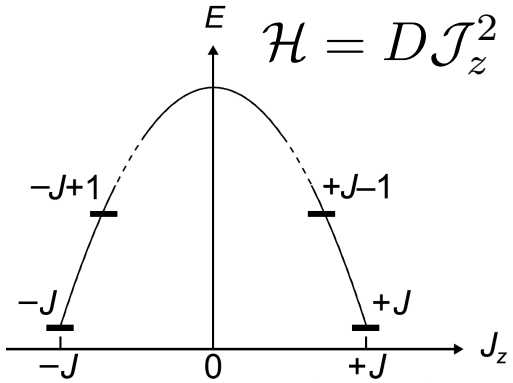

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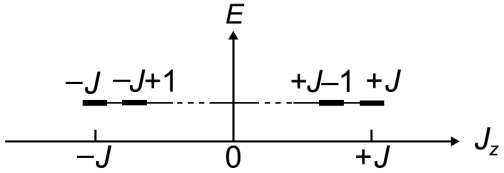
- polynomials of order n in the operator $\mathcal{J}_z$ with order m in ladder operators $\mathcal{J}_+$ and $\mathcal{J}_-$ (acting on $|JM\rangle$)

Free atoms:



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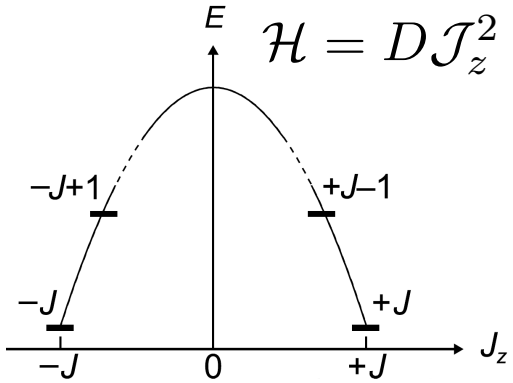

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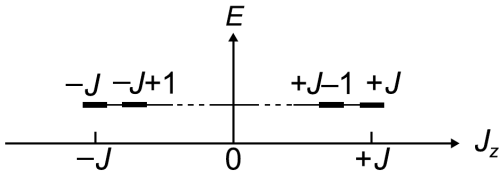
- only even powers of $n \leq 2l$

II. Real systems from first-principles

Fe Ho atoms on Pt(111) surface

Free atoms:



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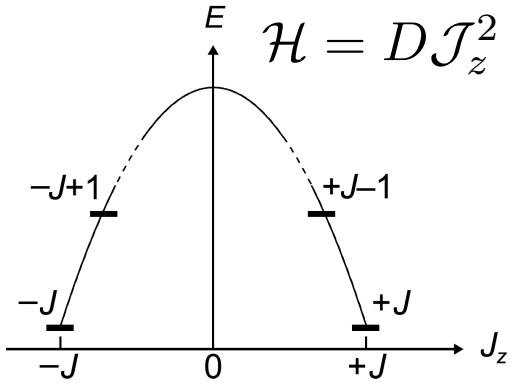

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$\mathcal{O}_n^m$ Crystal field or Stevens operators

- polynomials of order n in the operator $\mathcal{J}_z$ with order m in ladder operators $\mathcal{J}_+$ and $\mathcal{J}_-$ (acting on $|JM\rangle$)
- only even powers of $n \leq 2l$
- terms with $m = 0$ contain only powers of $\mathcal{J}_z$ → not mixes eigenstates

First order perturbation theory:

$|R_{4f}; JM'\rangle$ - unperturbed $4f$ states with n_{4f} unfilled f shells

$V(\mathbf{r})$ - total electrostatic potential

Expectation value $$E_{4f}(M) = \langle R_{4f}; JM| \sum_{i}^{n_{4f}} V(\mathbf{r}_i) |R_{4f}; JM'\rangle \,.$$

First order perturbation theory:

$|R_{4f}; JM'\rangle$ - unperturbed $4f$ states with n_{4f} unfilled f shells

$V(\mathbf{r})$ - total electrostatic potential

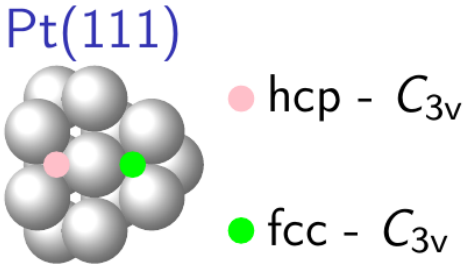
Expectation value $$E_{4f}(M) = \langle R_{4f}; JM| \sum_i^{n_{4f}} V(\mathbf{r}_i) |R_{4f}; JM'\rangle \,.$$

Expansion into real spherical harmonics $Y_{n,m}$:

$$E_{4f}(M) = \sum_{n=0} \sum_{m=0}^{n} \langle R_{4f}|V_{n,m}(r)|R_{4f}\rangle \langle JM| \sum_i^{n_{4f}} Y_{n,m}(\hat{\mathbf{r}}_i)|JM'\rangle$$

II. Real systems from first-principles

Fe Ho atoms on Pt(111) surface



Open core approximation:

Unfilled f states

- Treated as core electrons
- Calculated with SIC

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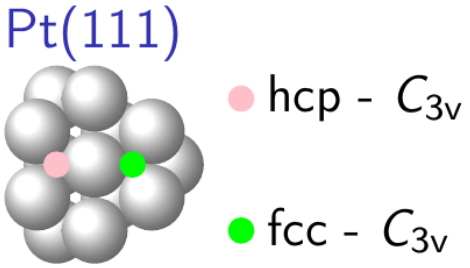

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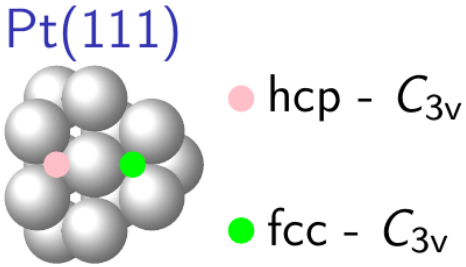
$$\mathcal{H}_{C_{3v}} = B_2^0\mathcal{O}_2^0 + B_4^0\mathcal{O}_4^0 + B_6^0\mathcal{O}_6^0 + B_4^3\mathcal{O}_4^3 + B_6^3\mathcal{O}_6^3 + B_6^6\mathcal{O}_6^6$$



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With Stevens operators:

$$\mathcal{O}_2^0 = 3\mathcal{J}_z^2 - J(J+1)\,,$$
$$\mathcal{O}_4^0 = \mathcal{O}_4^0(J, \mathcal{J}_z^2, \mathcal{J}_z^4)\,,$$
$$\mathcal{O}_4^3 = \mathcal{O}_4^3(\mathcal{J}_z, \mathcal{J}_+^3, \mathcal{J}_-^3)\,,$$
$$\mathcal{O}_6^0 = \mathcal{O}_6^0(J, \mathcal{J}_z^2, \mathcal{J}_z^4, \mathcal{J}_z^6)\,,$$
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Fe Ho atoms on Pt(111) surface

CFP	Value [neV]	CFP	Value [neV]
B_2^0	-239×10^3	B_6^0	0.186
B_4^0	86	B_6^3	-1.967
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Exact diagonalization

Eigenvalue problem:

$$\mathcal{H}_{C_{3v}} \boldsymbol{\Psi} = E \boldsymbol{\Psi}$$

$\boldsymbol{\Psi} = |\Psi_{-8}\rangle, |\Psi_{-7}\rangle, \ldots, |\Psi_{+8}\rangle$

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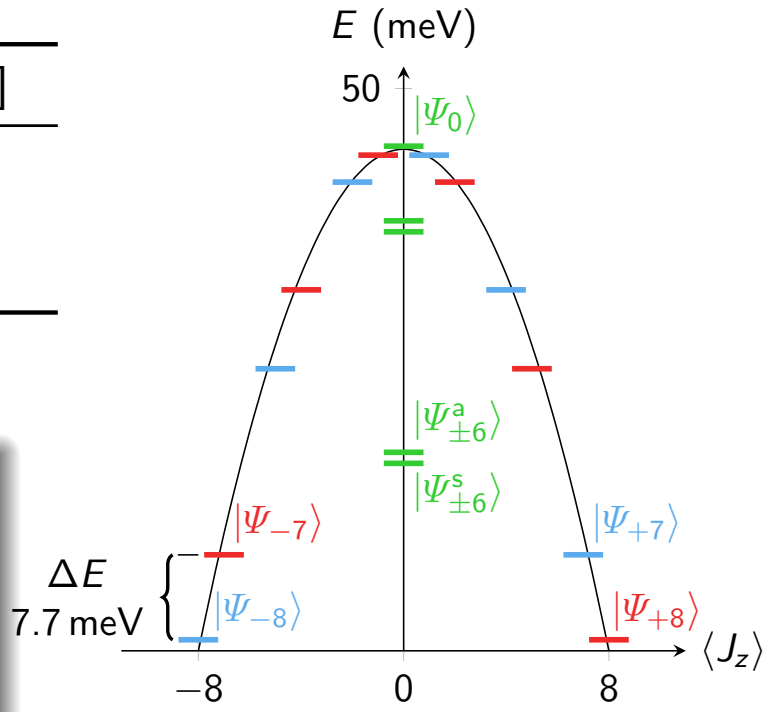

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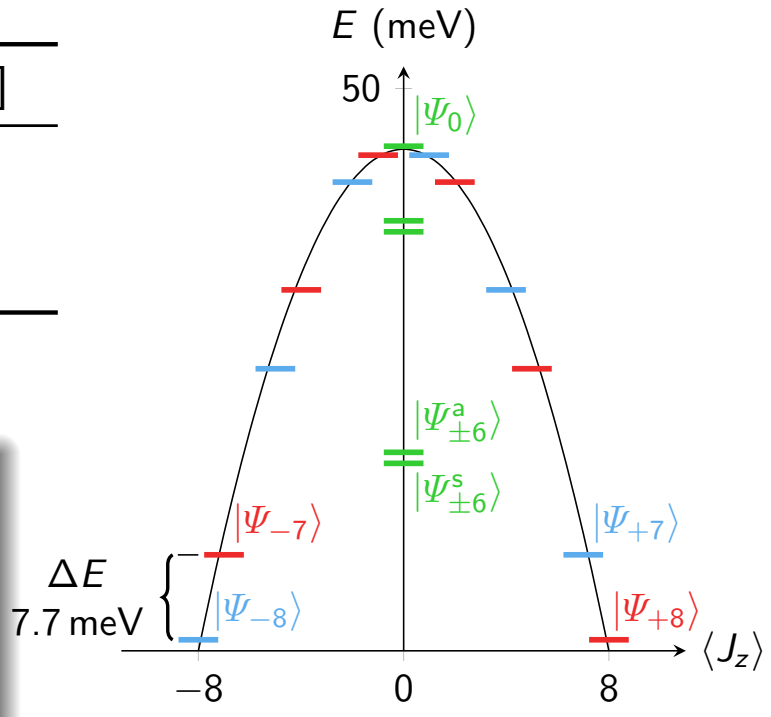

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- Different colors: Spin-flip is forbidden

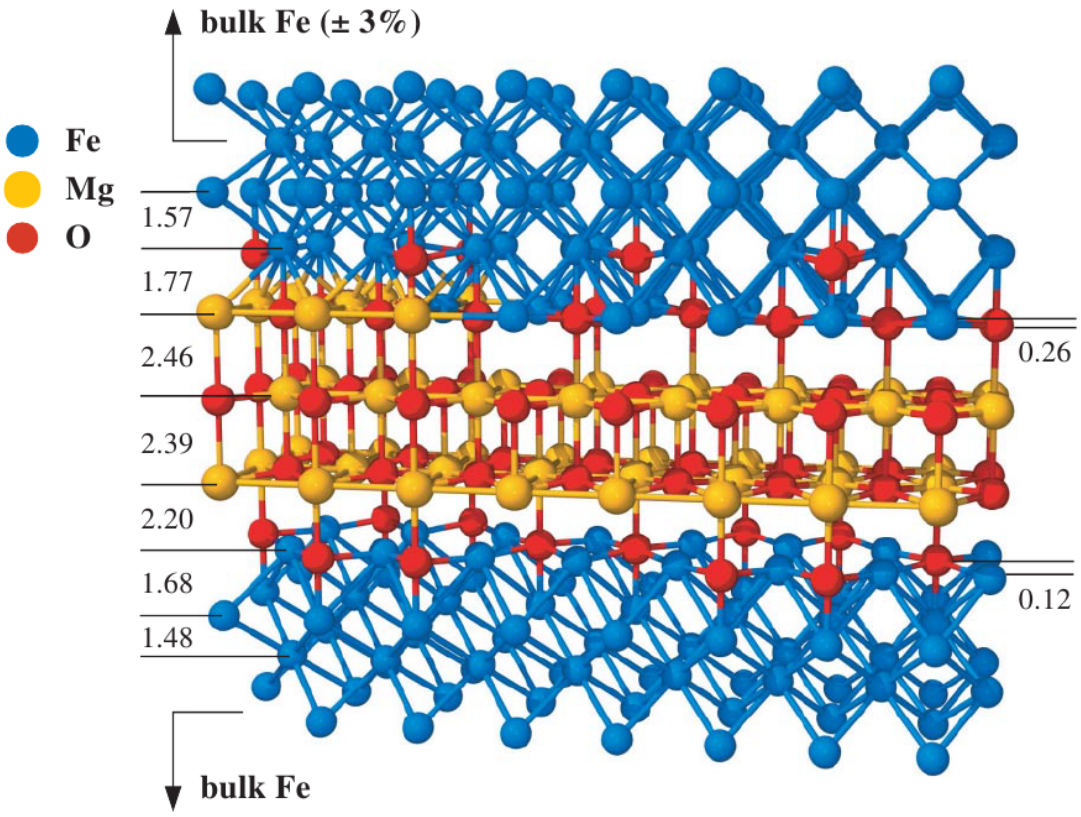
→ Long lifetime

→ Scattering only via intermediate state

Complexity of oxides

- Crystalline structure
- Chemical composition
- Defects & vacancies
- Valency of cations
- Electronic correlations
- Band gap problem of DFT

Fe/MgO/Fe(001) tunnel junction



Some possible approaches for complex oxides

- Crystalline structure: Total energy calculations

  Structure optimization of oxides is rather difficult because of the size of the problem
- Valency of cations: Self-interaction correction method (SIC)
- Electronic correlations:
  - SIC
  - LDA+U
  - DMFT
- Band gap problem of DFT: go beyond the DFT$\rightarrow$ GW

  GW approximation is time demanding for complex materials

Pragmatic approach

Fit crystalline & electronic structure to available experimental data

- **What can be fitted:**
  XAS & XNCD, Curie or Néel temperature
- **Fitting parameters:**
  - Structure
  - Chemical composition
  - U in the LDA+U method as a strength of correlations
  - Cation valency
- **How to proceed:**
  Varying relevant parameters to reach good agreement with experiment

Motivation: magnetism in thin oxide films without magnetic ions

Venkatesan (2004), Khalid (2010)

Models

I. Magnetism is induced by unsaturated p states of oxygen

Cation vacancies or acceptor doping induced magnetism

Elfimiov et al. (2001), C. Das Pemmaraju et al. (2005), H. Pan et al. (2007)

Problem: a high T_C requires defect concentrations incompatible with the stability of the material

II. Magnetism is induced by unsaturated p states of the oxide surface

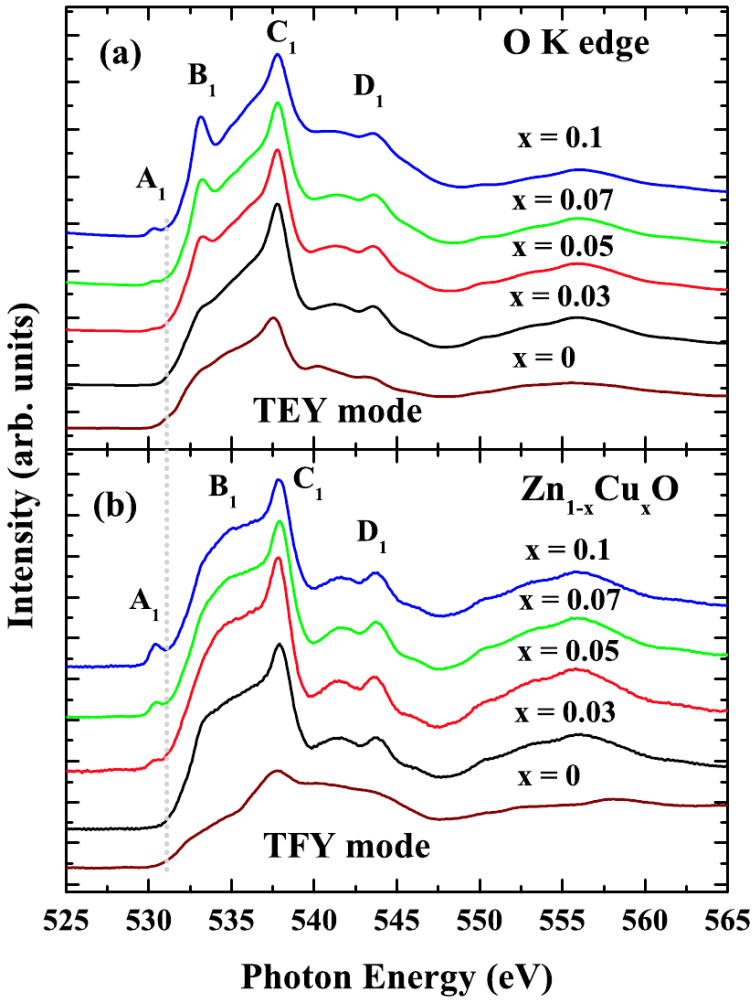
Breaking symmetry, unsaturated bonds or uncompensated ionic charges

S. Gallego et al. (2005), N. Sanchez et al. (2008)

Experimental indication: FM signal is mostly concentrated in the near surface region, grain boundaries or nanostructure interfaces

Representative system: **Surface of ZnO(0001)**

(ZnCu)O (0001): XAS experiment by Thakur *et al.* (2010)



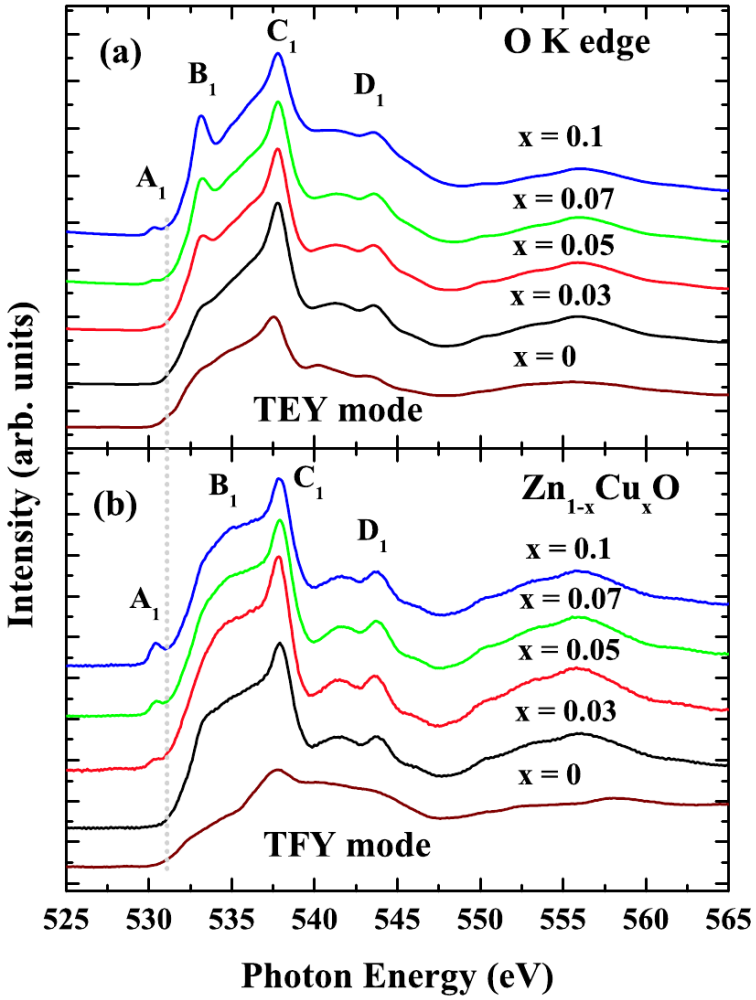
ZnO doped with Cu

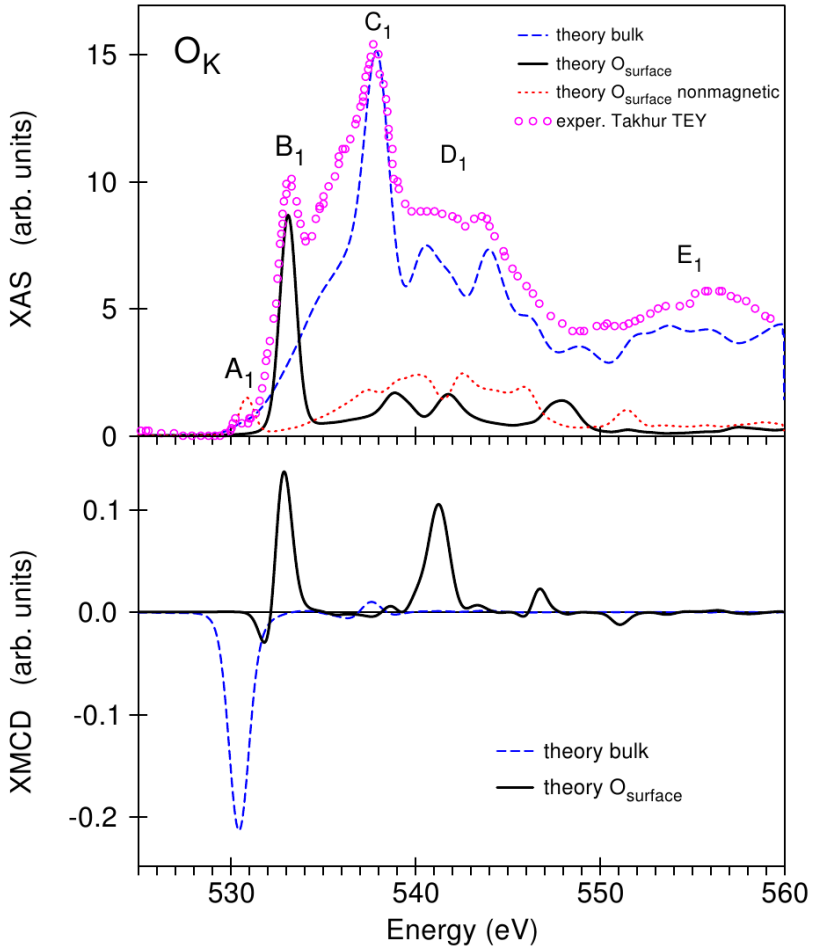
- TFY: bulk sensitive measurement
- TEY: surface sensitive measurement
- For TEY: Increase of B_1 peak with increase of Cu concentration
- Only XAS was measured

Results of our simulations

- We found several Cu ions in the system
  - regular Cu^{2+}_{Zn}
  - Cu^{1+}_{Zn} with oxygen vacancy
  - Cu^{1+}_{Zn} with Zn excess
  - Cu^{3+}_{Zn} surface ions
- Free oxygen due to Cu^{1+}_{Zn} is accumulated on the surface
- The peak B_1 is due to O atoms on the surface: O is magnetic with a moment of 1.2 μ_B

(ZnCu)O (0001): XAS & XMCD simulations





V. N. Antonov, L. Bekenov, and A. Ernst, to be submitted (2014)

Summary & Outlook

First-principles approach is a powerful tool to study various properties of condensed matter

- Ground state properties: the DFT
- Excited state properties: the TDDFT
- Correlated materials: SIC, LDA+U, DMFT
- Simulations of real experiments
- New material design

Future

- Non-equilibrium states within the DFT and TDDFT
- Self-consistent parameter free many-body calculations
- Large systems

Acknowledgment

Theory (MPI)

- Pawel Buczek
- Leonid Sandratskii

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- Tzu-Hung Chuang
- Khalil Zakeri

Experiment (KIT)

- Timofey Balashov
- Wulf Wulfhekel