The Munich SPRKKR-program package

A spin polarized relativistic Korringa-Kohn-Rostoker (SPR-KKR) code for Calculating Solid State Properties

H. Ebert, M. Battocletti, D. Benea, S. Bornemann, J. Braun, S. Chadov, M. Deng, H. Freyer, T. Huhne, D. Ködderitzsch, M. Kosuth, S. Lowitzer, S. Mankovskyy, J. Minar, A. Perlov, V. Popescu, O. Sipr, Ch. Zecha
and many others

Hubert.Ebert@cup.uni-muenchen.de

Universität München, Physikalische Chemie
München, Germany

Standard Band Structure Problem

- Born-Oppenheimer Approximation
- reduction of many-particle problem
  to single-particle problem
  e.g. via density functional theory (DFT)

$$\left[-\vec{\nabla}^2 + V(\vec{r})\right] \psi(\vec{r}, E) = E\psi(\vec{r}, E)$$

periodic potential $V(\vec{r}) = V(\vec{r} + \vec{R}_n)$

leads to the Bloch theorem

$$T_{\vec{R}_n} \psi_{\vec{k}}(\vec{r}, E) = e^{-i\vec{k}\vec{R}_n} \psi_{\vec{k}}(\vec{r}, E)$$

Why using the KKR band structure method?

KKR represents electronic structure in terms of single particle Green's function

$$G^{+}(\vec{r},\vec{r}\,',E) \;=\; \lim_{\epsilon\to 0}\sum_{i}\frac{\phi_i(\vec{r})\phi_i^{*}(\vec{r})}{E-E_i+i\epsilon}$$

- Dyson equation $G = G_0 + G\Delta\mathcal{H}G_0$
  - linear response formalism
  - treatment of complex structures: surfaces, nano-structures
- CPA alloy theory
- description of spectroscopic quantities
- central quantity of many-body theories

Munich SPR-KKR Package

Systems

- Arbitrary ordered/disordered three dimensionally periodic systems
- Slab configuration **NEW**
- Half-infinite solid **NEW**
- Embedded impurities in 3D host **NEW**

Calculation Mode

- Spin-polarised Scalar- and Fully relativistic
- Non-collinear spin configurations
- Spin spirals **NEW**
- Full potential **NEW**

Default: Spin-polarised relativistic Dirac formalism

Features

Electronic Properties

- SCF-potential
- Dispersion relation
- Bloch spectral Function
- Density of states
- ...

Ground State Properties

- Spin- and Orbital Moments
- Hyperfine Fields
- Magnetic Form Factors
- ...

Features

Response Functions

- Spin- and orbital susceptibility
- Knight-shift
- Field-induced XMCD
- Residual resistivity of alloys

Spectroscopic Properties

Spectroscopic Properties – including magnetic dichroism

- Valence Band Photoemission
  fully relativistic ARPES **NEW**
- Core level Photoemission
- non-relativistic Appearance Potential Spectroscopy
- non-/fully relativistic Auger Electron Spectroscopy
- X-ray absorption
- X-ray emission
- X-ray magneto-optics
- X-ray scattering
- Magnetic Compton scattering
- Positron annihilation

The Dirac Equation

$$\left[\frac{\hbar}{i}c\vec{\alpha}\cdot\vec{\nabla}+\beta mc^2+\bar{V}(\vec{r})+\underbrace{\beta\vec{\sigma}\cdot\vec{B}_{\mathrm{eff}}(\vec{r})}_{V_{\mathrm{spin}}(\vec{r})}\right]\Psi(\vec{r},E)=E\,\Psi(\vec{r},E)$$

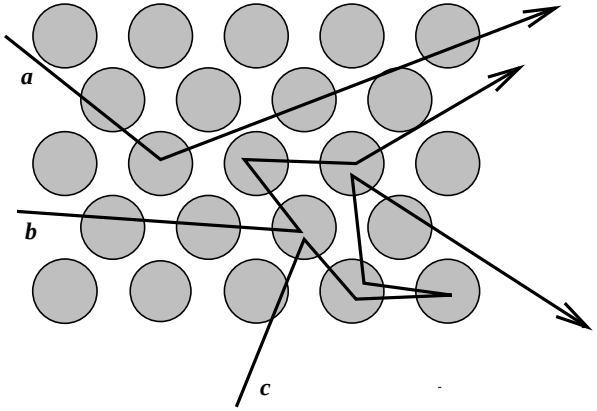
with an effective magnetic field

$$\vec{B}_{\mathrm{eff}}(\vec{r})=\frac{\partial E_{\mathrm{xc}}[n,\vec{m}]}{\partial\vec{m}(\vec{r})}$$

that is determined by the spin magnetisation $\vec{m}(\vec{r})$
within spin density functional theory (SDFT)
Within an atomic cell one can always choose $\hat{z}'$ to have:

$$V_{\mathrm{spin}}(\vec{r})=\beta\sigma_{z'}\,B_{\mathrm{eff}}(r)$$

Multiple scattering



scattering T-matrix operator of the crystal $\hat{T}$

$$\hat{T} = \sum_{n} \hat{t}^{n} + \sum_{n,m} \hat{t}^{n}\,\hat{G}_0\,\hat{t}^{m} + \sum_{\substack{n,m,k \\ n,m\neq k}} \hat{t}^{n}\,\hat{G}_0\,\hat{t}^{m}\,\hat{G}_0\,\hat{t}^{k} + \cdots$$

decomposition into scattering path operator $\hat{\tau}^{nm}$

$$\hat{T} = \sum_{n,m} \hat{\tau}^{nm}$$

Scattering path operator $\hat{\tau}^{nm}$

self-consistent requirement for $\hat{\tau}^{nm}$
in angular momentum representation

$$\tau^{nm}_{\Lambda\Lambda'} = t^n_{\Lambda\Lambda'}\delta_{nm} + \sum_{\Lambda''\Lambda'''} t^n_{\Lambda\Lambda''} \sum_{k\neq n} G^{0\,nk}_{\Lambda''\Lambda'''}\tau^{km}_{\Lambda'''\Lambda'}$$

$$\underline{\tau}^{nm} = \underline{t}^n\delta_{nm} + \underline{t}^n \sum_{k\neq n} \underline{G}^{0\,nk}\underline{\tau}^{km}$$

formal solution

$$\underline{\underline{\tau}} = [\underline{t}^{-1} - \underline{\underline{G}}]^{-1}$$

Electronic Green's function

$$G(\vec{r},\vec{r}\,',E) = \sum_{\Lambda\Lambda'} Z^n_\Lambda(\vec{r},E)\tau^{nn'}_{\Lambda\Lambda'}(E)Z^{n'\times}_{\Lambda'}(\vec{r}\,',E)$$
$$-\sum_\Lambda \Big[\, Z^n_\Lambda(\vec{r},E)J^{n\times}_\Lambda(\vec{r}\,',E)\Theta(r'-r)$$
$$+J^n_\Lambda(\vec{r},E)Z^{n\times}_\Lambda(\vec{r}\,',E)\Theta(r-r')\,\Big]\,\delta_{nn'}$$

normalisation of wave functions for $|\vec{r}| \geq r_{mt}$

regular solution

$$Z_\Lambda(\vec{r},E) = \sum_{\Lambda'} j_{\Lambda'}(p\vec{r})t^{-1}_{\Lambda'\Lambda}(E) - iph^+_\Lambda(p\vec{r})$$

irregular solution

$$J_\Lambda(\vec{r},E) = j_\Lambda(p\vec{r})$$

Expectation values

charge density $n(\vec{r})$

$$n(\vec{r}) = -\frac{1}{\pi}\Im \,\mathrm{Trace} \int^{E_F} dE\, G(\vec{r},\vec{r},E)$$

spin magnetization $m(\vec{r})$

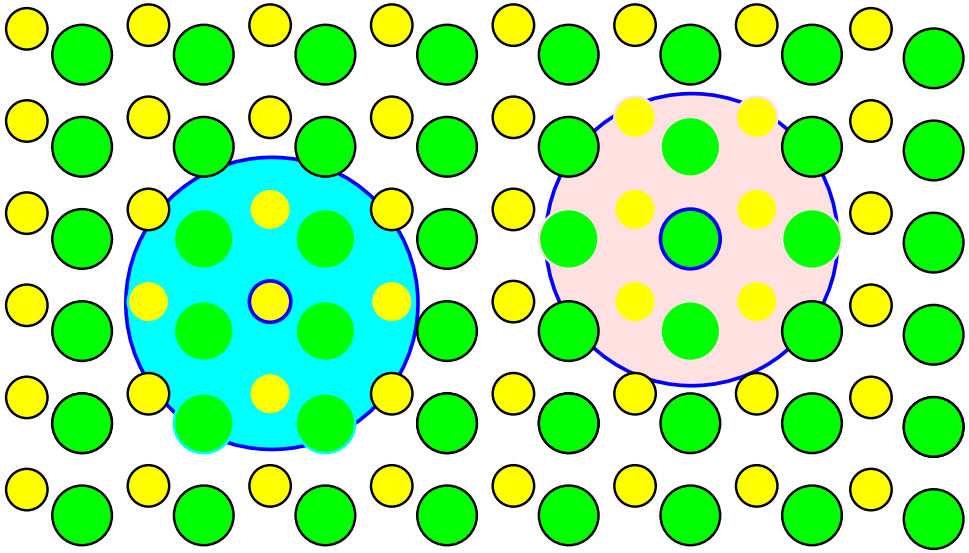
$$m(\vec{r}) = -\frac{1}{\pi}\Im \,\mathrm{Trace} \int^{E_F} dE\, \beta\sigma_z\, G(\vec{r},\vec{r},E)$$

spin and orbital magnetic moments μ_{spin} and μ_{orb}

$$\mu_{\mathrm{spin}} = -\frac{\mu_B}{\pi}\Im \,\mathrm{Trace} \int^{E_F} dE \int_V d^3r\, \beta\sigma_z\, G(\vec{r},\vec{r},E)$$

$$\mu_{\mathrm{orb}} = -\frac{\mu_B}{\pi}\Im \,\mathrm{Trace} \int^{E_F} dE \int_V d^3r\, \beta l_z\, G(\vec{r},\vec{r},E)$$

Cluster approximation



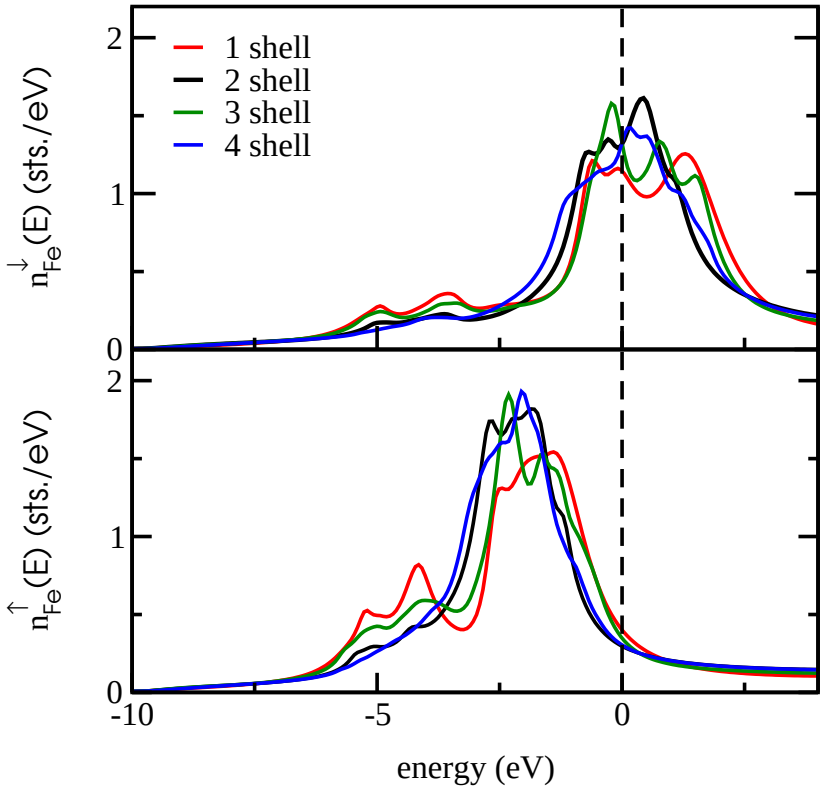
cut a finite cluster out of the infinite system centred on the atom of interest

$$\underline{\underline{\tau}}(E) = [\ \underbrace{\underline{\underline{t}}^{-1}(E) - \underline{\underline{G}}(E)}_{\text{real space KKR matrix } M(E)}\ ]^{-1}$$

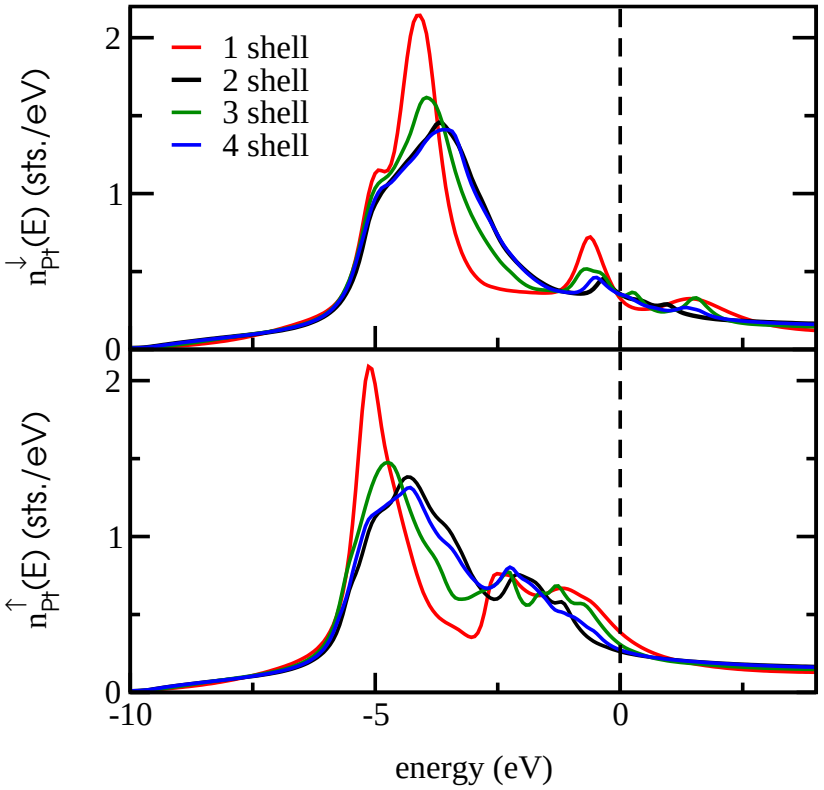
DOS in cluster approximation

DOS as a function of number of atomic shells in cluster

Fe in Fe_3Pt



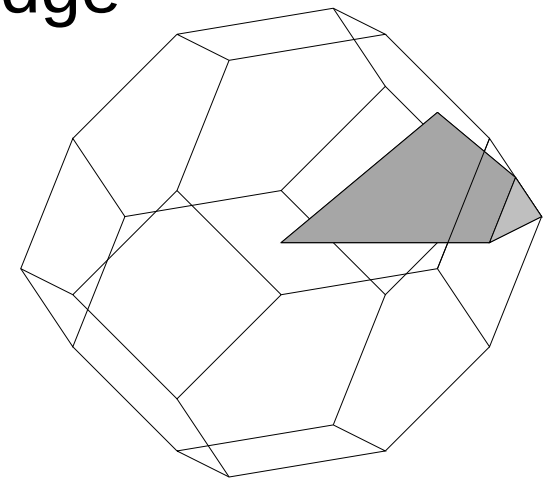
Pt in Fe_3Pt



Brillouin zone integration

$$\tau^{nn'}_{\Lambda\Lambda'}(E) = \frac{1}{\Omega_{\mathrm{BZ}}} \int_{\Omega_{\mathrm{BZ}}} d^3k \; e^{i\vec{k}(\vec{R}_n - \vec{R}_{n'})} \times [\underbrace{\underline{t}^{-1}(E) - \underline{G}(\vec{k}, E)}_{\mathrm{KKR\ \ matrix\ \ } M(\vec{k},E)}]^{-1}_{\Lambda\Lambda'}$$

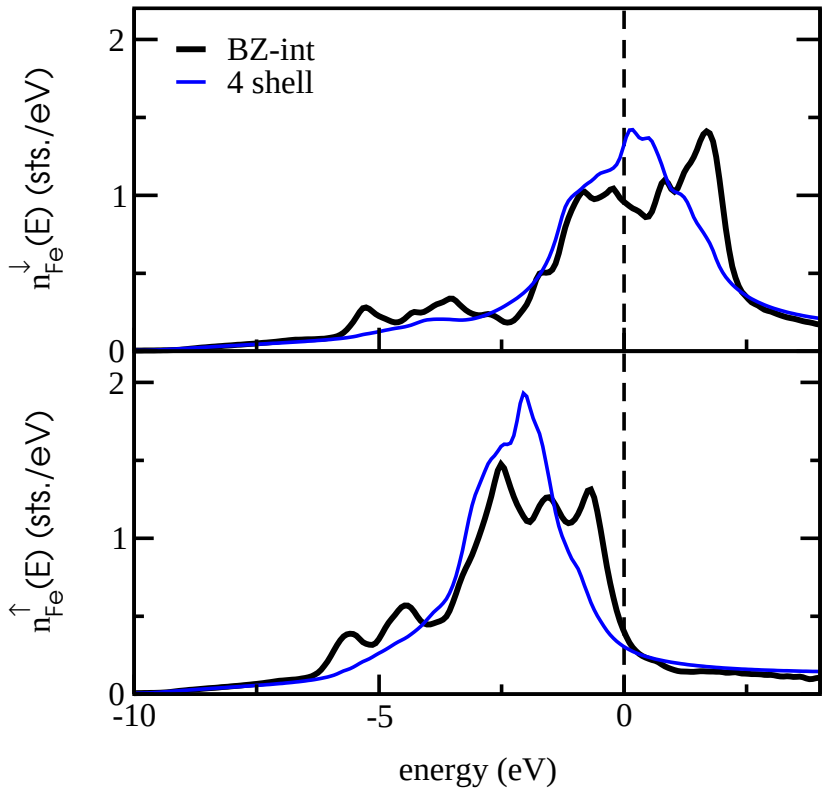
Symmetry allows to reduce the integration regime Ω_{BZ} to an irreducible wedge



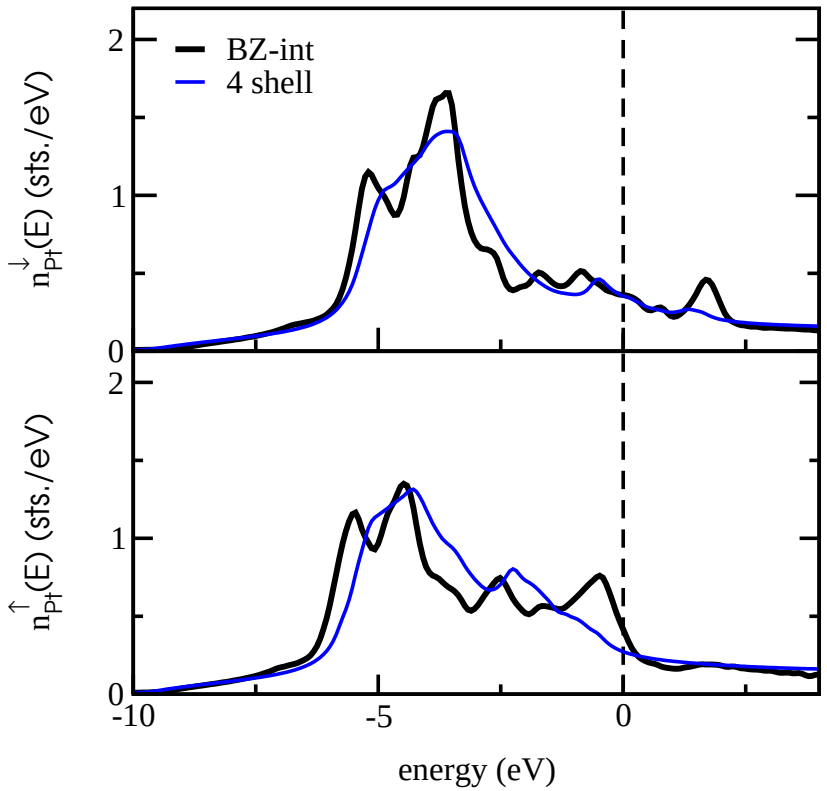
DOS with full Brillouin zone integration

comparison with results for 4 shell cluster

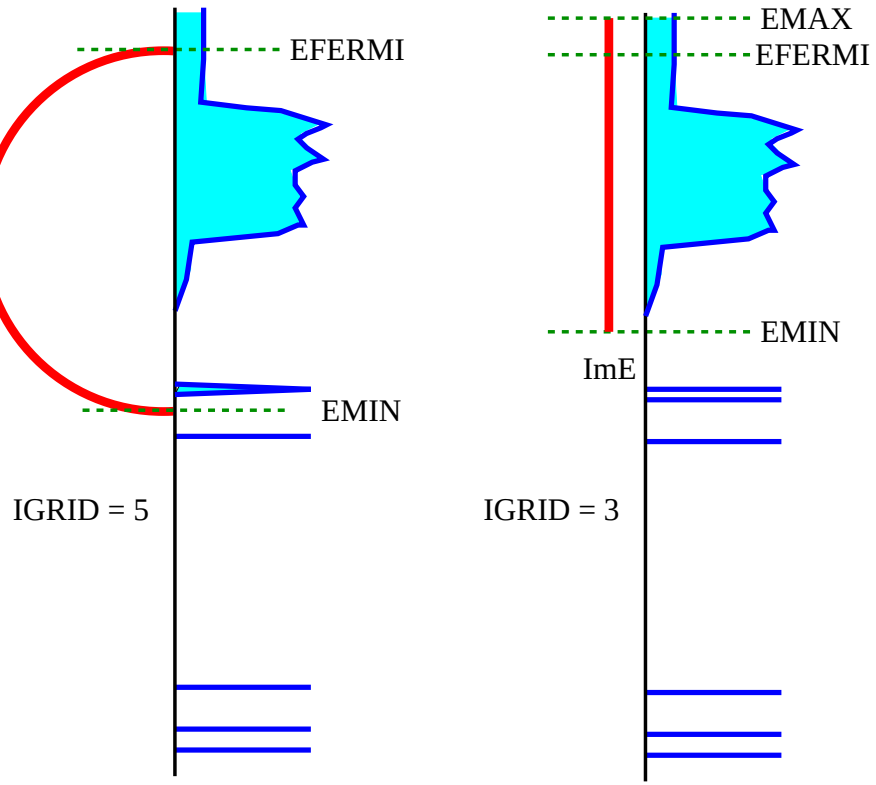
Fe in Fe_3Pt



Pt in Fe_3Pt



Energy paths

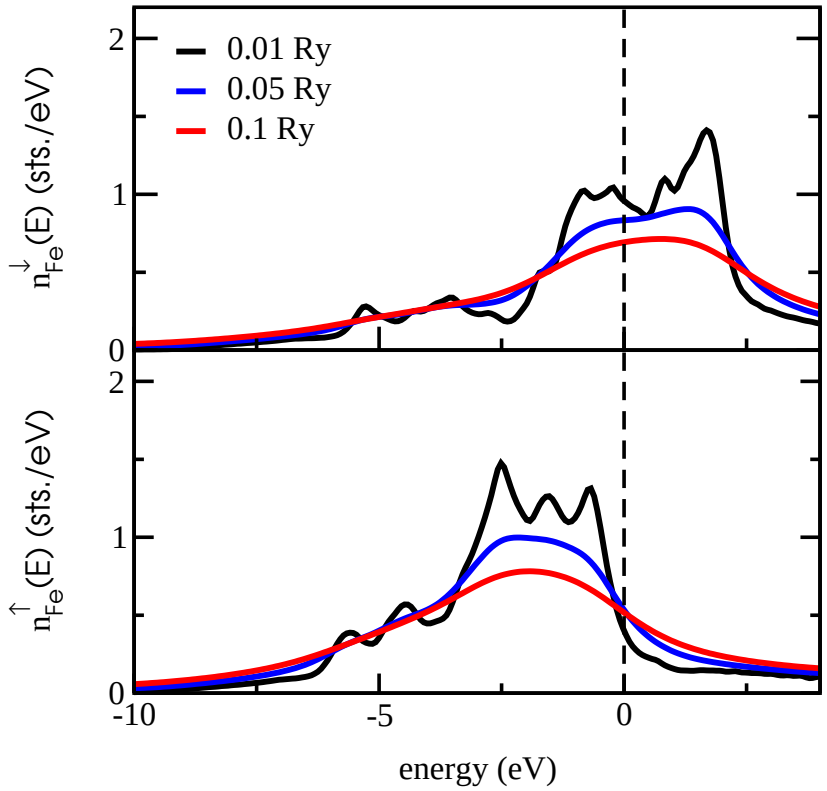


- SCF: arc in the complex plane used for integration
- DOS: straight path along real axis
- XAS: special straight path starting at E_F
- ...

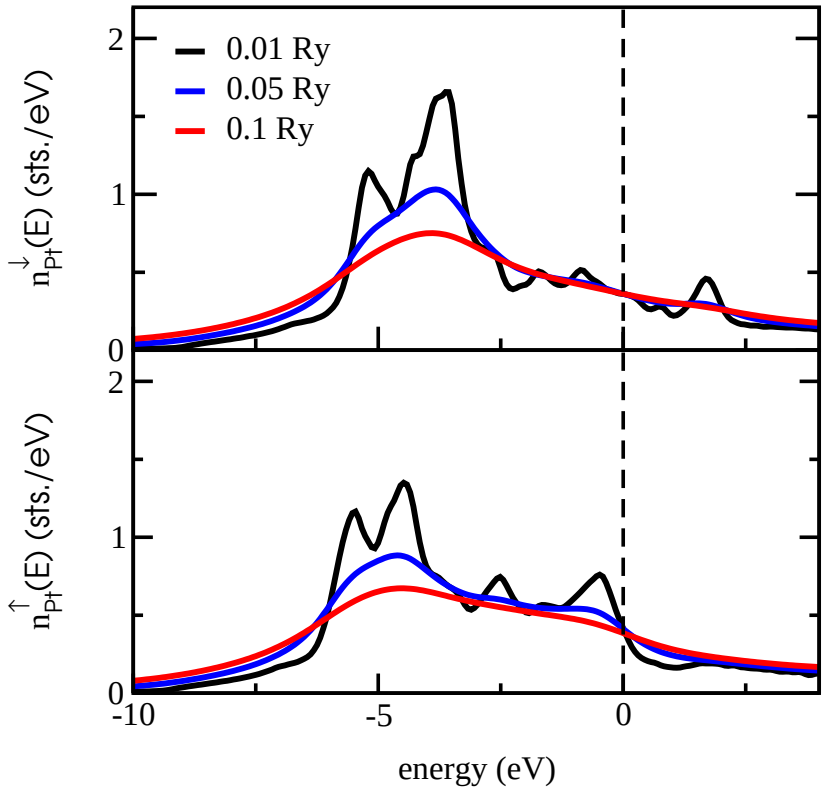
DOS for complex energies

DOS as a function of imaginary part of energy E

Fe in Fe_3Pt



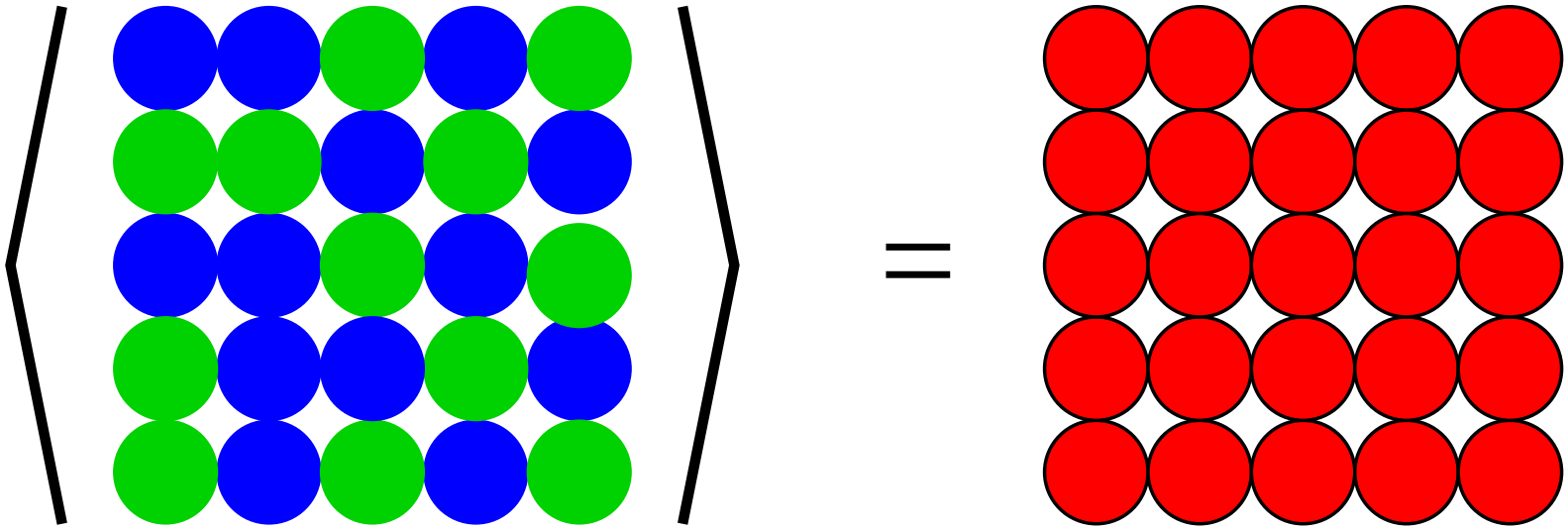
Pt in Fe_3Pt



Coherent Potential Approximation – CPA

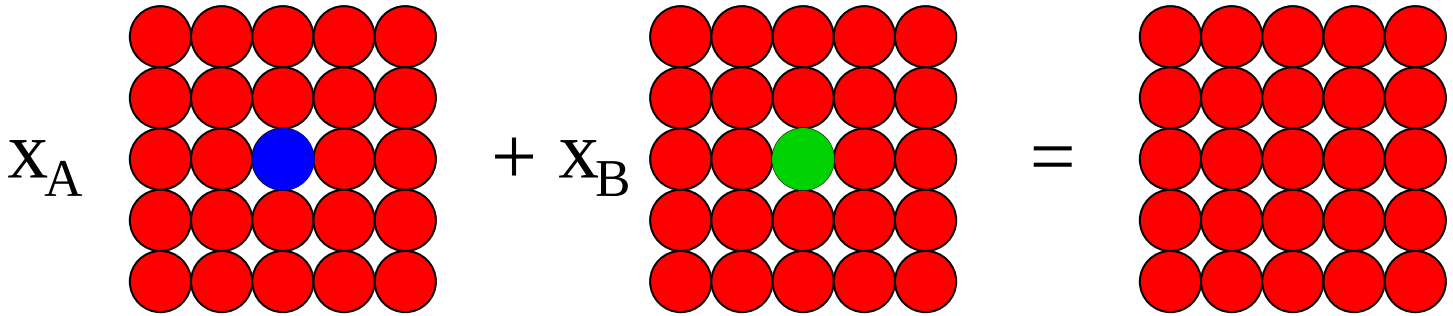
Idea

find an effective CPA medium that represents the electronic structure of an configurationally averaged substitutionally random alloy $A_x B_{1-x}$



CPA condition

Embedding of an A- or B-atom into the CPA-medium – in the average – should not give rise to additional scattering



$$x_{\mathrm{A}} \underline{\tau}^{nn,\mathrm{A}} + x_{\mathrm{B}} \underline{\tau}^{nn,\mathrm{B}} = \underline{\tau}^{nn,\mathrm{CPA}}$$

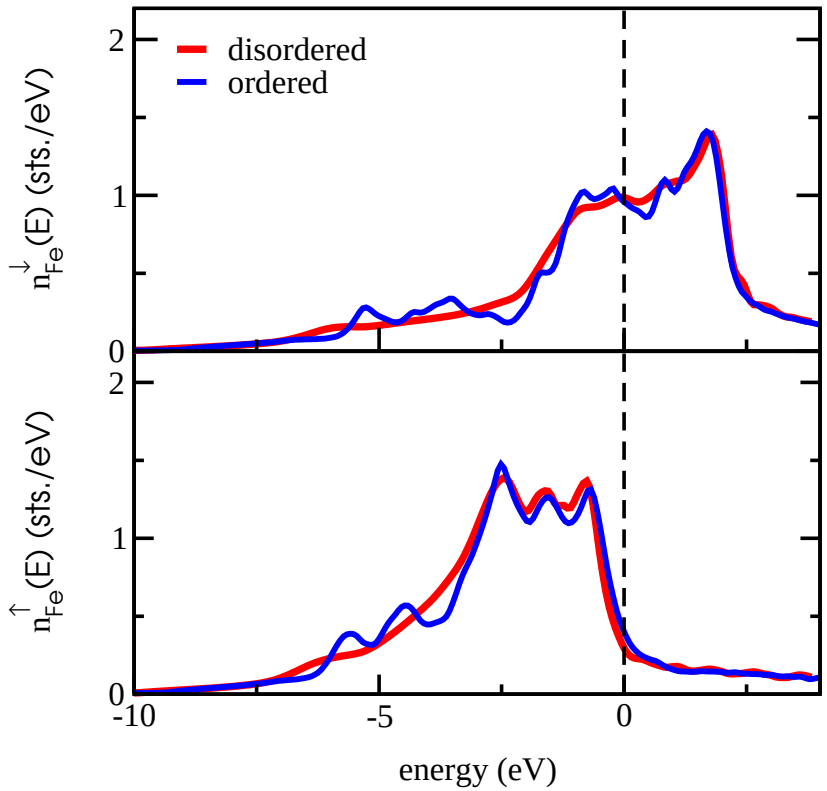
with the projected scattering path operator $\underline{\tau}^{nn,\alpha}$

$$\underline{\tau}^{nn,\alpha} = \underline{\tau}^{nn,\mathrm{CPA}} \left[1 + \left(\underline{t}_{\alpha}^{-1} - \underline{t}_{\mathrm{CPA}}^{-1} \right) \underline{\tau}^{nn,\mathrm{CPA}} \right]^{-1}$$

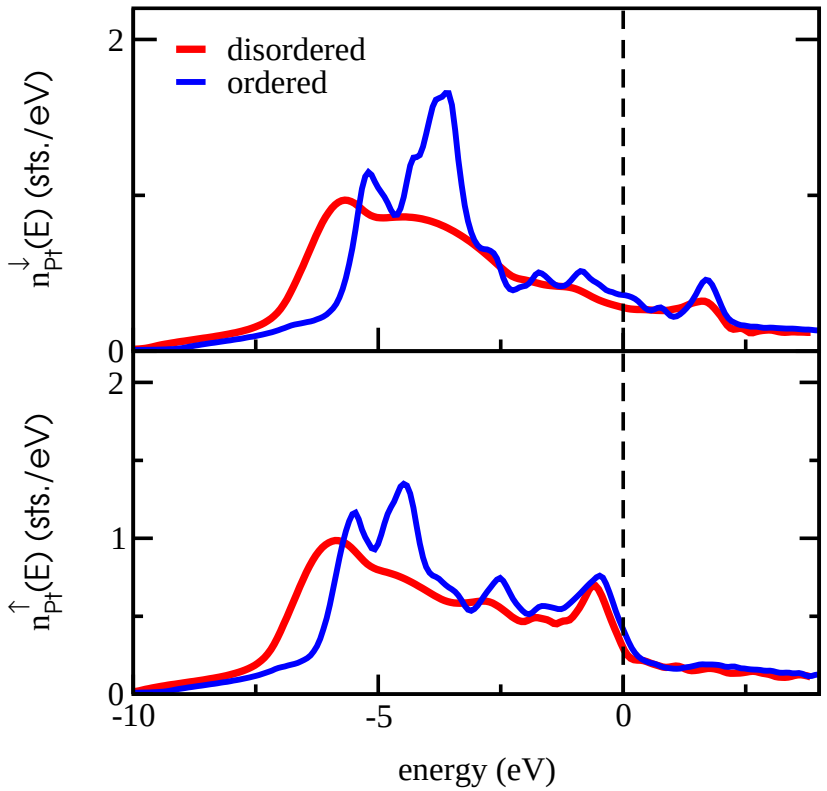
DOS in disordered systems

comparison of results for ordered and disordered case

Fe in Fe_3Pt



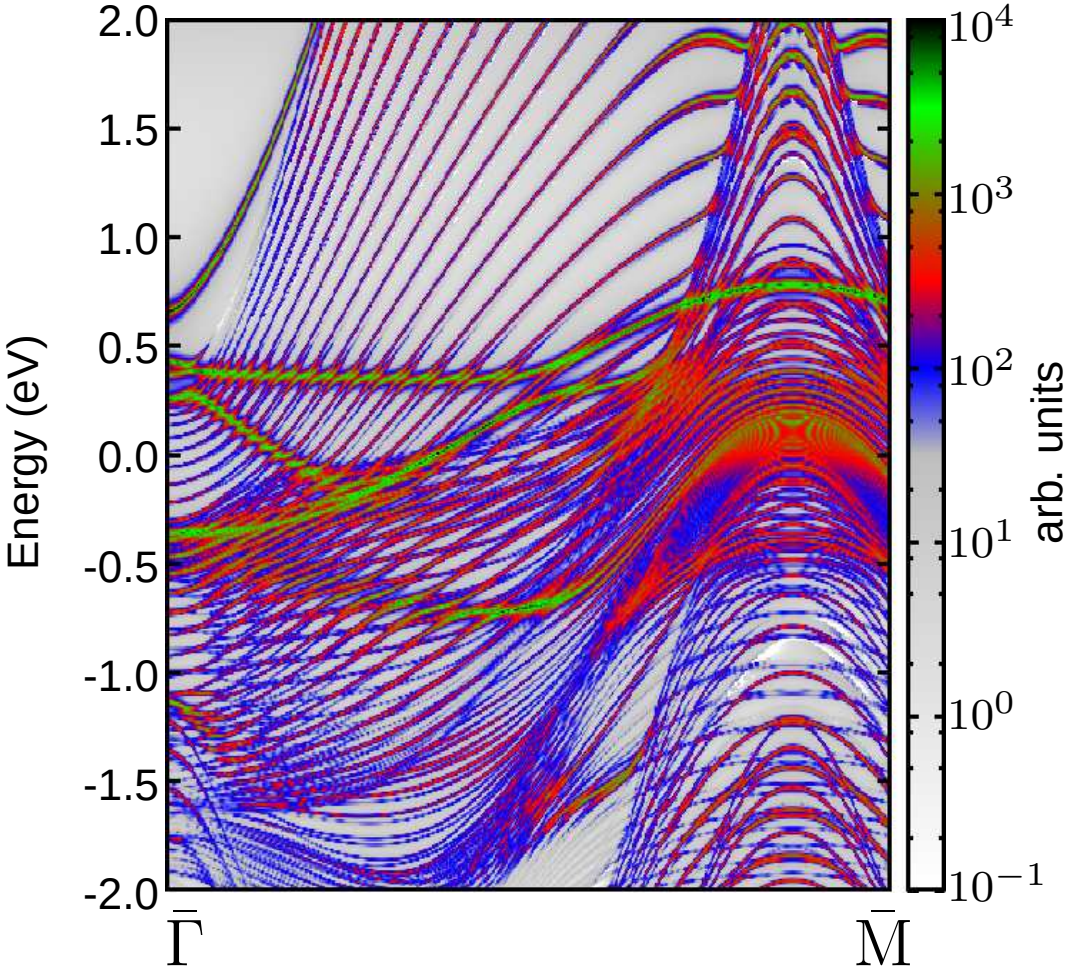
Pt in Fe_3Pt



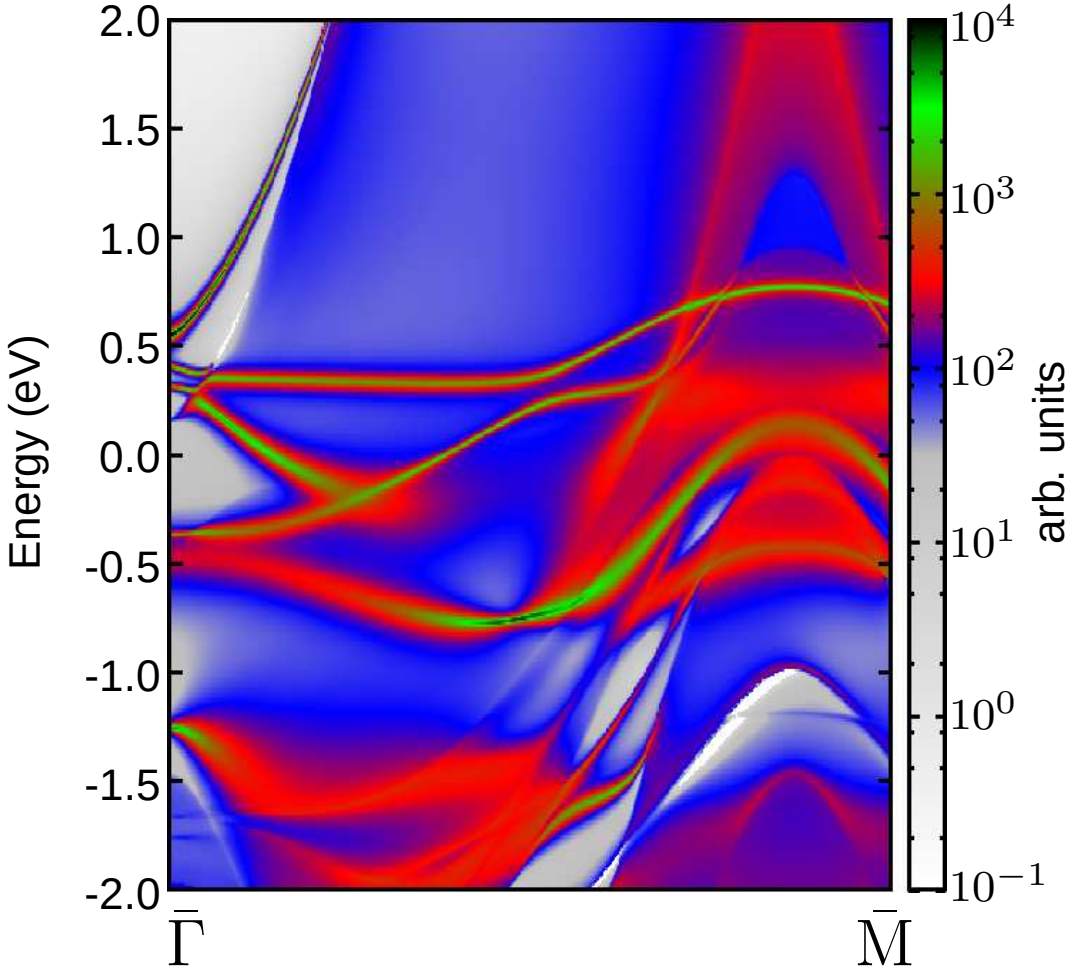
$\vec{k}_{||}$-resolved DOS for Co on Pt(III)

Projected band structure of a Co monolayer on Pt(111)

slab with 38 Pt layers



12 Pt layers + decimation



Anhang

Scattering path operator

decomposition into site-indexed
scattering path operator $\hat{\tau}^{nm}$

$$\hat{T} = \sum_{n,m} \hat{\tau}^{nm}$$

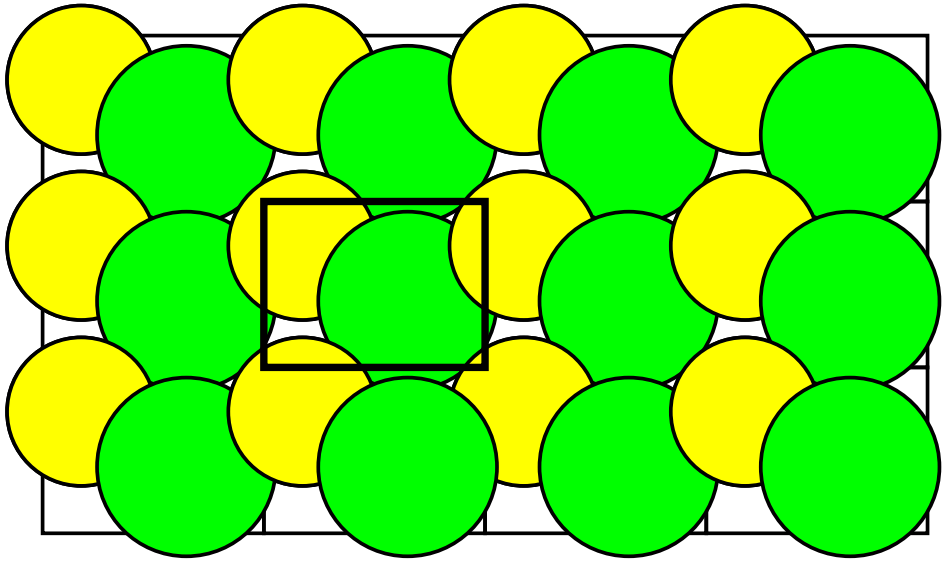
self-consistent requirement for $\hat{\tau}^{nm}$
in angular momentum representation

$$\underline{\tau}^{nm} = \underline{t}^{n}\delta_{nm} + \underline{t}^{n}\sum_{k\neq n}\underline{G}_{0}^{nk}\underline{\tau}^{km}$$

formal solution

$$\underline{\underline{\tau}} = [\underline{\underline{t}}^{-1} - \underline{\underline{G}}_{0}]^{-1}$$

Atomic sphere approximation – ASA

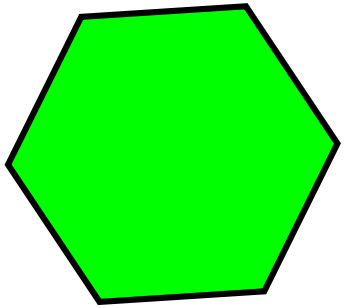


- replace atomic cells by atom centred spheres
- keep the volume of the unit cell constant
- assume a spherical symmetric potential within sphere:

$$\bar{V}(\vec{r}) = \bar{V}(r) \text{ and } \vec{B}_{\text{eff}}(\vec{r}) = \vec{B}_{\text{eff}}(r)$$

Single site Dirac equation

- restrict potential to a single atomic cell for atom type t:



$$\bar{V}^{\mathrm{t}}(\vec{r}) = 0 \text{ and } \vec{B}^{\mathrm{t}}_{\mathrm{eff}}(\vec{r}) = 0 \text{ for } \vec{r} \notin \Omega^{\mathrm{t}}$$

- Single site Dirac equation for atom type t

$$\left[\frac{\hbar}{i} c\vec{\alpha}\cdot\vec{\nabla} + \beta mc^2 + \bar{V}^{\mathrm{t}}(\vec{r}) + \beta\vec{\sigma}\cdot\vec{B}^{\mathrm{t}}_{\mathrm{eff}}(\vec{r})\right] \Psi(\vec{r}, E) = E\,\Psi(\vec{r}, E)$$

Ansatz to solve the single site Dirac equation

$$\psi_\nu(\vec{r}, E) = \sum_\Lambda \psi_{\Lambda\nu}(\vec{r}, E)$$

with

$$\psi_{\Lambda\nu}(\vec{r}, E) = \begin{pmatrix} g_{\Lambda\nu}(r, E)\, \chi_\Lambda(\hat{\vec{r}}) \\ i f_{\Lambda\nu}(r, E)\, \chi_{-\Lambda}(\hat{\vec{r}}) \end{pmatrix}$$

spin-angular functions

$$\chi_\Lambda(\hat{r}) = \sum_{m_s = \pm 1/2} C(l\tfrac{1}{2}j; \mu - m_s, m_s)\, Y_l^{\mu - m_s}(\hat{r})\, \chi_{m_s}$$

short hand notation $\Lambda = (\kappa, \mu)$ and $-\Lambda = (-\kappa, \mu)$

Relativistic quantum numbers

total angular momentum operator $\vec{j} = \vec{l} + \frac{1}{2}\vec{\sigma}$

$$\begin{aligned} \vec{j}^2 \chi_\Lambda(\hat{r}) &= j(j+1)\chi_\Lambda(\hat{r}) \\ j_z \chi_\Lambda(\hat{r}) &= \mu \chi_\Lambda(\hat{r}) \end{aligned}$$

total angular momentum quantum number j

$$j = l \pm 1/2$$

magnetic quantum number μ

$$\mu = -j \quad \ldots \quad +j$$

Relativistic quantum numbers

Spin-orbit operator $\hat{K}$

$$\hat{K}\chi_\Lambda(\hat{r}) = (1 + \vec{\sigma}\cdot\vec{l})\chi_\Lambda(\hat{r}) = -\kappa\chi_\Lambda(\hat{r})$$

Spin-obit quantum number κ

$$\kappa = \begin{cases} l = j + \frac{1}{2} & \text{if} \quad j = l - \frac{1}{2} \\ -l - 1 = -j - \frac{1}{2} & \text{if} \quad j = l + \frac{1}{2} \end{cases}$$

κ	-1	$+1$	-2	$+2$	-3	$+3$	-4
j	$1/2$	$1/2$	$3/2$	$3/2$	$5/2$	$5/2$	$7/2$
l	0	1	1	2	2	3	3
symbol	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$	$f_{5/2}$	$f_{7/2}$

Radial Differential Equations

$$P'_{\Lambda\nu} = -\frac{\kappa}{r}P_{\Lambda\nu} + \left[\frac{E-V}{c^2} + 1\right] Q_{\Lambda\nu} + \frac{B}{c^2}\sum_{\Lambda'}\langle\chi_{-\Lambda}|\sigma_z|\chi_{-\Lambda'}\rangle Q_{\Lambda'\nu}$$

$$Q'_{\Lambda\nu} = \frac{\kappa}{r}Q_{\Lambda\nu} - [E-V]\, P_{\Lambda\nu} + B\sum_{\Lambda'}\langle\chi_{\Lambda}|\sigma_z|\chi_{\Lambda'}\rangle P_{\Lambda'\nu}$$

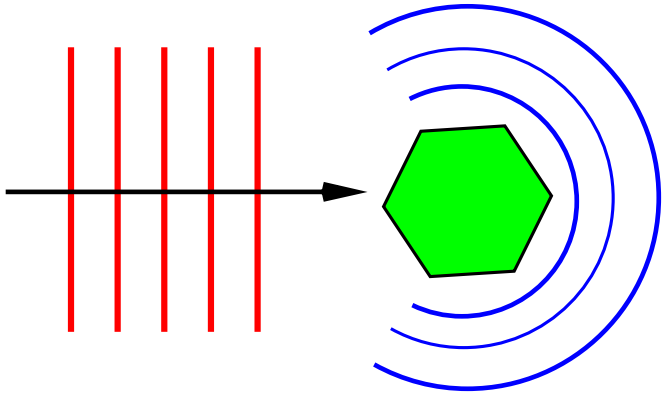
with $P_{\Lambda\nu}(r,E) = r\, g_{\Lambda\nu}(r,E)$
and $Q_{\Lambda\nu}(r,E) = cr\, f_{\Lambda\nu}(r,E)$

The coupling is restricted to $\mu - \mu' = 0$ and $l - l' = 0$

$\longrightarrow$ 4 coupled functions for $|\mu| < j$; e.g. $d_{3/2,\mu}$ — $d_{5/2,\mu}$

$\longrightarrow$ 2 coupled functions for $|\mu| = j$; e.g. $d_{5/2,\mu=\pm 5/2}$

Single site t-matrix



scattering amplitude $f(\hat{p})$

$$\Psi(\vec{r}, E) = e^{i\vec{p}\cdot\vec{r}} + f(\hat{p})\frac{e^{ipr}}{r}$$

spherical basis

$$\psi_\Lambda(\vec{r}, E) = j_\Lambda(\vec{r}, E) + ip \sum_{\Lambda'} t_{\Lambda\Lambda'}(E)\, h^+_{\Lambda'}(\vec{r}, E)$$

Single site t-matrix

single site t-matrix $t_{\Lambda\Lambda'}(E)$

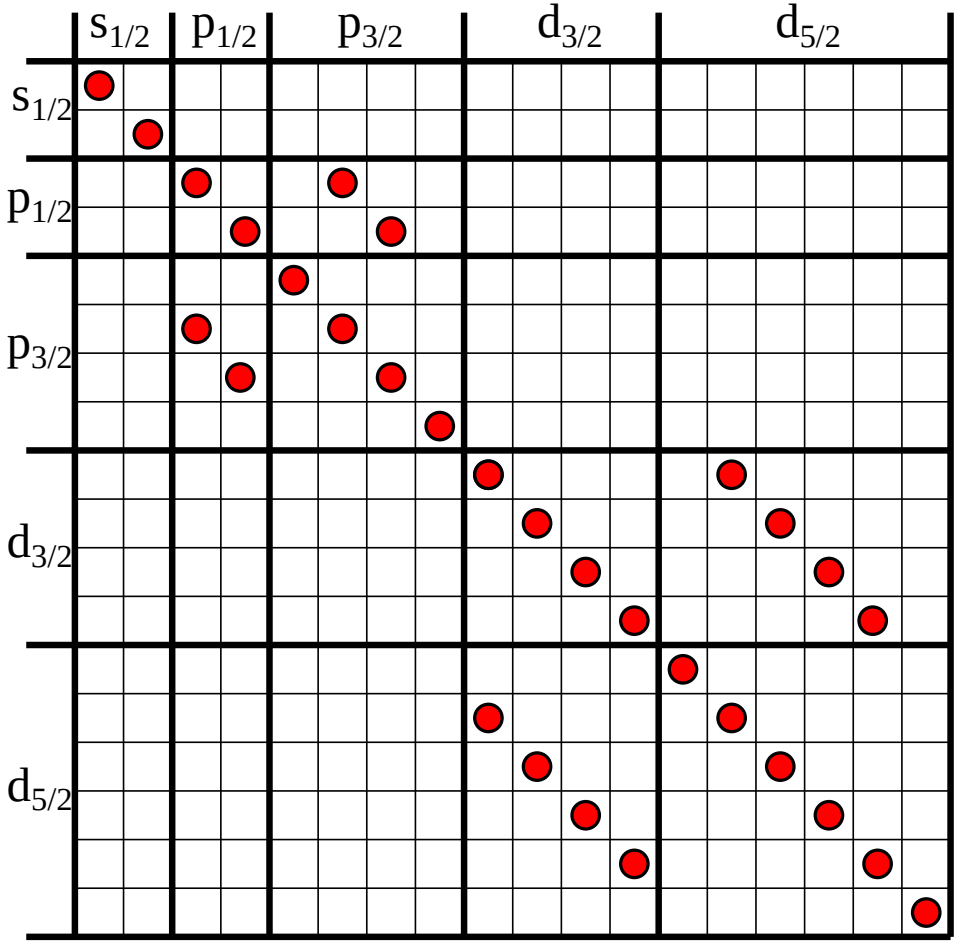
$$\begin{aligned} \underline{t}(E) &= \frac{i}{2p}\left[\underline{a}(E) - \underline{b}(E)\right]\underline{b}(E)^{-1} \\ a_{\Lambda\Lambda'}(E) &= -ipr^2[h^-_\Lambda, \phi_{\Lambda\Lambda'}]_r \\ b_{\Lambda\Lambda'}(E) &= -ipr^2[h^+_\Lambda, \phi_{\Lambda\Lambda'}]_r \end{aligned}$$

relativistic Wronskian

$$[h^+_\Lambda, \phi_{\Lambda\Lambda'}]_r = h^+_l c f_{\Lambda\Lambda'} - \frac{p}{1 + E/c^2} S_\kappa h^+_{\bar{l}} g_{\Lambda\Lambda'}$$

Single site t-matrix

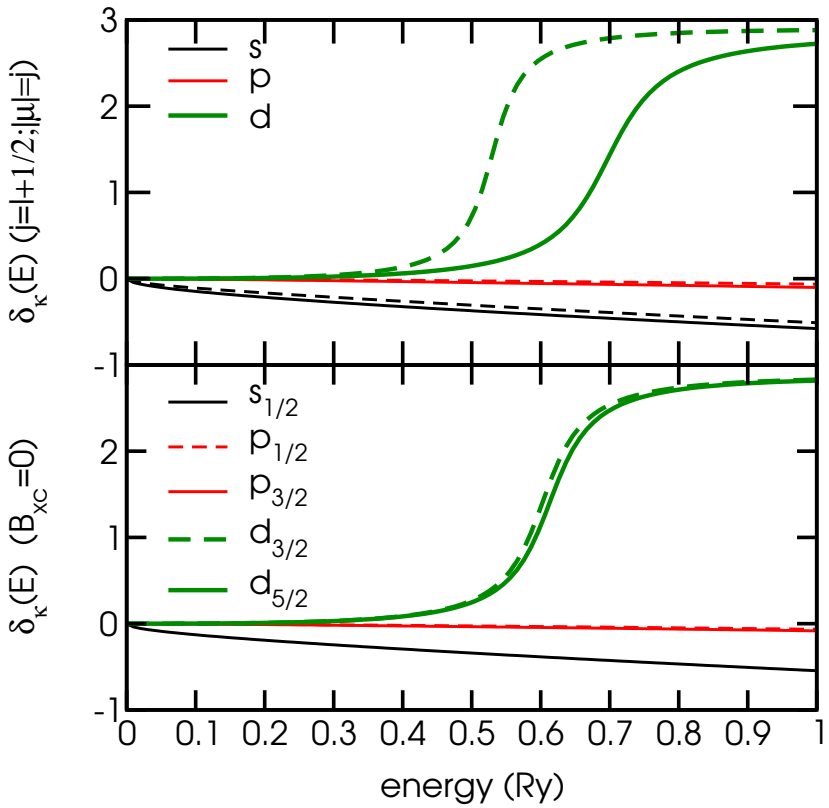
spherical spin-dependent potential ($\vec{M} \| \hat{z}$)



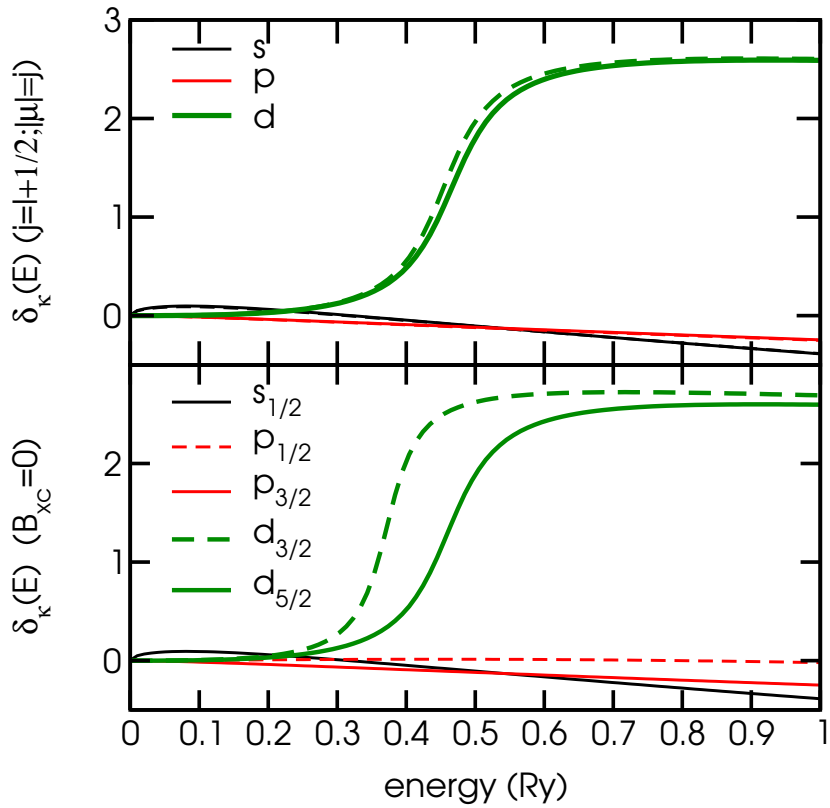
Single site t-matrix – phase shift δ_κ

for a spherical potential $t_\kappa = -\frac{1}{p}\,\sin(\delta_\kappa)\,e^{i\delta_\kappa}$

Fe in Fe_3Pt



Pt in Fe_3Pt



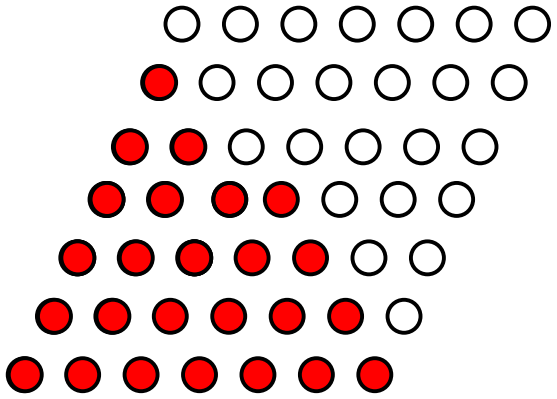
Special point sampling method

$$\underline{\tau}^{nn,\alpha\alpha}(E) = \sum_{j=1,\ldots,n_U} \underline{U}^j \underline{\tau}_0^{nn,\alpha'\alpha'}(E) \underline{U}^{j-1} + \sum_{j=1,\ldots,n_A} \underline{U}^j \underline{\tau}_0^{nn,\alpha'\alpha'T}(E) \underline{U}^{j-1}$$

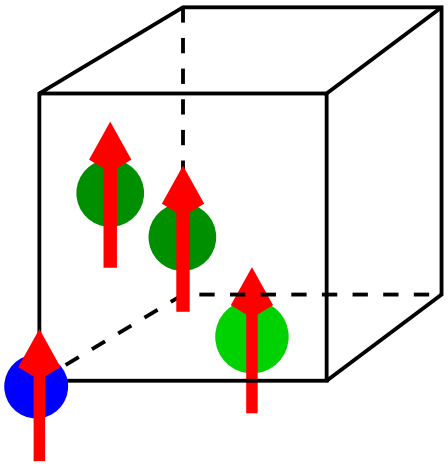
with $\underline{\tau}_0^{nn,\alpha\alpha}(E) = \sum_{\vec{k}} w_{\vec{k}} \underline{\tau}^{\alpha\alpha}(\vec{k}, E)$

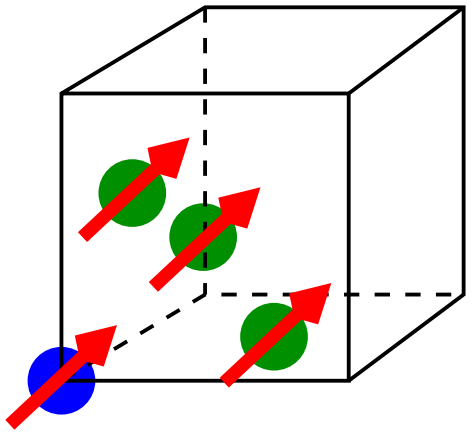
U: (anti-)unitary symmetry operations

Special point mesh



Symmetry considerations

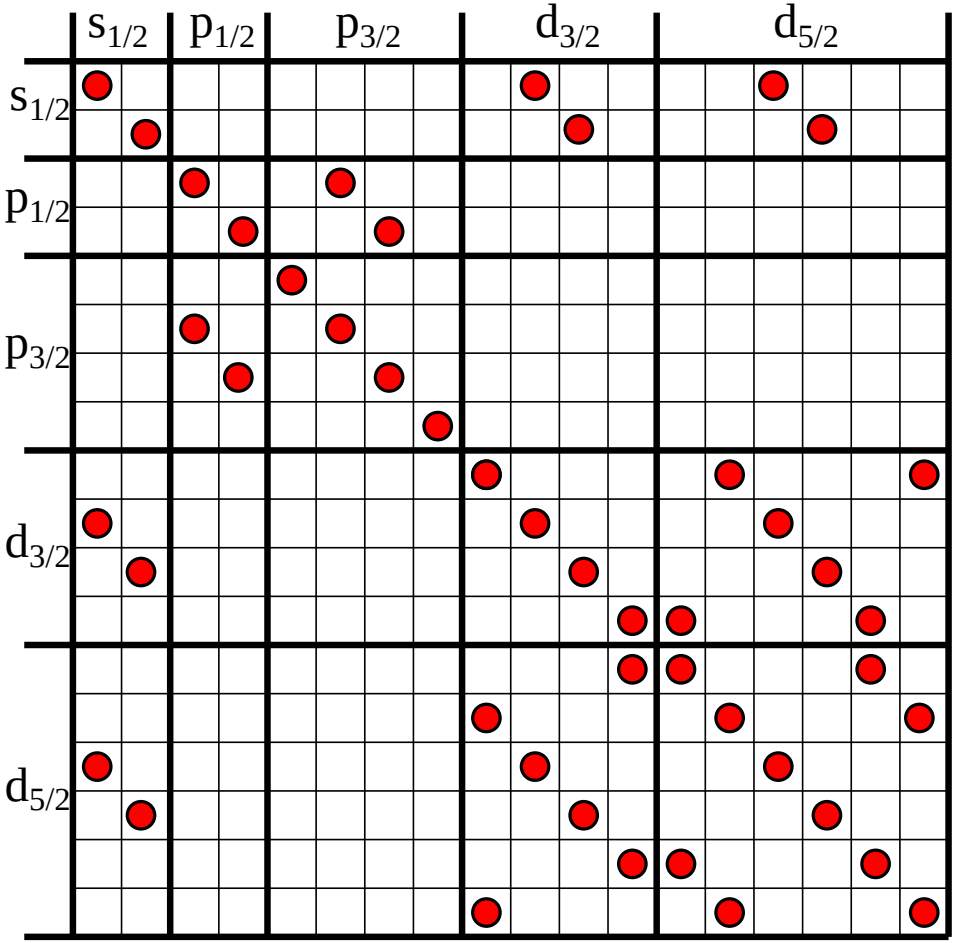




$\hat{M}\|\|[001]$	E	C_{2z}	C_{4z}^{+}	C_{4z}^{-}	I	σ_z	S_{4z}^{-}	S_{4z}^{+}
	TC_{2x}	TC_{2y}	TC_{2a}	TC_{2b}	$T\sigma_x$	$T\sigma_y$	$T\sigma_{da}$	$T\sigma_{db}$
$\hat{M}\|\|[111]$	E	C_{31}^{+}	C_{31}^{-}	I	S_{61}^{-}	S_{61}^{+}		
	TC_{2b}	TC_{2e}	TC_{2f}	$T\sigma_{db}$	$T\sigma_{de}$	$T\sigma_{df}$		

Scattering path matrix τ^{ii}

cubic spin-dependent system ($\vec{M} \| \hat{z}$)



Outlook

- Full potential version
- treatment of correlation effects
  - LSDA+U
  - DMFT
- Tight binding (TB) version
  for arbitrary layered systems
  in collaboration with P. H. Dederichs and R. Zeller
- free magnetic clusters
  in collaboration with O. Sipr
- ...

Expectation values

Starting for example from the identity:

$$\Im\, G(E) = -\pi \sum_{\alpha} |\alpha\rangle \langle\alpha|\, \delta(E - E_\alpha) \ ,$$

for the Green's function $G(E)$ in operator form one finds:
Expectation value of operator $\mathcal{A}$

$$\langle \mathcal{A} \rangle = -\frac{1}{\pi} \Im \,\text{Trace} \int^{E_F} dE\, \mathcal{A} G(\vec{r}, \vec{r}, E)$$

Trace-operation:

- take the trace with respect to the 4×4-matrices

Electronic Green's function

$$G(\vec{r},\vec{r}\,',E) = \sum_{\Lambda\Lambda'} Z^n_\Lambda(\vec{r},E)\tau^{nn'}_{\Lambda\Lambda'}(E)Z^{n'\times}_{\Lambda'}(\vec{r}\,',E)$$
$$-\sum_\Lambda \Big[\, Z^n_\Lambda(\vec{r},E)J^{n\times}_\Lambda(\vec{r}\,',E)\Theta(r'-r)$$
$$+J^n_\Lambda(\vec{r},E)Z^{n\times}_\Lambda(\vec{r}\,',E)\Theta(r-r')\,\Big]\,\delta_{nn'}$$

normalisation of wave functions for $|\vec{r}| \geq r_{mt}$

regular solution

$$Z_\Lambda(\vec{r},E) = \sum_{\Lambda'} j_{\Lambda'}(p\vec{r})t^{-1}_{\Lambda'\Lambda}(E) - iph^+_\Lambda(p\vec{r})$$

irregular solution

$$J_\Lambda(\vec{r},E) = j_\Lambda(p\vec{r})$$

Scattering path matrix τ^{ii}

cubic spin-dependent system ($\vec{M} \| \hat{z}$)