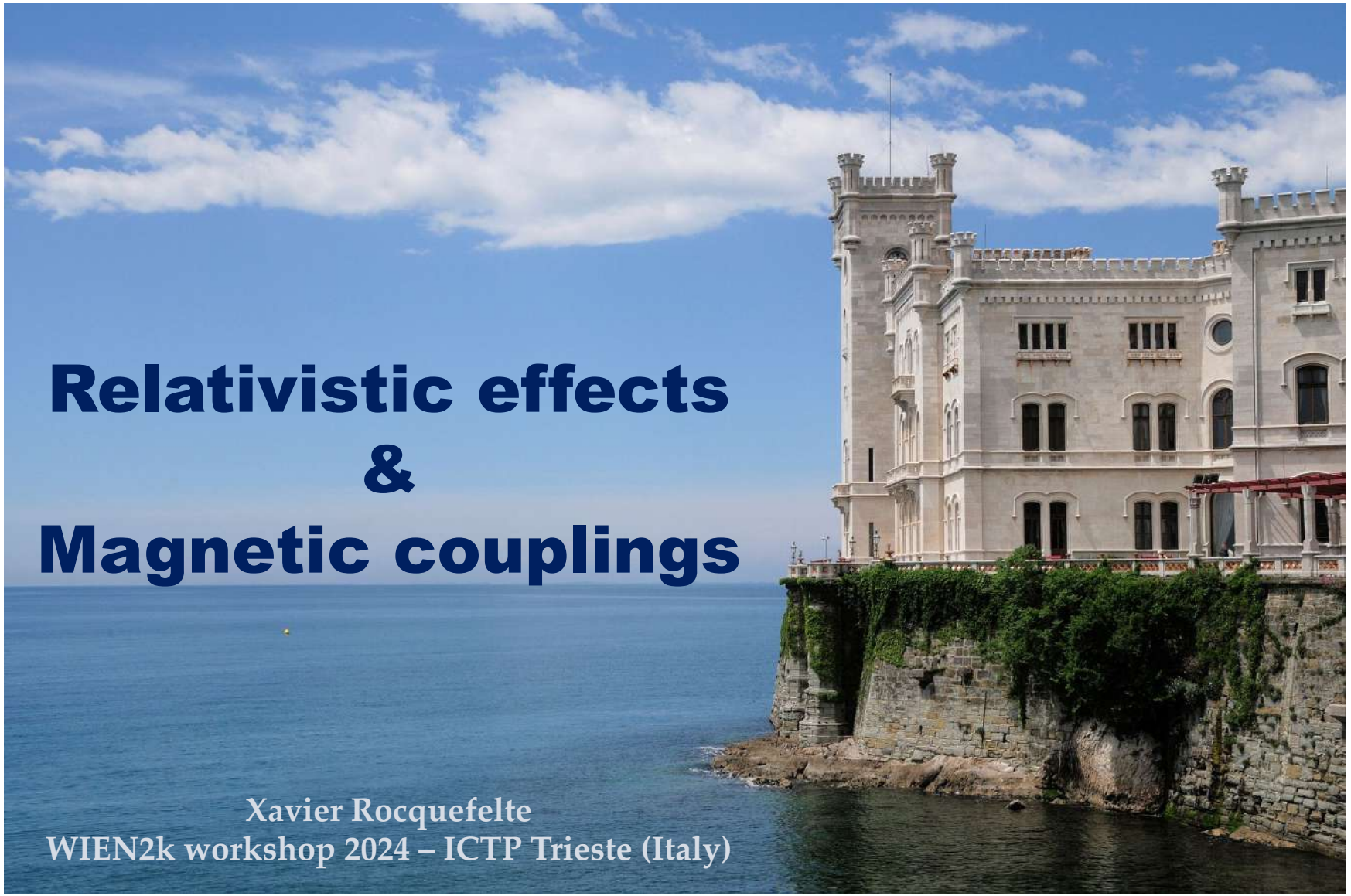


Relativistic effects & Magnetic couplings

Xavier Rocquefelte
WIEN2k workshop 2024 – ICTP Trieste (Italy)

I. Introduction

Talk constructed using the following documents:

Slides of:

- *Robert Laskowski, Stefaan Cottenier, Peter Blaha and Georg Madsen*

Notes of:

- *Pavel Novak (Calculation of spin-orbit coupling)* *http://www.wien2k.at/reg_user/textbooks/*

Books:

- *WIEN2k userguide, ISBN 3-9501031-1-2*
- *Electronic Structure: Basic Theory and Practical Methods, Richard M. Martin ISBN 0 521 78285 6*
- *Relativistic Electronic Structure Theory. Part 1. Fundamentals, Peter Schewerdtfeger, ISBN 0 444 51249 7*

web:

-*wienlist digest - http://www.wien2k.at/reg_user/index.html*

- *wikipedia …*

I. Introduction — Few words about Special Theory of Relativity

Light

Composed of photons (no mass)

Speed of light = constant

Atomic units:
$\hbar = m_e = e = 1$

$c \approx 137$ au

Matter

Composed of atoms (mass)

v = f(mass)

Speed of matter ⇄ mass

mass = f(v)

Lorentz Factor (measure of the relativistic effects)

$$\gamma = \frac{1}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} \geq 1$$

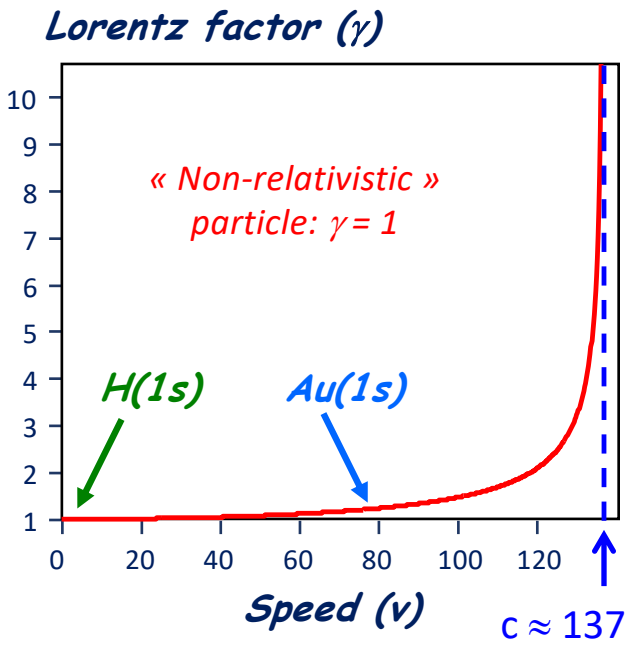
Relativistic mass: $M = \gamma m$ (m: rest mass)

Momentum: $p = \gamma m v = M v$

Total energy: $E^2 = p^2c^2 + m^2c^4$

$E = \gamma mc^2 = Mc^2$

I. Introduction — Few words about Special Theory of Relativity



Speed of the 1s electron (Bohr model):

$$v_e \propto \frac{Z}{n} \begin{cases} \text{H}: v_e(1s) = 1\,\text{au} \rightarrow \gamma = 1.00003 \\ \text{Au}: v_e(1s) = 79\,\text{au} \rightarrow \gamma = 1.22 \end{cases}$$

Details for Au atom:

$$v_e(1s) = \frac{79}{137}c = 0.58c$$

$$\gamma = \frac{1}{\sqrt{1-\left(\frac{v_e}{c}\right)^2}} = \frac{1}{\sqrt{1-(0.58)^2}} = 1.22$$

1s electron of Au atom = relativistic particle

$M_e(1s\text{-}Au) = 1.22m_e$

I. Introduction

Few words about Special Theory of Relativity

1) The mass-velocity correction

Relativistic increase in the mass of an electron with its velocity (when $v_e \rightarrow c$)

2) The Darwin term

It has no classical relativistic analogue
Due to small and irregular motions of an electron about its mean position (*Zitterbewegung*)

3) The spin-orbit coupling

It is the interaction of the spin magnetic moment (s) of an electron with the magnetic field induced by its own orbital motion (l)

4) Indirect relativistic effect

The change of the electrostatic potential induced by relativity is an indirect effect of the core electrons on the valence electrons

II. Equations

One electron radial Schrödinger equation

HARTREE ATOMIC UNITS

$$H_S\Psi = \left[-\frac{1}{2}\nabla^2 + V\right]\Psi = \varepsilon\Psi$$

$$V = -\frac{Z}{r}$$

INTERNATIONAL UNITS

$$H_S\Psi = \left[-\frac{\hbar^2}{2m_e}\nabla^2 + V\right]\Psi = \varepsilon\Psi$$

$$V = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

In a spherically symmetric potential

$$\Psi_{n,l,m} = R_{n,l}(r)Y_{l,m}(\theta,\varphi)$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\left[\sin(\theta)\frac{\partial}{\partial\theta}\right] + \frac{1}{r^2\sin^2(\theta)}\left(\frac{\partial^2}{\partial\varphi^2}\right)$$

$$-\frac{1}{2r^2}\frac{d}{dr}\left(r^2\frac{dR_{n,l}}{dr}\right) + \left[V + \frac{l(l+1)}{2r^2}\right]R_{n,l} = \varepsilon R_{n,l}$$

$$-\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_{n,l}}{dr}\right) + \left[V + \frac{\hbar^2}{2m_e}\frac{l(l+1)}{r^2}\right]R_{n,l} = \varepsilon R_{n,l}$$

Dirac Hamiltonian: a brief description

Dirac relativistic Hamiltonian provides a quantum mechanical description of electrons, consistent with the theory of special relativity.

$E^2 = p^2c^2 + m^2c^4$

Momentum operator

Rest mass

$$H_D\Psi = \varepsilon\Psi \quad \textit{with} \quad H_D = c\vec{\alpha}\cdot\vec{p} + \beta m_e c^2 + V$$

Electrostatic potential

$$\alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix} \qquad \beta_k = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}$$

(2×2) unit and zero matrices

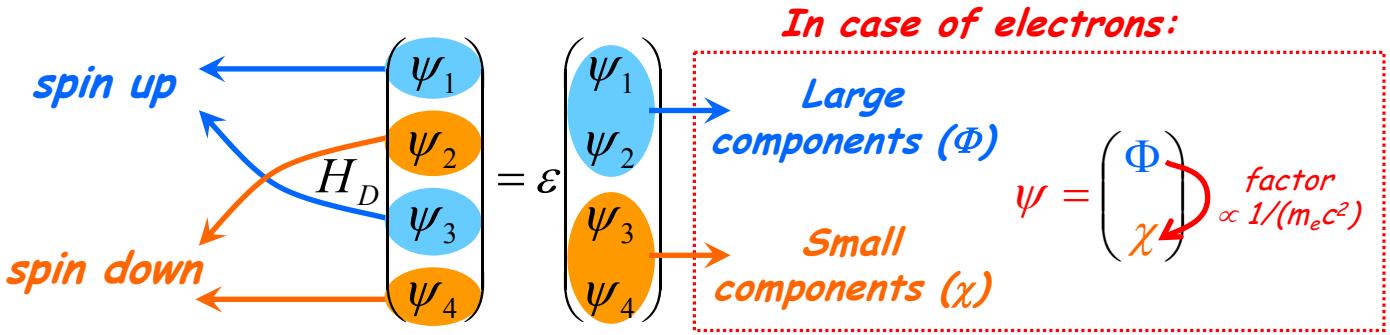
$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

(2×2) Pauli spin matrices

II. Equations

Dirac equation: H_D and Ψ are 4-dimensional

Ψ is a four-component single-particle wave function that describes spin-1/2 particles.



Φ and χ are time-independent two-component spinors describing the spatial and spin-1/2 degrees of freedom

→ Leads to a set of coupled equations for Φ and χ:

$$c(\sigma \cdot \vec{p})\chi = (\varepsilon - V - m_e c^2)\phi$$

$$c(\sigma \cdot \vec{p})\phi = (\varepsilon - V + m_e c^2)\chi$$

II. Equations

Dirac equation: H_D and Ψ are 4-dimensional

For a free particle (i.e. V = 0)

$$\begin{pmatrix} \varepsilon - m_e c^2 & 0 & -\hat{p}_z & -(\hat{p}_x - i\hat{p}_y) \\ 0 & \varepsilon - m_e c^2 & -(\hat{p}_z + i\hat{p}_y) & \hat{p}_z \\ -\hat{p}_z & -(\hat{p}_z - i\hat{p}_y) & \varepsilon + m_e c^2 & 0 \\ -(\hat{p}_z + i\hat{p}_y) & \hat{p}_z & 0 & \varepsilon + m_e c^2 \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix} = 0$$

Solution in the slow particle limit (p=0)

Non-relativistic limit decouples Ψ_1 from Ψ_2 and Ψ_3 from Ψ_4

Particles: up & down

$$\uparrow\ m_e c^2, \begin{pmatrix} \phi^{\uparrow} \\ 0 \\ 0 \\ 0 \end{pmatrix} \qquad \downarrow\ m_e c^2, \begin{pmatrix} 0 \\ \phi^{\downarrow} \\ 0 \\ 0 \end{pmatrix}$$

Antiparticles: up & down

$$\uparrow\ -m_e c^2, \begin{pmatrix} 0 \\ 0 \\ \chi^{\uparrow} \\ 0 \end{pmatrix} \qquad \downarrow\ -m_e c^2, \begin{pmatrix} 0 \\ 0 \\ 0 \\ \chi^{\downarrow} \end{pmatrix}$$

For a spherical potential (i.e. V(r))

$$\Psi = \begin{pmatrix} \Phi \\ \chi \end{pmatrix} = \begin{pmatrix} g_{n\kappa}(r)\, Y_{\kappa\sigma} \\ -i\, f_{n\kappa}(r)\, Y_{\kappa\sigma} \end{pmatrix}$$

$g_{n\kappa}$ and $f_{n\kappa}$ are Radial functions

$Y_{\kappa\sigma}$ are angular-spin functions

$$j = l + s/2$$
$$\kappa = -s(j + 1/2)$$
$$s = +1, -1$$

Dirac equation in a spherical potential

For a spherical potential (i.e. V(r)

The resulting equations for the radial functions ($g_{n\kappa}$ and $f_{n\kappa}$) are simplified if we define:

Energy: $\varepsilon' = \varepsilon - m_e c^2$ Radially varying mass: $M_e(r) = m_e + \frac{\varepsilon' - V(r)}{2c^2}$

Then the coupled equations can be written in the form of the radial eq.:

$$-\frac{\hbar^2}{2M_e}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dg_{n\kappa}}{dr}\right)+\left[V+\frac{\hbar^2}{2M_e}\frac{l(l+1)}{r^2}\right]g_{n\kappa}-\frac{\hbar^2}{4M_e^2c^2}\frac{dV}{dr}\frac{dg_{n\kappa}}{dr}-\frac{\hbar^2}{4M_e^2c^2}\frac{dV}{dr}\frac{(1+\kappa)}{r}g_{n\kappa}=\varepsilon' g_{n\kappa}$$

Mass-velocity effect **Darwin term** **Spin-orbit coupling**

$$-\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_{n,l}}{dr}\right)+\left[V+\frac{\hbar^2}{2m_e}\frac{l(l+1)}{r^2}\right]R_{n,l}=\varepsilon R_{n,l}$$

One electron radial Schrödinger equation in a spherical potential

Note that: $\kappa(\kappa+1)=l(l+1)$

Dirac equation in a spherical potential

For a spherical potential (i.e. V(r)

The resulting equations for the radial functions ($g_{n\kappa}$ and $f_{n\kappa}$) are simplified if we define:

Energy: $\varepsilon' = \varepsilon - m_e c^2$ Radially varying mass: $M_e(r) = m_e + \frac{\varepsilon' - V(r)}{2c^2}$

Then the coupled equations can be written in the form of the radial eq.:

$$-\frac{\hbar^2}{2M_e}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dg_{n\kappa}}{dr}\right)+\left[V+\frac{\hbar^2}{2M_e}\frac{l(l+1)}{r^2}\right]g_{n\kappa}-\frac{\hbar^2}{4M_e{}^2c^2}\frac{dV}{dr}\frac{dg_{n\kappa}}{dr}-\frac{\hbar^2}{4M_e{}^2c^2}\frac{dV}{dr}\frac{(1+\kappa)}{r}g_{n\kappa}=\varepsilon' g_{n\kappa}$$

Darwin term — Spin-orbit coupling

and

$$\frac{df_{nk}}{dr}=\frac{1}{\hbar c}(V-\varepsilon')g_{n\kappa}+\frac{(\kappa-1)}{r}f_{n\kappa}$$

→ Due to spin-orbit coupling, Ψ is not an eigenfunction of spin (s) and angular orbital moment (l).

Instead the good quantum numbers are j and κ

Note that: $\kappa(\kappa+1)=l(l+1)$

No approximation has been made so far

Dirac equation in a spherical potential

Scalar relativistic approximation

Approximation that the spin-orbit term is small
⇒ neglect SOC in radial functions (and treat it by perturbation theory)

No SOC ⇒ Approximate radial functions: $g_{n\kappa} \to \tilde{g}_{nl}$ $f_{n\kappa} \to \tilde{f}_{nl}$

$$-\frac{\hbar^2}{2M_e}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\tilde{g}_{nl}}{dr}\right)+\left[V+\frac{\hbar^2}{2M_e}\frac{l(l+1)}{r^2}\right]\tilde{g}_{nl}-\frac{\hbar^2}{4M_e{}^2c^2}\frac{dV}{dr}\frac{d\tilde{g}_{nl}}{dr}=\varepsilon'\tilde{g}_{nl}$$

and $\tilde{f}_{nl}=\frac{\hbar}{2M_e c}\frac{d\tilde{g}_{nl}}{dr}$ *with the normalization condition:* $\int\left(\tilde{g}_{nl}^2+\tilde{f}_{nl}^2\right)r^2dr=1$

→ *The four-component wave function is now written as:*

$$\tilde{\Psi}=\begin{pmatrix}\tilde{\Phi}\\ \tilde{\chi}\end{pmatrix}=\begin{pmatrix}\tilde{g}_{nl}(r)\,Y_{lm}\\ -i\,\tilde{f}_{nl}(r)\,Y_{lm}\end{pmatrix}$$

→ *Inclusion of the spin-orbit coupling in "second variation" (on the large component only)*

$$H\tilde{\psi}=\varepsilon\tilde{\psi}+H_{SO}\tilde{\psi}$$

with

$$H_{SO}=\frac{\hbar^2}{4M_e{}^2c^2}\frac{1}{r}\frac{dV}{dr}\begin{pmatrix}\vec{\sigma}\vec{l} & 0\\ 0 & 0\end{pmatrix}$$

$\tilde{\Phi}$ *is a pure spin state*

$\tilde{\chi}$ *is a mixture of up and down spin states*

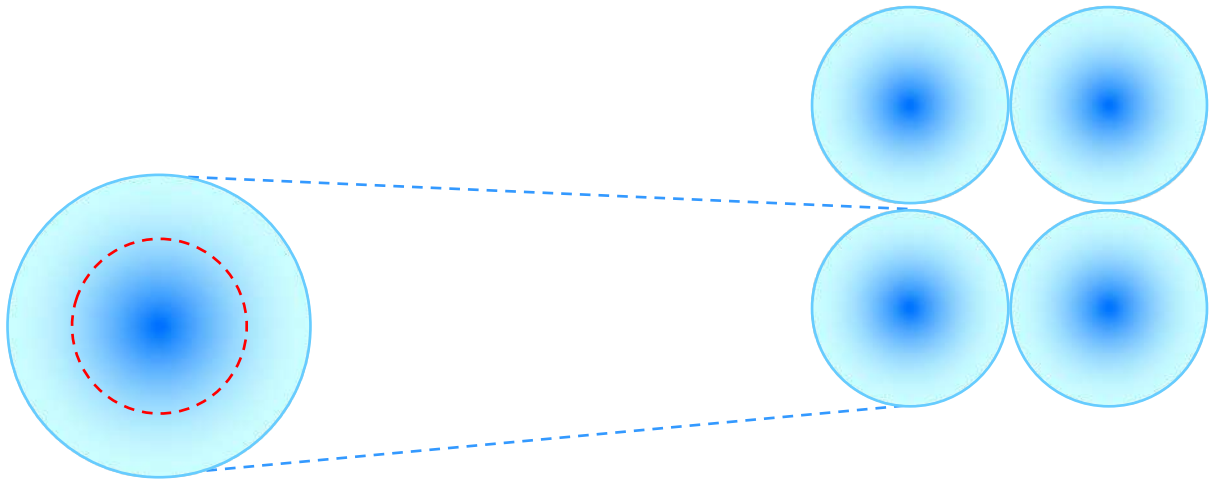
Relativistic effects in a solid

➡ *For a molecule or a solid:*

Relativistic effects originate deep inside the core.

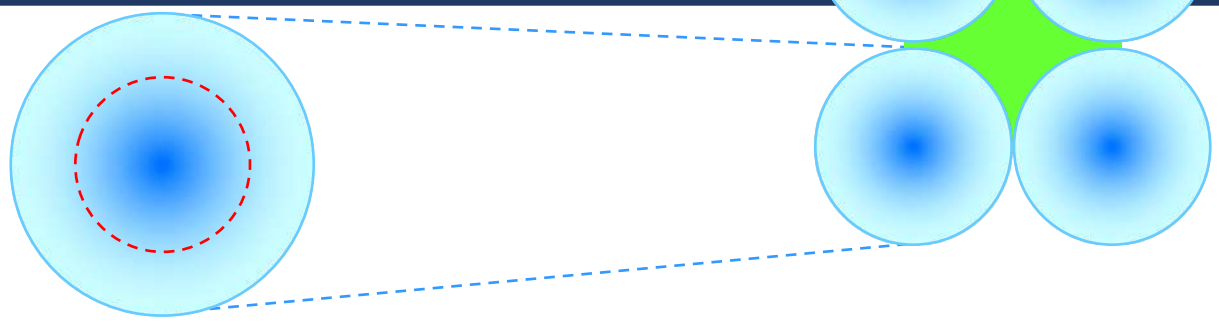
It is then sufficient to solve the relativistic equations in a spherical atomic geometry (inside the atomic spheres of WIEN2k).

⇨ *Justify an implementation of the relativistic effects only inside the muffin-tin atomic spheres*



III. Implementation

Relativistic effects in a solid



Atomic sphere (RMT) Region

Interstitial Region

Core electrons

Valence electrons

Valence electrons

« Fully » relativistic

Scalar relativistic (no SOC)

Not relativistic

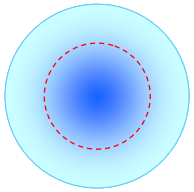
Spin-compensated Dirac equation

Possibility to add SOC (2nd variational)

SOC: Spin orbit coupling

III. Implementation

Treatment of the core electrons



Core states: fully occupied → spin-compensated Dirac equation (include SOC)

Atomic sphere (RMT) Region

Core electrons

« Fully » relativistic

Spin-compensated Dirac equation

For spin-polarized potential, spin up and spin down are calculated separately, the density is averaged according to the occupation number specified in case.inc file.

	l	j=l+s/2 s=-1	j=l+s/2 s=+1	κ=-s(j+1/2) s=-1	κ=-s(j+1/2) s=+1	occupation s=-1	occupation s=+1
s	0		1/2		-1		2
p	1	1/2	3/2	1	-2	2	4
d	2	3/2	5/2	2	-3	4	6
f	3	5/2	7/2	3	-4	6	8

case.inc for Au atom

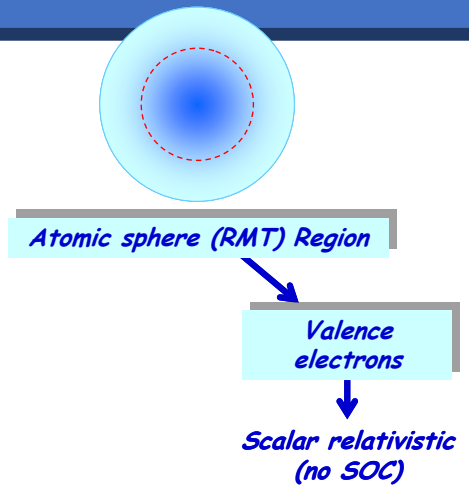
```
                17 0.00  0
1s1/2 →         1,-1,2    ( n,κ,occup)
2s1/2           2,-1,2    ( n,κ,occup)
2p1/2 →         2, 1,2    ( n,κ,occup)
2p3/2 →         2,-2,4    ( n,κ,occup)
3s1/2           3,-1,2    ( n,κ,occup)
3p1/2           3, 1,2    ( n,κ,occup)
3p3/2           3,-2,4    ( n,κ,occup)
3d3/2 →         3, 2,4    ( n,κ,occup)
3d5/2 →         3,-3,6    ( n,κ,occup)
4s1/2           4,-1,2    ( n,κ,occup)
4p1/2           4, 1,2    ( n,κ,occup)
4p3/2           4,-2,4    ( n,κ,occup)
4d3/2           4, 2,4    ( n,κ,occup)
4d5/2           4,-3,6    ( n,κ,occup)
5s1/2           5,-1,2    ( n,κ,occup)
4f5/2 →         4, 3,6    ( n,κ,occup)
4f7/2 →         4,-4,8    ( n,κ,occup)
                0
```

III. Implementation

Treatment of the valence electrons

Valence electrons INSIDE atomic spheres are treated within scalar relativistic approximation [1] if RELA is specified in case.struct file (by default).

```
Title
F    LATTICE,NONEQUIV.ATOMS:  1 225 Fm-3m
MODE OF CALC=RELA unit=bohr
   7.670000  7.670000  7.670000 90.000000 90.000000 90.000000
ATOM   1: X=0.00000000 Y=0.00000000 Z=0.00000000
          MULT= 1          ISPLIT= 2
Au1        NPT=  781  R0=0.00000500 RMT=    2.6000   Z: 79.0
LOCAL ROT MATRIX:    1.0000000 0.0000000 0.0000000
                     0.0000000 1.0000000 0.0000000
                     0.0000000 0.0000000 1.0000000
  48      NUMBER OF SYMMETRY OPERATIONS
```



- *no κ dependency of the wave function, (n,l,s) are still good quantum numbers*
- *all relativistic effects are included except SOC*
- *small component enters normalization and calculation of charge inside spheres*
- *augmentation with large component only*
- *SOC can be included in « second variation »*

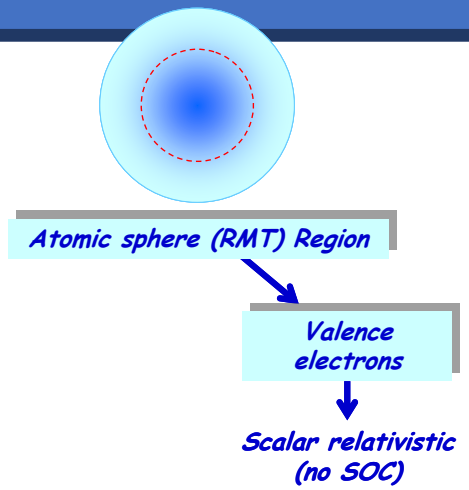
Valence electrons in interstitial region are treated classically

[1] Koelling and Harmon, J. Phys. C (1977)

Treatment of the valence electrons

SOC is added in a second variation (lapwso):

- *First diagonalization (lapw1):* $H_1\Psi_1 = \varepsilon_1\Psi_1$
- *Second diagonalization (lapwso):* $(H_1 + H_{SO})\Psi = \varepsilon\Psi$



The second equation is expanded in the basis of first eigenvectors (Ψ_1)

$$\sum_i^N \left(\delta_{ij}\varepsilon_1^j + \left\langle \Psi_1^j \middle| H_{SO} \middle| \Psi_1^i \right\rangle\right)\left\langle \Psi_1^i \middle| \Psi \right\rangle = \varepsilon \left\langle \Psi_1^j \middle| \Psi \right\rangle$$

sum include both up/down spin states

→ ***N is much smaller than the basis size in lapw1***

♦ SOC is active only inside atomic spheres, only spherical potential (V_{MT}) is taken into account, in the polarized case spin up and down parts are averaged.

♦ Eigenstates are not pure spin states, SOC mixes up and down spin states

♦ Off-diagonal term of the spin-density matrix is ignored. It means that in each SCF cycle the magnetization is projected on the chosen direction (from case.inso)

V_{MT}: Muffin-tin potential (spherically symmetric)

Controlling spin-orbit coupling in WIEN2k

- Do a regular scalar-relativistic "scf" calculation
- save_lapw
- initso_lapw
  - case.inso:

```
WFFIL
 4  1  0                          llmax,ipr,kpot
 -10.0000   1.50000               emin,emax (output energy window)
   0.  0.  1.                     direction of magnetization (lattice vectors)
 NX                               number of atoms for which RLO is added
 NX1   -4.97      0.0005          atom number,e-lo,de (case.in1), repeat NX times
 0 0 0 0 0                        number of atoms for which SO is switch off; atoms
```

  - case.in1(c):

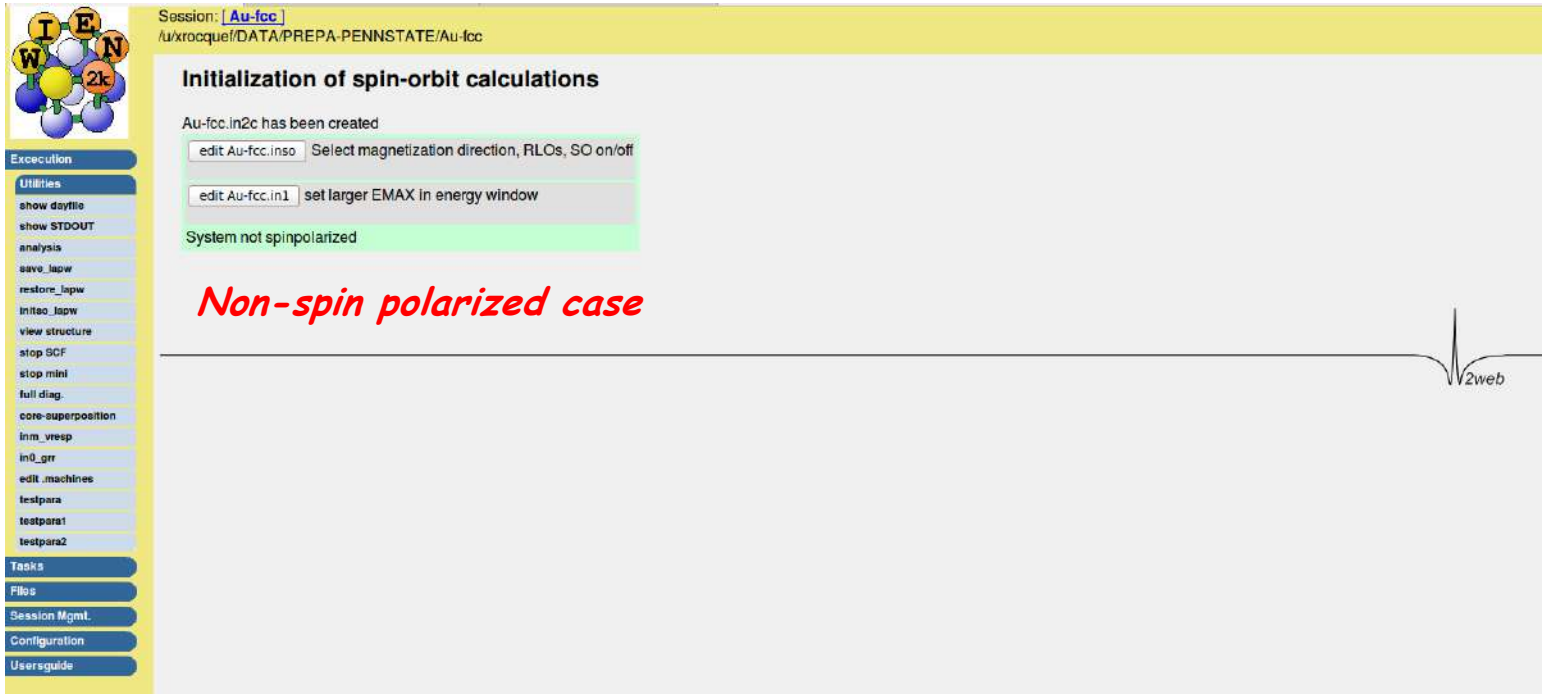
```
(…)
 2     0.30       0.005 CONT 1
 0     0.30       0.000 CONT 1
K-VECTORS FROM UNIT:4   -9.0       4.5     65    emin/emax/nband
```

  - symmetso (for spin-polarized calculations only)
- run(sp)_lapw -so ⟵ -so switch specifies that scf cycles will include SOC

III. Implementation

Controlling spin-orbit coupling in WIEN2k

➡ *The w2web interface is helping you*



III. Implementation

Controlling spin-orbit coupling in WIEN2k

The w2web interface is helping you

Session: [Co-hcp]
/u/xrocquef/DATA/PREPA-PENNSTATE/Co-hcp

Initialization of spin-orbit calculations

Co-hcp.in2c has been created

edit Co-hcp.inso — Select magnetization direction, RLOs, SO on/off

edit Co-hcp.in1 — set larger EMAX in energy window

This is a spin-polarized system. SO may reduce symmetry. ← *Spin polarized case*

x symmetso — Determines symmetry in spinpolarized case

edit Co-hcp.outsymso — view Co-hcp.outsymso

A new setup for SO calculations has been created (_so). If you commit the next step will create new Co-hcp.struct, in1, in2c, inc, clmsum/up/dn files. PLEASE "save_lapw" any previous calculation.

Prepare new input files

The number of symmetry operations may have changed, then you must run KGEN.

x kgen — Generate k-mesh with proper SO-symmetry

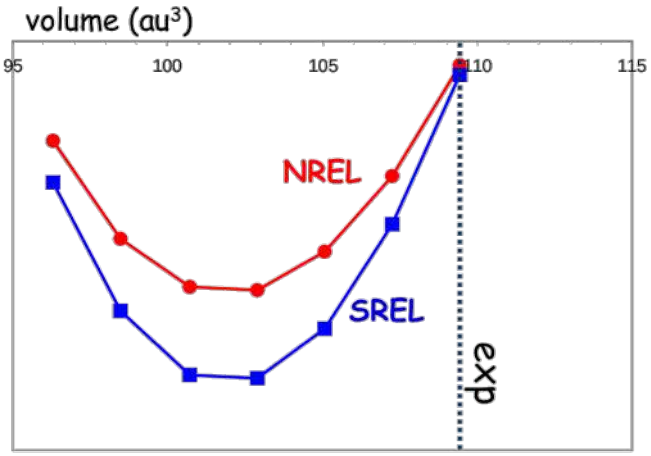
edit Co-hcp.klist — view Co-hcp.klist

Execution
Utilities
show dayfile
show STDOUT
analysis
save_lapw
restore_lapw
initso_lapw
view structure
stop SCF
stop mini
full diag.
core-superposition
inm_vresp
in0_grr
edit .machines
testpara
testpara1
testpara2
Tasks
Files
Session Mgmt.
Configuration
Usersguide

w2web

Relativistic effects: Illustration

hcp-Be
Z = 4

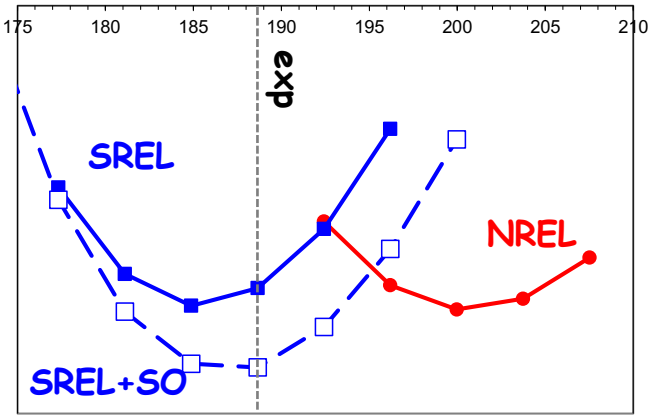


LDA overbinding (7%)

No difference NREL/SREL

Bulk modulus:
- NREL: 131.4 GPa
- SREL: 131.5 GPa
- Exp.: 130 GPa

hcp-Os
Z = 76



♦ **Scalar-relativistic** (SREL):
- LDA overbinding (2%)
- Bulk modulus: 447 GPa

\+ **spin-orbit coupling** (SREL+SO):
- LDA overbinding (1%)
- Bulk modulus: 436 GPa

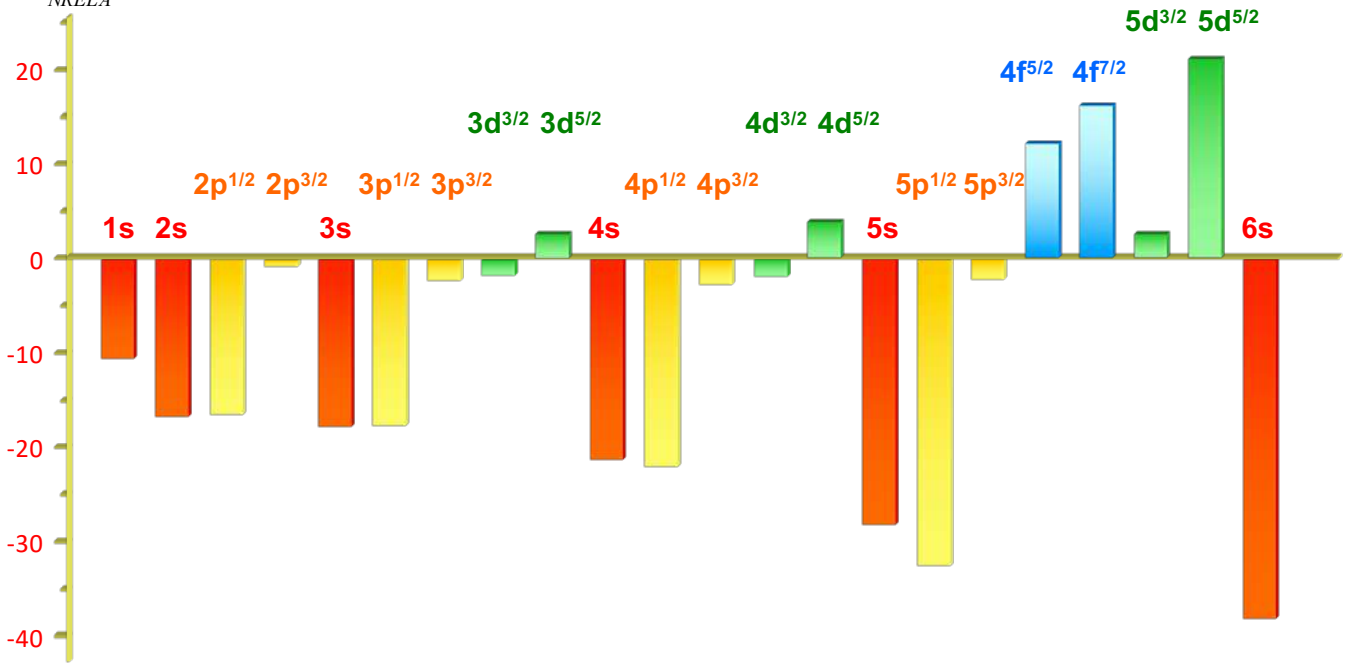
⇒ **Exp. Bulk modulus: 462 GPa**

Relativistic effects: Illustration

Au: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 4f^{14}\ 5d^{10}\ 6s^1$

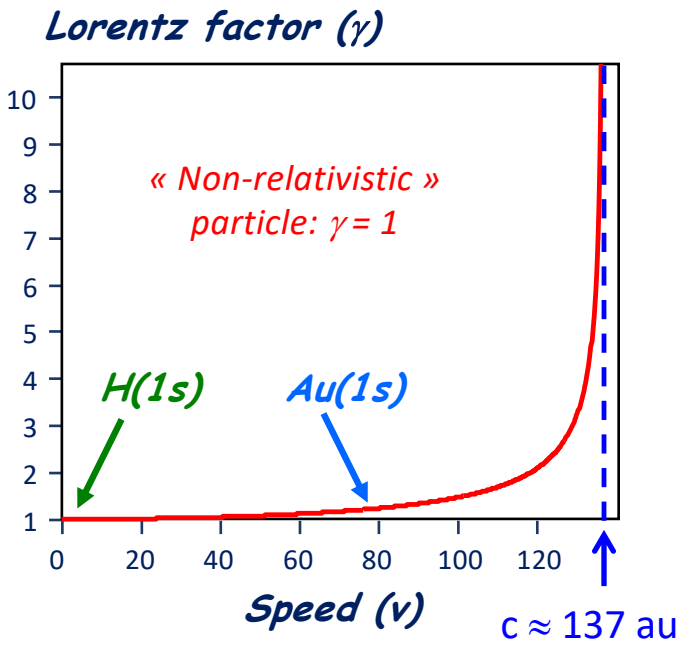
Relativistic correction (%)

$$\frac{(E_{RELA} - E_{NRELA})}{E_{NRELA}}$$



III. Implementation

(1) Relativistic orbital contraction



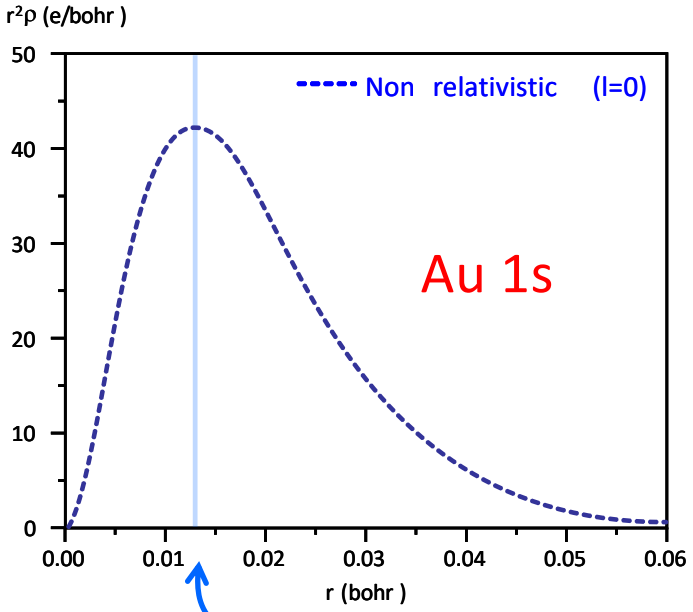
$$\gamma = \frac{1}{\sqrt{1-\left(\frac{v}{c}\right)^2}} \geq 1$$

Speed of the 1s electron (Bohr model):

$$v_e \propto \frac{Z}{n} \begin{cases} \mathrm{H}: v_e(1s) = 1\,\mathrm{au} \rightarrow \gamma = 1.00003 \\ \mathrm{Au}: v_e(1s) = 79\,\mathrm{au} \rightarrow \gamma = 1.22 \end{cases}$$

III. Implementation

(1) Relativistic orbital contraction



Radius of the 1s electron (Bohr model):

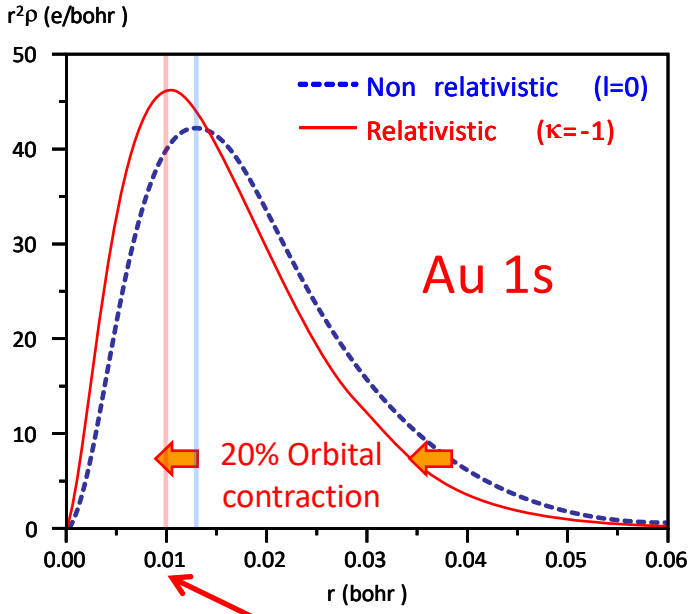
$$r(1s) = \frac{n^2 a_0}{Z} \quad \text{AND} \quad a_0 = \frac{\hbar}{m_e c \alpha} = 1\,\text{bohr}$$

$$r(1s) = \frac{1}{79} = 0.013\,\text{bohr}$$

Atomic units:
$\hbar = m_e = e = 1$
$c = 1/\alpha \approx 137$ au

III. Implementation

(1) Relativistic orbital contraction



Radius of the 1s electron (Bohr model):

$$r(1s)=\frac{n^2 a_0}{Z} \quad \text{AND} \quad a_0=\frac{\hbar}{m_e c\alpha}=1\,\text{bohr}$$

$$r(1s)=\frac{1}{79}=0.013\,\text{bohr}$$

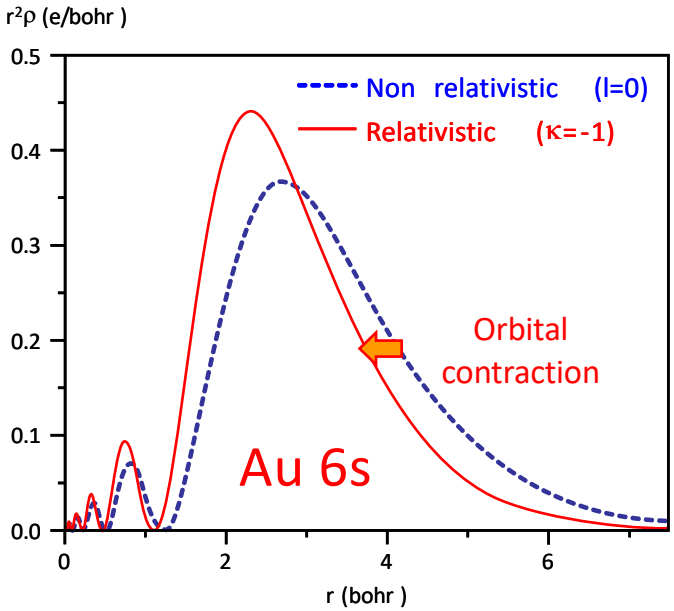
In Au atom, the relativistic mass (M) of the 1s electron is 22% larger than the rest mass (m)

$$r(1s)=\frac{n^2}{Z}\frac{a_0}{\gamma}=\frac{1}{79}\frac{1}{1.22}=0.010\,\text{bohr} \quad \Leftarrow \quad M=\gamma\cdot m_e=1.22 m_e$$

$$a_0[RELA]=\frac{\hbar}{M_e c\alpha}=\frac{a_0}{\gamma}$$

III. Implementation

(1) Relativistic orbital contraction



Speed of the 6s electron (Bohr model):

$$v_e(6s) = \frac{Z}{n} = \frac{79}{6} = 13.17 = 0.096c$$

$$\gamma = \frac{1}{\sqrt{1-\left(\frac{v_e}{c}\right)^2}} = \frac{1}{\sqrt{1-(0.096)^2}} = 1.0046$$

Direct relativistic effect (mass enhancement) → contraction of 0.46% only

However, the relativistic contraction of the 6s orbital is large (>20%)

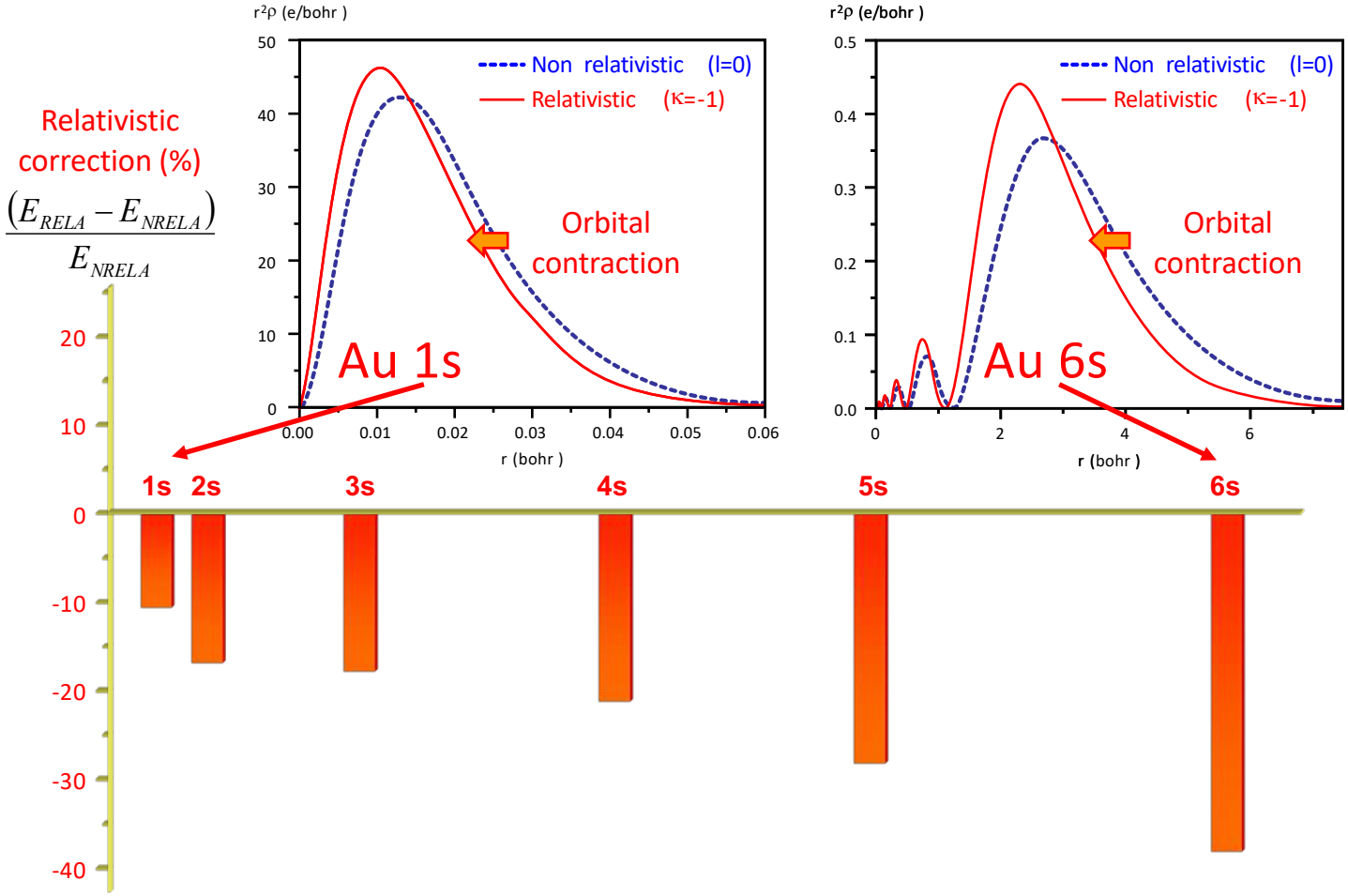
ns orbitals (with n > 1) contract due to orthogonality to 1s

III. Implementation

(1) Relativistic orbital contraction

Relativistic correction (%)

$$\frac{(E_{RELA} - E_{NRELA})}{E_{NRELA}}$$

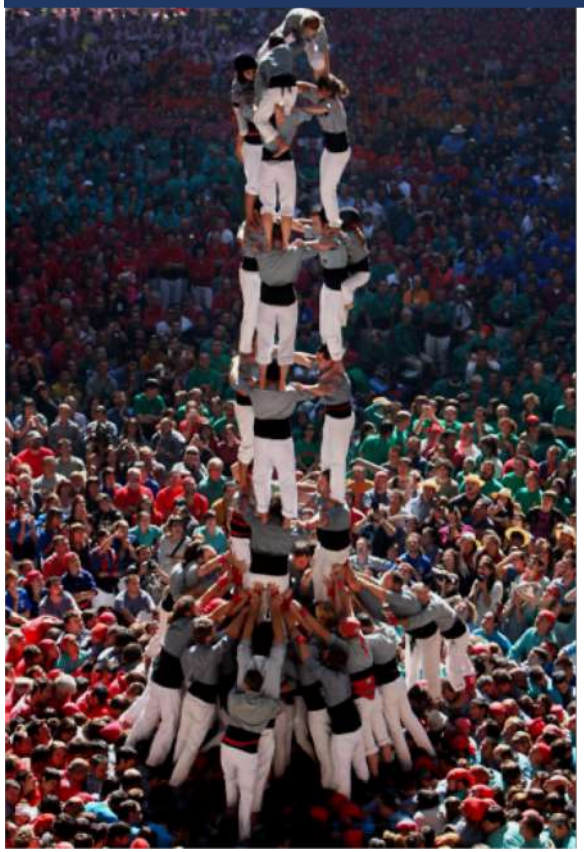


III. Implementation

Let's travel to Tarragona to understand!

III. Implementation

Let's travel to Tarragona to understand!



Human pyramid at Tarragona (Spain)
Santa Tecla festival

n = 6 *Indirect Impact*

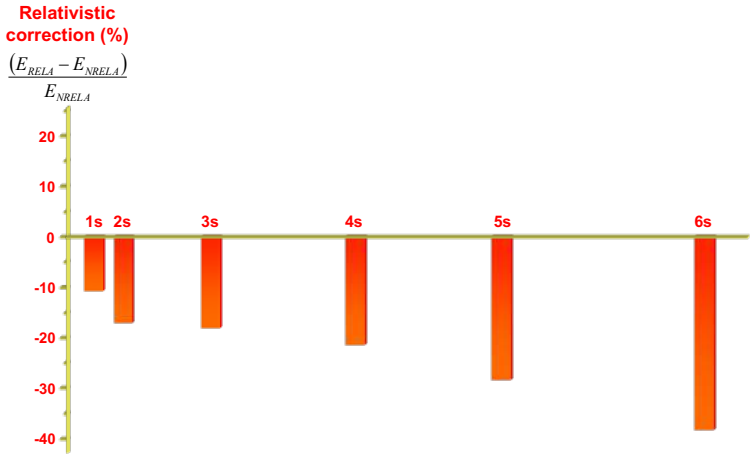
n = 5

n = 4

n = 3

n = 2

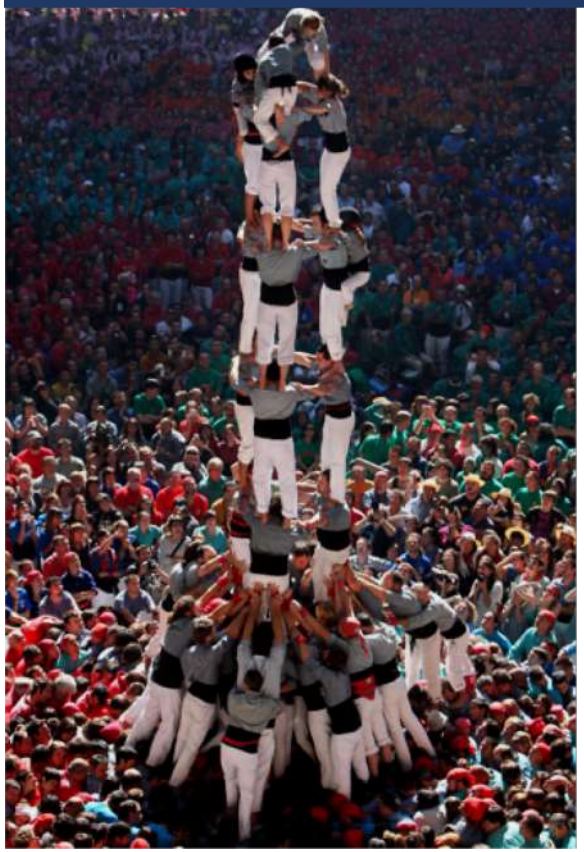
n = 1 *Direct Impact*



« Relativistic » perturbation !

III. Implementation

Let's travel to Tarragona to understand!



Human pyramid at Tarragona (Spain)
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n = 6 *Indirect Impact*

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n = 4

n = 3

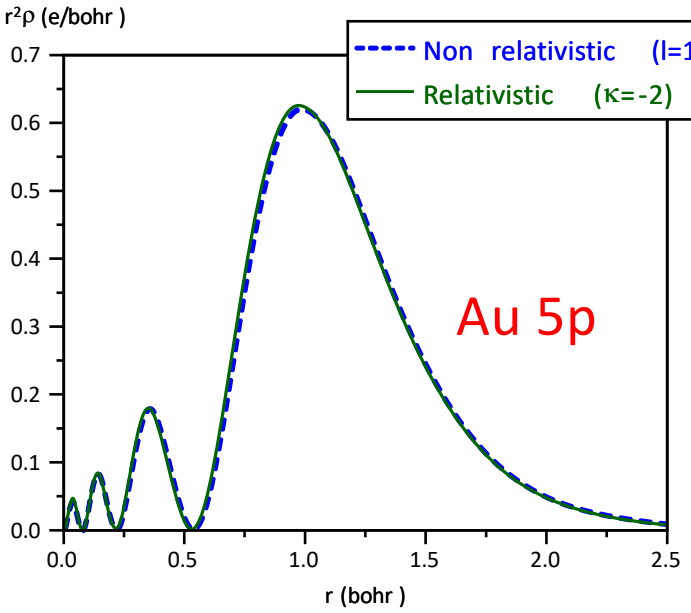
n = 2

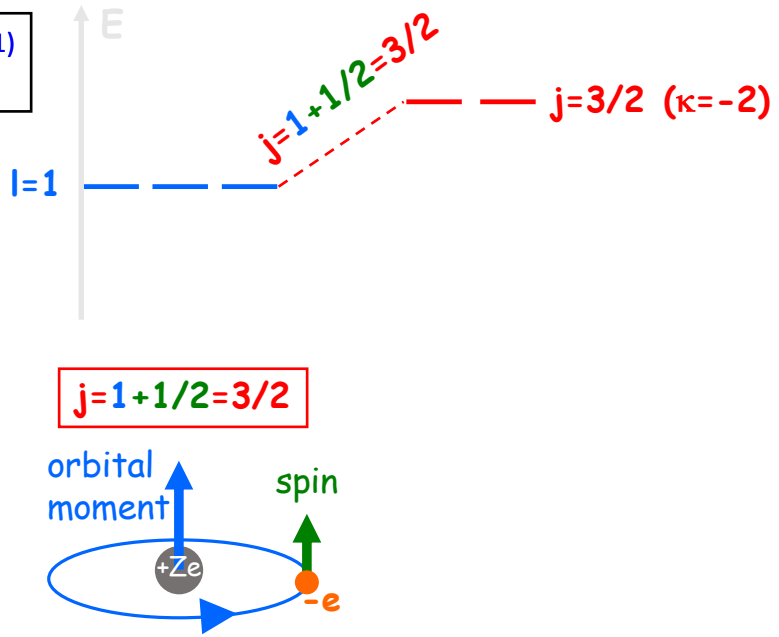
n = 1 *Direct Impact*

« Relativistic » perturbation !

(2) Spin-orbit splitting of p states

♦ Spin-orbit splitting of l-quantum number

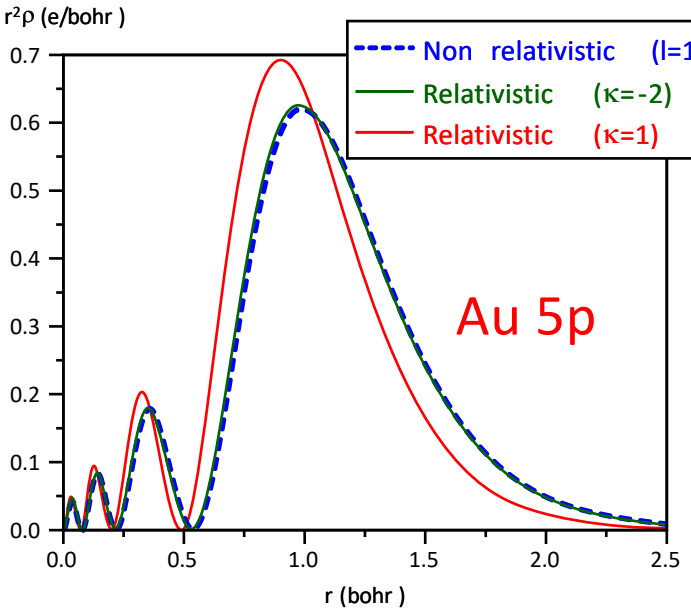


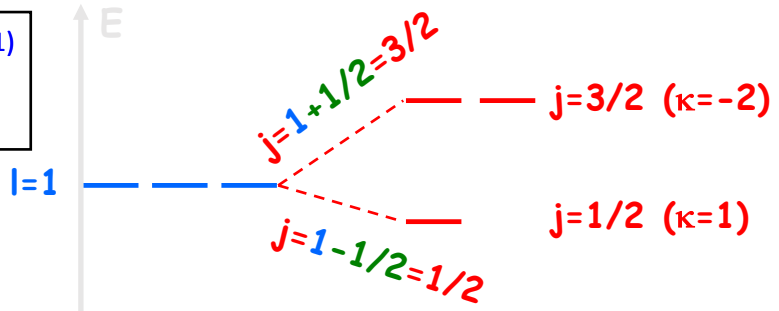


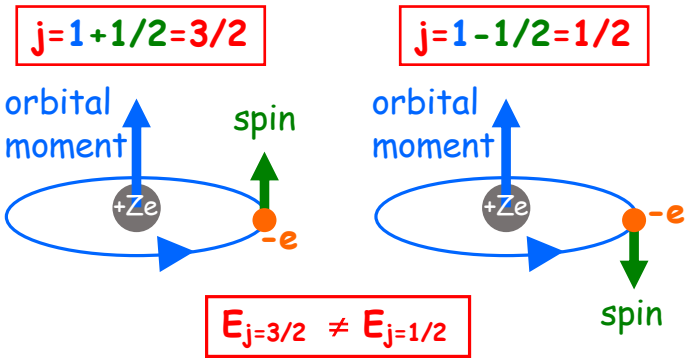
♦ $p_{3/2}$ (κ=-2): nearly same behavior than non-relativistic p-state

(2) Spin-orbit splitting of p states

♦ Spin-orbit splitting of l-quantum number







$E_{j=3/2} \neq E_{j=1/2}$

♦ $p_{1/2}$ ($\kappa=1$): markedly different behavior than non-relativistic p-state

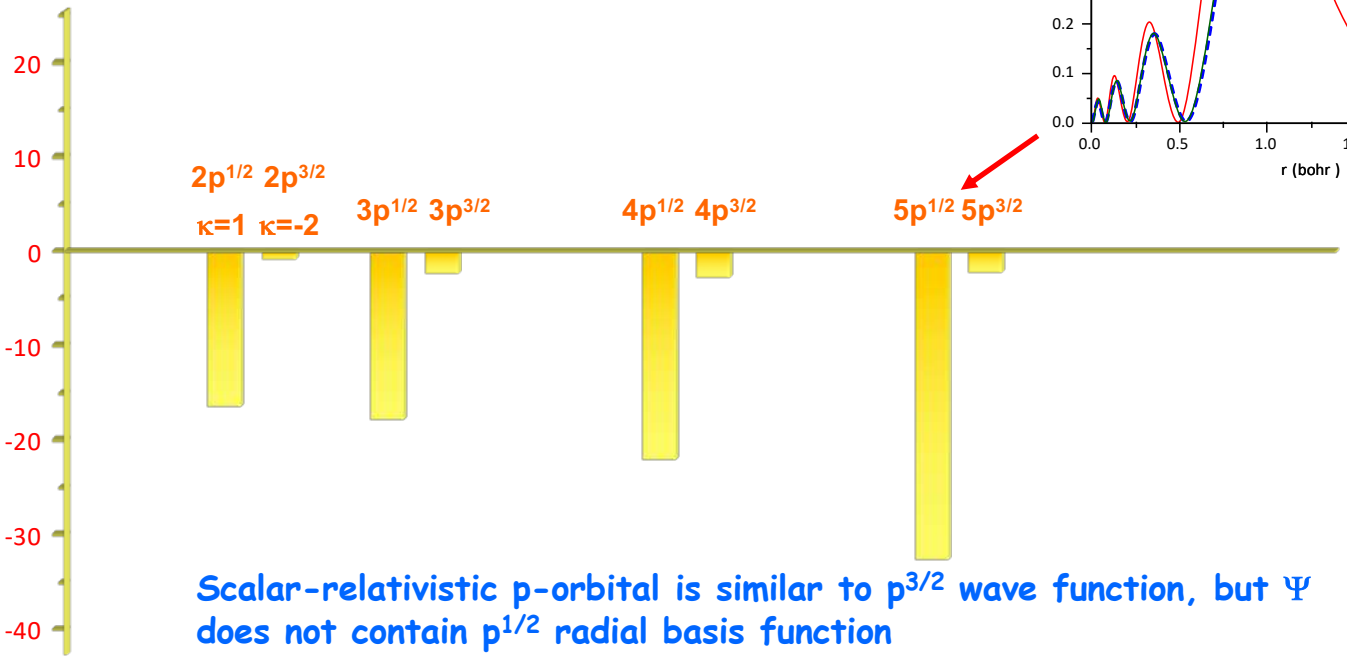
$g_{\kappa=1}$ is non-zero at nucleus

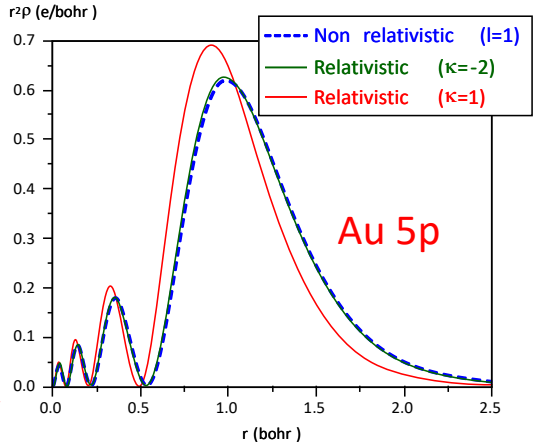
III. Implementation

(2) Spin-orbit splitting of p states

Relativistic correction (%)

$$\frac{(E_{RELA} - E_{NRELA})}{E_{NRELA}}$$

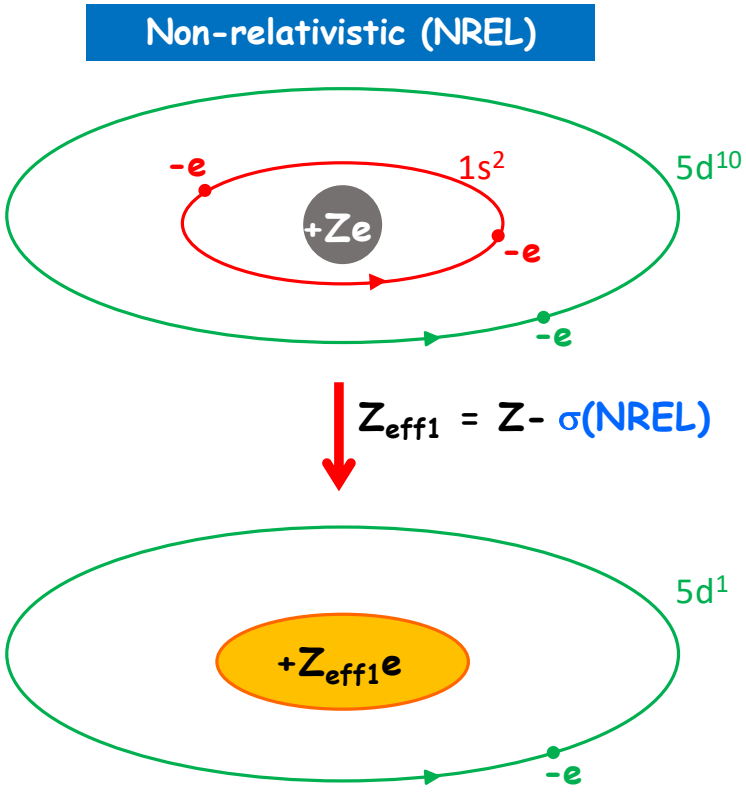




Scalar-relativistic p-orbital is similar to $p^{3/2}$ wave function, but Ψ does not contain $p^{1/2}$ radial basis function

(3) Orbital expansion: Au(d) states

Higher l-quantum number states expand due to better shielding of nucleus charge from contracted s-states



III. Implementation

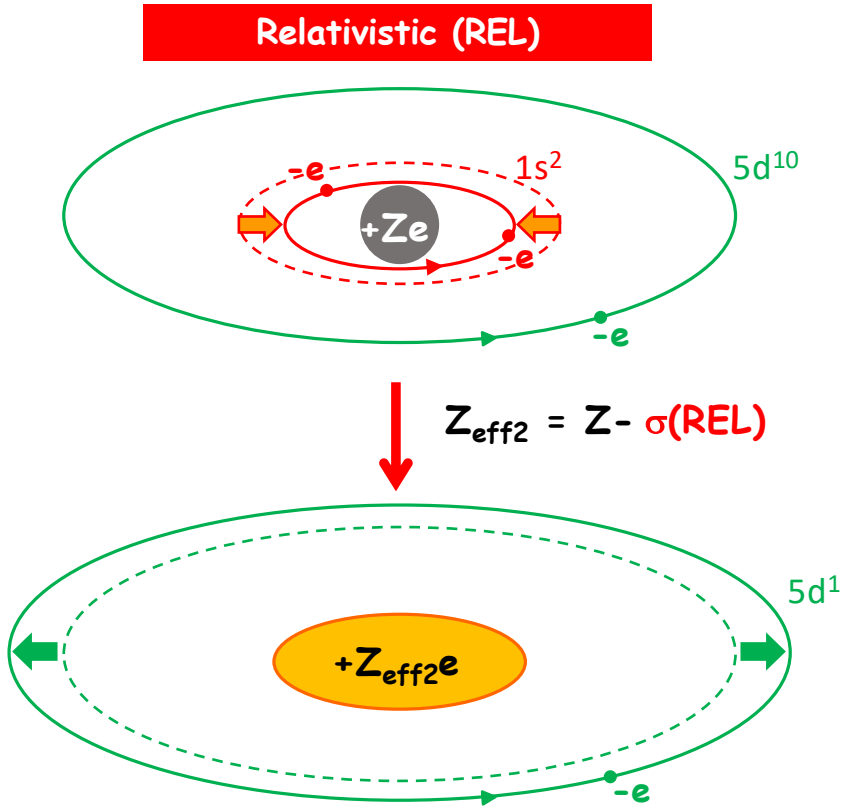
(3) Orbital expansion: Au(d) states

Higher l-quantum number states expand due to better shielding of nucleus charge from contracted s-states

1s electrons closer to the nucleus

Better shielding $Z_{eff2} > Z_{eff1}$

Valence electron less attracted (= Indirect relativistic effect) ⇒ Orbital expansion

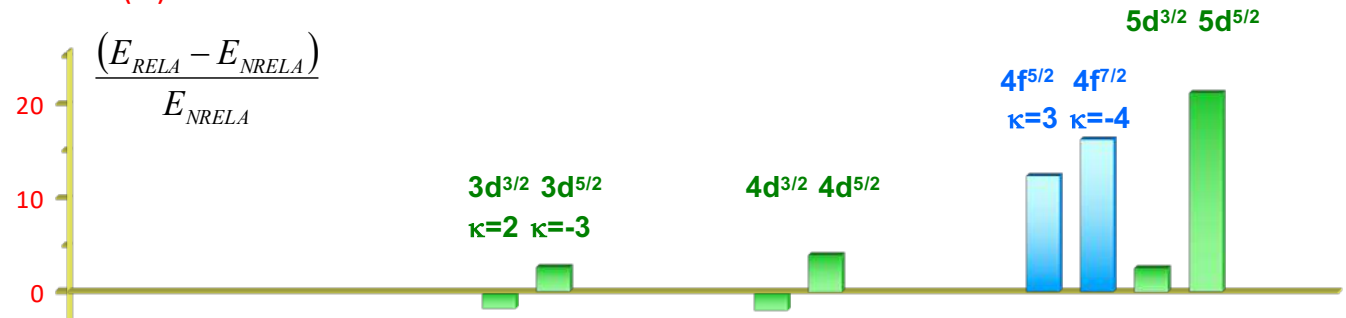


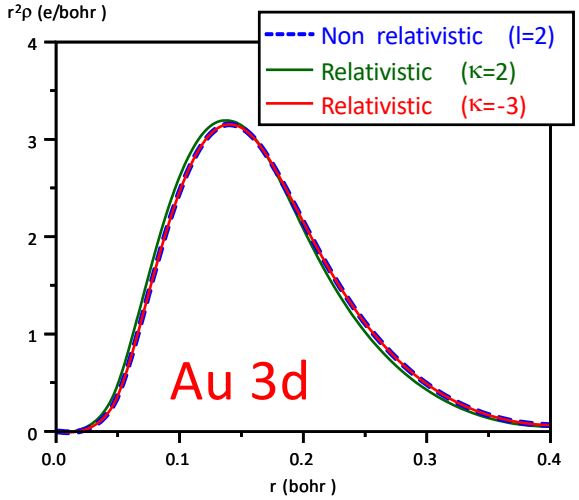
III. Implementation

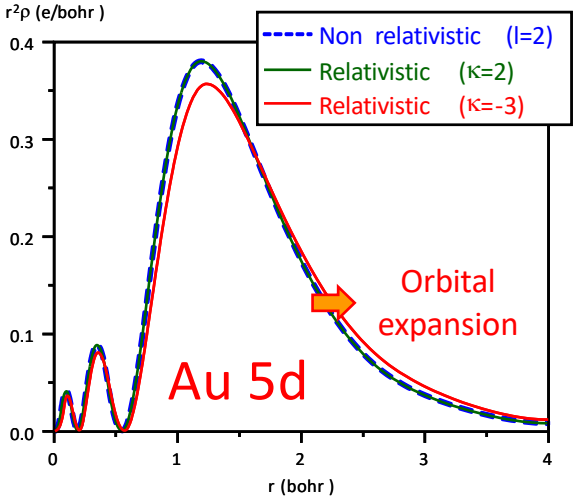
(3) Orbital expansion: Au(d) states

Relativistic correction (%)

$$\frac{(E_{RELA} - E_{NRELA})}{E_{NRELA}}$$





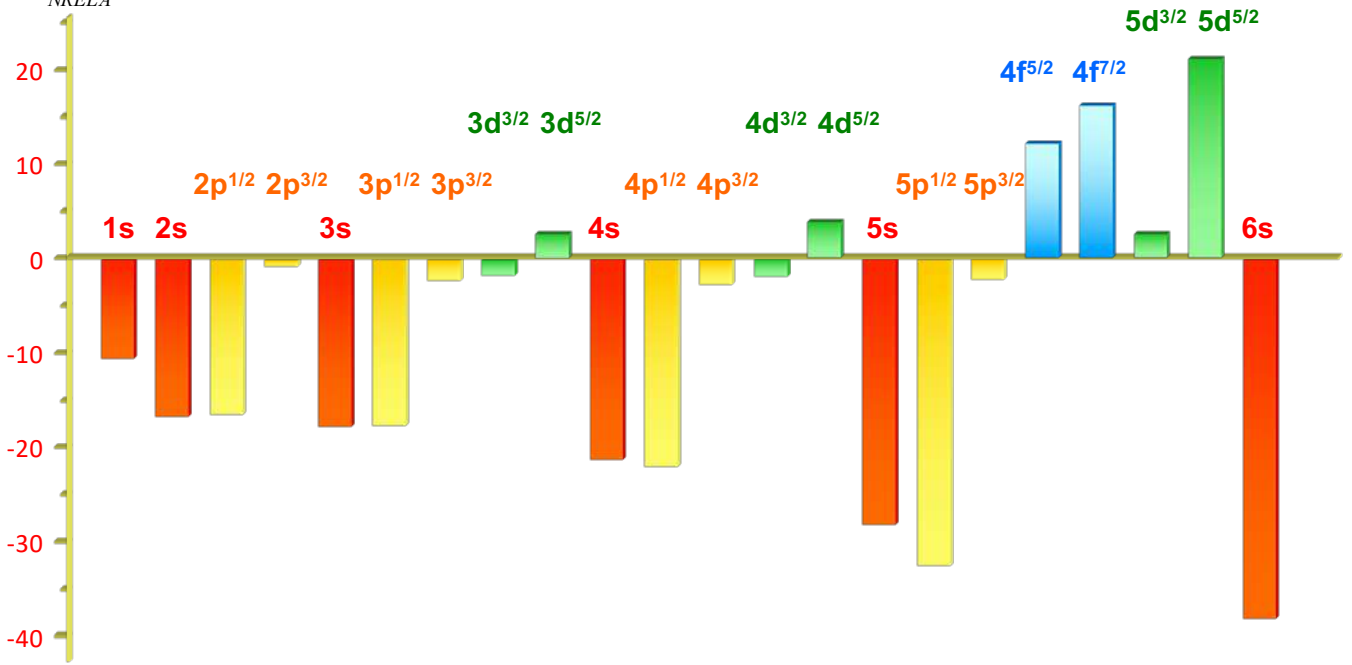


Relativistic effects: Illustration

Au: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 4f^{14}\ 5d^{10}\ 6s^1$

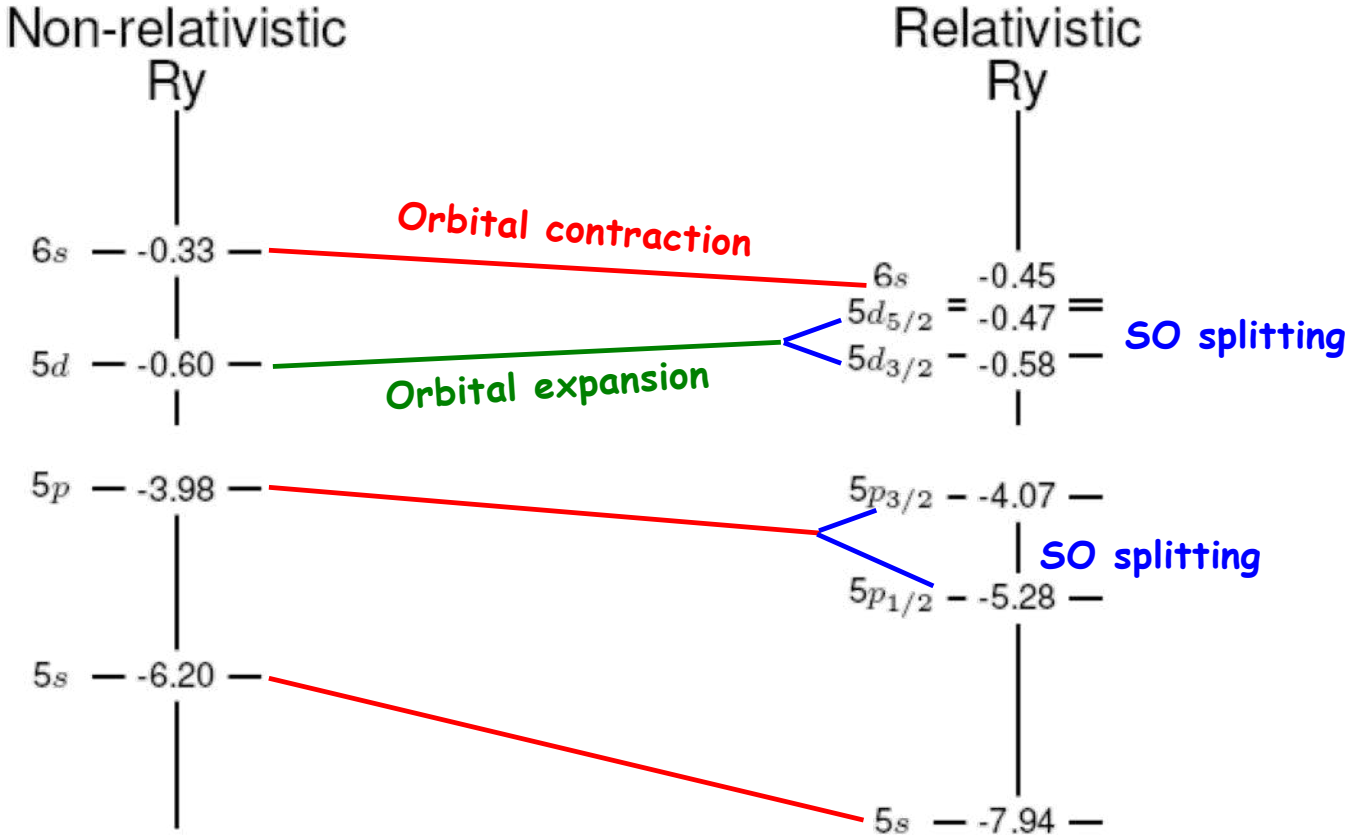
Relativistic correction (%)

$$\frac{(E_{RELA} - E_{NRELA})}{E_{NRELA}}$$



Relativistic effects: Illustration

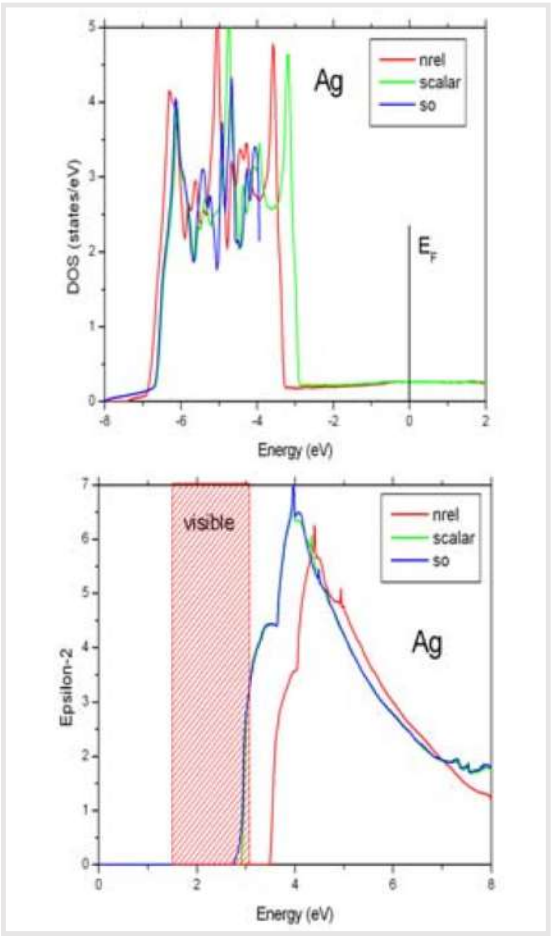
Atomic spectra of gold

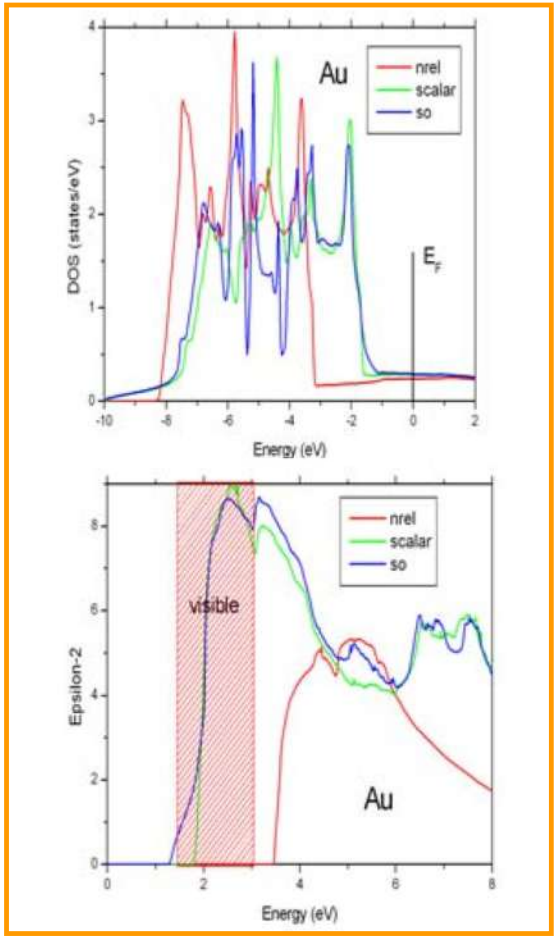


III. Implementation

Ag – Au: the differences (DOS & optical prop.)

Ag



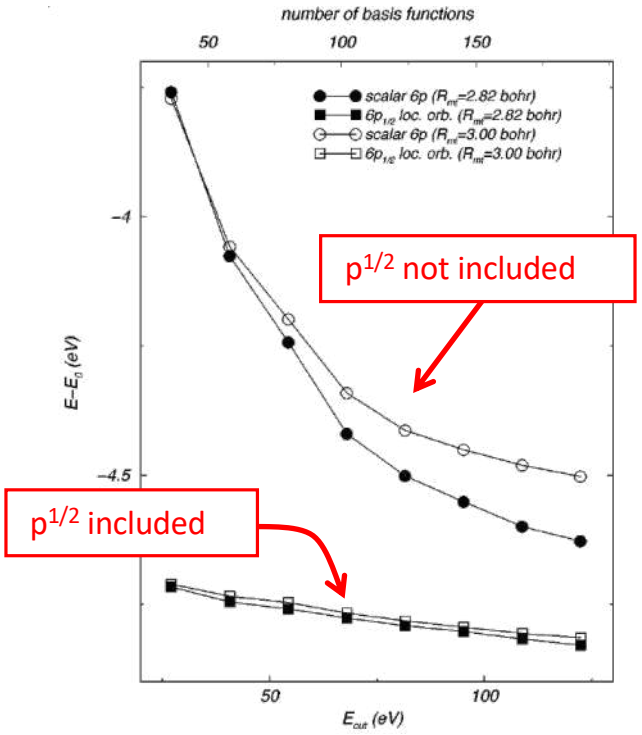


Au

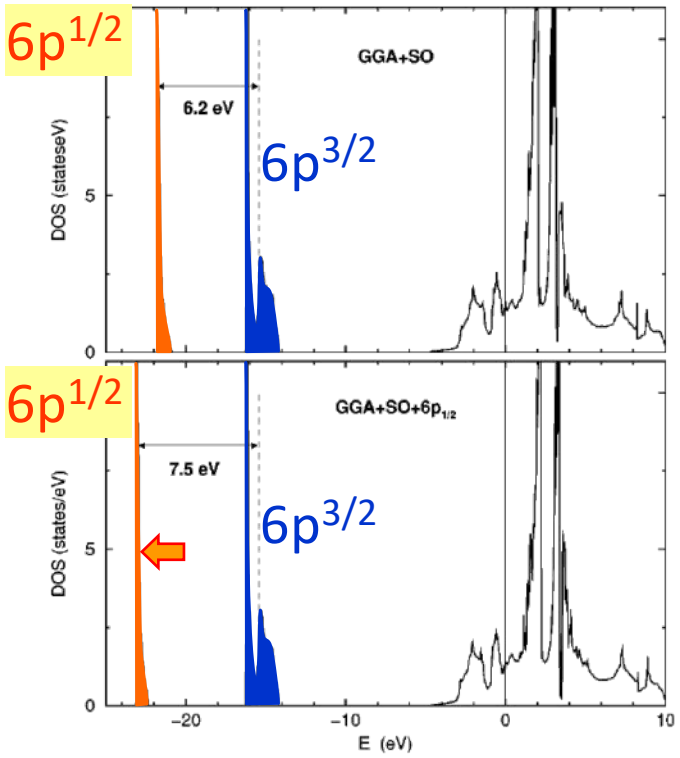
Relativistic semicore states: $p^{1/2}$ orbitals

Electronic structure of fcc Th, SOC with $6p^{1/2}$ local orbital

Energy vs. basis size



DOS with and without $p^{1/2}$



J.Kuneš, P.Novak, R.Schmid, P.Blaha, K.Schwarz, Phys.Rev.B. 64, 153102 (2001)

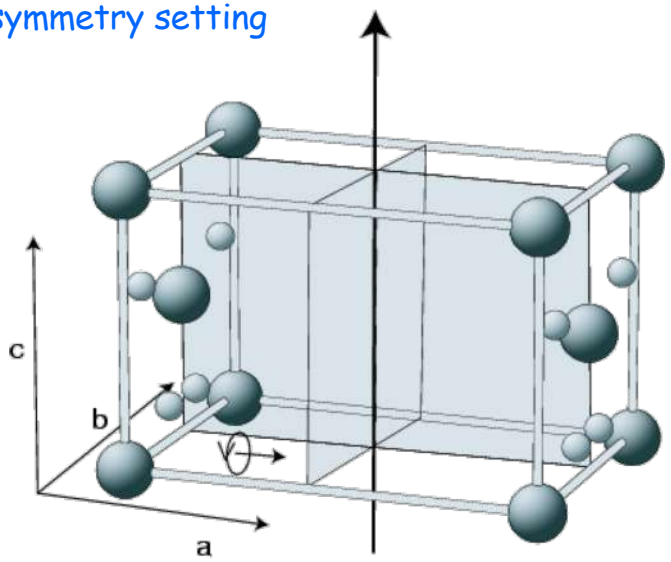
➡ ***SOC couples magnetic moment to the lattice***

- direction of the exchange field matters (input in case.inso)

➡ ***Symmetry operations acts in real and spin space***

- number of symmetry operations may be reduced (reflections act differently on spins than on positions)
- time inversion is not symmetry operation (do not add an inversion for klist)
- initso_lapw (must be executed) detects new symmetry setting

	Direction of magnetization			
	[100]	[010]	[001]	[110]
1	A	A	A	A
m_x	A	B	B	-
m_y	B	A	B	-
2_z	B	B	A	B



Relativity in WIEN2k: Summary

WIEN2k offers several levels of treating relativity:

- **non-relativistic:** select NREL in case.struct (not recommended)
- **standard:** fully-relativistic core, scalar-relativistic valence

  mass-velocity and Darwin s-shift, no spin-orbit interaction
- **"fully"-relativistic:**

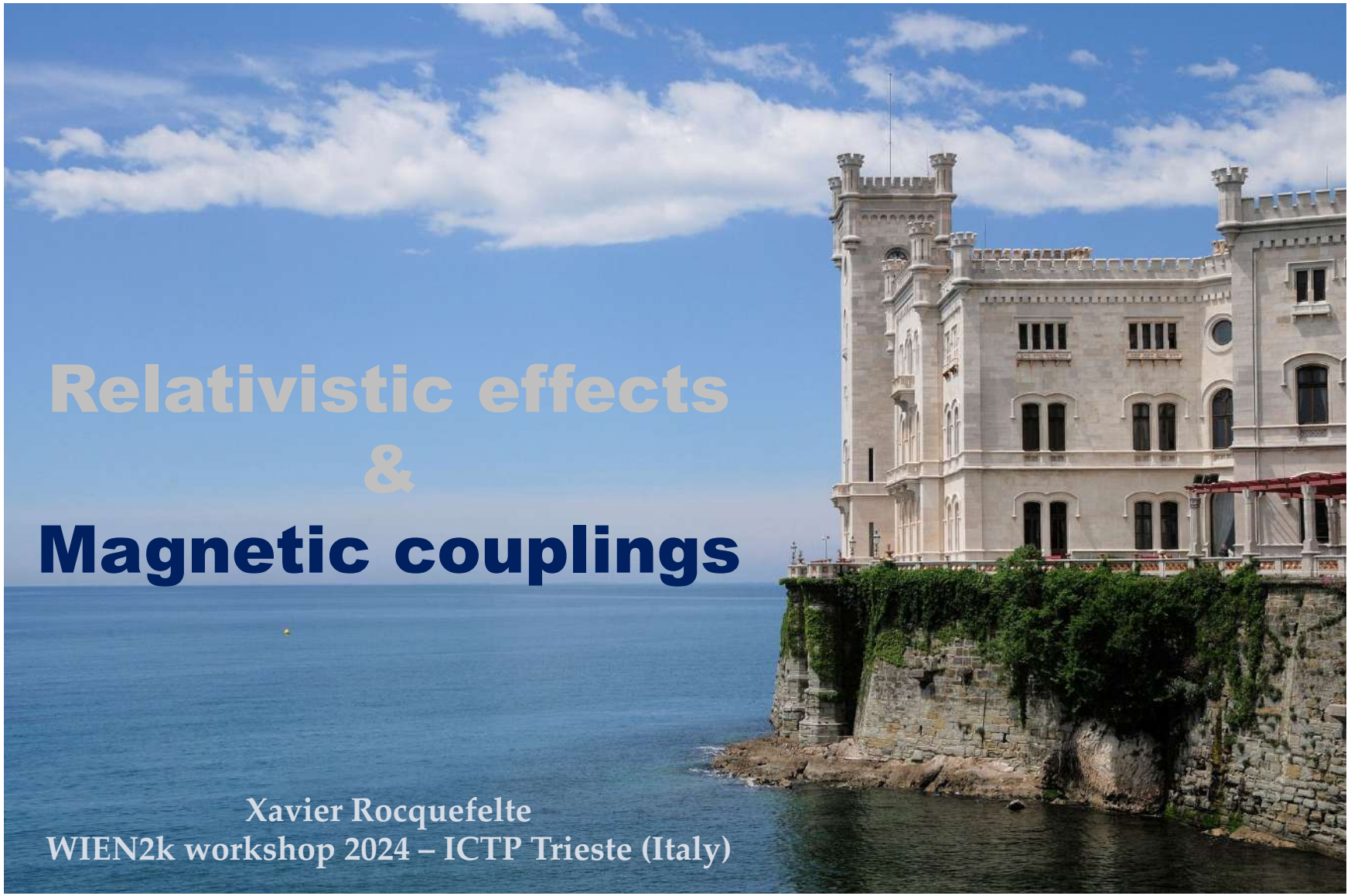
  adding SO in "second variation" (using previous eigenstates as basis)

  adding $p^{1/2}$ LOs to increase accuracy (caution!!!)

  x lapw1 (increase E-max for more eigenvalues, to have
  x lapwso basis for lapwso)
  x lapw2 -so -c SO **ALWAYS** needs **complex lapw2** version
- **Non-magnetic systems:**

  SO does NOT reduce symmetry. initso_lapw just generates case.inso and case.in2c.
- **Magnetic systems:**

  symmetso detects proper symmetry and rewrites case.struct/in*/clm*



Relativistic effects & Magnetic couplings

Xavier Rocquefelte
WIEN2k workshop 2024 – ICTP Trieste (Italy)

I. Introduction

To learn and practice

Dalton Transactions

RSC Publishing

PERSPECTIVE

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Magnetic properties and energy-mapping analysis

Cite this: *Dalton Trans.*, 2013, **42**, 823

Hongjun Xiang,*[a] Changhoon Lee,†[b] Hyun-Joo Koo,[c] Xingao Gong[a] and Myung-Hwan Whangbo*[b]

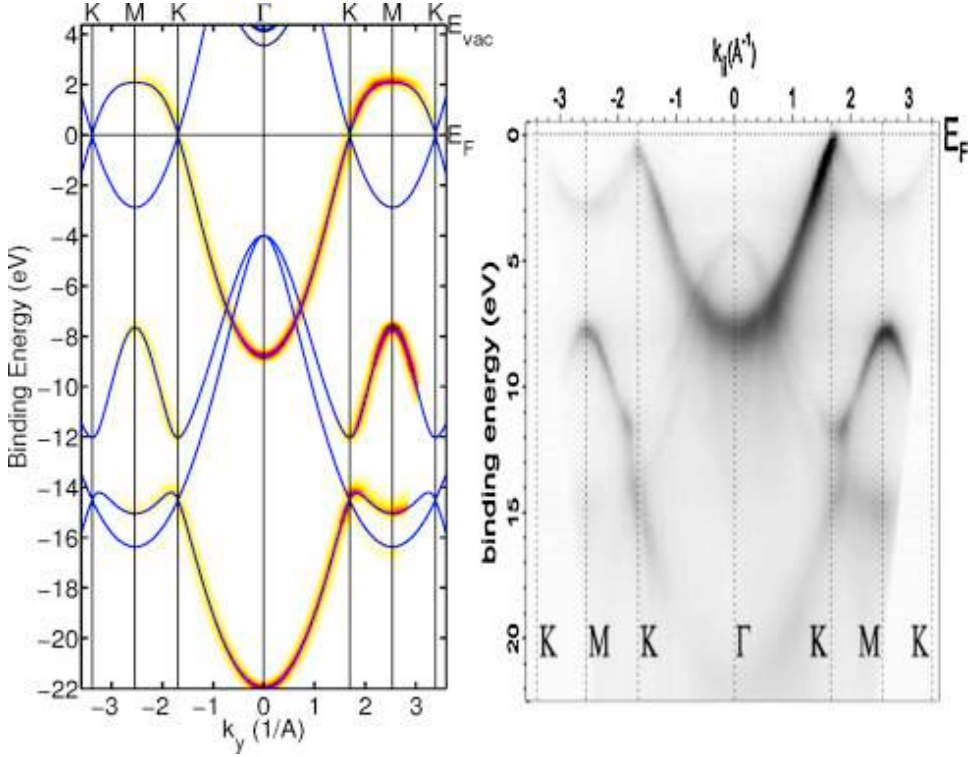
M.-H. Whangbo

The magnetic energy levels of a given magnetic solid are closely packed in energy because the interactions between magnetic ions are weak. Thus, in describing its magnetic properties, one needs to generate its magnetic energy spectrum by employing an appropriate spin Hamiltonian. In this review article we discuss how to determine and specify a necessary spin Hamiltonian in terms of first principles electronic structure calculations on the basis of energy-mapping analysis and briefly survey important concepts and phenomena that one encounters in reading the current literature on magnetic solids. Our discussion is given on a qualitative level from the perspective of magnetic energy levels and electronic structures. The spin Hamiltonian appropriate for a magnetic system should be based on its spin lattice, *i.e.*, the repeat pattern of its strong magnetic bonds (strong spin exchange paths), which requires one to evaluate its Heisenberg spin exchanges on the basis of energy-mapping analysis. Other weaker energy terms such as Dzyaloshinskii–Moriya (DM) spin exchange and magnetocrystalline anisotropy energies, which a spin Hamiltonian must include in certain cases, can also be evaluated by performing energy-mapping analysis. We show that the spin orientation of a transition-metal magnetic ion can be easily explained by considering its split d-block levels as unperturbed states with the spin–orbit coupling (SOC)

I. Introduction

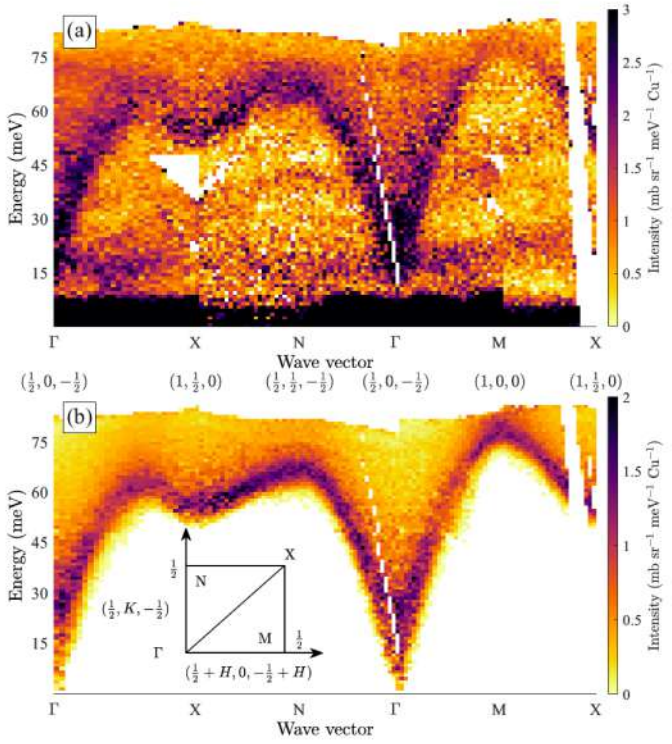
Let's talk about order of magnitude

Band structure & ARPES of graphene



https://doi.org/10.1016/j.elspec.2015.06.003

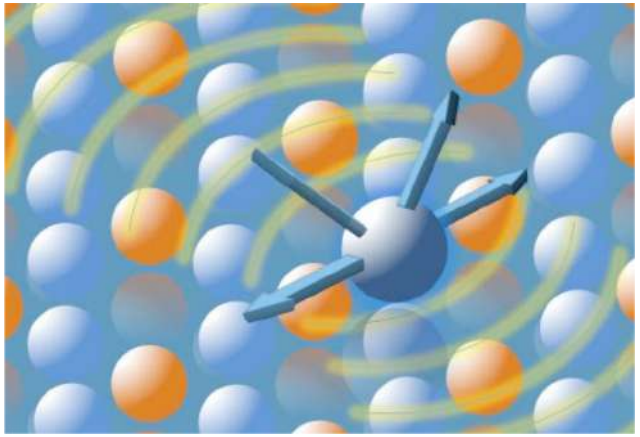
Magnetic dispersion of CuO at 6K (neutron scattering)



https://doi.org/10.1103/PhysRevB.97.144401

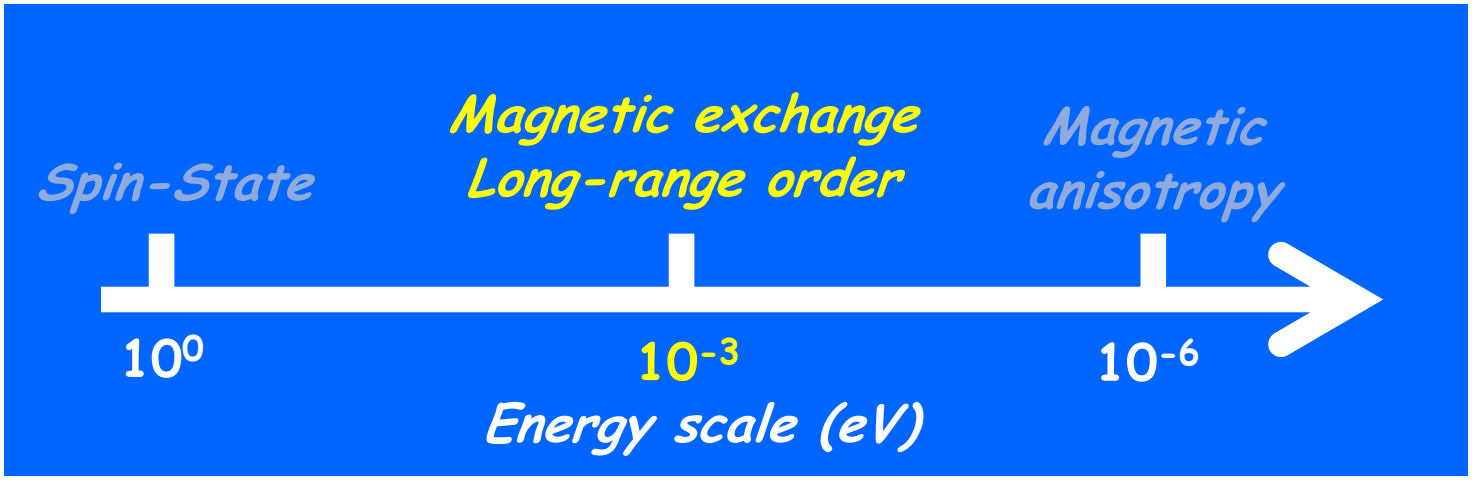
I. Introduction

1 meV
=
11.6 K
=
8.06 cm^{-1}



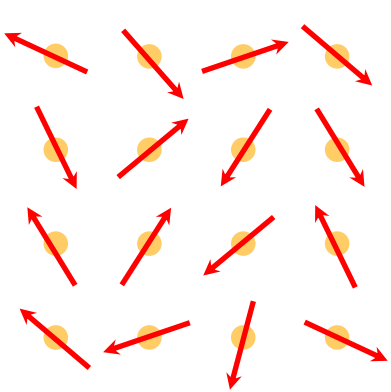
Magnetic properties:

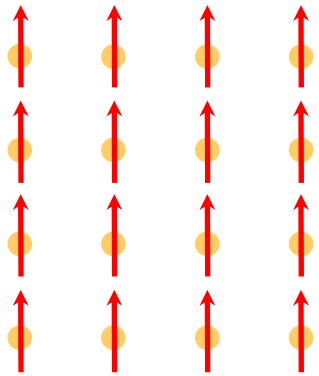
- ✓ *Spin-state (high/low)*
- ✓ *Long-range/short-range orders*
- ✓ *Collinear / non-collinear*
- ✓ *Magnetic anisotropy*
- ✓ *Magnetic frustration*
- ✓ *Magnetic exchange*



I. Introduction

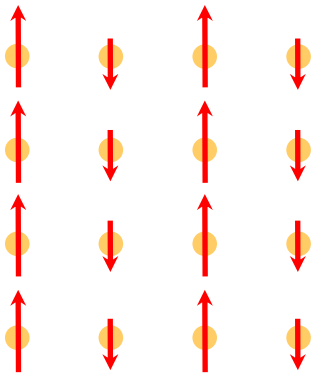
Paramagnetic (PM)

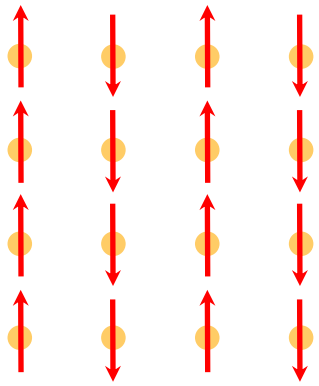




Ferromagnetic (FM) order

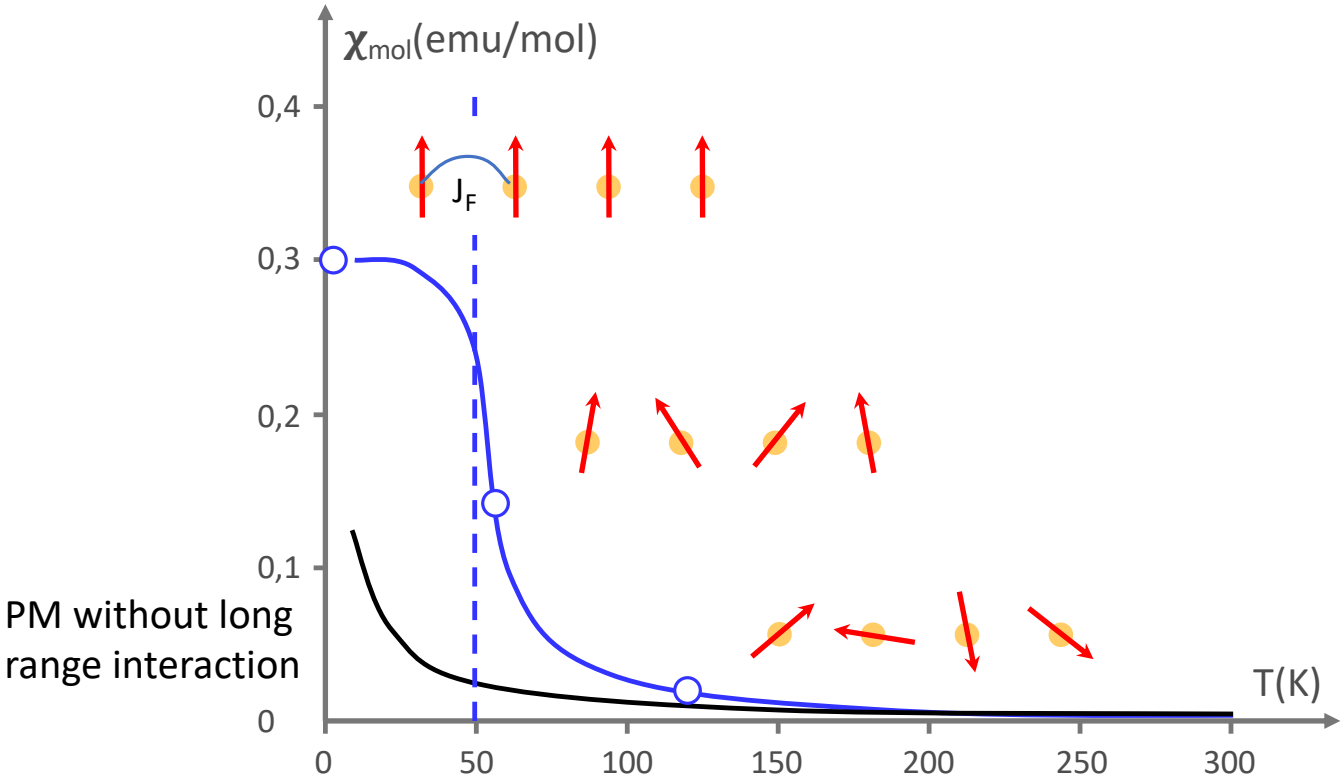
Ferrimagnetic order



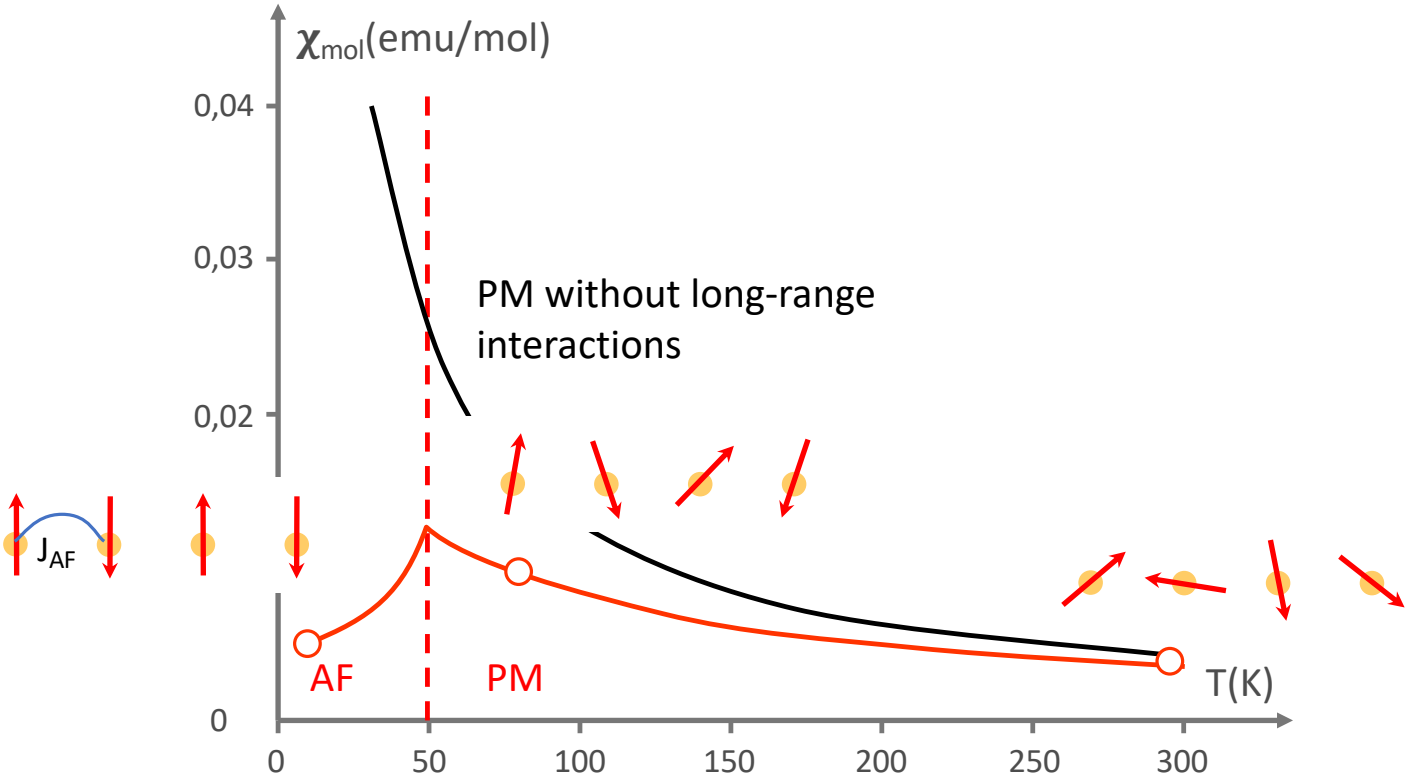


Antiferromagnetic (AFM) order

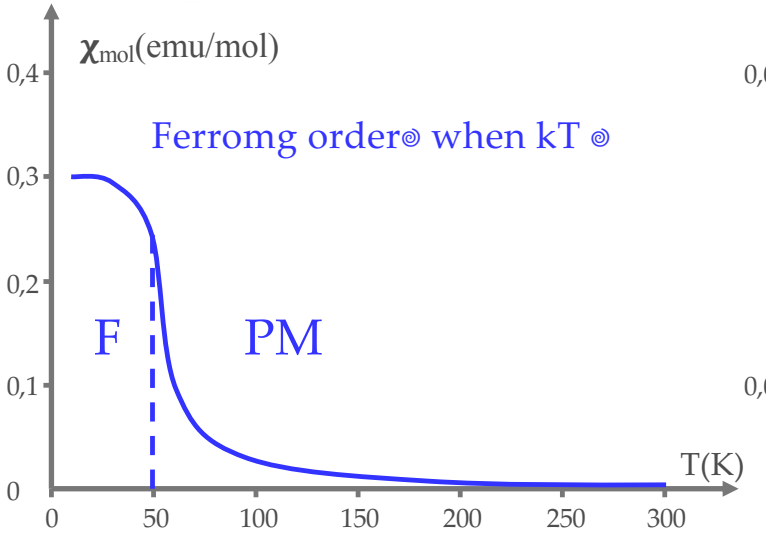
Magnetic susceptibility of a ferromagnetic (FM) compound



Magnetic susceptibility of an antiferromagnetic (AFM) compound



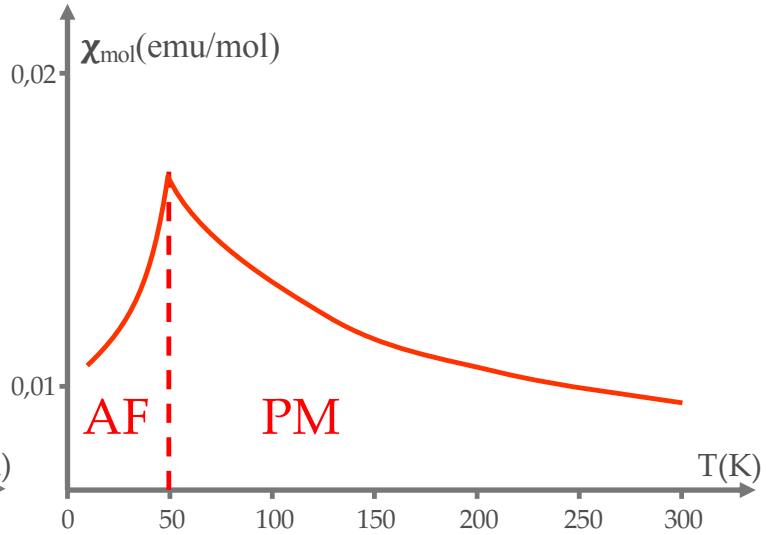
Ferromagnetic



T_C Curie temperature

Ferromagnetic exchange: $J_F < 0$

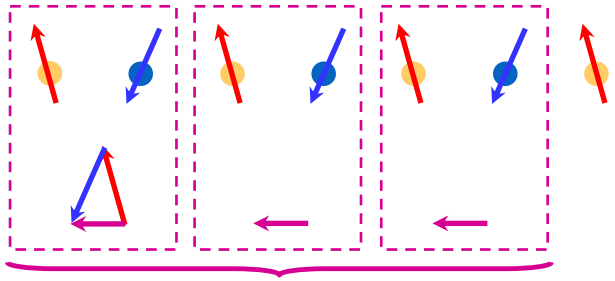
Antiferromagnetic



T_N Néel temperature

Antiferromagnetic exchange: $J_{AF} > 0$

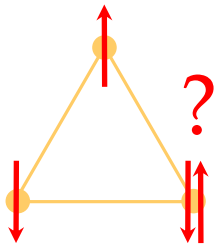
AFM with 2 subnetworks having different magnetization directions



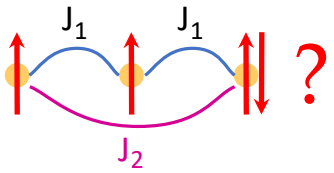
◎ weak ferromagnetism

Frustrated AFM

Topologic frustration

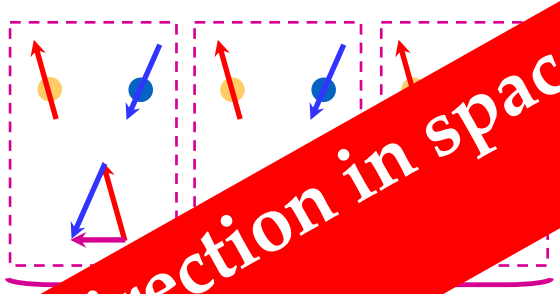


FM-AFM competition



J_1 : FM J_2 : AFM

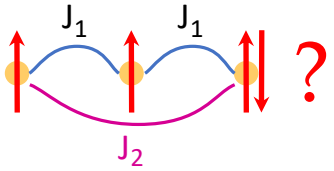
AFM with 2 subnetworks having different magnetization directions



Frustrated AFM

Topologic frustrati… FM-AFM competition

Magnetic moment has a direction in space ➔ spin-orbit coupling



J_1 : FM J_2 : AFM

II. Magnetic coupling J

Estimation of J can be done by mapping energy differences onto the general Heisenberg Spin Hamiltonian:

J_{ij}: spin exchange parameter between the spin sites i and j

$$\hat{H} = \hat{H}_0 + \sum_{i<j} J_{ij} \vec{S}_i . \vec{S}_j$$

$J_{ij} > 0 \Rightarrow$ AFM

$J_{ij} < 0 \Rightarrow$ FM

Long-range order

$$E_\alpha = \langle \alpha | H | \alpha \rangle = E_0 + S^2 \sum_{i<j} J_{ij} \sigma_i \sigma_j$$

S: Spin hold by the magnetic center
$\sigma_i = \pm 1$ (up or down spin)

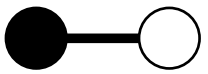
Example of a spin-half dimer (S = ½)

To estimate the J_{12} value, 2 total energy calculations are needed:

$\sigma_1 = +1$ $\sigma_2 = +1$

$$E_{FM} = E_0 + \frac{1}{4} J_{12}$$

$\sigma_1 = +1$ $\sigma_2 = -1$

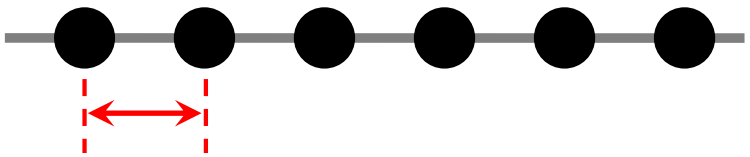


$$E_{AFM} = E_0 + -\frac{1}{4} J_{12}$$

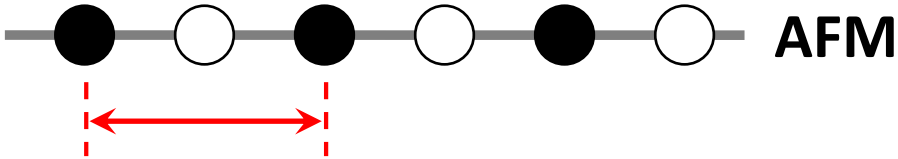
$$J_{12} = 2\left(E_{FM} - E_{AFM}\right)$$

Illustration: 1D system – Method A

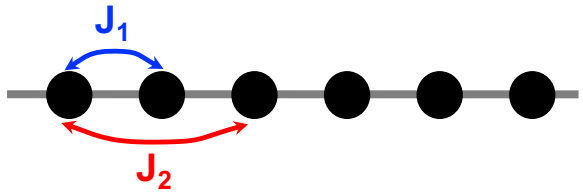
Estimation of only J_1 needs 2 magnetic orders



$a_{FM} = a_{cryst}$



$a_{AFM} = 2a_{FM}$



2 DFT calculations using

same supercell

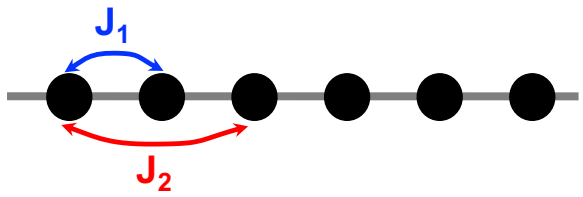
same symmetry

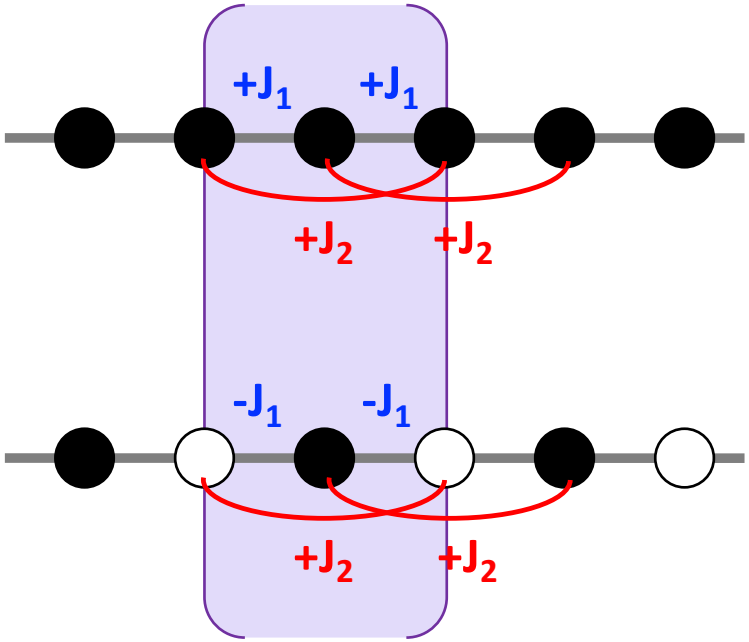
same precision

E_{FM}^{DFT} E_{AFM}^{DFT}

Illustration: 1D system – Method A

Estimation of only J_1 needs 2 magnetic orders



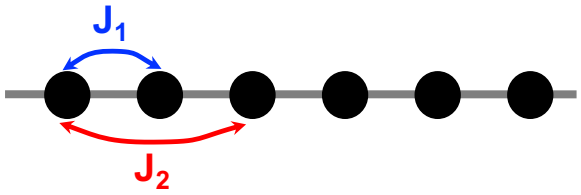


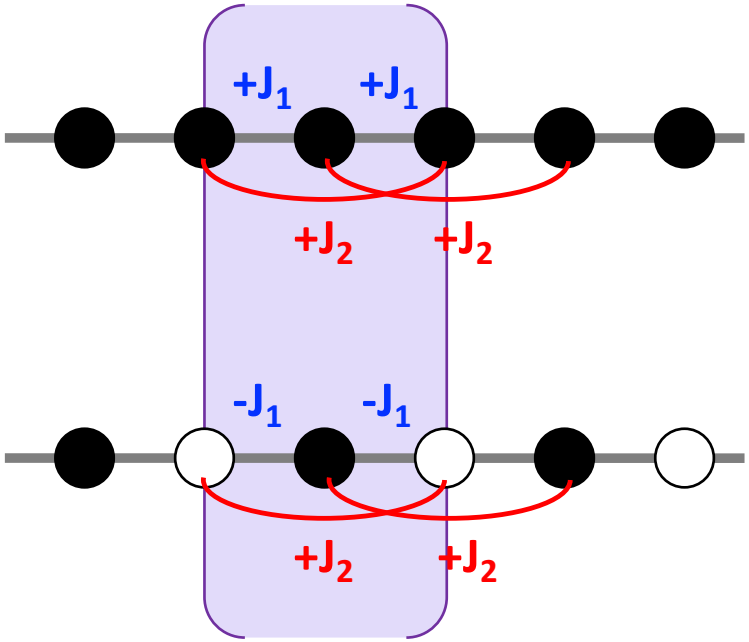
$$E_{FM}^{Mapping} = 2J_1 + 2J_2$$

$$E_{AFM}^{Mapping} = -2J_1 + 2J_2$$

Illustration: 1D system – Method A

Estimation of only J_1 needs 2 magnetic orders





$$E_{FM}^{Mapping} = 2J_1 + 2J_2 = E_{FM}^{DFT}$$

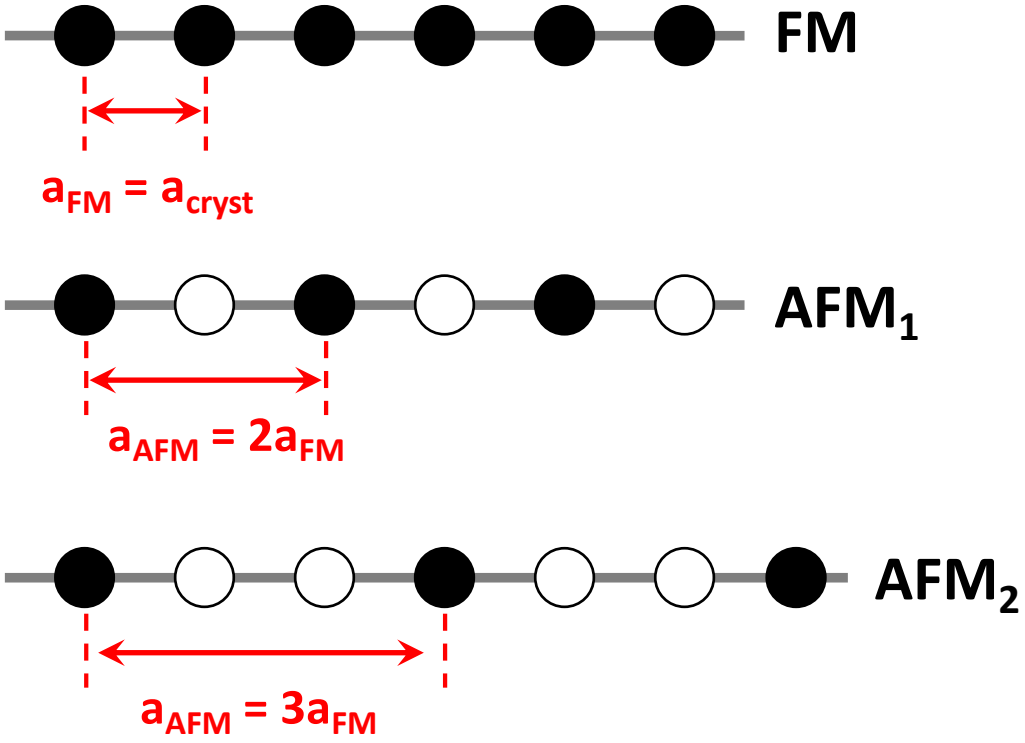
$$E_{AFM}^{Mapping} = -2J_1 + 2J_2 = E_{AFM}^{DFT}$$

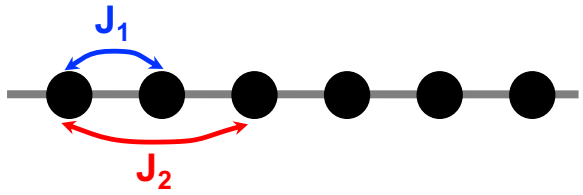
$$E_{FM}^{Mapping} - E_{AFM}^{Mapping} = 4J_1 \Rightarrow J_1 = \frac{E_{FM}^{DFT} - E_{AFM}^{DFT}}{4}$$

BUT J_2?

Illustration: 1D system – Method A

Estimation of J_1 and J_2





3 DFT calculations using

same supercell

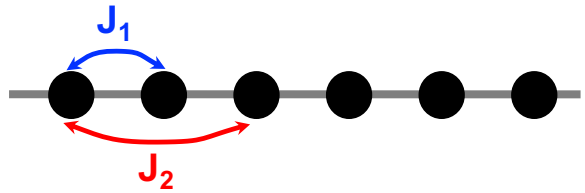
same symmetry

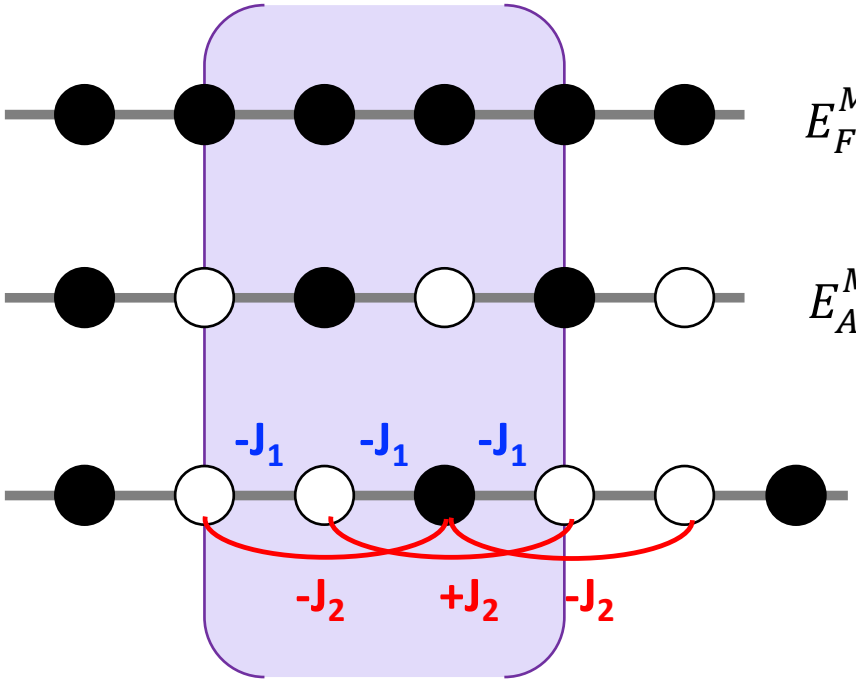
same precision

E_{FM}^{DFT} $E_{AFM_1}^{DFT}$ $E_{AFM_2}^{DFT}$

Illustration: 1D system – Method A

Estimation of J_1 and J_2





$$E_{FM}^{Mapping} = 3J_1 + 3J_2 = E_{FM}^{DFT}$$

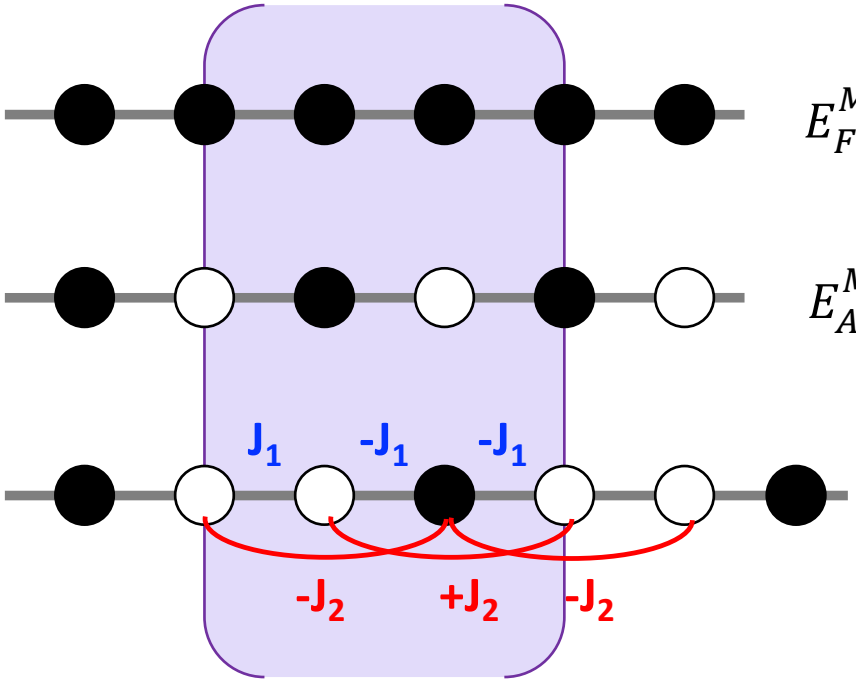
$$E_{AFM_1}^{Mapping} = -3J_1 + 3J_2 = E_{AFM_1}^{DFT}$$

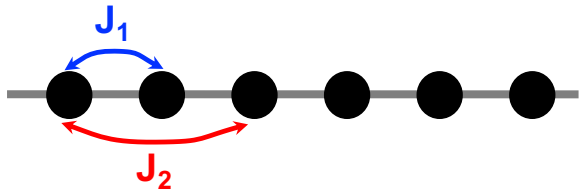
$$E_{AFM_2}^{Mapping} = -J_1 - 3J_2 = E_{AFM_2}^{DFT}$$

$$E_{FM}^{Mapping} - E_{AFM_1}^{Mapping} = 6J_1 \quad \Rightarrow \quad J_1 = \frac{E_{FM}^{DFT} - E_{AFM}^{DFT}}{6}$$

Illustration: 1D system – Method A

Estimation of J_1 and J_2





$$E_{FM}^{Mapping} = 3J_1 + 3J_2 = E_{FM}^{DFT}$$

$$E_{AFM_1}^{Mapping} = -3J_1 + 3J_2 = E_{AFM_1}^{DFT}$$

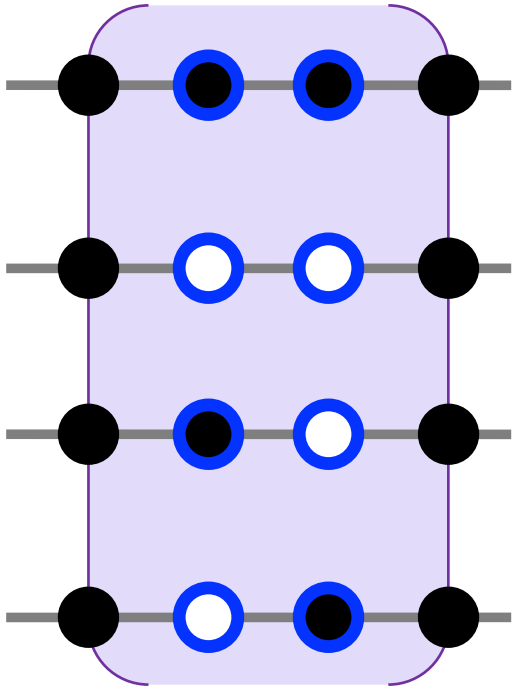
$$E_{AFM_2}^{Mapping} = -J_1 - J_2 = E_{AFM_2}^{DFT}$$

$$E_{AFM_1}^{Mapping} - 3E_{AFM_2}^{Mapping} = 6J_2 \quad \Rightarrow \quad J_2 = \frac{E_{AFM_1}^{DFT} - 3E_{AFM_2}^{DFT}}{6}$$

II. Magnetic coupling J

Illustration: 1D system – Method B

Estimation of J_1



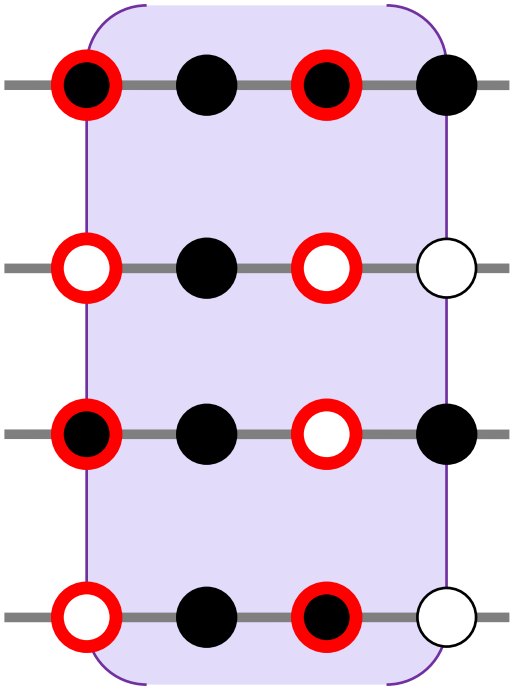
up - up

down - down

up - down

down - up

Estimation of J_2



$$J_1 = \frac{E_{uu} + E_{dd} - E_{ud} - E_{du}}{4S^2}$$

$$J_2 = \frac{E_{uu} + E_{dd} - E_{ud} - E_{du}}{4S^2}$$

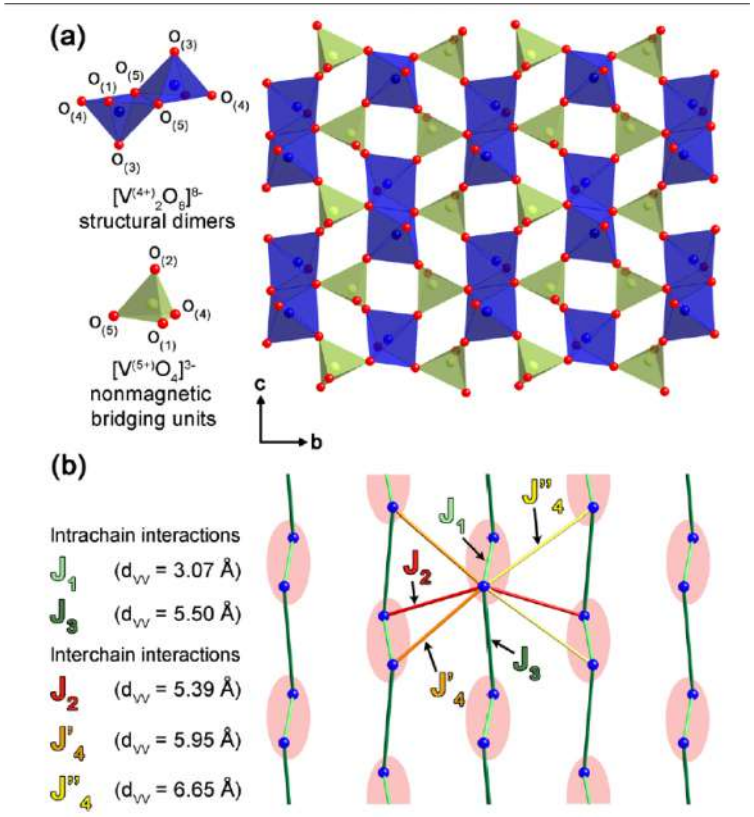
II. Magnetic coupling J

METHOD A

PRL 106, 177203 (2011) PHYSICAL REVIEW LETTERS week ending 29 APRIL 2011

Magnetic Couplings in CsV_2O_5: A New Picture

A. Saúl[1,*] and G. Radtke[2]
[1]CINaM, UPR 3118 CNRS, Campus de Luminy, case 913, 13288 Marseille cedex 9, France
[2]IM2NP, UMR 6242 CNRS, Faculté des Sciences de Saint-Jérôme, Case 262, 13397 Marseille cedex 20, France
(Received 7 March 2011; published 29 April 2011)



64-atoms supercell

↓

8 magnetic ions

↓

2^8 = 256 possible magnetic configurations

↓ Spin reversal ↓ Cristalline symmetry

28 inequivalent magnetic configurations

Least-squares fit procedure
(28 equations → 4 parameters)

II. Magnetic coupling J

METHOD A

PRL 106, 177203 (2011) PHYSICAL REVIEW LETTERS week ending 29 APRIL 2011

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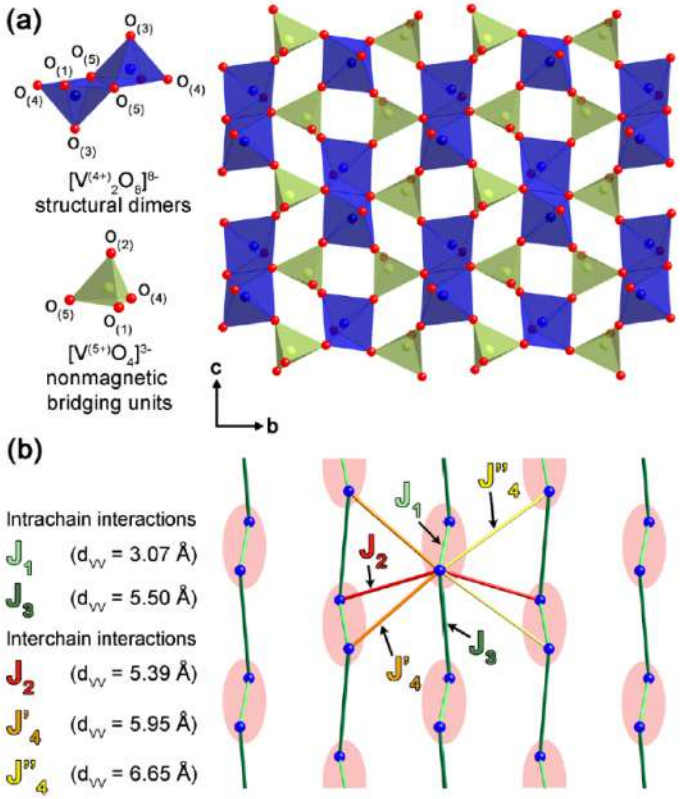


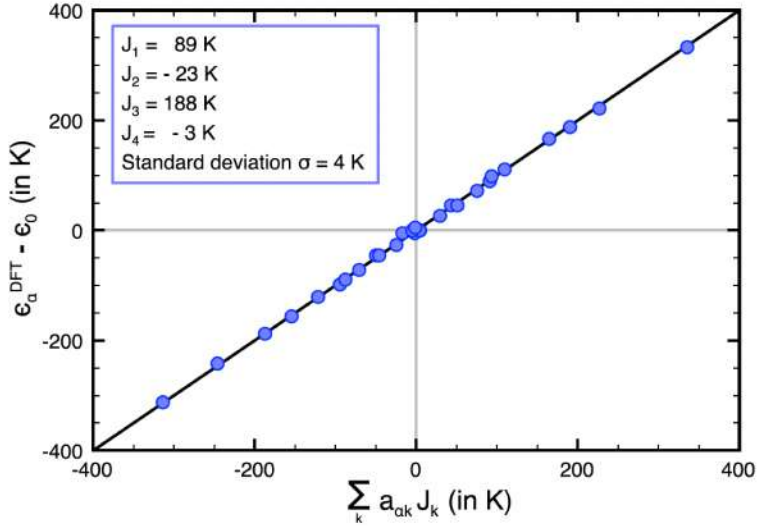


FIG. 2 (color online). Graphical representation of the results obtained by using the least-squares fit procedure: For each configuration, the DFT relative energy ϵ_α^{DFT}-ϵ_0 is represented as a function of the optimized Ising energy. The best fit values are shown in the inset. According to the convention used in Eq. (1), positive couplings correspond to AFM interactions.

II. Magnetic coupling J

CuO Cu^{2+} (d^9) $magnetic\ orb.\ d_{x^2-y^2}$

METHOD A

PRL 106, 026401 (2011) PHYSICAL REVIEW LETTERS week ending 14 JANUARY 2011

High-T_c Ferroelectricity Emerging from Magnetic Degeneracy in Cupric Oxide

Gianluca Giovannetti,[1,2] Sanjeev Kumar,[3,4] Alessandro Stroppa,[5] Jeroen van den Brink,[3] Silvia Picozzi,[1] and José Lorenzana[2]

[1]*Consiglio Nazionale delle Ricerche CNR-SPIN L'Aquila, Italy*
[2]*ISC-CNR, Dipartimento di Fisica, Università "La Sapienza", Piazzale Aldo Moro 5, Roma, Italy*
[3]*Institute for Theoretical Solid State Physics, IFW Dresden, 01171 Dresden, Germany*
[4]*Indian Institute of Science Education and Research Mohali, MGSIPAP Complex, Sector 26, Chandigarh 160019, India*
[5]*CNISM- Department of Physics, University of L'Aquila, Via Vetoio 10, 67010 Coppito, L'Aquila, Italy*

(Received 26 July 2010; published 12 January 2011)

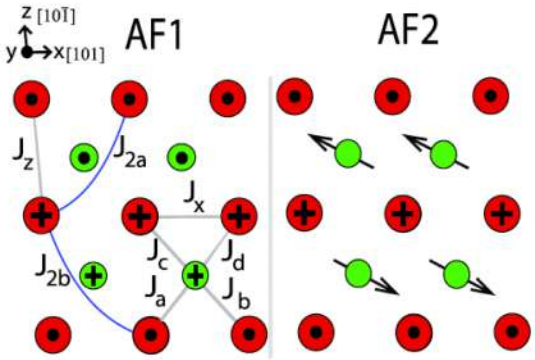


TABLE I. Exchange coupling parameters (meV) calculated within SGGA + U and hybrid functional calculations. The structure allows for $J_a \neq J_d$ and $J_b \neq J_c$ but we take them equal for simplicity. This is inessential for our conclusions. For the notations see Fig. 1 and Ref. [8].

	J_z	J_x	J_{2a}	J_{2b}	$J_a = J_d$	$J_b = J_c$	J_y
$U_{\text{eff}} = 5.5$	107.76	−15.76	6.89	16.18	7.98	15.82	−21.48
$\alpha = 0.15$	120.42	−24.33	4.99	14.27	4.19	13.17	−23.02

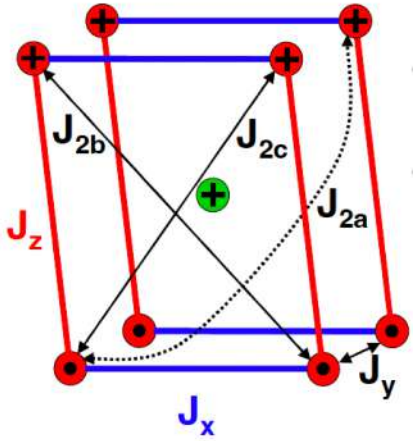
II. Magnetic coupling J

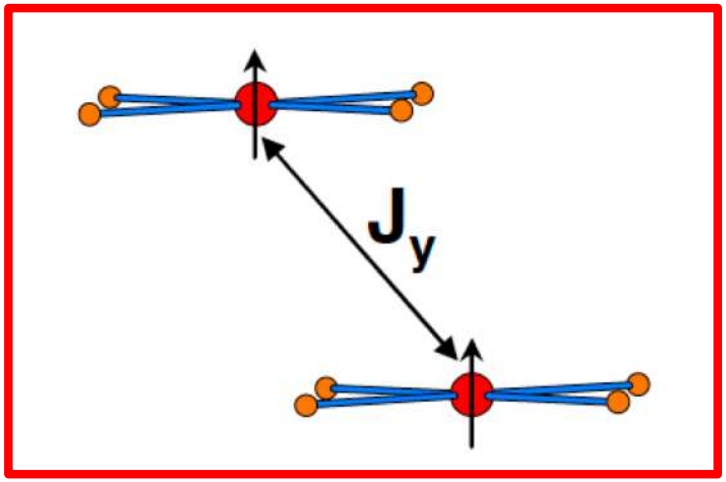
CuO

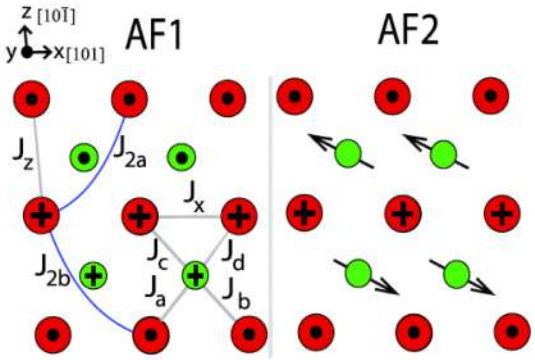
Cu^{2+} (d^9)

$magnetic\ orb.\ d_{x^2-y^2}$

METHOD A







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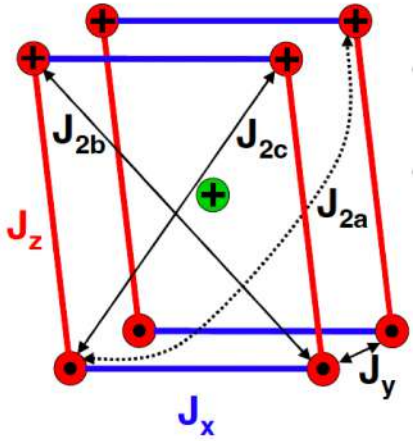
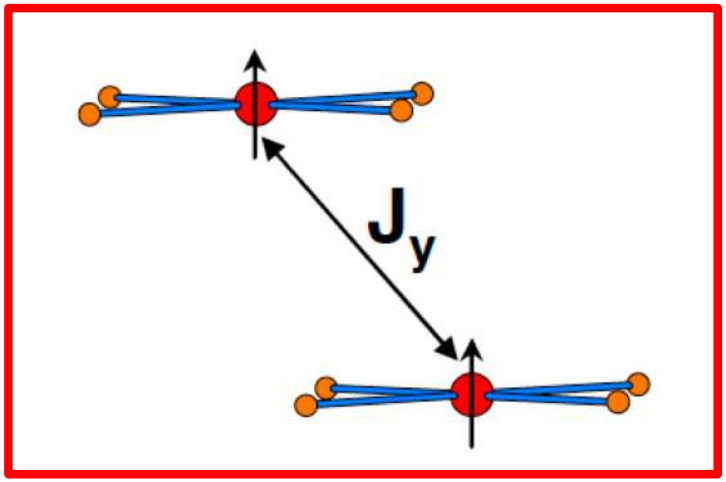
II. Magnetic coupling J

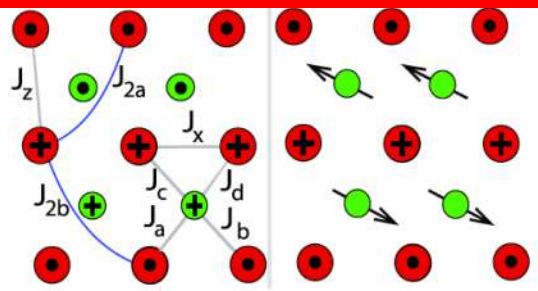
CuO Cu^{2+} (d^9) $magnetic\ orb.\ d_{x^2-y^2}$

METHOD A





NO PHYSICAL MEANING! WHAT IS THE PROBLEM?



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II. Magnetic co

METHOD A

Comment on "High-T_c Ferroelectricity Emerging from Magnetic Degeneracy in Cupric Oxide"

The origin of the multiferroicity in cupric oxide was addressed in a recent Letter [1], in which Giovannetti *et al.* performed classical Monte Carlo simulations on a 3D Hamiltonian to estimate the spin-current susceptibility χ_{jj} for the CuO structure. However, they used incorrect exchange parameters J_{ij} as inputs. Giovannetti *et al.* [2] have done the following. (i) They introduced a new ferromagnetic (FM) J parameter, namely, J_y, but neglected an important antiferromagnetic (AFM) supersuperexchange interaction with a dihedral Cu-O-O-Cu angle of 0°, previously defined as J_{nnn} in Ref. [3] and J_{2a} in Ref. [4]. (ii) They mentioned that they used the notations of Ref. [4], which is not true and leads to severe confusions. In particular, they interchanged J_a with J_b, J_{2b} with J_{2a}, and J_{2c} with J_{2b}. (iii) They used incorrect coefficients for their J_b parameter in their energy expressions (twice too much). (iv) They performed their mapping analysis such that the number of equations is equal to the number of unknown parameters, which does not guarantee the robustness of the so-obtained J parameters.

We used for our total energy calculations the same conditions as specified in Ref. [1]. However, we considered 23 different magnetic states and a least-squares fit procedure and not only a minimal set of equations as in Ref. [1]. The discussion in the present Comment is based on the

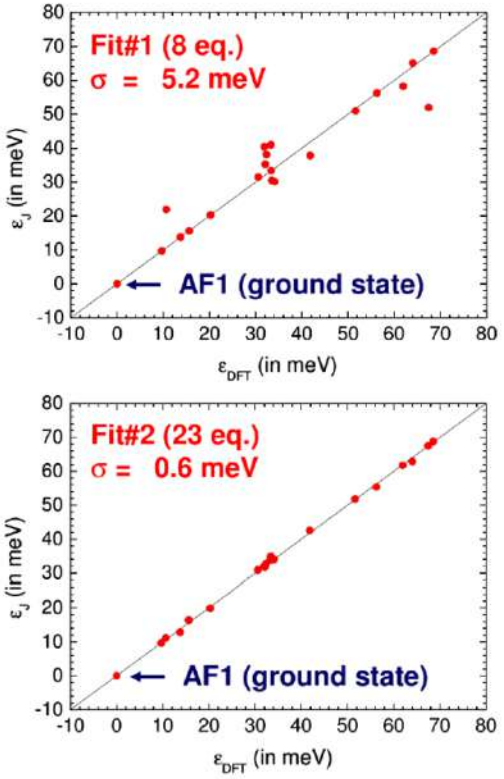

FIG. 1 (color online). Graphical representation of fit#1 and fit#2 results. $\varepsilon_{\mathrm{DFT}}$ and ε_J are, respectively, the relative energies (with respect to the ground state, labeled "AF1" in Ref. [1]) deduced from the density-functional theory (DFT) calculations and the J parameters.

II. Magnetic co

METHOD A

PRL **107,** 239701 (2011) PHYSICAL REVIEW LETTERS week ending 2 DECEMBER 2011

Comment on "High-T_c Ferroelectricity Emerging from Magnetic Degeneracy in Cupric Oxide"

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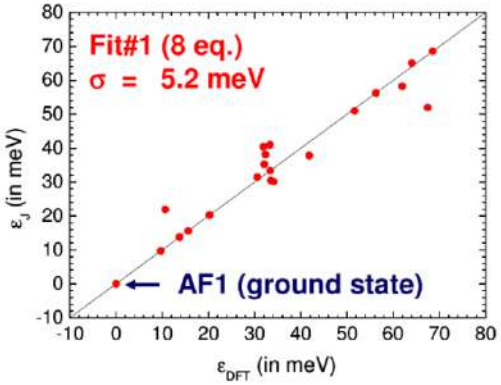


TABLE I. Exchange-coupling parameters (meV) calculated using DFT + U calculations.

Refs. [4,5]	J_z	J_x	J_a	J_b	J_{2a}	J_{2b}	J_{2c}	J_y
Ref. [1]	J_z	J_x	J_b	J_a	⋯	J_{2a}	J_{2b}	J_y
d_{Cu-Cu} (Å)	3.748	3.173	2.901	3.083	5.801	5.129	4.684	3.423
J_{ij} fit#1	99.53	−13.04	23.13	5.07	⋯	6.23	14.80	−19.42
J_{ij} fit#2	107.12	−3.65	8.32	−2.92	20.05	10.11	−1.04	0.77

Illustration: NiO (Ex. 13 & 14)

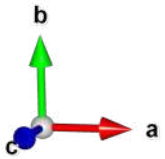
Experiment data:

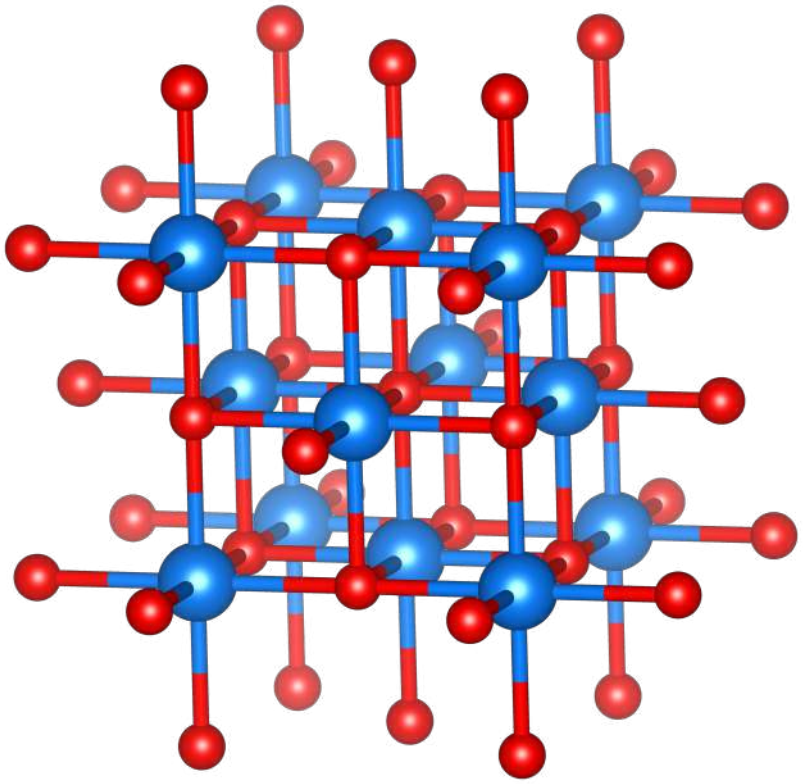
Ni^{2+}: d^8 electronic configuration
Octahedral environment

Rock-salt structure
Space group: Fm-3m (#225)

Optical gap: 4-4.3 eV

Magnetic properties:
- **AFM order**
- **μ(Ni) = 1.7-1.9 μ_B**





II. Magnetic coupling J

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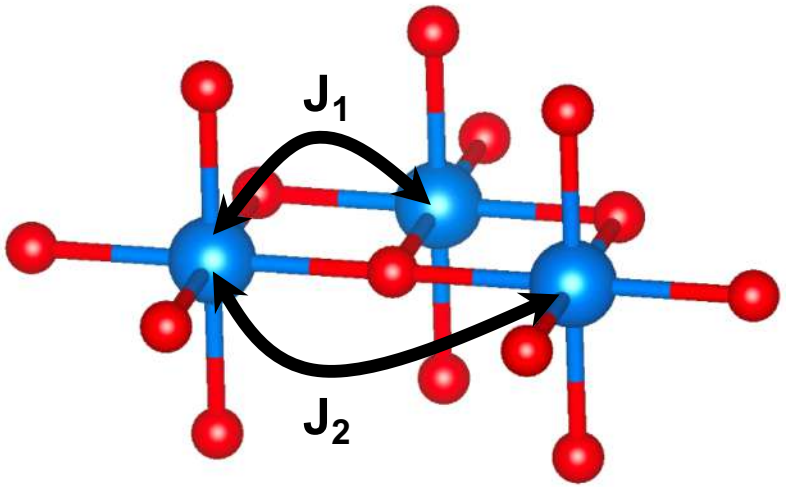

II. Magnetic coupling J

Illustration: NiO (Ex. 13 & 14)

PHYSICAL REVIEW B VOLUME 6, NUMBER 9 1 NOVEMBER 1972

Measurement of Spin-Wave Dispersion in NiO by Inelastic Neutron Scattering and Its Relation to Magnetic Properties

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and

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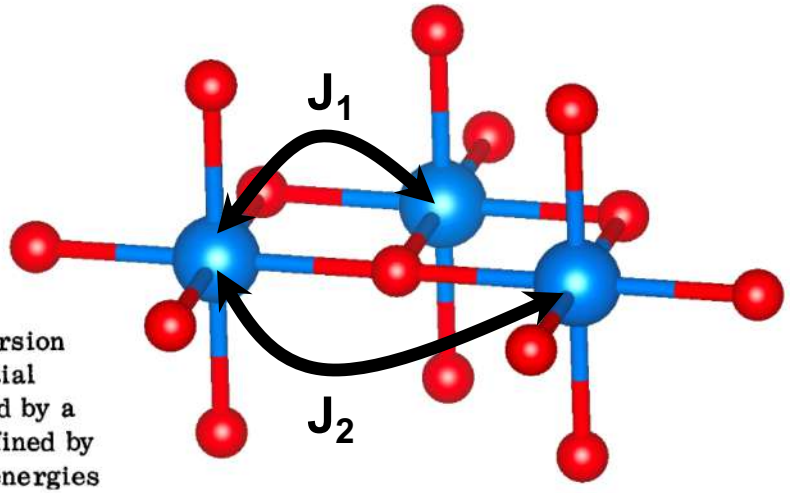
(Received 12 June 1972)

Inelastic neutron scattering techniques have been used to measure the spin-wave dispersion relations at 78 °K in the fcc antiferromagnet NiO. The energy dispersion has a steep initial slope (~ 250 meV Å) and a high maximum energy (~ 117 meV) and is further characterized by a relatively low zone boundary energy in certain directions. The exchange parameters defined by $\mathcal{H}^{1,2} = J_j \vec{S}^{(1)} \cdot \vec{S}^{(2)}$ were determined by fitting the theoretical expression for the spin-wave energies to the experimental data corrected for instrumental resolution effects. The predominant interaction is a large antiferromagnetic exchange $J_2 = 221$ °K (19.01 meV) between next-nearest neighbors, which are linked by a 180° superexchange path. The interaction between nearest neighbors, linked by a 90° Ni^{2+}—O^{2-}—Ni^{2+} configuration, is much smaller and ferromagnetic in sign, $J_1 = -15.9$ °K (−1.37 meV). A consequence of the relatively small value of J_1 is that the spin waves from the four domains present in the sample can only be resolved in a limited region of reciprocal space. These values of exchange interactions are in accord with simple ideas of covalency and overlap, and the results emphasize the behavior of NiO as a weakly covalent insulator. The density of magnon states, estimates of the transition temperature, and several thermomagnetic properties of NiO have been calculated from the measured exchange parameters using molecular field and random-phase-approximation Green's-function formulas.



nn J_1 = -1.37 meV (FM)

Ni-Ni = 2.966 Å

nnn J_2 = 19.01 meV (AFM)

Ni-Ni = 4.195 Å

II. Magnetic coupling J

Illustration: NiO (Ex. 13 & 14)

- Learn how to estimate the magnetic coupling J
- Learn 2 different approaches to extract J:
  - (A) Energy-mapping analysis based on two ordered spin states (FM and AFM)
  - (B) Energy-mapping analysis based on four ordered spin states (uu, dd, ud and du)

Ref. Dalton Trans., 2013, 42, 823

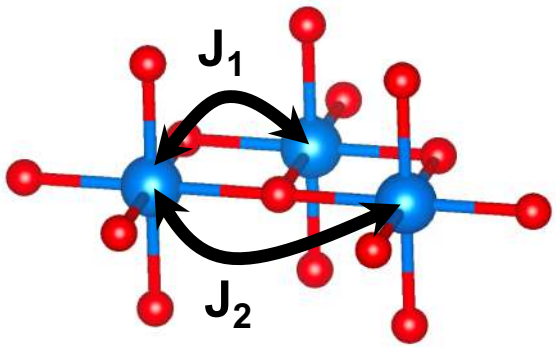
Spin hamiltonian: $\hat{H}_{spin} = \sum_{i<j} J_{ij}\vec{S}_i\vec{S}_j$

(A) $J_{ij} = (E_{FM} - E_{AFM})/2N$

with N: number of J_{ij}

(B) $J_{ij} = \frac{E_{uu} + E_{dd} - E_{ud} - E_{du}}{4S^2}$

with S: Total spin of Ni in NiO



J_1: nearest-neighbors exchange coupling

J_2: next nearest-neighbors exchange coupling

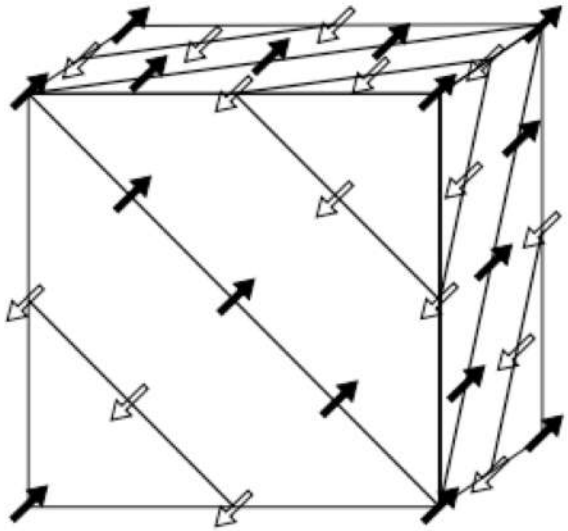
Exp. Values from neutron scattering:

J_1 = -1.37 meV and J_2 = +19.01 meV

FM: J < 0 **AFM: J > 0**

II. Magnetic coupling J

Illustration: NiO (Ex. 13 & 14)



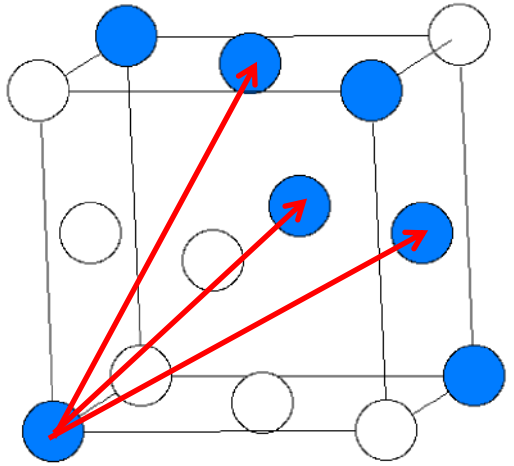
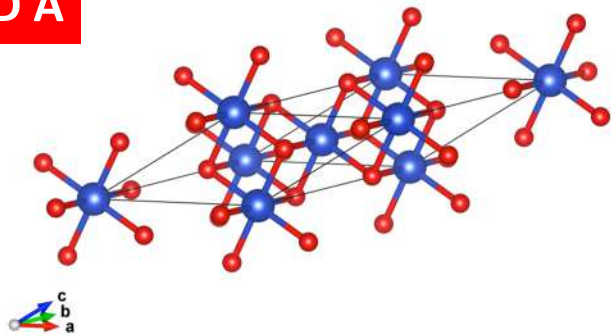


Figure 4.4 Basic spin ordering in the TM monoxides MnO, FeO, CoO and NiO. The spins are ferromagnetically ordered within {111} planes, and AF in neighboring {111} planes in all four compounds. The orientation of the spins with respect to the crystallographic axes, however, is different. In NiO and MnO, the spins are oriented in $\langle 11\bar{2} \rangle$ directions (as is actually shown in the above figure), in FeO in the [111] direction, and in CoO slightly tilted away from the cubic axes. All materials have structures that are slightly distorted to lower than cubic symmetries, which are consistent with these orientations.

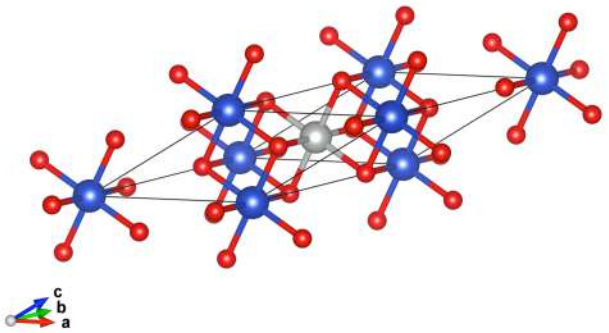
Illustration: NiO (Ex. 13 & 14)

J2 FROM METHOD A

Illustration with NiO: NaCl structure, A-type AFM along [111]



$$E_{FM}^{Mapping} = ?\,J_1 + ?\,J_2 = E_{FM}^{DFT}$$



$$E_{AFM}^{Mapping} = ?\,J_1 + ?\,J_2 = E_{AFM}^{DFT}$$

$$E_{FM}^{Mapping} - E_{AFM}^{Mapping} = ?\,J_2 \quad \Rightarrow \quad J_2 = \frac{E_{FM}^{DFT} - E_{AFM}^{DFT}}{?}$$

II. Magnetic coupling J

Illustration: NiO (Ex. 13 & 14)

x nn -> 2

vi NiO.outputnn

```
ATOM:  1  EQUIV.  1  Ni1        AT   0.00000   0.00000   0.00000
RMT(  1)=2.05000 AND RMT(  3)=1.77000
SUMS TO 3.82000  LT.  NN-DIST= 3.96370
ATOM:  3  O 1       AT -0.2500 -0.2500  0.7500 IS  3.96370 A.U.   2.09750 ANG
ATOM:  3  O 1       AT  0.2500  0.2500 -0.7500 IS  3.96370 A.U.   2.09750 ANG 180.00
ATOM:  3  O 1       AT -0.2500  0.7500 -0.2500 IS  3.96370 A.U.   2.09750 ANG  90.00  90.00
ATOM:  3  O 1       AT -0.7500  0.2500  0.2500 IS  3.96370 A.U.   2.09750 ANG  90.00  90.00  90.00
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ATOM:  3  O 1       AT  0.2500 -0.7500  0.2500 IS  3.96370 A.U.   2.09750 ANG  90.00  90.00 180.00
ATOM:  2  Ni2       AT -0.5000 -0.5000  0.5000 IS  5.60552 A.U.   2.96631 ANG
ATOM:  2  Ni2       AT -0.5000  0.5000 -0.5000 IS  5.60552 A.U.   2.96631 ANG
ATOM:  2  Ni2       AT -0.5000  0.5000  0.5000 IS  5.60552 A.U.   2.96631 ANG
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ATOM:  2  Ni2       AT  0.5000 -0.5000  0.5000 IS  5.60552 A.U.   2.96631 ANG
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ATOM:  1  Ni1       AT -1.0000  1.0000  0.0000 IS  5.60552 A.U.   2.96631 ANG
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ATOM:  1  Ni1       AT  1.0000  0.0000 -1.0000 IS  5.60552 A.U.   2.96631 ANG
ATOM:  3  O 1       AT -0.2500 -0.2500 -0.2500 IS  6.86533 A.U.   3.63298 ANG
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ATOM:  3  O 1       AT -0.7500 -0.7500  1.2500 IS  6.86533 A.U.   3.63298 ANG
ATOM:  3  O 1       AT -0.7500  1.2500 -0.7500 IS  6.86533 A.U.   3.63298 ANG
ATOM:  3  O 1       AT  0.7500 -1.2500  0.7500 IS  6.86533 A.U.   3.63298 ANG
ATOM:  3  O 1       AT  0.7500  0.7500 -1.2500 IS  6.86533 A.U.   3.63298 ANG
ATOM:  3  O 1       AT  1.2500 -0.7500 -0.7500 IS  6.86533 A.U.   3.63298 ANG
Atom   1 equiv  1 Ni1        Bond-Valence Sum     2.40    2.55
```
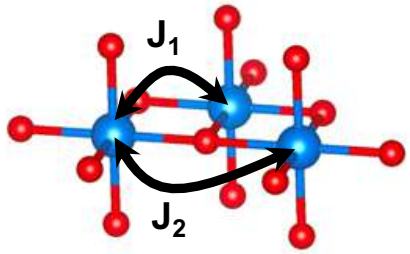

Ni-Ni (J_1) = 2.966 Å

Ni-Ni (J_2) = 4.195 Å



12 J_1 / Ni

6 Ni1-Ni2

6 Ni1-Ni1

II. Magnetic coupling J

Illustration: NiO (Ex. 13 & 14)

x nn -> 3

vi NiO.outputnn

```
ATOM:   1  EQUIV.  1  Ni1        AT   0.00000   0.00000   0.00000
RMT(  1)=2.05000 AND RMT(  3)=1.77000
SUMS TO 3.82000  LT.  NN-DIST= 3.96370
ATOM:   3  O 1       AT -0.2500 -0.2500  0.7500 IS  3.96370 A.U.   2.09750 ANG
ATOM:   3  O 1       AT  0.2500  0.2500 -0.7500 IS  3.96370 A.U.   2.09750 ANG
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ATOM:   3  O 1       AT  0.7500 -0.2500 -0.2500 IS  3.96370 A.U.   2.09750 ANG
ATOM:   3  O 1       AT  0.2500 -0.7500  0.2500 IS  3.96370 A.U.   2.09750 ANG
ATOM:   2  Ni2       AT -0.5000 -0.5000  0.5000 IS  5.60552 A.U.   2.96631 ANG
ATOM:   2  Ni2       AT -0.5000  0.5000 -0.5000 IS  5.60552 A.U.   2.96631 ANG
                                    .
                                    .
                                    .
ATOM:   3  O 1       AT  0.7500 -1.2500  0.7500 IS  6.86533 A.U.   3.63298 ANG
ATOM:   3  O 1       AT  0.7500  0.7500 -1.2500 IS  6.86533 A.U.   3.63298 ANG
ATOM:   3  O 1       AT  1.2500 -0.7500 -0.7500 IS  6.86533 A.U.   3.63298 ANG
ATOM:   2  Ni2       AT -0.5000 -0.5000  1.5000 IS  7.92740 A.U.   4.19500 ANG
ATOM:   2  Ni2       AT  0.5000  0.5000 -1.5000 IS  7.92740 A.U.   4.19500 ANG
ATOM:   2  Ni2       AT -1.5000  0.5000  0.5000 IS  7.92740 A.U.   4.19500 ANG
ATOM:   2  Ni2       AT -0.5000  1.5000 -0.5000 IS  7.92740 A.U.   4.19500 ANG
ATOM:   2  Ni2       AT  0.5000 -1.5000  0.5000 IS  7.92740 A.U.   4.19500 ANG
ATOM:   2  Ni2       AT  1.5000 -0.5000 -0.5000 IS  7.92740 A.U.   4.19500 ANG
ATOM:   3  O 1       AT -1.2500 -0.2500  0.7500 IS  8.86311 A.U.   4.69015 ANG
ATOM:   3  O 1       AT -1.2500  0.7500 -0.2500 IS  8.86311 A.U.   4.69015 ANG
```

6/2 → **3 J_2 / Ni 3 Ni1-Ni2**

Ni-Ni (J_1) = 2.966 Å

Ni-Ni (J_2) = 4.195 Å

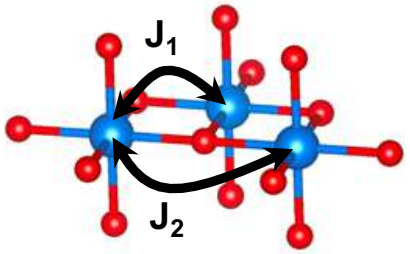
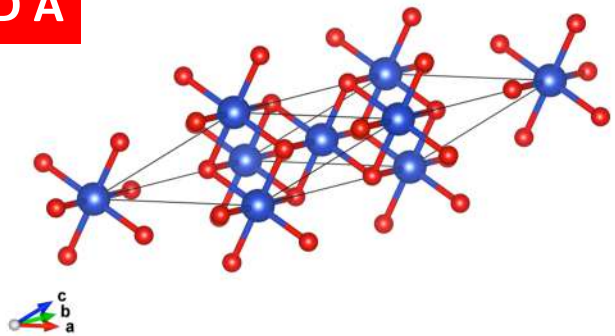
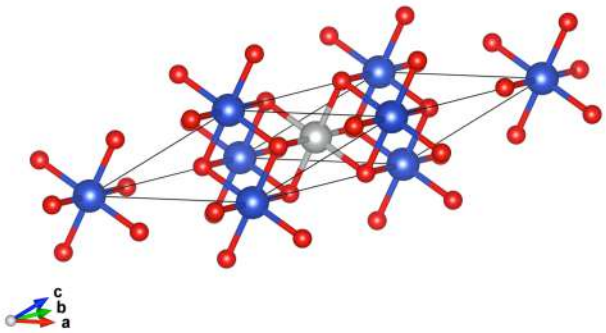


Illustration: NiO (Ex. 13 & 14)

J2 FROM METHOD A

Illustration with NiO: NaCl structure, A-type AFM along [111]





$$E_{FM}^{Mapping} = 12J_1 + 3J_2 = E_{FM}^{DFT}$$

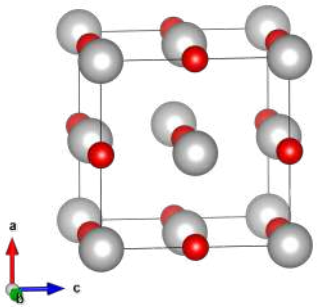
$$E_{AFM}^{Mapping} = 0J_1 - 3J_2 = E_{AFM}^{DFT}$$

$$E_{FM}^{Mapping} - E_{AFM}^{Mapping} = 12J_1 + 6J_2 \approx 6J_2 \quad \Rightarrow \quad J_2 \approx \frac{E_{FM}^{DFT} - E_{AFM}^{DFT}}{6}$$

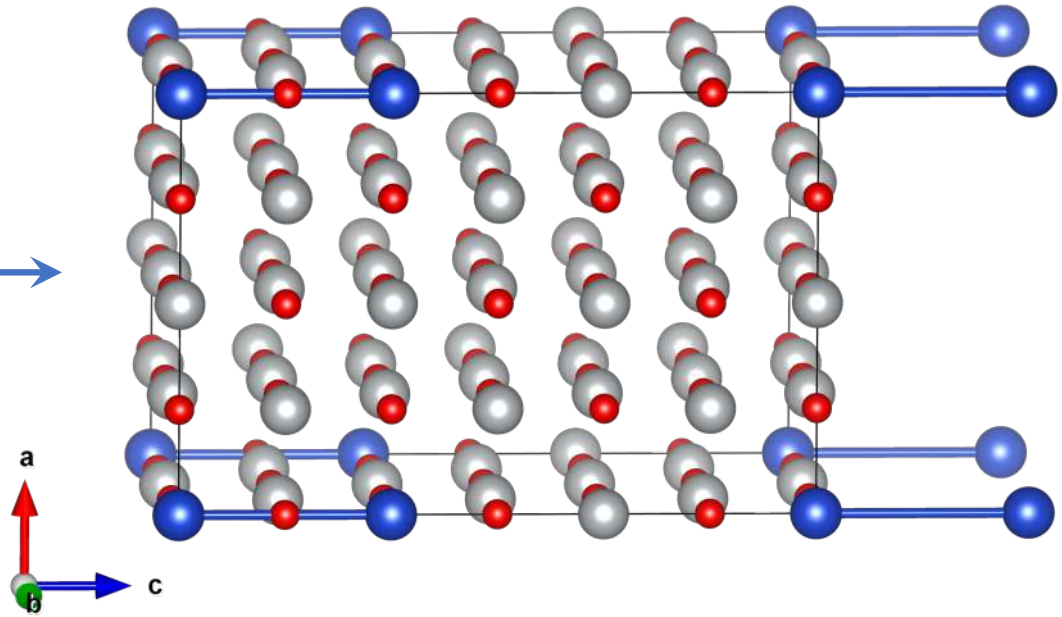
Illustration: NiO (Ex. 13 & 14)

J2 FROM METHOD B

NiO
F lattice

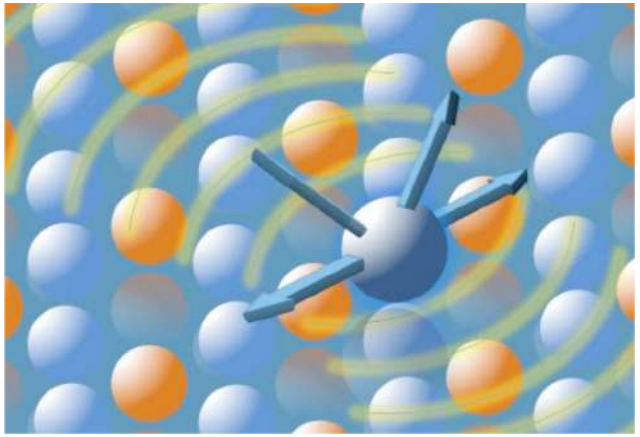


Supercell
2a x 2b x 3c



$$J_2 = \frac{E_{uu} + E_{dd} - E_{ud} - E_{du}}{4S^2}$$

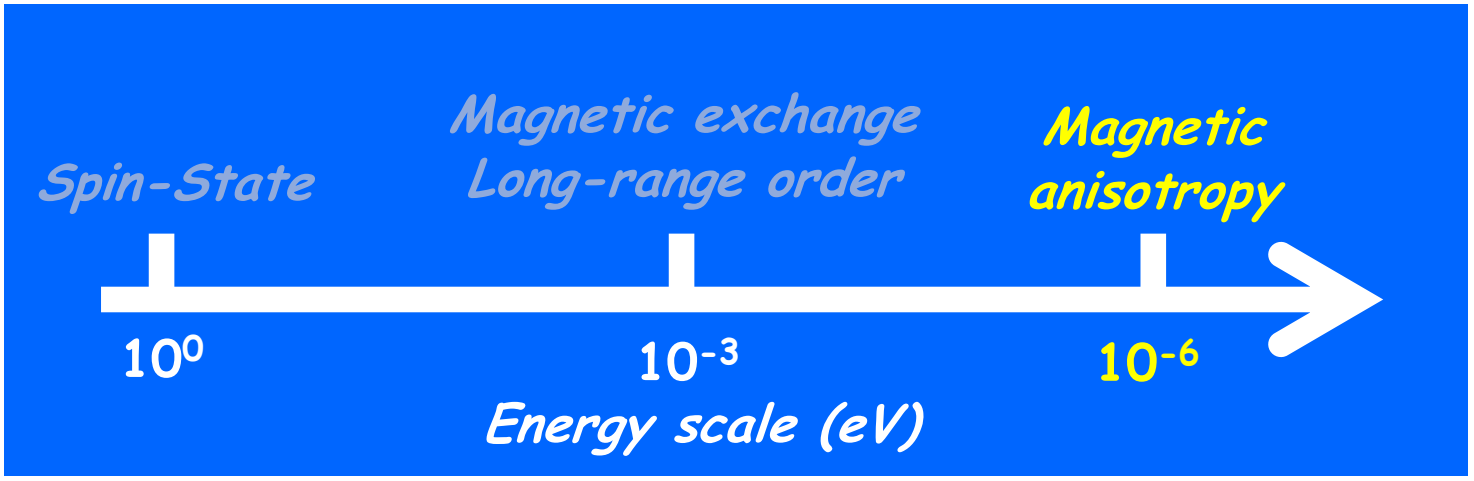
III. Magnetic anisotropy



Magnetic properties:

- ✓ Spin-state (high/low)
- ✓ Long-range/short-range orders
- ✓ Collinear / non-collinear
- ✓ **Magnetic anisotropy**
- ✓ Magnetic frustration
- ✓ Magnetic exchange

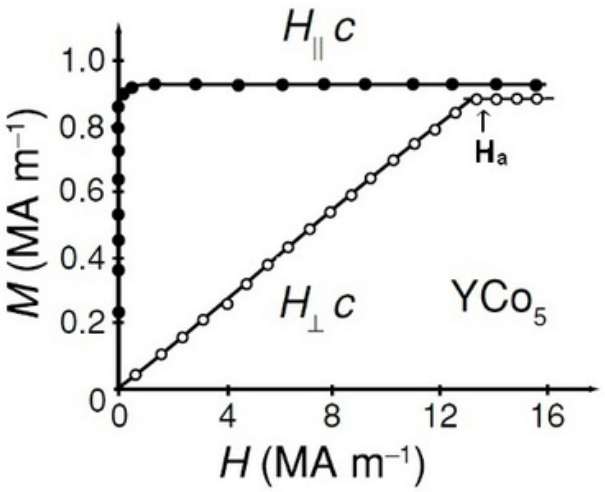
1 meV
=
11.6 K
=
8.06 cm^{-1}



III. Magnetic anisotropy

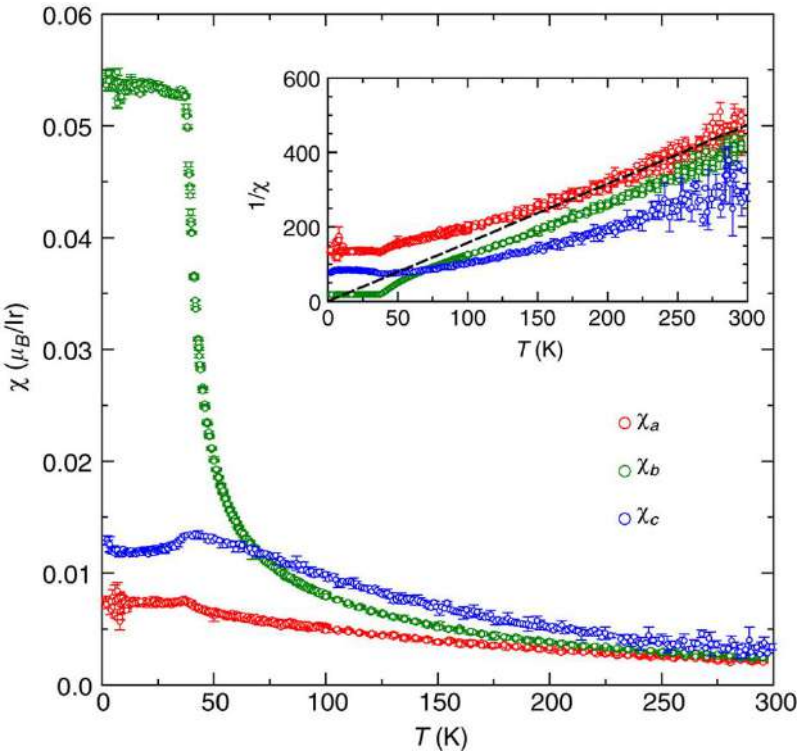
Different response as function of the direction of the applied magnetic field
(consequence of the spin-orbit coupling)

Magnetization of a single crystal of YCo_5



http://www.tara.tcd.ie/handle/2262/83258

Magnetic susceptibility of a single crystal of Li_2IrO_3



https://doi.org/10.1038/ncomms5203

III. Magnetic anisotropy

Estimation in WIEN2k

- Do a regular scalar-relativistic "scf" calculation
- save_lapw
- initso_lapw
  - case.inso:

```
WFFIL
 4  1  0                        llmax,ipr,kpot
 -10.0000   1.50000             emin,emax (output energy window)
   0.  0.  1.                   direction of magnetization (lattice vectors)
 NX                             number of atoms for which RLO is added
 NX1   -4.97      0.0005        atom number,e-lo,de (case.in1), repeat NX times
 0 0 0 0 0                      number of atoms for which SO is switch off; atoms
```

  - case.in1(c):

```
(…)
 2     0.30       0.005 CONT 1
 0     0.30       0.000 CONT 1
K-VECTORS FROM UNIT:4   -9.0        4.5     65    emin/emax/nband
```

  - symmetso (for spin-polarized calculations only)
- run(sp)_lapw -so ⟵ -so switch specifies that scf cycles will include SOC

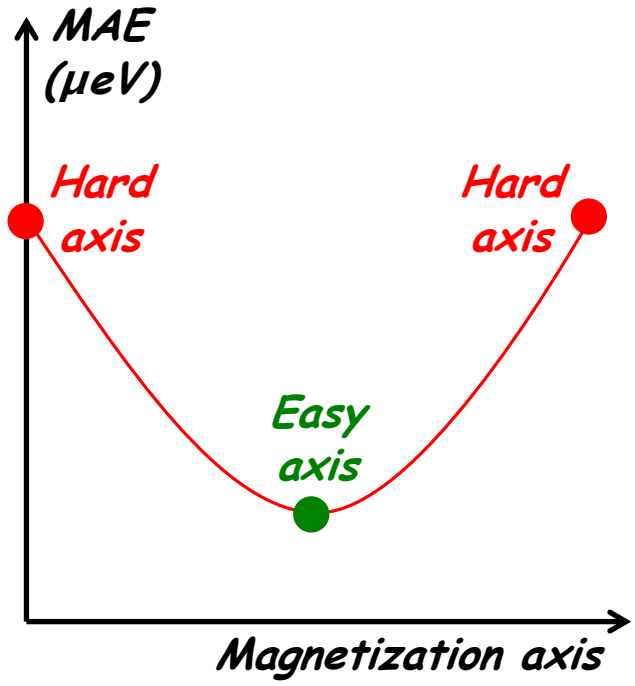
Estimation of the Magneto-crystalline Anisotropy Energy (MAE) of CuO

Allows to define the magnetization easy and hard axes

Here we have considered the following expression:

$$MAE = E[u\ v\ w] - E[easy\ axis]$$

E[uvw] is the energy deduced from spin-orbit calculations with the magnetization along the [uvw] crystallographic direction



[1] X. Rocquefelte, P. Blaha, K. Schwarz, S. Kumar, J. van den Brink, Nature Comm. **4**, 2511 (2013)

III. Magnetic anisotropy

Estimation in WIEN2k

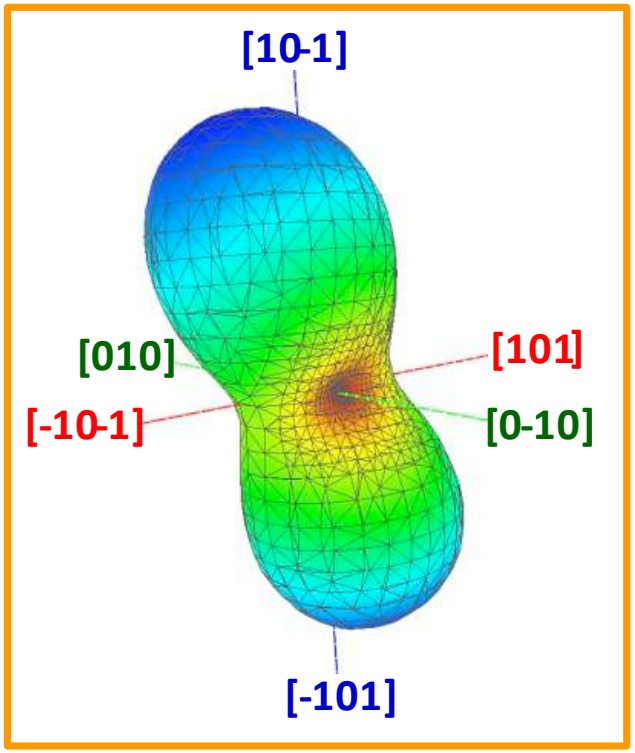
Estimation of the Magneto-crystalline Anisotropy Energy (MAE) of CuO

Allows to define the magnetization easy and hard axes

Here we have considered the following expression:

$$MAE = E[u\ v\ w] - E[easy\ axis]$$

E[uvw] is the energy deduced from spin-orbit calculations with the magnetization along the [uvw] crystallographic direction



[1] X. Rocquefelte, P. Blaha, K. Schwarz, S. Kumar, J. van den Brink, Nature Comm. **4**, 2511 (2013)

III. Magnetic anisotropy

Estimation in WIEN2k

PHYSICAL REVIEW B **82**, 220402(R) (2010)

J dependence in the LSDA+*U* treatment of noncollinear magnets

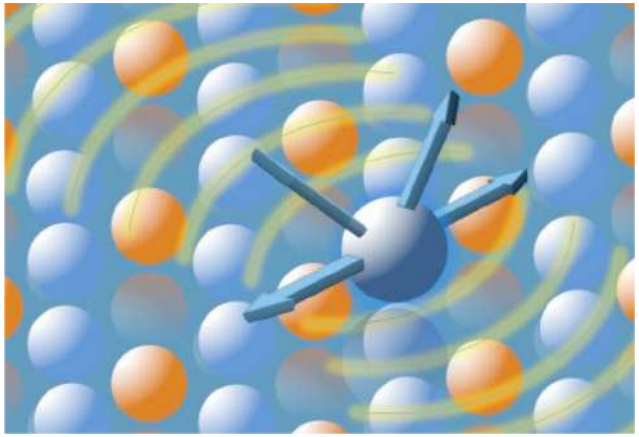
Eric Bousquet[1,2] and Nicola Spaldin[3]
[1]*Materials Department, University of California, Santa Barbara, California 93106, USA*
[2]*Physique Théorique des Matériaux, Université de Liège, B-4000 Sart Tilman, Belgium*
[3]*Department of Materials, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland*
(Received 30 October 2010; published 13 December 2010)

We re-examine the commonly used density-functional theory plus Hubbard *U* (DFT+*U*) method for the case of noncollinear magnets. While many studies neglect to explicitly include the exchange-correction parameter *J*, or consider its exact value to be unimportant, here we show that in the case of noncollinear magnetism calculations the *J* parameter can strongly affect the magnetic ground state. We illustrate the strong *J* dependence of magnetic canting and magnetocrystalline anisotropy by calculating trends in the magnetic lithium orthophosphate family LiMPO$_4$ (M=Fe and Ni) and difluorite family MF$_2$ (M=Mn, Fe, Co, and Ni). Our results can be readily understood by expanding the usual DFT+*U* equations within the spinor scheme, in which the *J* parameter acts directly on the off-diagonal components which determine the spin canting.

DOI: 10.1103/PhysRevB.82.220402 PACS number(s): 75.30.−m, 71.10.−w

Be careful! No ideal functional to deals with non-collinear magnetism

IV. Last but not the least



Magnetic properties:

- ✓ Spin-state (high/low)
- ✓ Long-range/short-range orders
- ✓ Collinear / non-collinear
- ✓ Magnetic anisotropy
- ✓ Magnetic frustration
- ✓ Magnetic exchange

Which model Hamiltonian?

Open question for the data treatment of both experimental and theoretical investigations!

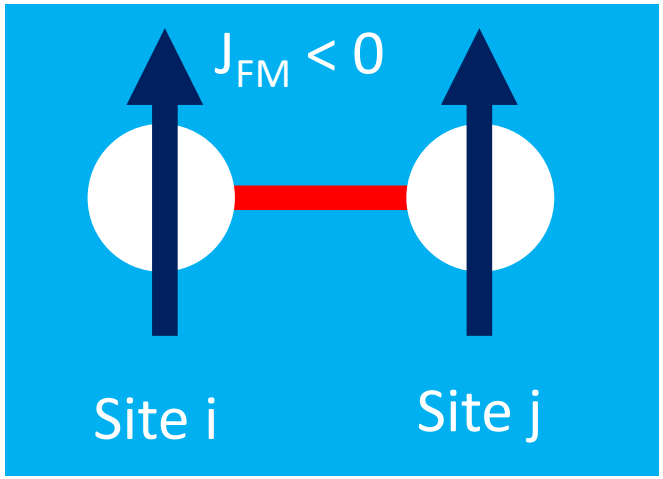
IV. Last but not the least

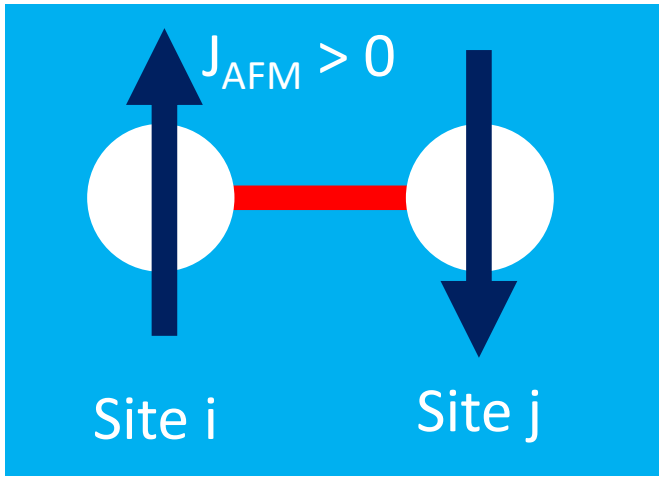
General spin Hamiltonian describing the magnetic properties of a material with localized electrons

$$\hat{H}_{spin}=\sum_{i<j} J_{ij}\left(\hat{S}_i.\hat{S}_j\right)$$

J_{ij} : Symmetric exchange interaction

(Heisenberg exchange interaction)





DOI: 10.1039/c2dt31662e

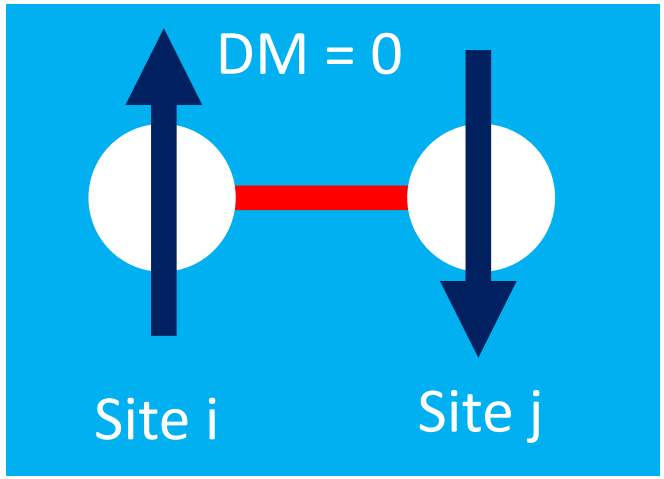
IV. Last but not the least

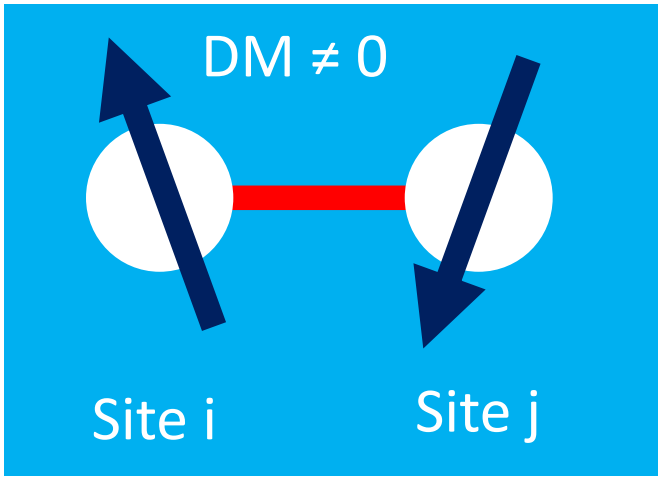
General spin Hamiltonian describing the magnetic properties of a material with localized electrons

$$\hat{H}_{spin}=\sum_{i<j} J_{ij}\left(\hat{S}_i.\hat{S}_j\right)+\sum_{i<j}\vec{D}_{ij}\left(\hat{S}_i\times\hat{S}_j\right)$$

$\vec{D}_{ij}$: Antisymmetric exchange interaction

(Dzyaloshinskii-Moriya interaction)





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IV. Last but not the least

General spin Hamiltonian describing the magnetic properties of a material with localized electrons

$$\hat{H}_{spin} = \sum_{i<j} J_{ij}\left(\hat{S}_i.\hat{S}_j\right) + \sum_{i<j} \vec{D}_{ij}\left(\hat{S}_i \times \hat{S}_j\right) + \sum_i A_i S_{iz}^2 + \sum_{i<j} K_{ij}\left(\hat{S}_i.\hat{S}_j\right)^2 + \cdots$$

J_{ij} : Symmetric exchange interaction
(Heisenberg exchange interaction)

$\vec{D}_{ij}$: Antisymmetric exchange interaction
(Dzyaloshinskii-Moriya interaction)

A_i : « Single-ion » anisotropy
(Easy/hard axes of magnetization)

K_{ij} : Biquadratic interaction
(fourth-order perturbation to the Hubbard model)

} $Spin - orbit\ coupling$

Grazie per l'attenzione
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