Relativistic effects and non-collinear DFT

- What is relativistic effects?
- Dirac equation
- Relativistic effects in an atom
- Spin-orbit coupling
- Hund's 3rd rule
- Orbital magnetic moment
- Non-collinear DFT
- Relativistic pseudopotentials
- Non-collinear DFT+U method
- Constraint DFT
- Examples

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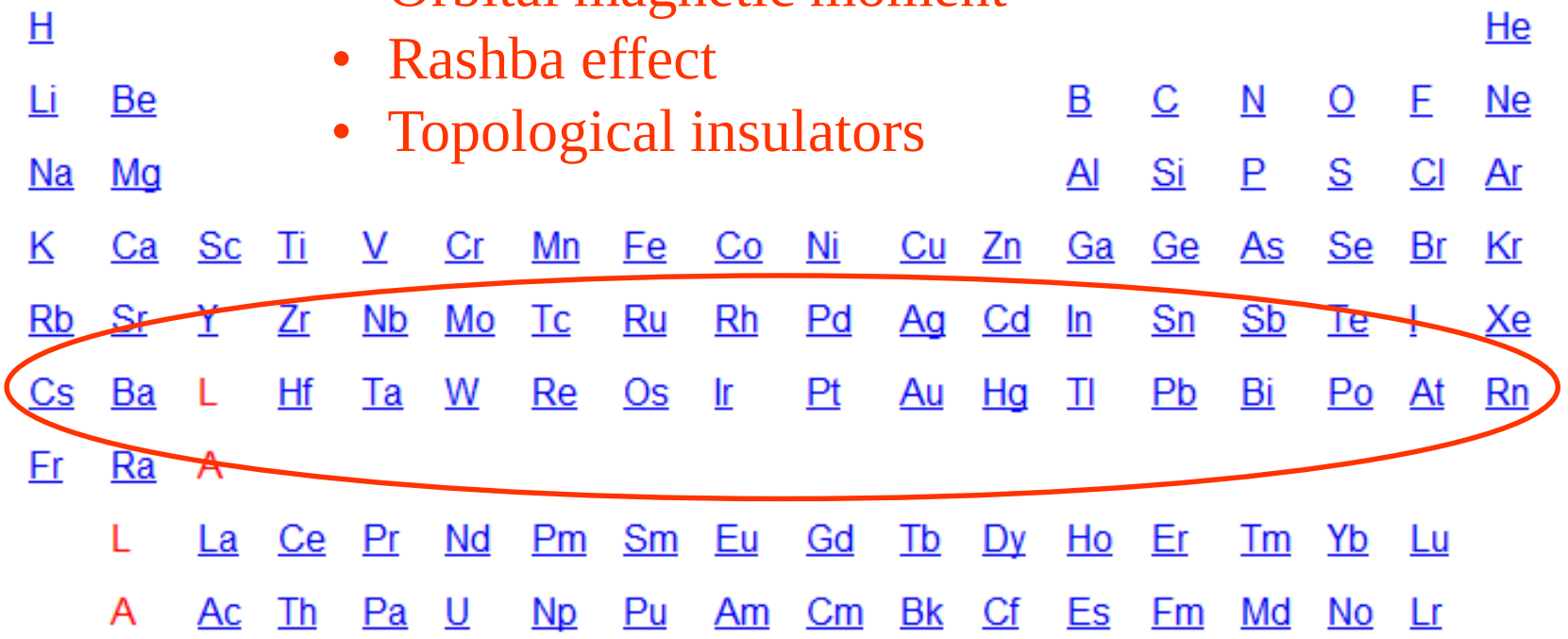
Relativistic effects

- Difference between Schrodinger and Dirac equations
- Large for heavy elements
- Correct prediction of d-band which is important for catalysts
- Spin-orbit coupling leading to many interesting physics:
  - Anisotropy energy of magnets
  - Orbital magnetic moment
  - Rashba effect
  - Topological insulators



Dirac equation

$$\left(\varepsilon - eV - mc^2\right)\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix} = c\sigma\cdot(\mathbf{p}+e\mathbf{A})\begin{pmatrix}\varphi_3\\ \varphi_4\end{pmatrix}$$

$$\left(\varepsilon - eV + mc^2\right)\begin{pmatrix}\varphi_3\\ \varphi_4\end{pmatrix} = c\sigma\cdot(\mathbf{p}+e\mathbf{A})\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix}$$

Large components	Small components
φ_1	φ_3
φ_2	φ_4

Pauli matrices

$$\sigma_1 = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \qquad \sigma_2 = \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} \qquad \sigma_3 = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

- Under the Lorentz transformation, the equation is invariant.

e.g., in case two coordinate systems move with a relative velocity v along x-direction

$$x = \frac{x' + vt'}{\sqrt{1-\frac{v^2}{c^2}}} \qquad y = y' \qquad z = z' \qquad t = \frac{t' + \frac{v}{c^2}x'}{\sqrt{1-\frac{v^2}{c^2}}}$$

- It contains the first order derivatives with respect to space and time.
- It includes spin automatically without ad-hoc treatments.

Equations for atom

Schrodinger equation

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}+V\right]P_{nl}=\varepsilon_{nl}P_{nl}$$

Dirac equation

$$\left[-\frac{1}{2M(r)}\left(\frac{d^2}{dr^2}+\frac{a^2}{2M(r)}\frac{dV}{dr}\frac{d}{dr}+\frac{a^2}{2M(r)}\frac{\kappa}{r}\frac{dV}{dr}-\frac{\kappa(\kappa+1)}{r^2}\right)+V\right]G_{nlj}=\varepsilon_{nlj}G_{nlj}$$

$j=l-\frac{1}{2}\quad \kappa=l$ Degeneracy: $2l$

$j=l+\frac{1}{2}\quad \kappa=-(l+1)$ Degeneracy: $2(l+1)$

$a \equiv 1/c$ (1/137.036 in a.u.).

$M(r) = 1+\frac{a^2(\varepsilon_{nlj}-V)}{2}$.

Scalar relativistic equation

$$\left[-\frac{1}{2M(r)}\left(\frac{d^2}{dr^2}+\frac{a^2}{2M(r)}\frac{dV}{dr}\frac{d}{dr}-\frac{a^2}{2M(r)}\frac{1}{r}\frac{dV}{dr}\right)+V\right]G_{nlj}=\varepsilon_{nlj}G_{nlj}$$

By considering the degeneracy, a mean κ can be calculated as

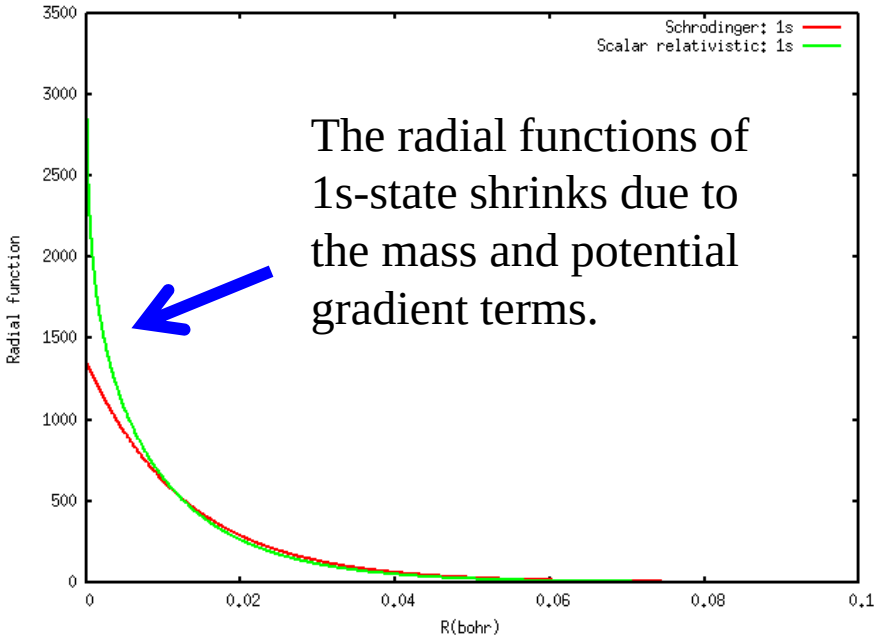
$$\kappa_{\mathrm{av}}=\frac{l\times 2l-(l+1)\times 2(l+1)}{2l+2(l+1)}=-1$$

By inserting the mean κ into the Dirac eq., one can derive the scalar relativistic equation.

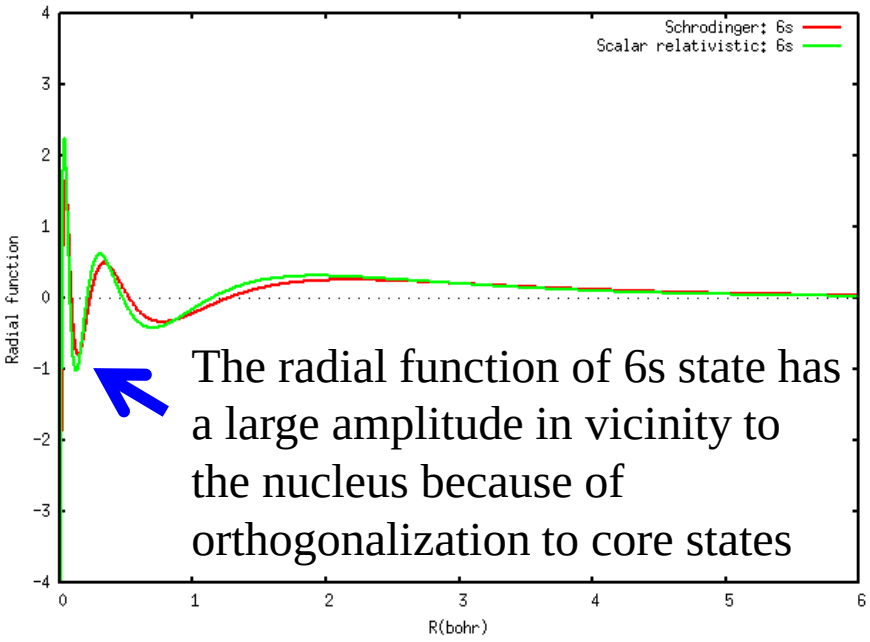
1s and 6s radial functions of Pt atom

Red: Schrodinger

Green: Scalar relativistic



The radial functions of 1s-state shrinks due to the mass and potential gradient terms.



The radial function of 6s state has a large amplitude in vicinity to the nucleus because of orthogonalization to core states

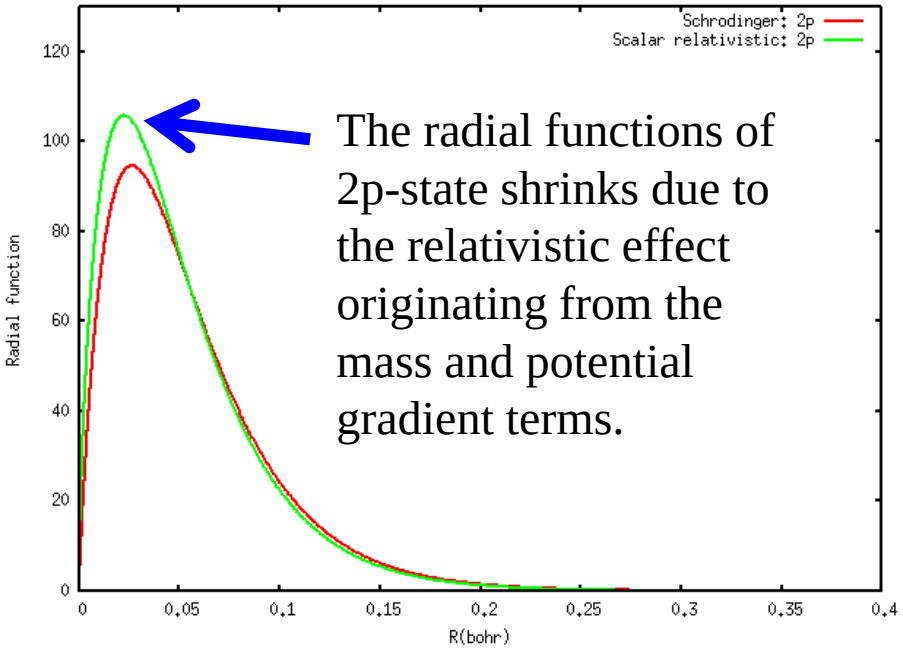
Relativistic effect for s-states:

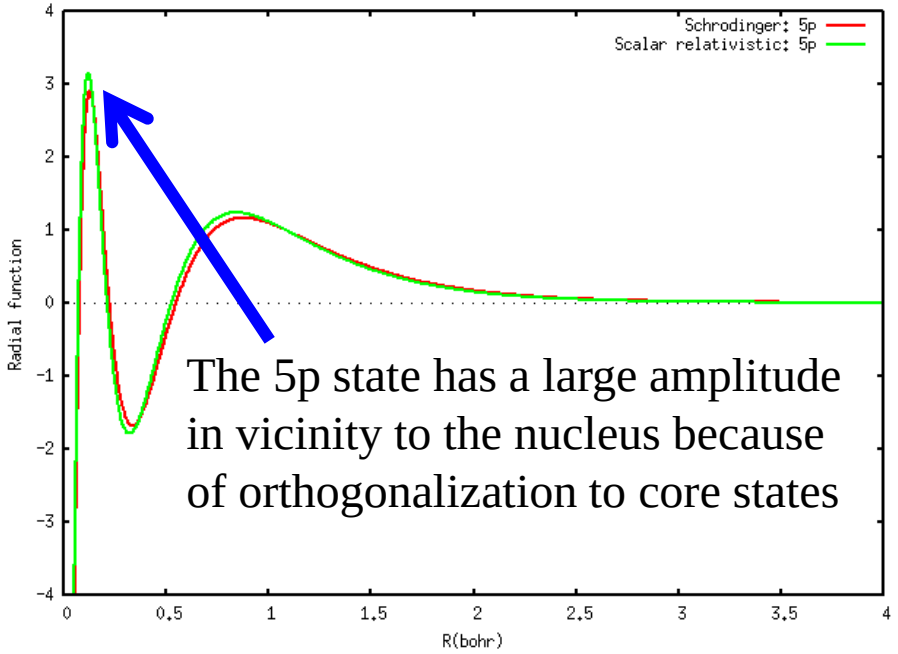
All the s-states shrink due to the mass and potential gradient terms.

2p and 5p radial functions of Pt atom

Red: Schrodinger

Green: Scalar relativistic





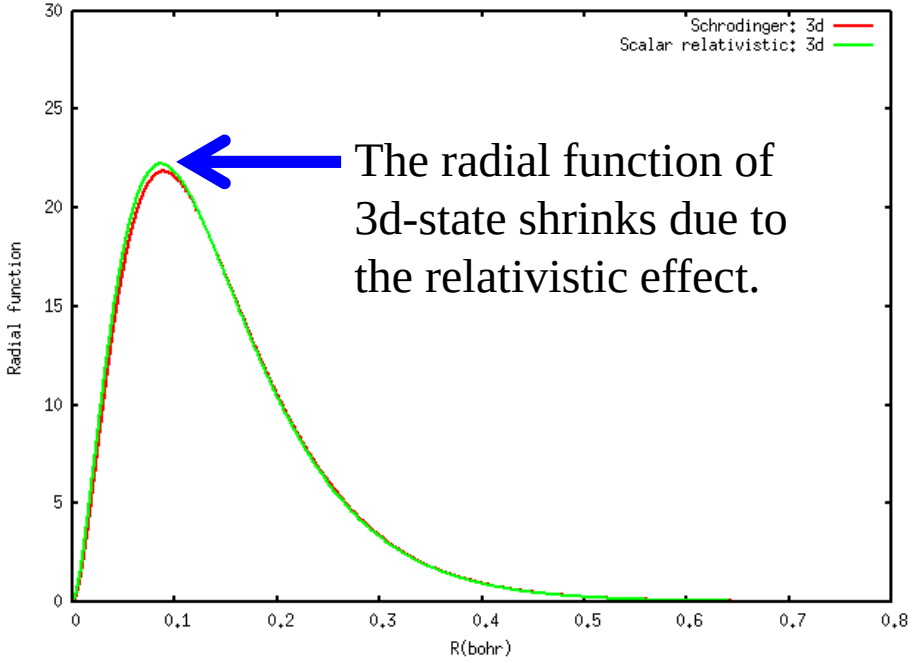
Relativistic effect for p-states:

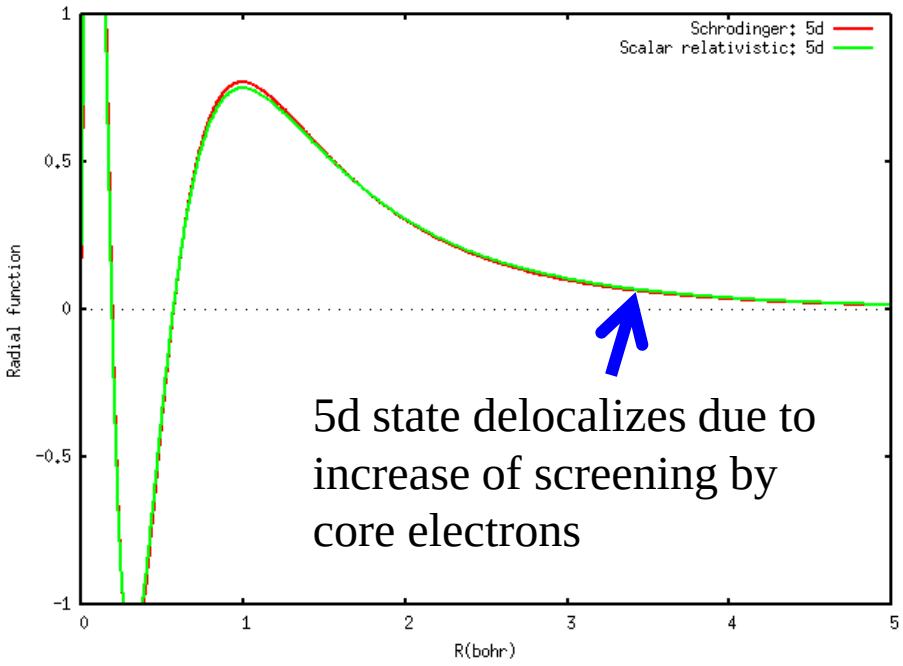
All the p-states shrink due to the mass and potential gradient terms.

3d and 5d radial functions of Pt atom

Red: Schrodinger

Green: Scalar relativistic





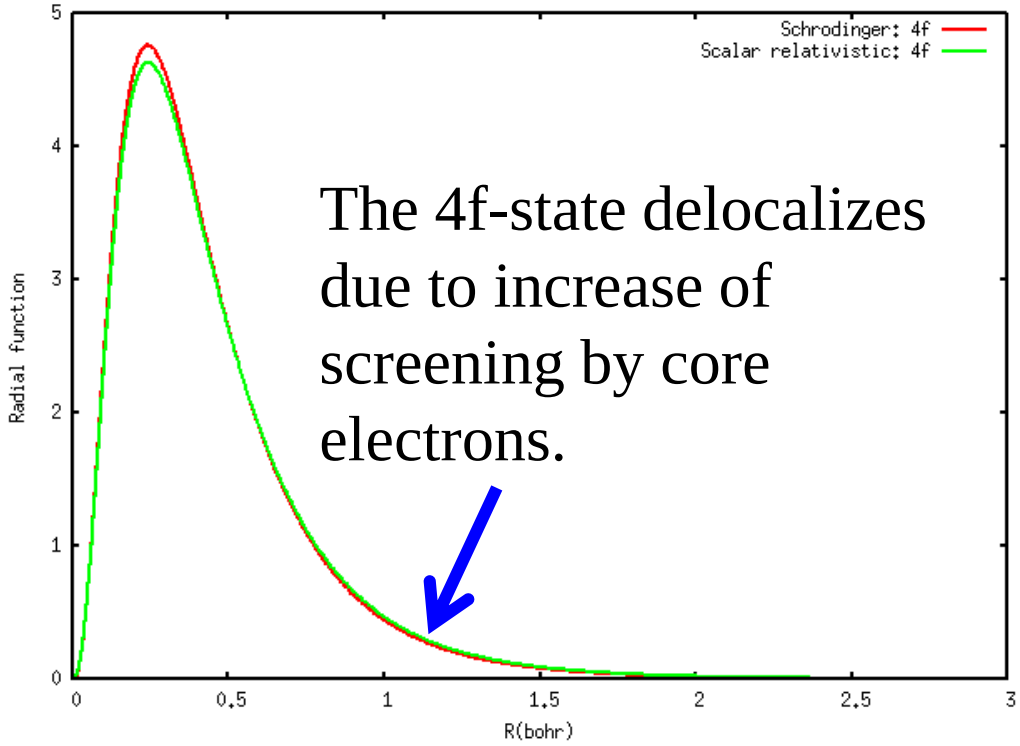
Relativistic effect for d-states:

There is a competition between the relativistic effect and screening effect by core electrons. In case of the 5d-state, the screening effect is larger than the former.

4f radial function of Pt atom

Red: Schrodinger

Green: Scalar relativistic



The 4f-state delocalizes due to increase of screening by core electrons.

Relativistic effect for f-states:

The screening effect is dominant, resulting in delocalization of f-states.

Eigenvalues of Pt atom

Eigenvalues (Hartree) of atomic platinum calculated by the Schrödinger equation, a scalar relativistic treatment, and a fully relativistic treatment of Dirac equation within GGA to DFT.

state	sch	sdirac	dirac	
			j=l+1/2	j=l-1/2
1s	-2612.2560	-2876.3416	-2868.8969	
2s	-434.7956	-505.1706	-503.1143	
2p	-418.0254	-438.1804	-419.1547	-482.3721
3s	-101.2589	-118.6671	-118.0772	
3p	-93.3171	-99.1367	-94.8406	-108.7310
3d	-78.3951	-77.8404	-76.1768	-79.1659
4s	-21.1326	-25.4989	-25.3346	
4p	-17.7166	-19.0862	-18.0570	-21.3626
4d	-11.4203	-11.2646	-10.9124	-11.5257
4f	-3.0221	-2.5775	-2.4568	-2.5821
5s	-2.9387	-3.7323	-3.6983	
5p	-1.8756	-2.0571	-1.8911	-2.43384
5d	-0.2656	-0.2259	-0.2020	-0.24966
6s	-0.1507	-0.2074	-0.2079	

It turns out from the comparison between 'sch' and 'sdirac' that

- The eigenvalues of the s- and p-states are always deepened by the relativistic effect.
- The eigenvalue of the 3d, 4d, 5d, and 4f states become shallower.

Scalar relativistic effects

- The mass and potential gradient terms affect largely core electrons, leading to localization of those electrons.
- Even the valence s- and p-states localize due to the orthogonalization to the core states.
- The d-states are affected by both the localization effect and screening effect with the core electrons.
- The 4f-state is mainly affected by the screening effect of the core electrons.

Spin-orbit coupling

The Dirac equation has a dependency on κ or j, the dependency produces a coupling between l and spin quantum number. This is so called 'spin-orbit coupling'.

Dirac equation

$$\left[-\frac{1}{2M(r)}\left(\frac{d^2}{dr^2}+\frac{a^2}{2M(r)}\frac{dV}{dr}\frac{d}{dr}+\frac{a^2}{2M(r)}\frac{\kappa}{r}\frac{dV}{dr}-\frac{\kappa(\kappa+1)}{r^2}\right)+V\right]G_{nlj}=\varepsilon_{nlj}G_{nlj}$$

$j = l - \frac{1}{2}$ $\kappa = l$ Degeneracy: $2l$

$j = l + \frac{1}{2}$ $\kappa = -(l+1)$ Degeneracy: $2(l+1)$

$a \equiv 1/c$ (1/137.036 in a.u.).

$M(r) = 1 + \frac{a^2(\varepsilon_{nlj} - V)}{2}$.

Pt atom

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5d	-0.2656	-0.2259	-0.2020	-0.24966
6s	-0.1507	-0.2074	-0.2079	

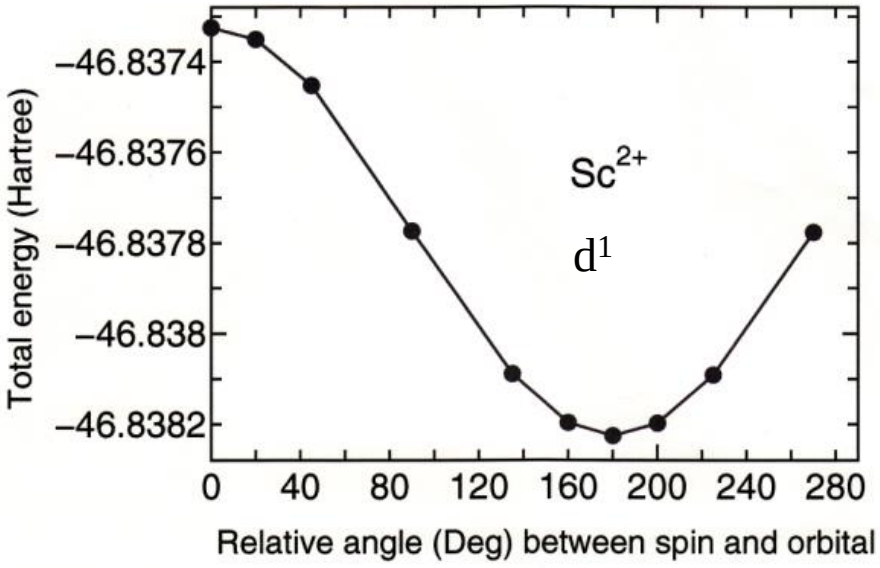
SO-splitting

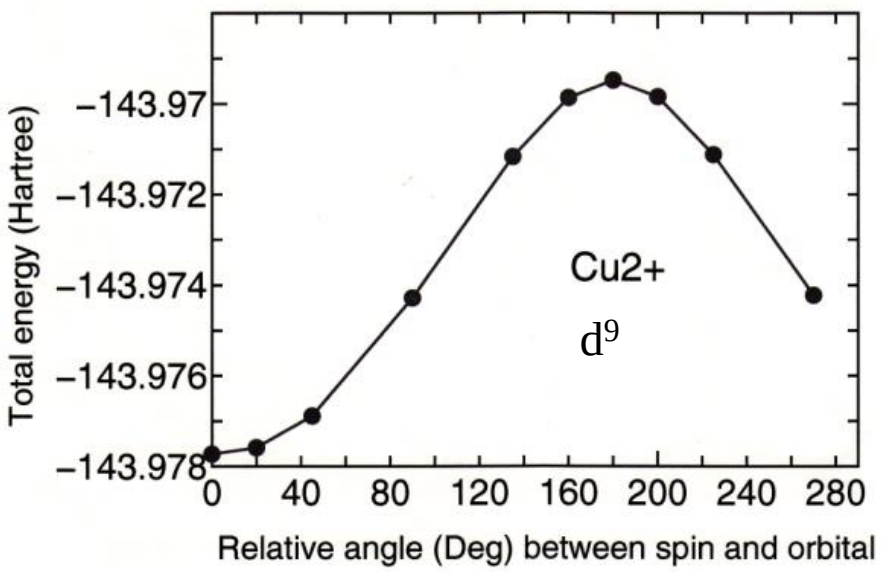
0
0
63.2174
0
13.8904
2.9891
0
3.3056
0.6133
0.1253
0
0.5427
0.0477
0

- The core states have a large SO-splitting.
- The s-stage has no SO-splitting.
- The SO-splitting decreases in order of p-, d-, f-…., when they are compared in a nearly same energy regime.

First-principle calculations of Hund's 3rd rule

By changing relative angle between spin and orbital moments, one can calculate how the total energy varies depending on the angle, leading to **a direct evaluation of Hund's third rule**.





Less than half in the shell structure ⇒ The anti-parallel is favored

More than half in the shell structure ⇒ The parallel is favored

Orbital magnetic moment

The orbital moment for localized electrons can be calculated by projecting wave functions onto the local angular momentum operator on each site as follows:

$$
\begin{aligned}
l_{iv} &= \int dE \sum_{\mathbf{k}} \sum_{\nu} f(E) \langle \psi_{\mathbf{k}\nu} | \hat{l}_v | \psi_{\mathbf{k}\nu} \rangle \delta(E - \varepsilon_{\mathbf{k}\nu}), \\
&= \int dE \sum_{\mathbf{k}} \sum_{\nu} f(E) \left[\langle \varphi^{\alpha}_{\mathbf{k}\nu} | \hat{l}_v | \varphi^{\alpha}_{\mathbf{k}\nu} \rangle + \langle \varphi^{\beta}_{\mathbf{k}\nu} | \hat{l}_v | \varphi^{\beta}_{\mathbf{k}\nu} \rangle \right] \delta(E - \varepsilon_{\mathbf{k}\nu}), \\
&= \sum_{\mathbf{k}} \sum_{\nu} f(\varepsilon_{\mathbf{k}\nu}) \left[\sum_{\kappa,\kappa'} c^{\alpha,*}_{\mathbf{k}\nu,i\kappa} c^{\alpha}_{\mathbf{k}\nu,i\kappa'} \langle \phi^{\alpha}_{i\kappa} | \hat{l}_v | \phi^{\alpha}_{i\kappa'} \rangle + c^{\beta,*}_{\mathbf{k}\nu,i\kappa} c^{\beta}_{\mathbf{k}\nu,i\kappa'} \langle \phi^{\beta}_{i\kappa} | \hat{l}_v | \phi^{\beta}_{i\kappa'} \rangle \right], \\
&= \sum \rho^{\alpha\alpha}_{i\kappa,i\kappa'} \langle \phi^{\alpha}_{i\kappa} | \hat{l}_v | \phi^{\alpha}_{i\kappa'} \rangle + \rho^{\beta\beta}_{i\kappa,i\kappa'} \langle \phi^{\beta}_{i\kappa} | \hat{l}_v | \phi^{\beta}_{i\kappa'} \rangle,
\end{aligned}
$$

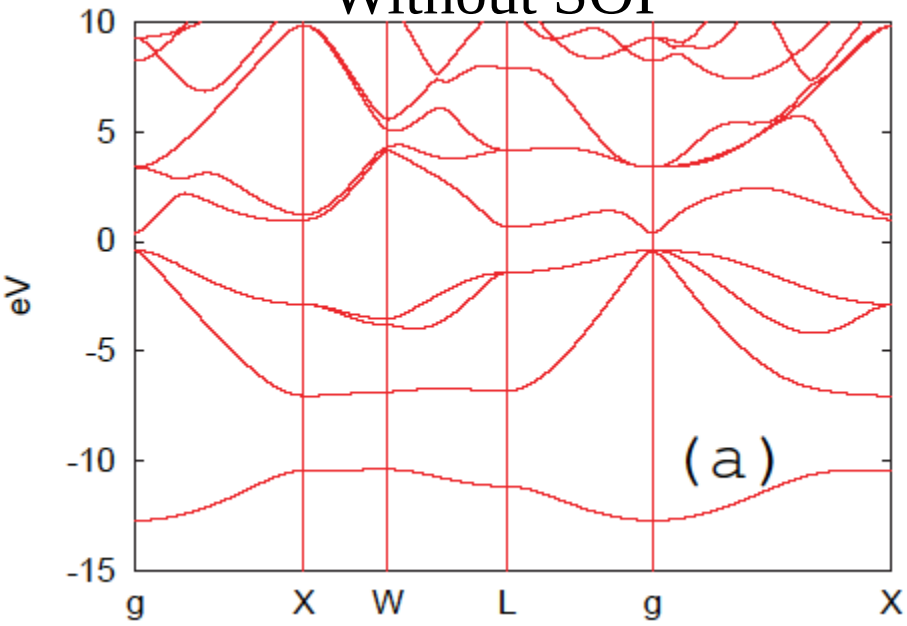
Compound	M_s OpenMX	M_s Other calc.	M_o OpenMX	M_o Other calc.	Expt. in total
MnO	4.560	4.49[1]	0.001	0.00[1]	4.79,4.58
FeO	3.586	3.54[1]	1.010	1.01[1]	3.32
CoO	2.685	2.53[1]	1.137	1.19[1]	3.35,3.8
NiO	1.603	1.53[1]	0.171	0.27[1]	1.77,1.64,1.90
Fe_2O_3	4.014		0.034		
$GaFeO_3$ (GGFF)	3.950-3.956		0.020-0.021		
$GaFeO_3$ (GFFF)	3.923-4.001		0.020-0.022		

[1] A. Svane and O. Gunnarsson, Phys. Rev. Lett. **65**, 1148 (1990).

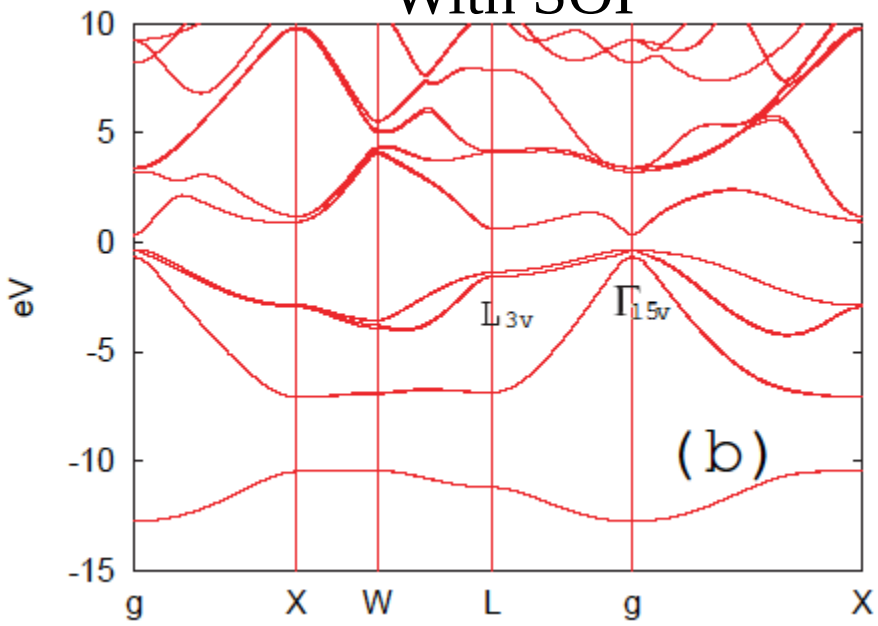
Spin-orbit splitting

e.g., GaAs

Without SOI



With SOI



Level	OpenMX	LMTO[(a)]	PP[(b)]	Expt.
Γ_{15v}	0.348	0.351	0.35	0.34
L_{3v}	0.218	0.213	0.22	

(a) M. Cardona, N. E. Christensen, and G. Gasol, Phys. Rev. B **38**, 1806 (1988).
(b) G. Theurich and N. A. Hill, Phys. Rev. B **64**, 073106 (2001).

Simplification of Dirac eq. (1)

$$\left(\varepsilon - eV - mc^2\right)\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix} = c\sigma\cdot(\mathbf{p}+e\mathbf{A})\begin{pmatrix}\varphi_3\\ \varphi_4\end{pmatrix}$$

$$\left(\varepsilon - eV + mc^2\right)\begin{pmatrix}\varphi_3\\ \varphi_4\end{pmatrix} = c\sigma\cdot(\mathbf{p}+e\mathbf{A})\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix}$$

$$\varepsilon = mc^2 + \varepsilon'$$

Assuming that

$$|\varepsilon'| \ll mc^2 \longrightarrow \begin{pmatrix}\varphi_3\\ \varphi_4\end{pmatrix} \approx \frac{v}{c}\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix}$$

With the assumption, the Dirac eq. can be simplified as

$$\left\{\frac{1}{2m}(\mathbf{p}+e\mathbf{A})^2 + \frac{e\hbar}{2m}\sigma\cdot\mathbf{B} + V\right\}\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix} = \varepsilon'\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix}$$

It looks Schrodinger eq., but the wave function is a two-component spinor.

Simplification of Dirac eq. (2)

By expanding explicitly the simplified eq., we obtain

$$\left\{\frac{1}{2m}(\mathbf{p}+e\mathbf{A})^2+\frac{e\hbar}{2m}\sigma\cdot\mathbf{B}+V\right\}\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix} = \varepsilon'\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix}$$

$$\left\{-\frac{1}{2m}\nabla^2+\frac{e}{2m}\mathbf{B}\cdot\mathrm{l}+\frac{e}{m}\mathbf{B}\cdot\frac{1}{2}\hbar\sigma+\text{Diamagnetic term}+V\right\}\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix} = \varepsilon'\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix}$$

This has the Zeeman and diamagnetic terms, but unfortunately does not take account of the spin-orbit interaction.

By ignoring the diamagnetic term, and giving j-dependence of *V*, we get the following eq:

$$\left\{-\frac{1}{2m}\nabla^2+\frac{e}{2m}\mathbf{B}\cdot\mathrm{l}+\frac{e}{m}\mathbf{B}\cdot\frac{1}{2}\hbar\sigma+V_j\right\}\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix} = \varepsilon'\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix}$$

This is the equation employed in a widely used non-collinear DFT method.

Relativistic pseudopotential

Radial Dirac eq. for the majority component

$$\left[\frac{1}{2M(r)}\left(\frac{d^2}{dr^2}+\frac{a^2}{2M(r)}\frac{dV}{dr}\frac{d}{dr}+\frac{a^2}{2M(r)}\frac{\kappa}{r}\frac{dV}{dr}-\frac{\kappa(\kappa+1)}{r^2}\right)+\varepsilon_{nlj}-V\right]G_{nlj}=0$$

$$M(r) = 1+\frac{a^2(\varepsilon_{nlj}-V)}{2} \qquad \kappa=l \text{ and } \kappa=-(l+1) \text{ for } j=l-\tfrac{1}{2} \text{ and } j=l+\tfrac{1}{2}$$

For each quantum number j, the Dirac eq. is solved numerically,
and its norm-conserving pseudopotential is constructed by the MBK scheme.

The unified pseudopotential is given by

$$V_{\rm ps} = \sum_{lm}\left[|\Phi_J^M\rangle V_{\rm ps}^{l+\frac{1}{2}}\langle\Phi_J^M| + |\Phi_{J'}^{M'}\rangle V_{\rm ps}^{l-\frac{1}{2}}\langle\Phi_{J'}^{M'}|\right]$$

with the analytic solution for spherical coordinate:

where for $J=l+\frac{1}{2}$ and $M=m+\frac{1}{2}$

$$|\Phi_J^M\rangle = \left(\frac{l+m+1}{2l+1}\right)^{\frac{1}{2}}|Y_l^m\rangle|\alpha\rangle+\left(\frac{l-m}{2l+1}\right)^{\frac{1}{2}}|Y_l^{m+1}\rangle|\beta\rangle,$$

and for $J'=l-\frac{1}{2}$ and $M'=m-\frac{1}{2}$

$$|\Phi_{J'}^{M'}\rangle = \left(\frac{l-m+1}{2l+1}\right)^{\frac{1}{2}}|Y_l^{m-1}\rangle|\alpha\rangle-\left(\frac{l+m}{2l+1}\right)^{\frac{1}{2}}|Y_l^{m}\rangle|\beta\rangle.$$

Non-collinear DFT (1)

Two-component spinor

$$|\psi_\nu\rangle \;=\; |\varphi_\nu^\alpha \alpha\rangle + |\varphi_\nu^\beta \beta\rangle,$$

The charge density operator is defined by

$$\hat{n} \;=\; \sum f_\nu |\psi_\nu\rangle\langle\psi_\nu|, \qquad \begin{pmatrix} n'_\uparrow & 0 \\ 0 & n'_\downarrow \end{pmatrix} \;=\; U n\, U^\dagger,$$

$$= \; U \begin{pmatrix} n_{\alpha\alpha} & n_{\alpha\beta} \\ n_{\beta\alpha} & n_{\beta\beta} \end{pmatrix} U^\dagger.$$

The total energy is a simple extension of the collinear case.

$$E_{\rm tot} \;=\; \sum_{\sigma=\alpha,\beta} \sum_\nu f_\nu \langle \varphi_\nu^\sigma | \hat{T} | \varphi_\nu^\sigma \rangle + \sum_{\sigma\sigma'} \int w_{\sigma\sigma'} n_{\sigma'\sigma} + \frac{1}{2} \int\int \frac{n'(\mathbf{r}) n'(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} dv dv' + E_{\rm xc}\left\{n_{\sigma\sigma'}\right\},$$

The variation of wave functions leads to

$$\left.\begin{array}{l} \frac{\delta F}{\delta \varphi_\mu^{\alpha,*}} = 0 \\ \frac{\delta F}{\delta \varphi_\mu^{\beta,*}} = 0 \end{array}\right\} \Rightarrow \begin{pmatrix} \hat{T} + w_{\alpha\alpha} + V_{\rm H} + V_{\rm xc}^{\alpha\alpha} & w_{\alpha\beta} + V_{\rm xc}^{\alpha\beta} \\ w_{\beta\alpha} + V_{\rm xc}^{\beta\alpha} & \hat{T} + w_{\beta\beta} + V_{\rm H} + V_{\rm xc}^{\beta\beta} \end{pmatrix} \begin{pmatrix} \varphi_\mu^\alpha \\ \varphi_\mu^\beta \end{pmatrix} \;=\; \varepsilon_\mu \begin{pmatrix} \varphi_\mu^\alpha \\ \varphi_\mu^\beta \end{pmatrix}$$

Non-collinear DFT (2)

The spin-1/2 matrix gives us the relation between the spin direction in real space and spinor.

$$D \equiv \exp\left(\frac{-i\hat{\sigma}\cdot\mathbf{h}\phi}{2}\right)$$

- First, rotate θ on the y-axis $\rightarrow \exp\left(-i\frac{\sigma_2\theta}{2}\right)$
- Second, rotate ϕ on the z-axis $\rightarrow \exp\left(-i\frac{\sigma_3\phi}{2}\right)$

$$\begin{pmatrix}1\\0\end{pmatrix} \Rightarrow \boxed{\exp\left(-i\frac{\sigma_3\phi}{2}\right)\exp\left(-i\frac{\sigma_2\theta}{2}\right)}\begin{pmatrix}1\\0\end{pmatrix}$$

U

Condition $\quad UnU^\dagger = \begin{pmatrix} n'_\uparrow & 0 \\ 0 & n'_\downarrow \end{pmatrix}.$

We would like to find U which diagonalizes the matrix n, after algebra, it is given by

$$\begin{aligned}
\phi &= -\arctan\frac{\mathrm{Im}\ n_{\alpha\beta}}{\mathrm{Re}\ n_{\alpha\beta}} \\
\theta &= \arctan\left(\frac{2(\mathrm{Re}\ n_{\alpha\beta}\cos(\phi) - \mathrm{Im}\ n_{\alpha\beta}\sin(\phi))}{n_{\alpha\alpha} - n_{\beta\beta}}\right) \\
n'_\uparrow &= \frac{1}{2}(n_{\alpha\alpha}+n_{\beta\beta}) + \frac{1}{2}(n_{\alpha\alpha}-n_{\beta\beta})\cos(\theta) + (\mathrm{Re}\ n_{\alpha\beta}\cos(\phi) - \mathrm{Im}\ n_{\alpha\beta}\sin(\phi))\sin(\theta) \\
n'_\downarrow &= \frac{1}{2}(n_{\alpha\alpha}+n_{\beta\beta}) - \frac{1}{2}(n_{\alpha\alpha}-n_{\beta\beta})\cos(\theta) - (\mathrm{Re}\ n_{\alpha\beta}\cos(\phi) - \mathrm{Im}\ n_{\alpha\beta}\sin(\phi))\sin(\theta)
\end{aligned}$$

LDA+U within NC-DFT

In conjunction with unrestricted Hartree-Fock theory, we introduce a Hubbard term.

$$E_{\mathrm{LDA+U}} = E_{\mathrm{LDA}} + E_{\mathrm{U}}$$

Starting from the diagonal occupation matrix, a rotational invariant formula can be obtained even for the NC case.

$$\begin{aligned} E_{\mathrm{U}} &= \frac{1}{2}\sum_s U_s \left[\mathrm{Tr}(A_s N_s A_s^\dagger) - \mathrm{Tr}(A_s N_s A_s^\dagger A_s N_s A_s^\dagger)\right], \\ &= \frac{1}{2}\sum_s U_s \left[\mathrm{Tr}(n_s) - \mathrm{Tr}(n_s n_s)\right], \\ &= \frac{1}{2}\sum_s U_s \left[\sum_{\sigma m} n^{\sigma\sigma}_{s,mm} - \sum_{\sigma m,\sigma' m'} n^{\sigma\sigma'}_{s,mm'} n^{\sigma'\sigma}_{s,m'm}\right], \end{aligned}$$

The occupation number operator is given by

$$\hat{n}^{\sigma\sigma'}_{smm'} = \frac{1}{2}\left(|s\tilde{m}\sigma\rangle\langle sm'\sigma'| + |sm\sigma\rangle\langle s\tilde{m'}\sigma'|\right),$$

Then, the effective potential operator becomes

$$\hat{v}_{\mathrm{U}} = \frac{1}{2}\sum_{\sigma\sigma'}\sum_{smm'}\left[|s\tilde{m}\sigma\rangle v^{\sigma\sigma'}_{\mathrm{U},smm'}\langle sm'\sigma'| + |sm\sigma\rangle v^{\sigma\sigma'}_{\mathrm{U},smm'}\langle s\tilde{m'}\sigma'|\right].$$

Constrained NC-DFT: a harmonic constraint

Each atomic site, (2 x 2) occupation matrices are constructed:

From two-component spinor

$$N = \begin{pmatrix} N_{\alpha\alpha} & N_{\alpha\beta} \\ N_{\beta\alpha} & N_{\beta\beta} \end{pmatrix}$$

Constraint matrix

$$N^{(0)} = U_0^{\dagger} \begin{pmatrix} N_{\uparrow} & 0 \\ 0 & N_{\downarrow} \end{pmatrix} U_0$$

Then, a constraint energy can be calculated by the following energy functional:

$$E_{cs} = v \sum_i \mathrm{Tr} \left((N_i - N_i^{(0)})^2 \right)$$

By specifying the spin direction and the magnitude at each site, one can control spin (orbital) magnetic moment self-consistently.

The effective Hamiltonian due to the constraints and LDA+U

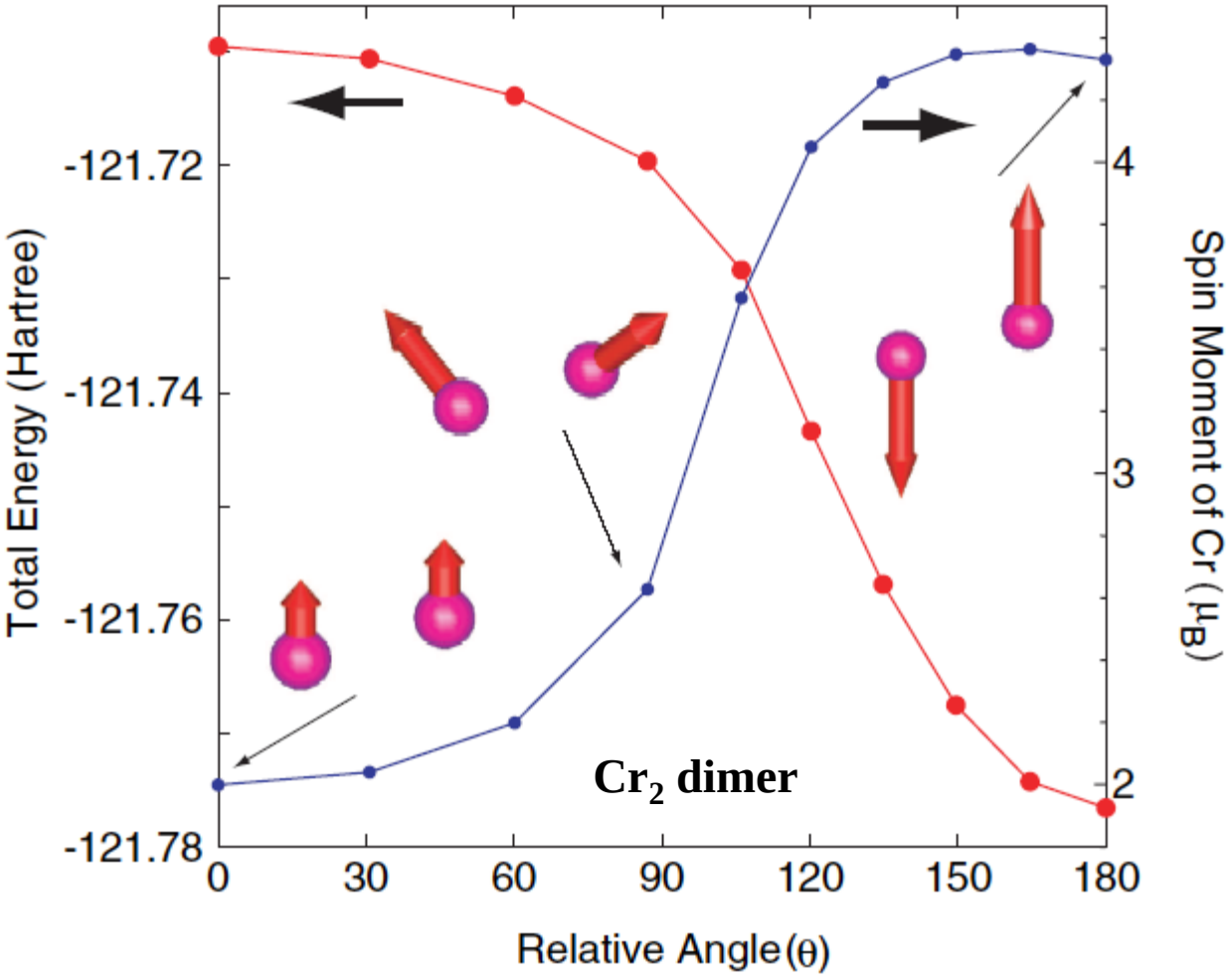
The effective Hamiltonian due to the constraints and LDA+U take the same form

$$\hat{v}_{\rm eff} = \frac{1}{2}\sum_{\sigma\sigma'}\sum_{smm'}\left[|s\tilde{m}\sigma\rangle v^{\sigma\sigma'}_{{\rm eff},smm'}\langle sm'\sigma'| + |sm\sigma\rangle v^{\sigma\sigma'}_{{\rm eff},smm'}\langle s\tilde{m'}\sigma'|\right].$$

$$v^{\sigma\sigma'}_{{\rm eff},smm'} = v^{\sigma\sigma'}_{{\rm U},smm'} + v^{\sigma\sigma'}_{{\rm constraint},smm'}$$

Thus, we only have to add each contribution, leading to that the implementation makes easier.

Example: a harmonic constraint



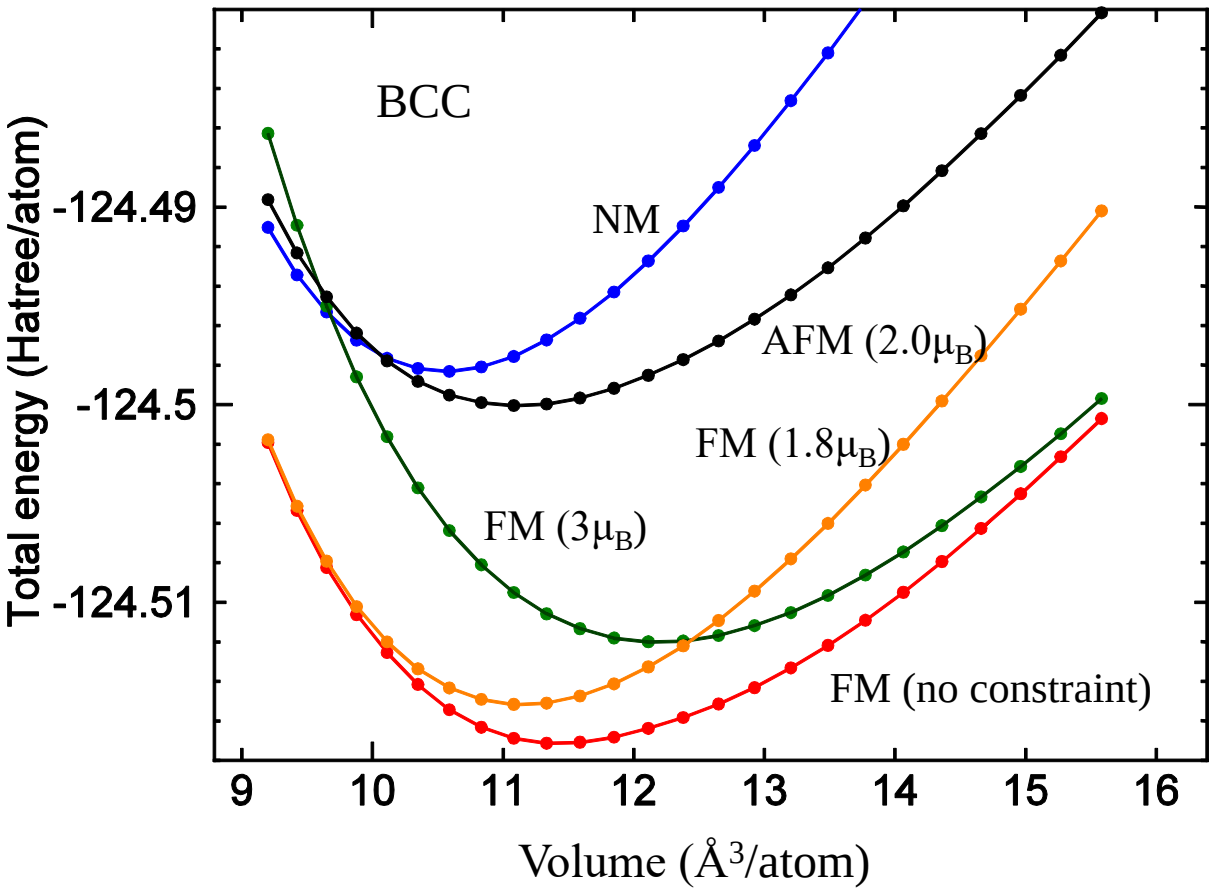
The spin direction is controlled by the harmonic constraint, and the spin moment is also determined self-consistenly.

bcc-Fe with various spin states

To take account of spin structures with arbitrary direction and magnitude, the total energy is calculated by a constraint scheme within non-collinear DFT (GGA).

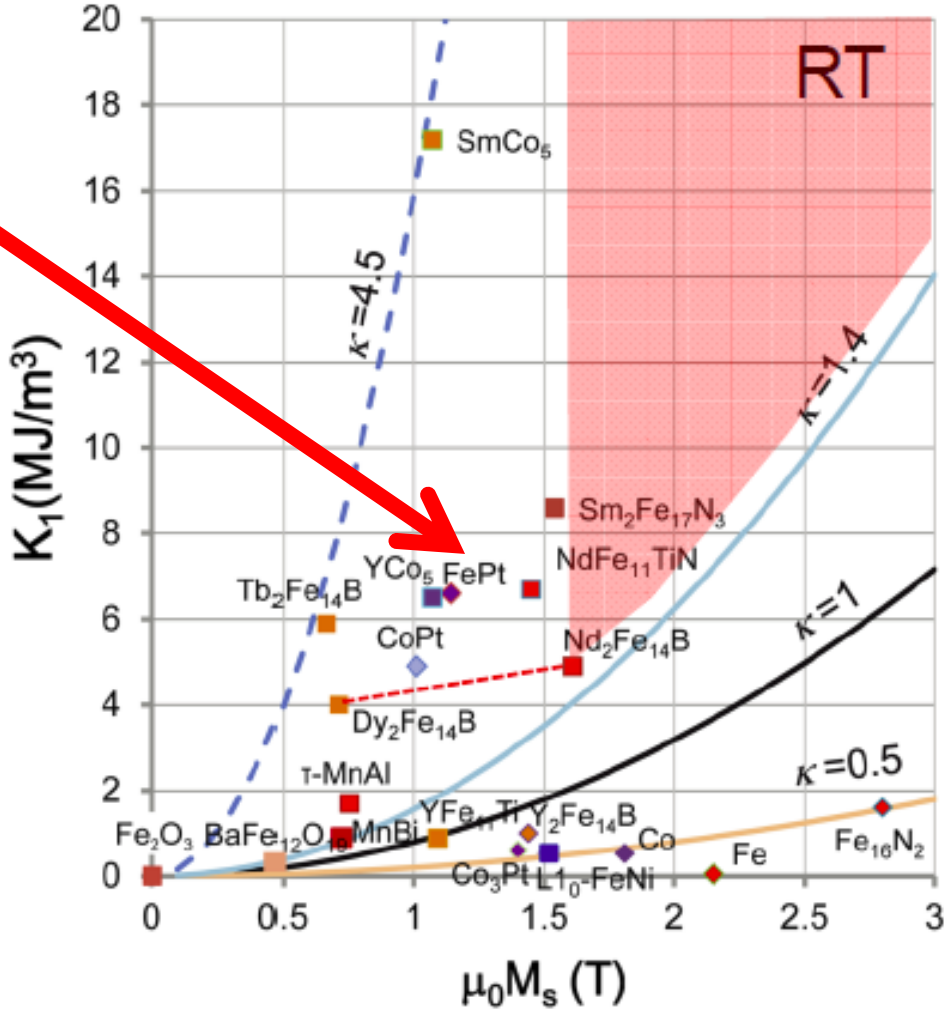
$$E_{DFT} = E^{(0)}{}_{DFT} + E_{CS}$$

$$E_{CS} = \nu \sum_i Tr[(N_i - N_i^{(CS)})^2]$$



Anisotropy and magnetization in magnets

FePt having a large K_1



K_1:
magnetic anisotropy constant

$\mu_0 M_s$:
Saturation magnetization

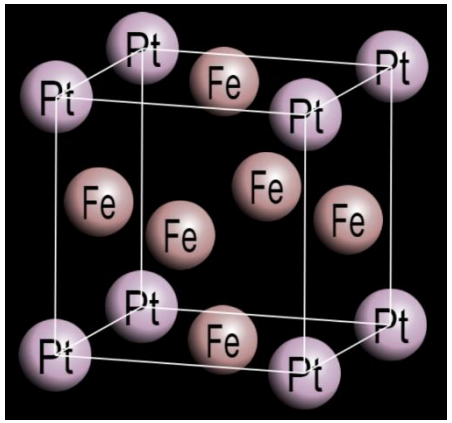
$\kappa = (K_1/\mu_0 M_s^2)^{1/2}$
hardness parameter

Hono@NIMS

Crystal structure of FePt

PtFe alloy is known to have three ordered phases.

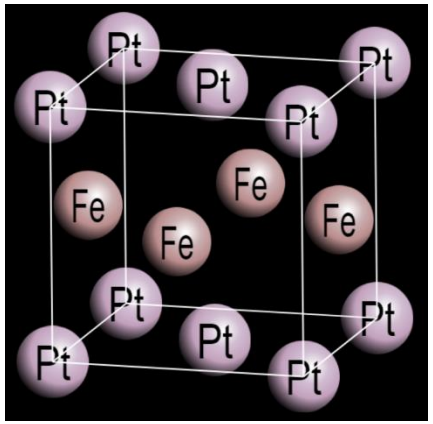
$L1_2$-Fe_3Pt ⇒ Ferromagnetic
$L1_0$-FePt ⇒ Ferromagnetic with high anisotropy
$L1_2$-$FePt_3$ ⇒ Anti-ferromagnetic



$L1_2$-Fe_3Pt

Expt.

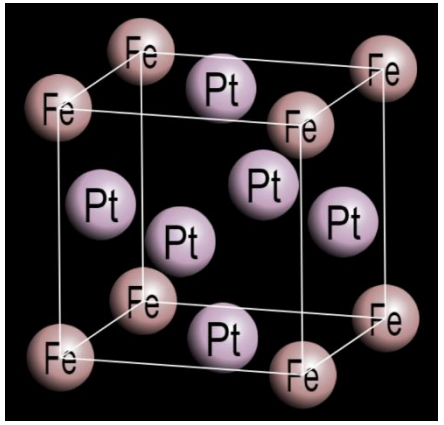
a=3.734Å



$L1_0$-FePt

Expt.

a=3.86Å, c=3.725Å

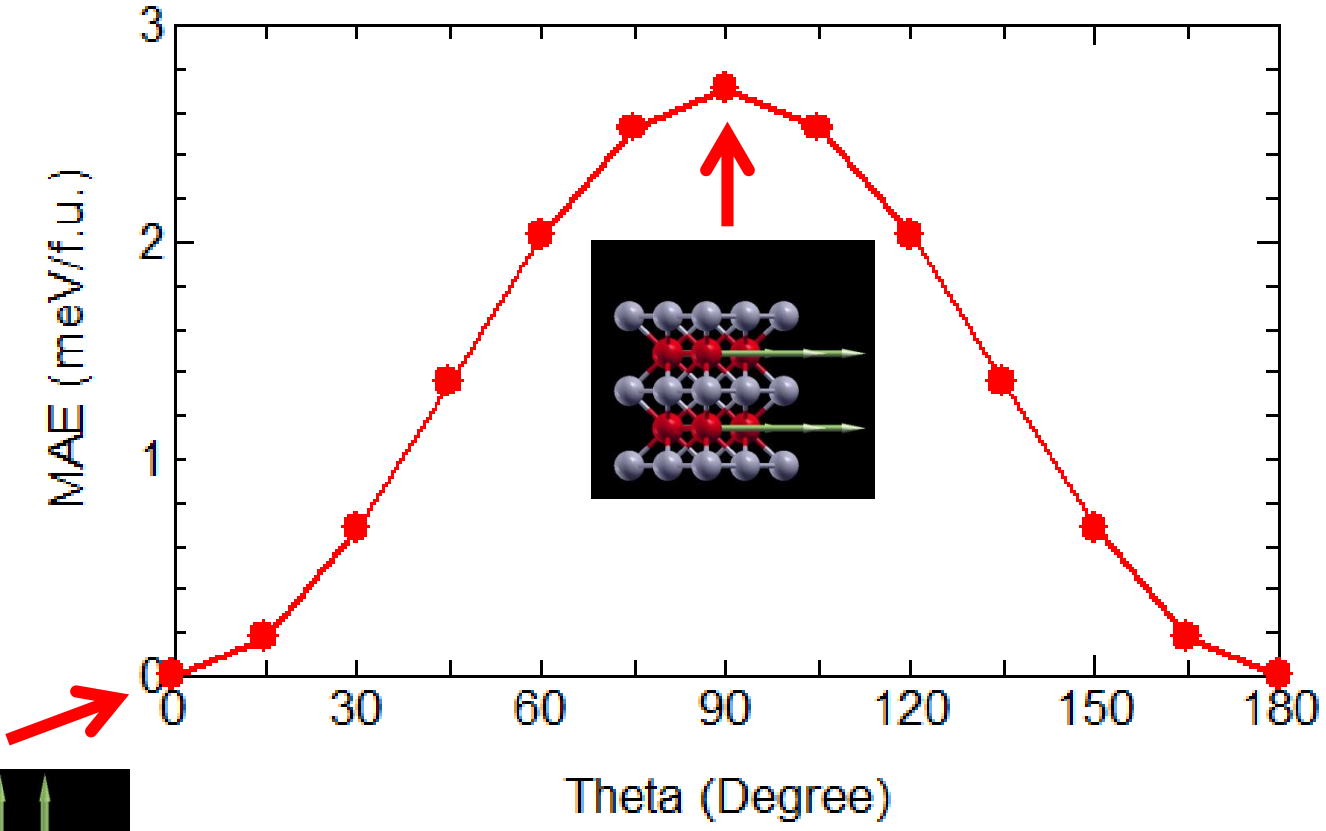


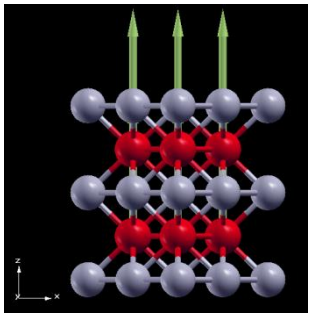
$L1_2$-$FePt_3$

Expt.

a=3.864Å

Exercise 7: Anisotropy energy of $L1_0$-FePt





Lattice constant from Expt.

	MAE (meV/f.u.)
OpenMX	2.7
VASP	2.6*
Expt.	1.1

* R.V. Chupulski et al, APL 100, 142405 (2012)

Relevant keywords for constraint scheme

To calculate an electronic structure with an arbitrary spin orientation in the non-collinear DFT, OpenMX Ver. 3.8 provides two kinds of constraint functionals which give a penalty unless the difference between the calculated spin orientation and the initial one is zero. The constraint DFT for the non-collinear spin orientation is available by the following keywords:

```
scf.Constraint.NC.Spin      on      # on|on2|off, default=off
scf.Constraint.NC.Spin.v    0.5      # default=0.0(eV)
```

The constraint is applied on each atom by specifying a flag as follows:

```
<Atoms.SpeciesAndCoordinates
  1   Cr    0.00000   0.00000   0.00000  7.0  5.0 -20.0 0.0  1  off
  2   Cr    0.00000   2.00000   0.00000  7.0  5.0  20.0 0.0  1  off
Atoms.SpeciesAndCoordinates>
```

See the manual for the details at

http://www.openmx-square.org/openmx_man3.8/node106.html

Outlook

The scalar relativistic effects

- Shrinking of core states by the mass and potential gradient terms
- Delocalization of valence electron due to screening by localization of core electrons

The spin-orbit coupling bridges real and spin spaces and produces many interesting physics such as

- Hund's 3rd rule
- Orbital magnetic moment
- Magnetic anisotropy in magnets
- Topological insulators
- Rashba effect
- etc.