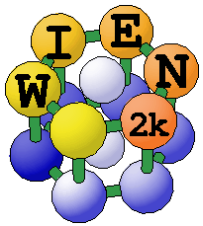

20th WIEN2k Workshop
PennStateUniversity – 2013

TU WIEN

Relativistic effects
&
Non-collinear magnetism

(WIEN2k / WIENncm)

Xavier Rocquefelte
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UNIVERSITÉ DE NANTES

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/
- Robert Laskowski (Non-collinear magnetic version of WIEN2k package)

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:

- http://www2.slac.stanford.edu/vvc/theory/relativity.html
- wienlist digest - http://www.wien2k.at/reg_user/index.html
- wikipedia …

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*

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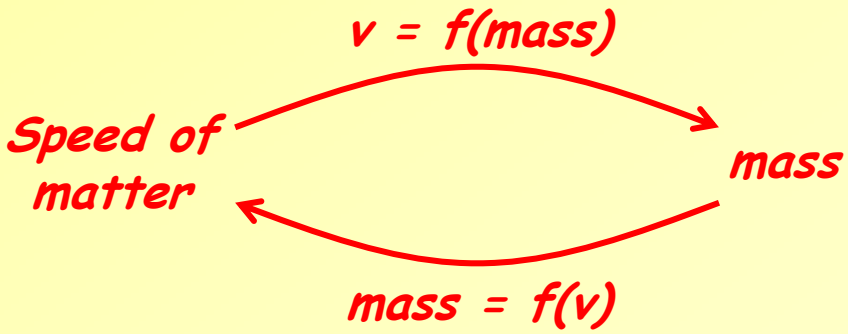
Composed of atoms (mass)



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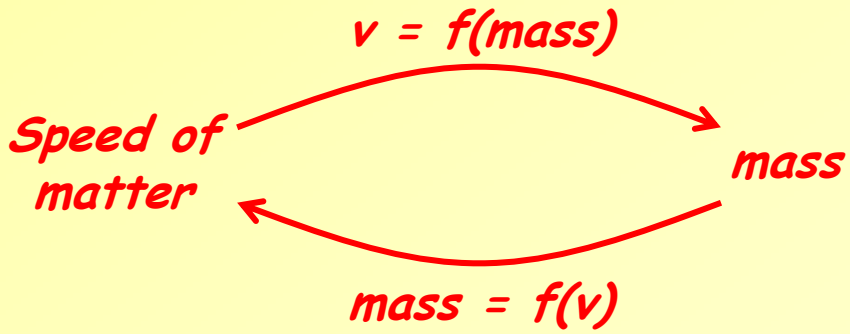


Lorentz Factor (measure of the relativistic effects)

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

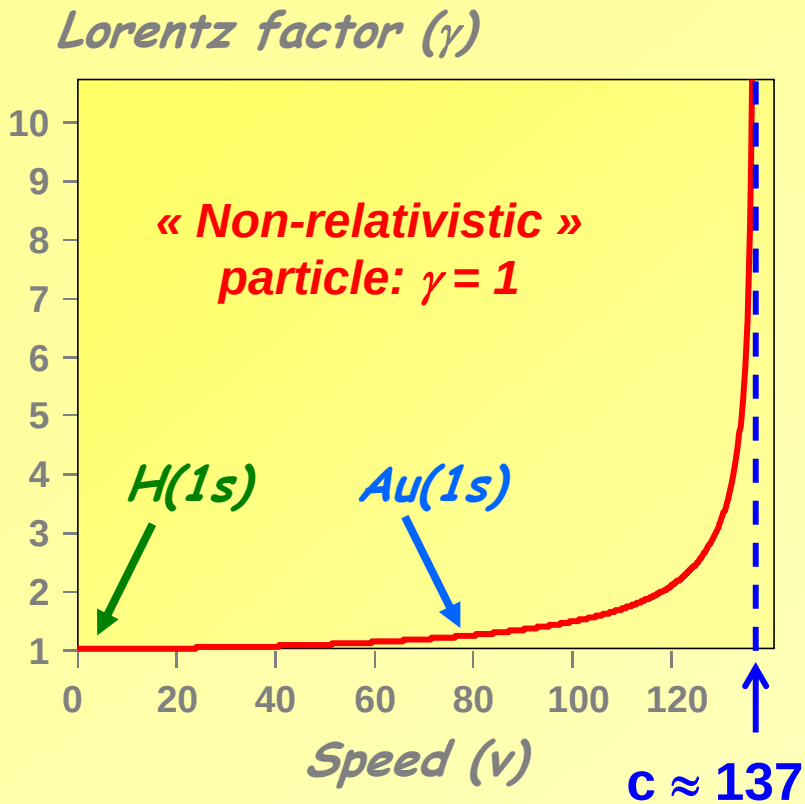
Relativistic mass: $M = \gamma m$ (m: rest mass)

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

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

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

Definition of a relativistic particle (Bohr model)



c ≈ 137 au

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

Relativistic effects

1) The mass-velocity correction

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

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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**)

**Analysis of Erwin Schrödinger of the wave packet solutions of the Dirac equation for relativistic electrons in free space: The interference between positive and negative energy states produces what appears to be a fluctuation (at the speed of light) of the position of an electron around the median.*

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

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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

One electron radial Schrödinger equation

HARTREE ATOMIC UNITS

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

Atomic units:
$\hbar = m_e = e = 1$
$1/(4\pi\varepsilon_0) = 1$
$c = 1/\alpha \approx 137$ au

INTERNATIONAL UNITS

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

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

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

In a spherically symmetric potential

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

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

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

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Dirac Hamiltonian: a brief description

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

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

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

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Momentum operator

Rest mass

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V → *Electrostatic potential*

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

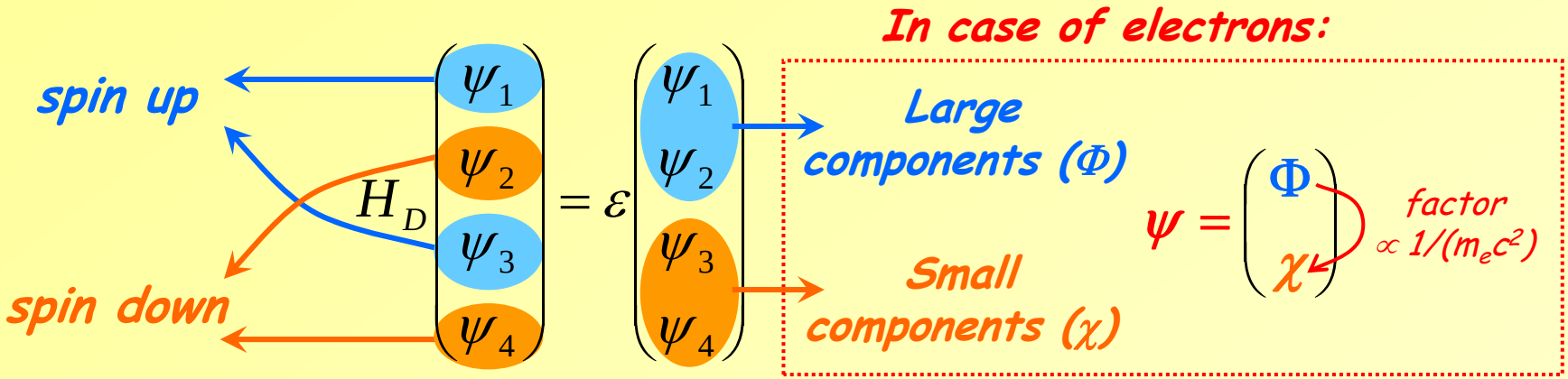
(2×2) unit and zero matrices

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

(2×2) Pauli spin matrices

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:

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

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

Dirac equation: H_D and Ψ are 4-dimensional

➡ *For a free particle (i.e. V = 0):*

Solution in the slow particle limit (p=0)

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

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

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

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

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

For a spherical potential 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 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: $M_e(r) = m_e + \dfrac{\varepsilon' - V(r)}{2c^2}$

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

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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

No approximation have been made so far

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

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: $\int\left(\tilde{g}_{nl}^2+\tilde{f}_{nl}^2\right)r^2dr=1$

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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*

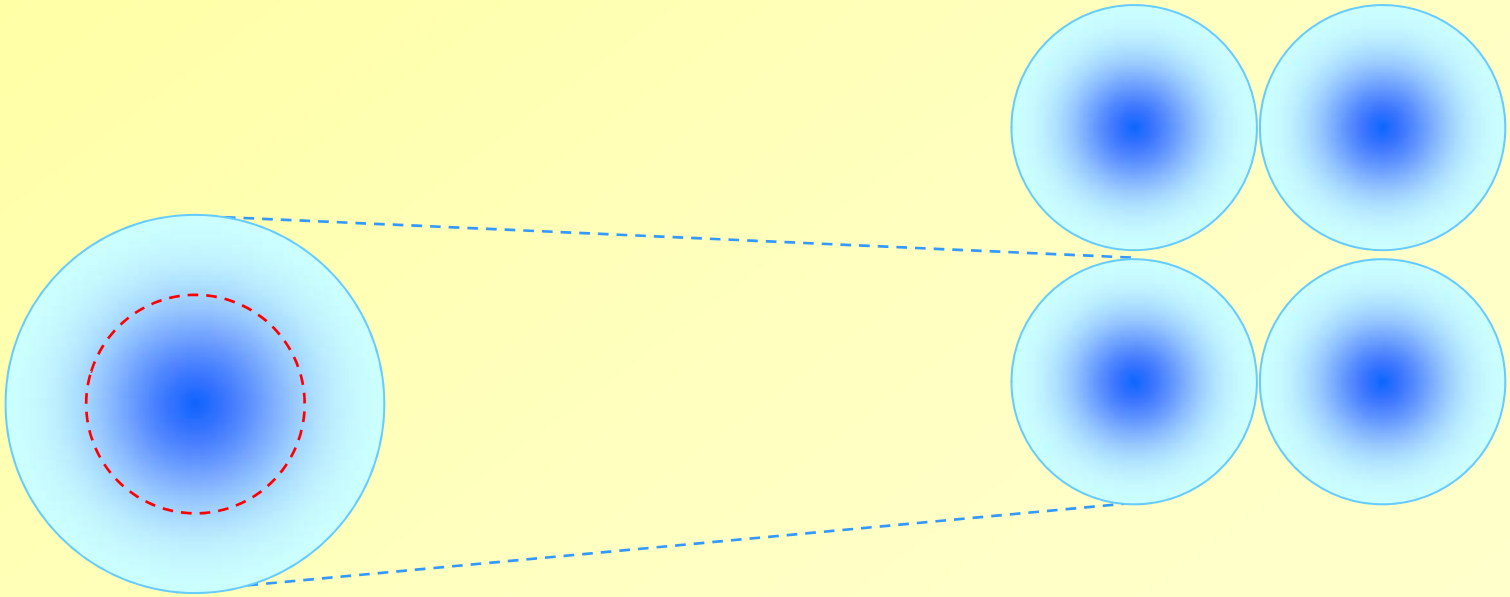
Relativistic effects in a solid

➡ *For a molecule or a solid:*

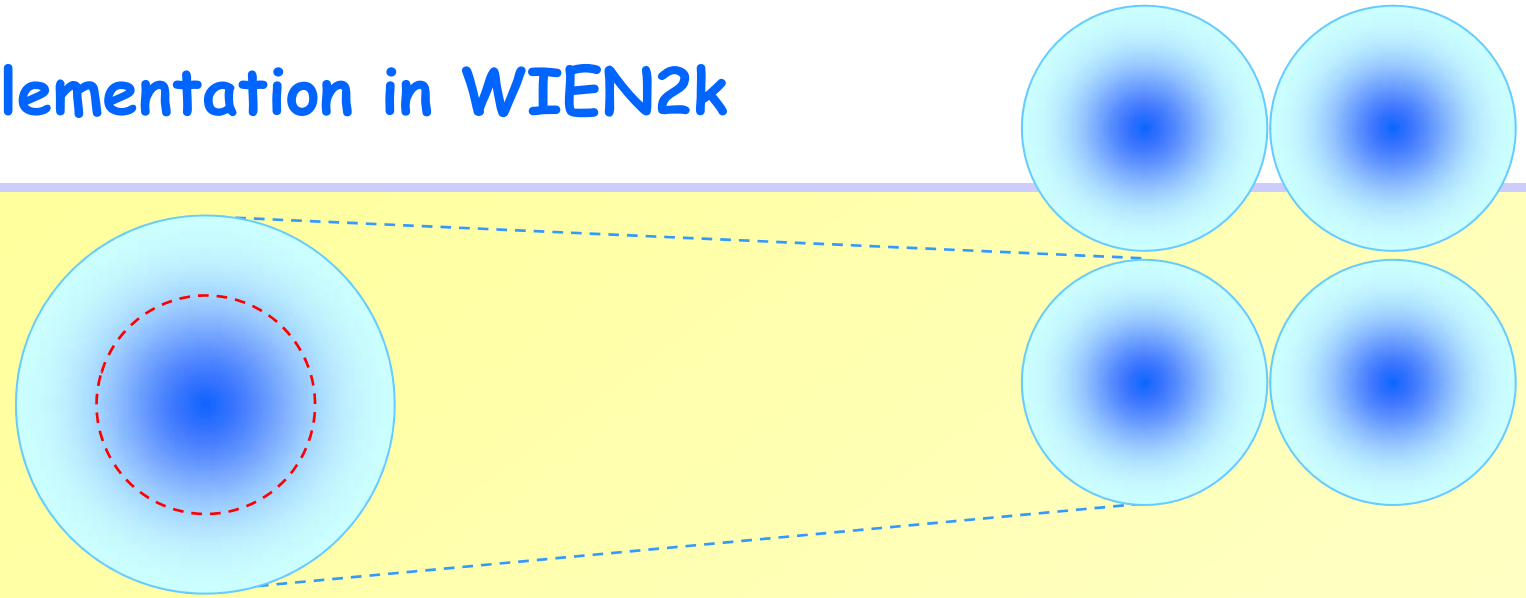
Relativistic effects originate deep inside the core.

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*



Implementation in WIEN2k



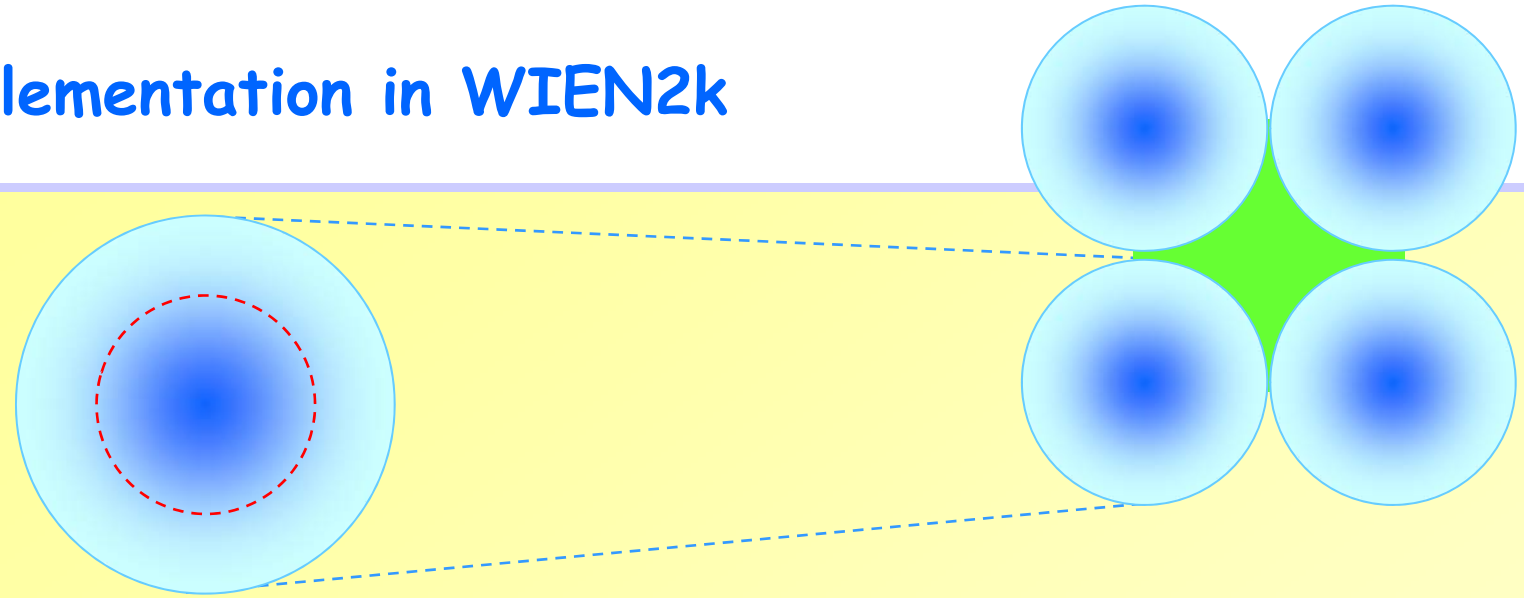
Atomic sphere (RMT) Region

Core electrons → *« Fully » relativistic* → *Spin-compensated Dirac equation*

Valence electrons → *Scalar relativistic (no SOC)* → *Possibility to add SOC (2nd variational)*

SOC: Spin orbit coupling

Implementation in WIEN2k



Atomic sphere (RMT) Region

Core electrons

« Fully » relativistic

Spin-compensated Dirac equation

Valence electrons

Scalar relativistic (no SOC)

Possibility to add SOC (2nd variational)

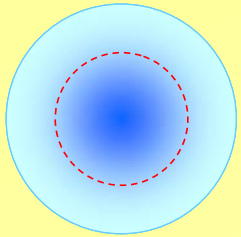
Interstitial Region

Valence electrons

Not relativistic

SOC: Spin orbit coupling

Implementation in WIEN2k: core electrons



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

Atomic sphere (RMT) Region

Core electrons

« Fully » relativistic

Spin-compensated Dirac equation

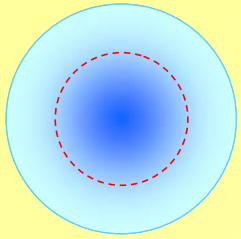
For spin-polarized potential, spin up and spin down are calculated separately, the density is averaged according to the occupation number specified in case.inc file.

	l	j=l+s/2		κ=-s(j+1/2)		occupation	
		s=-1	s=+1	s=-1	s=+1	s=-1	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
1,-1,2     ( n,κ,occup)
2,-1,2     ( n,κ,occup)
2, 1,2     ( n,κ,occup)
2,-2,4     ( n,κ,occup)
3,-1,2     ( n,κ,occup)
3, 1,2     ( n,κ,occup)
3,-2,4     ( n,κ,occup)
3, 2,4     ( n,κ,occup)
3,-3,6     ( n,κ,occup)
4,-1,2     ( n,κ,occup)
4, 1,2     ( n,κ,occup)
4,-2,4     ( n,κ,occup)
4, 2,4     ( n,κ,occup)
4,-3,6     ( n,κ,occup)
5,-1,2     ( n,κ,occup)
4, 3,6     ( n,κ,occup)
4,-4,8     ( n,κ,occup)
 0
```

Implementation in WIEN2k: core electrons



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Spin-compensated Dirac equation

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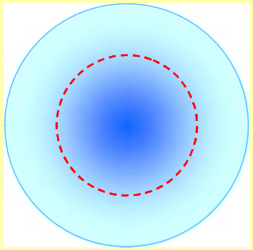
	l	j=l+s/2 s=-1	j=l+s/2 s=+1	κ=-s(j+1/2) s=-1	κ=-s(j+1/2) s=+1	occupation s=-1	occupation s=+1
s	0		1/2		-1		2
p	1	1/2	3/2	1	-2	2	4
d	2	3/2	5/2	2	-3	4	6
f	3	5/2	7/2	3	-4	6	8

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
```

Implementation in WIEN2k: valence electrons

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



Atomic sphere (RMT) Region

Valence electrons

Scalar relativistic (no SOC)

```
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)

Implementation in WIEN2k: valence electrons

SOC is added in a second variation (lapwso):

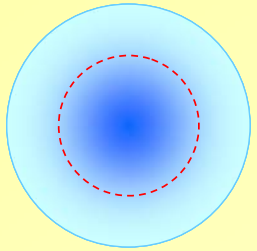
- *First diagonalization (lapw1):* $H_1\Psi_1 = \varepsilon_1\Psi_1$
- *Second diagonalization (lapwso):* $(H_1 + H_{SO})\Psi = \varepsilon\Psi$

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***



Atomic sphere (RMT) Region

Valence electrons

Scalar relativistic (no SOC)

Possibility to add SOC (2nd variational)

Implementation in WIEN2k: valence electrons

SOC is added in a second variation (lapwso):

- *First diagonalization (lapw1):* $H_1\Psi_1 = \varepsilon_1\Psi_1$
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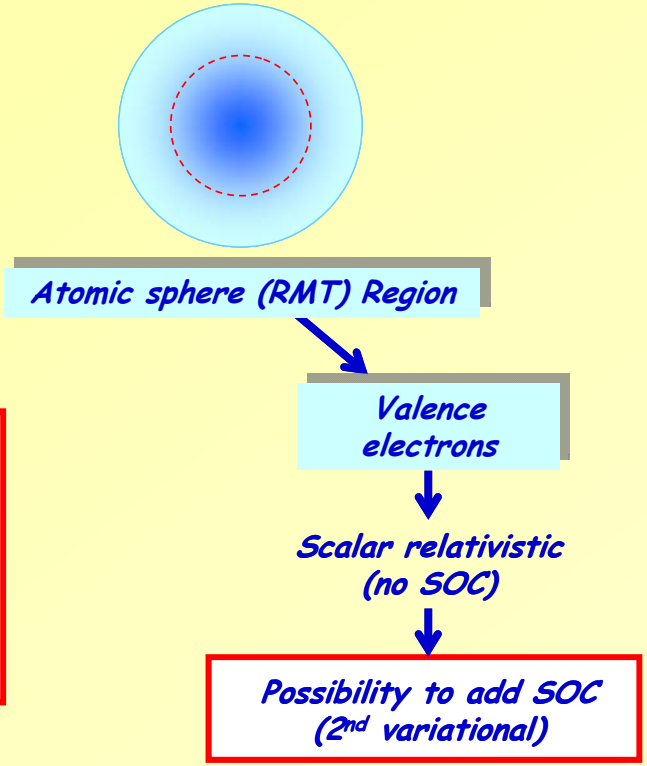
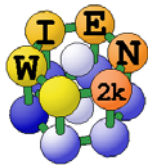


♦ SOC is active only inside atomic spheres, only spherical potential (V_{MT}) is taken into account, in the polarized case spin up and down parts are averaged.

♦ 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
```

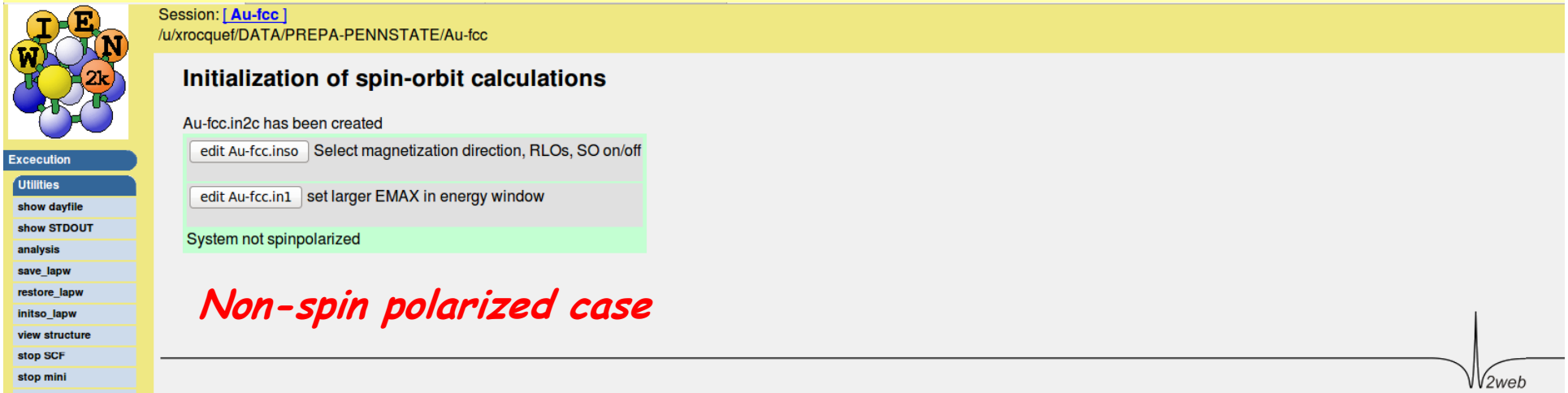
  - case.in1(c):

```
(…)
 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

Controlling spin-orbit coupling in WIEN2k

The w2web interface is helping you



Non-spin polarized case

Controlling spin-orbit coupling in WIEN2k

The w2web interface is helping you

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

- Excecution
- 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

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

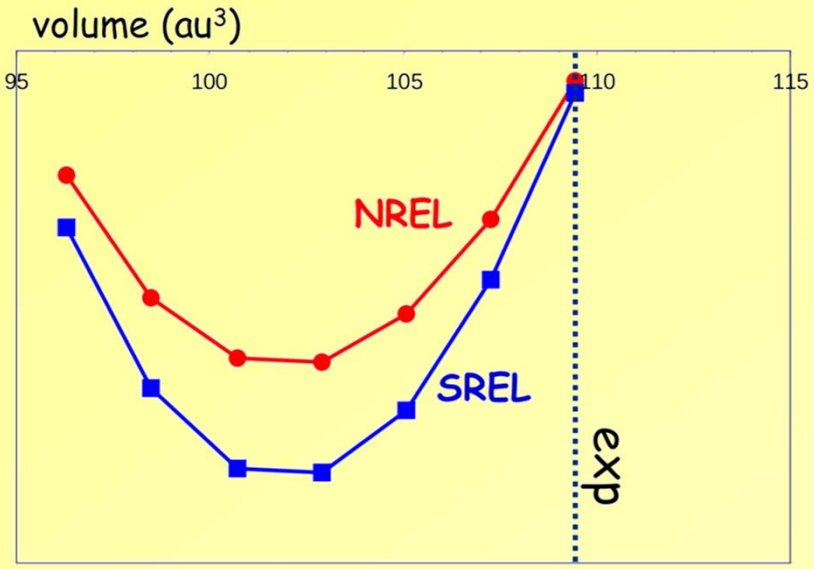
edit Co-hcp.klist — view Co-hcp.klist

w2web

Relativistic effects in the solid: Illustration

hcp-Be

Z = 4



LDA overbinding (7%)

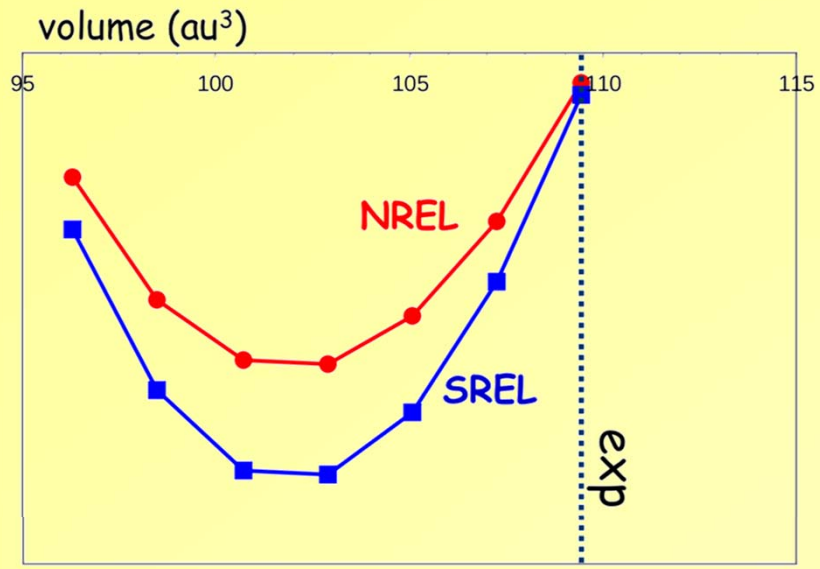
No difference NREL/SREL

Bulk modulus:

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

Relativistic effects in the solid: Illustration

hcp-Be
Z = 4



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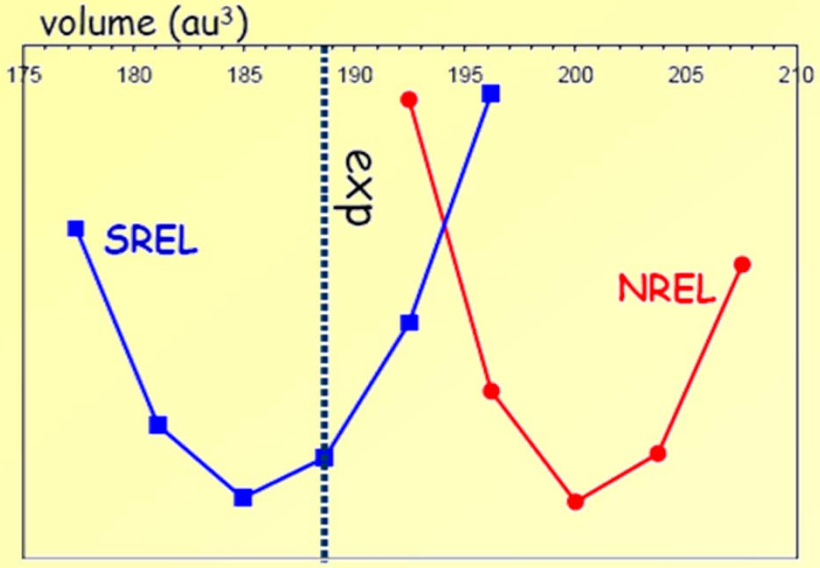
hcp-Os
Z = 76



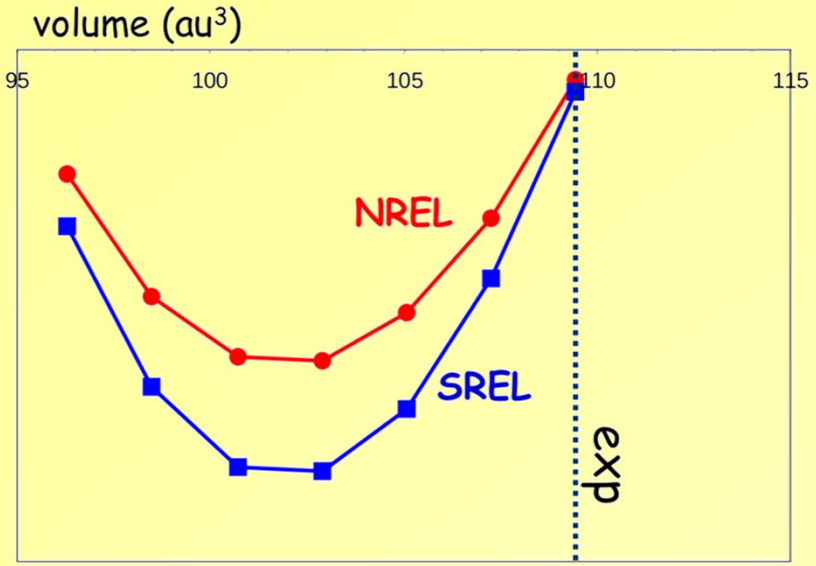
LDA overbinding (2%)

Clear difference NREL/SREL

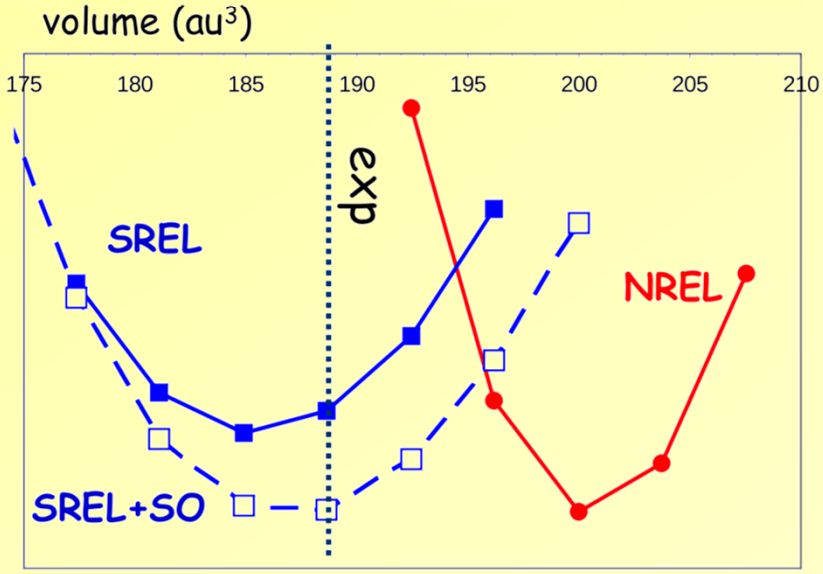
Bulk modulus:
- NREL: 344 GPa
- SREL: 447 GPa
- Exp.: 462 GPa

Relativistic effects in the solid: Illustration

hcp-Be
Z = 4



hcp-Os
Z = 76



♦ **Scalar-relativistic** (SREL):

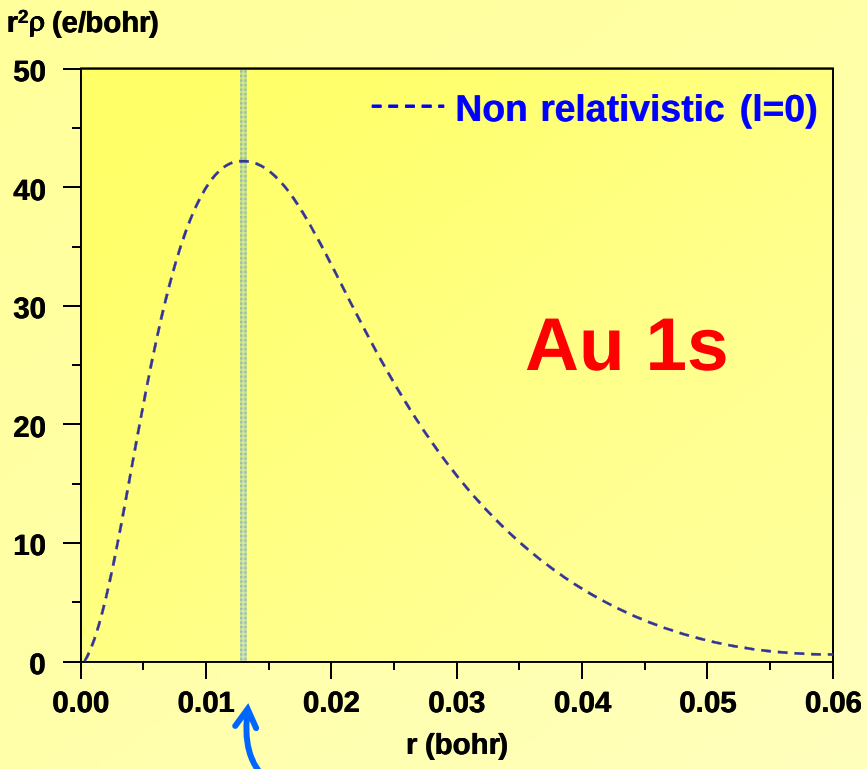
- LDA overbinding (2%)
- Bulk modulus: 447 GPa

\+ **spin-orbit coupling (SREL+SO):**

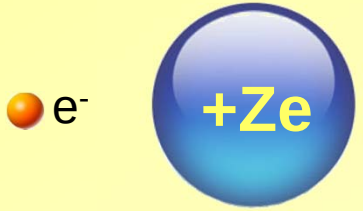
- LDA overbinding (1%)
- Bulk modulus: 436 GPa

⇒ **Exp. Bulk modulus: 462 GPa**

(1) Relativistic orbital contraction



Radius of the 1s orbit (Bohr model):

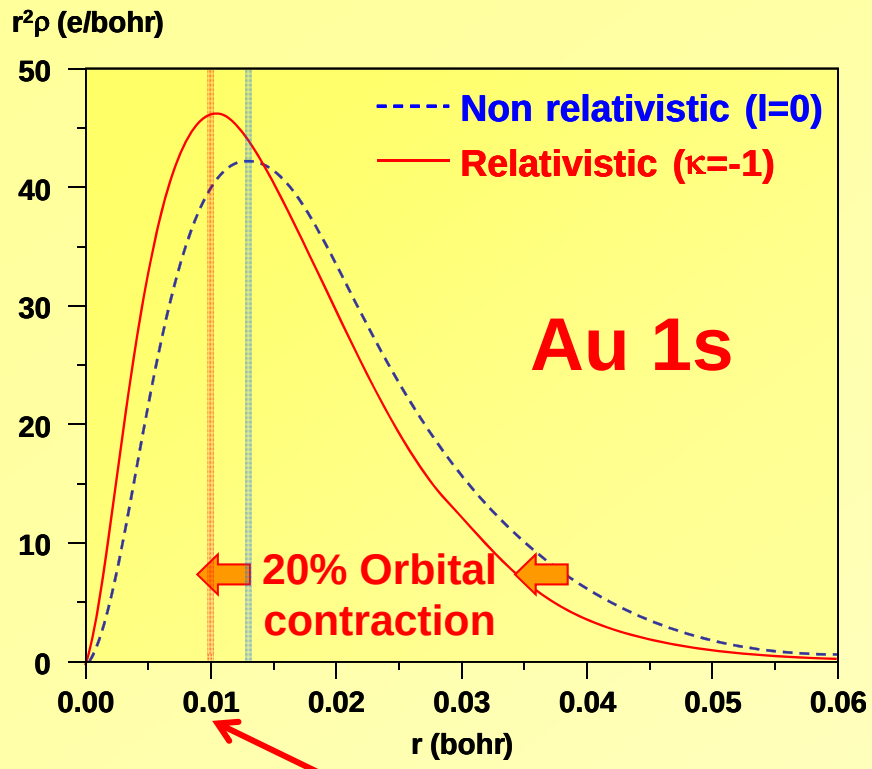


$$r(1s) = \frac{n^2 a_0}{Z} \quad \textbf{AND} \quad a_0 = \frac{\hbar}{m_e c \alpha} = 1\,\text{bohr}$$

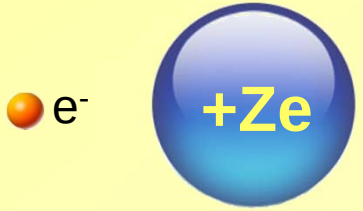
$$r(1s) = \frac{1}{79} = 0.013\,\text{bohr}$$

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

(1) Relativistic orbital contraction



Radius of the 1s orbit (Bohr model):



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

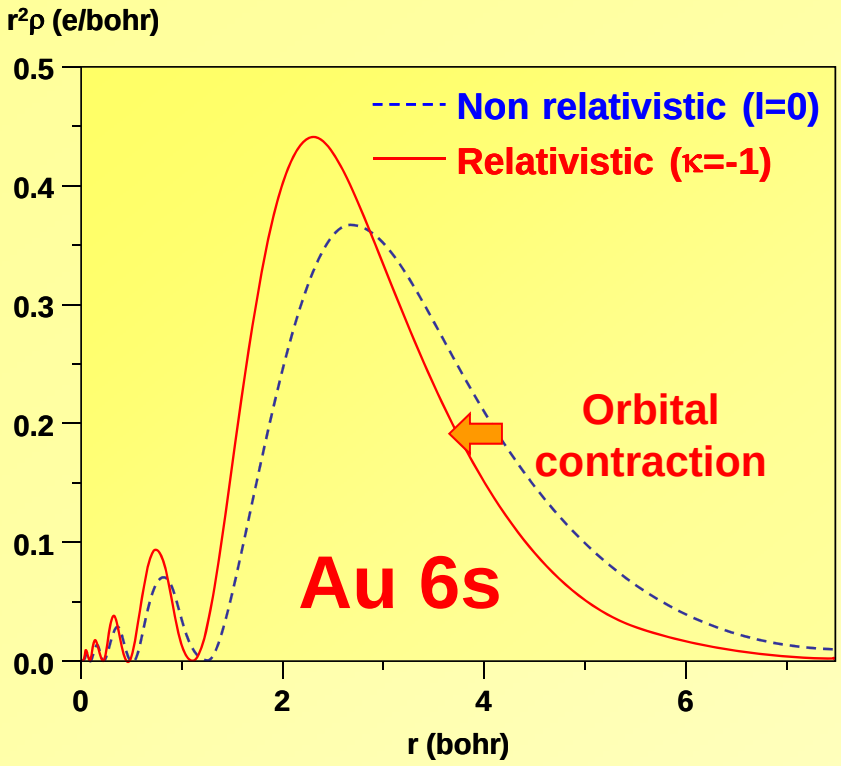
$$r(1s) = \frac{1}{79} = 0.013\,\text{bohr}$$

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

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

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

(1) Relativistic orbital contraction



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

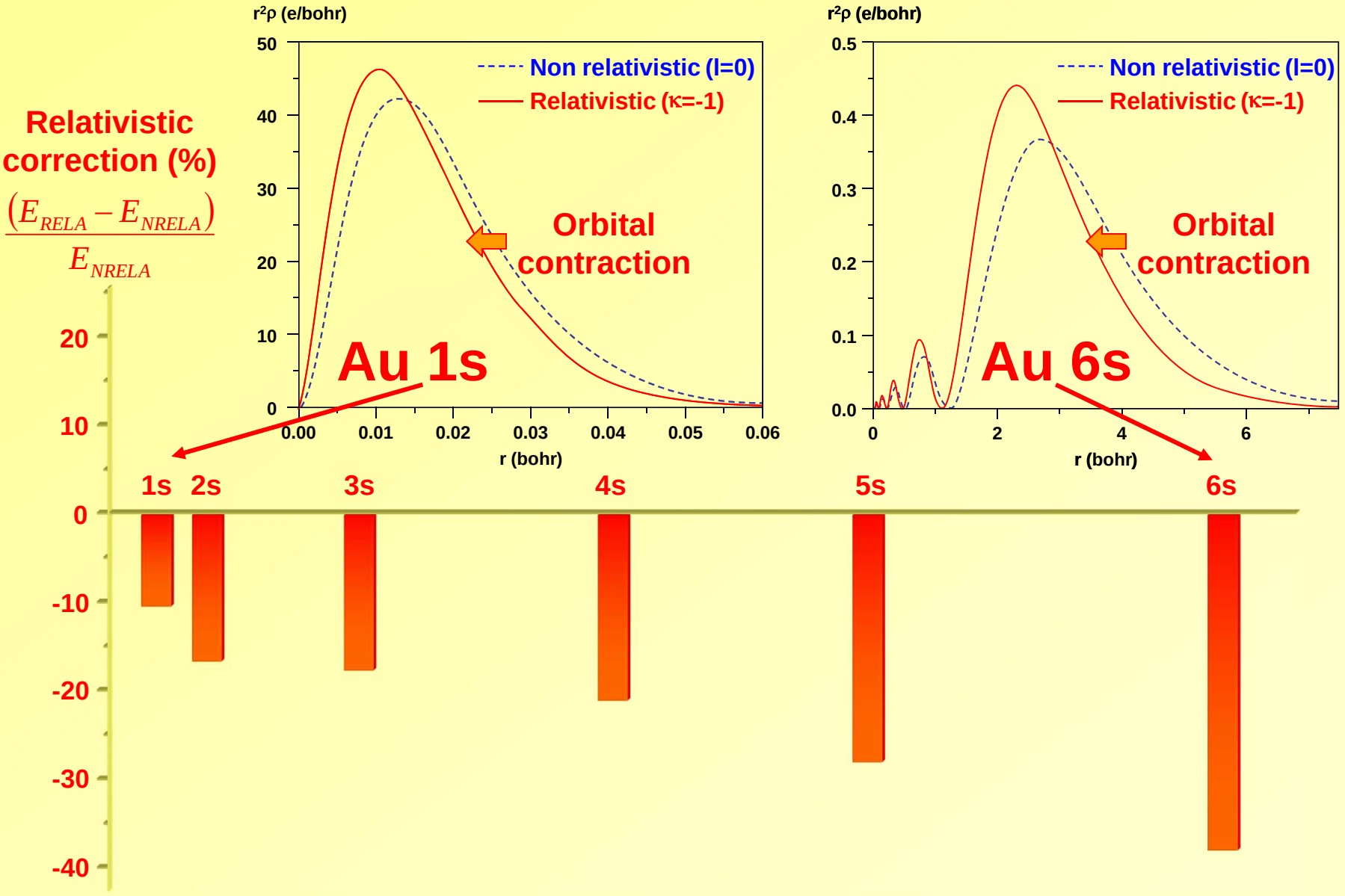
$$\gamma = \frac{1}{\sqrt{1-\left(\frac{v_e}{c}\right)^2}} = \frac{1}{\sqrt{1-(0.096)^2}} = 1.0046$$

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

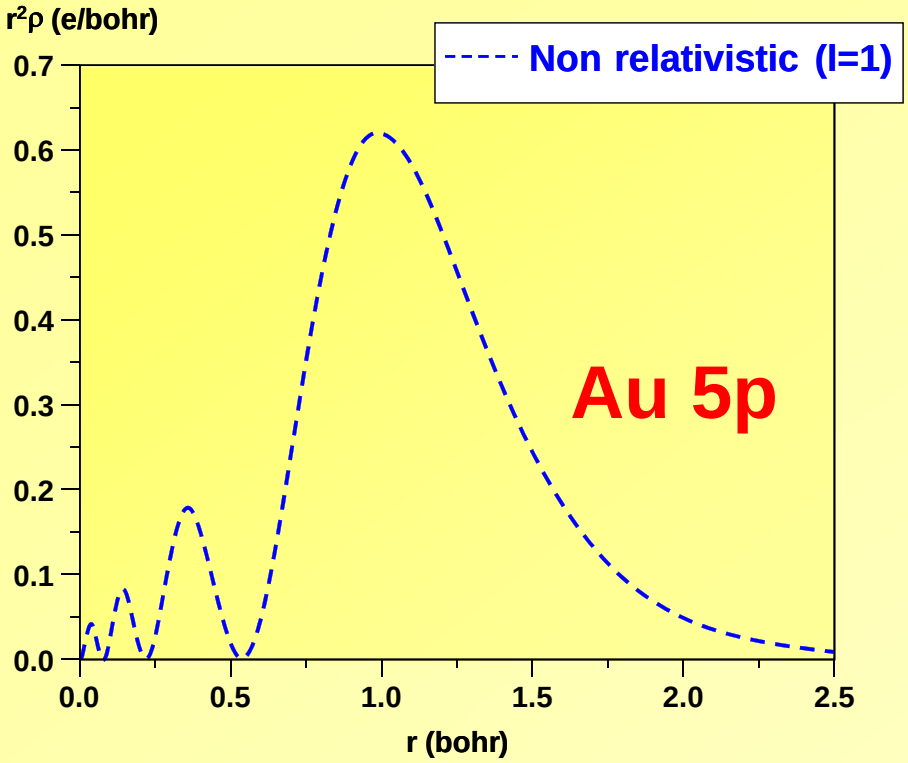
However, the relativistic contraction of the 6s orbital is large (>20%)

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

(1) Orbital Contraction: Effect on the energy

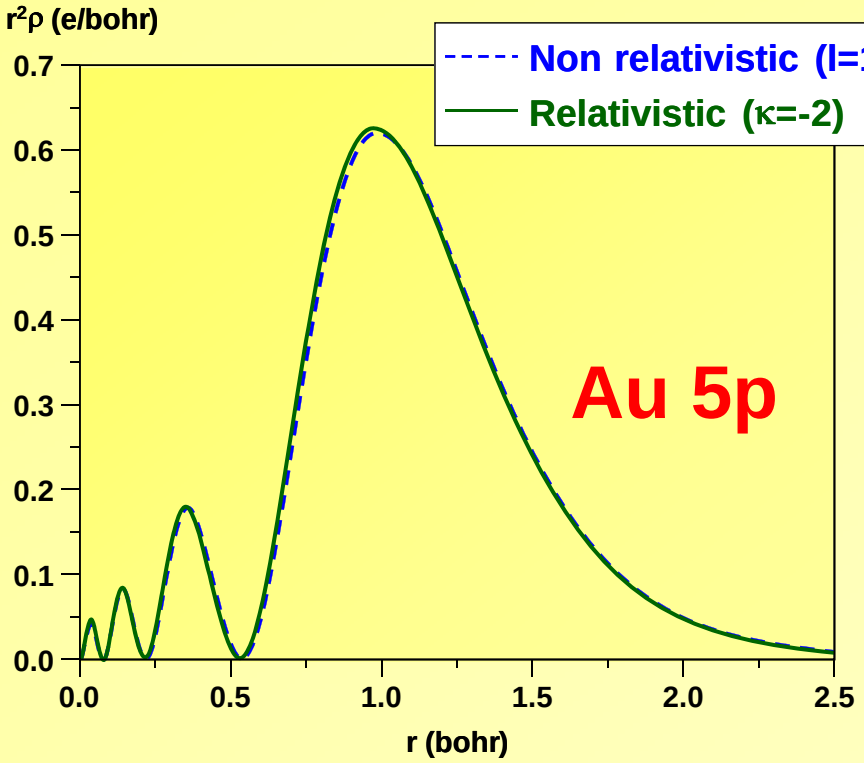


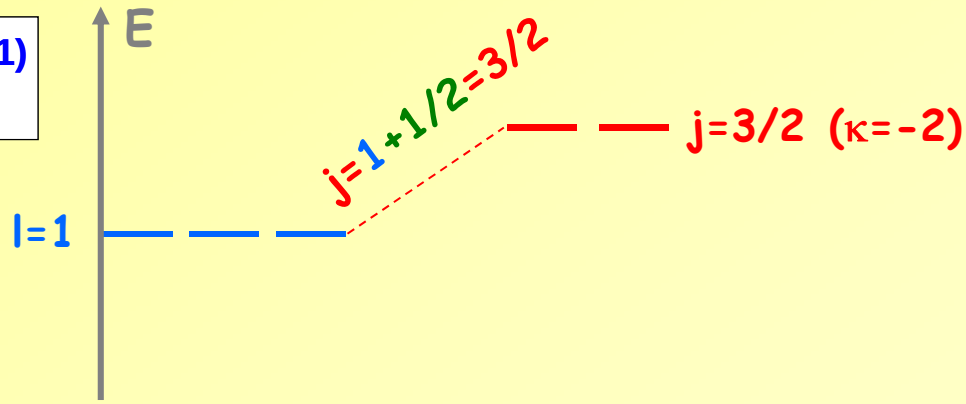
(2) Spin-Orbit splitting of p states



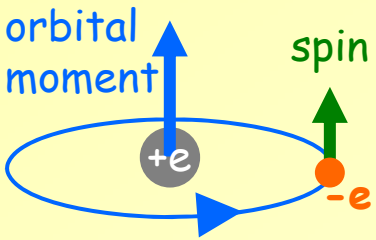
(2) Spin-Orbit splitting of p states

♦ Spin-orbit splitting of l-quantum number





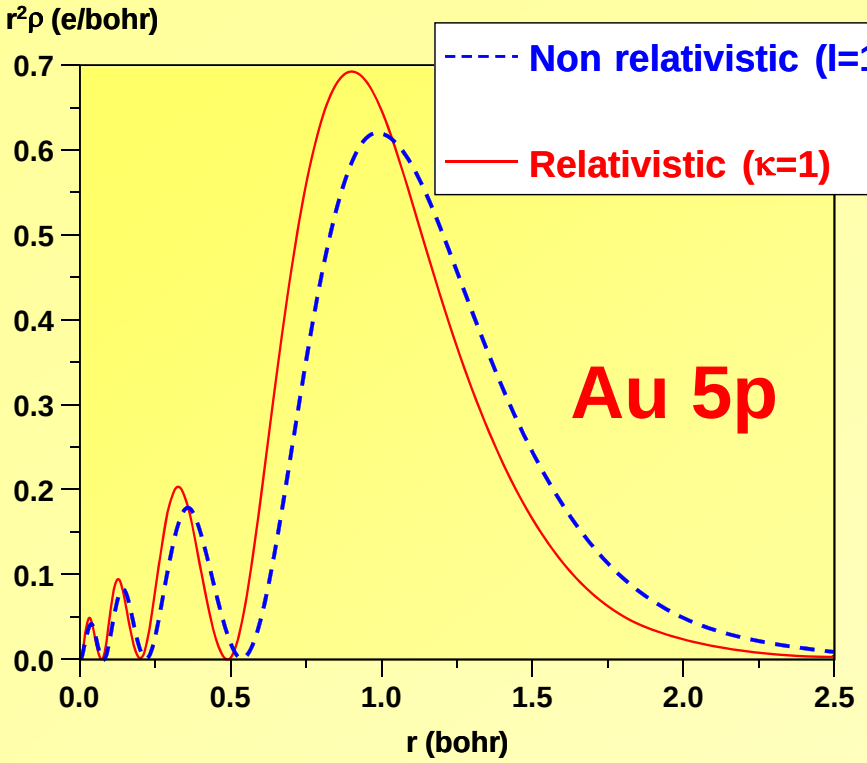
j=1+1/2=3/2

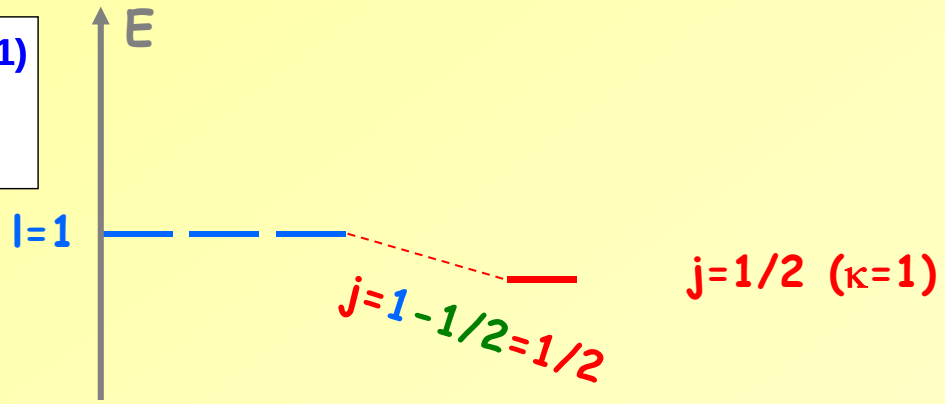


♦ $p_{3/2}$ (κ=-2): nearly same behavior than non-relativistic p-state

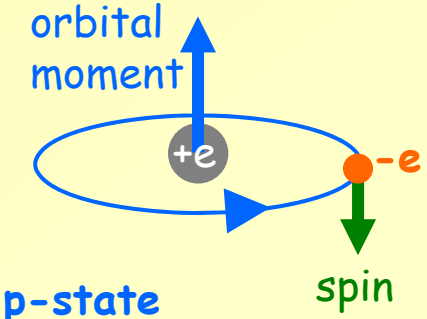
(2) Spin-Orbit splitting of p states

♦ Spin-orbit splitting of l-quantum number





j=1-1/2=1/2

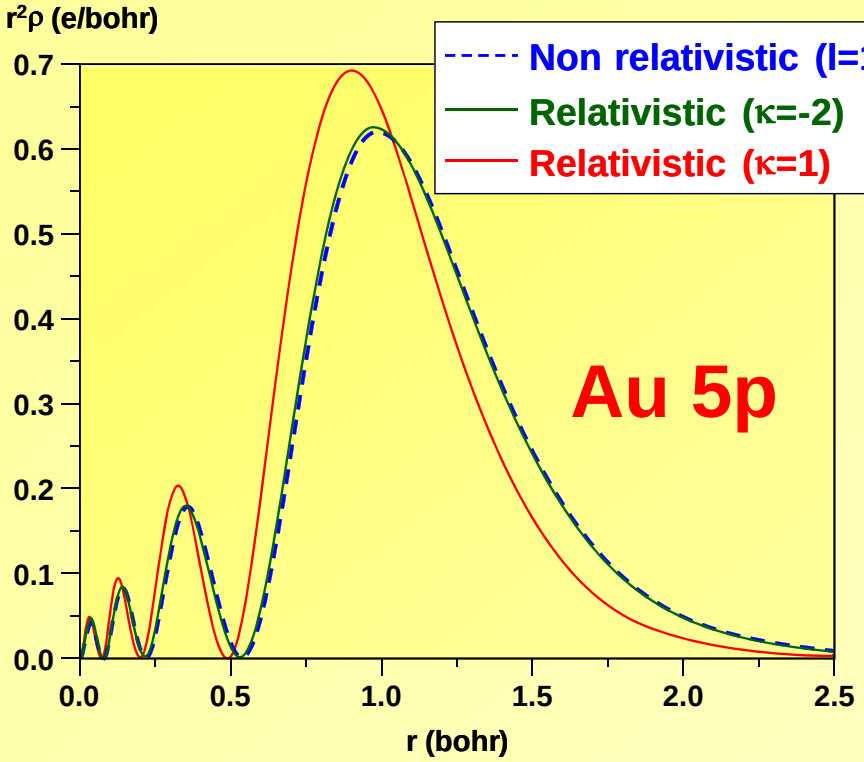


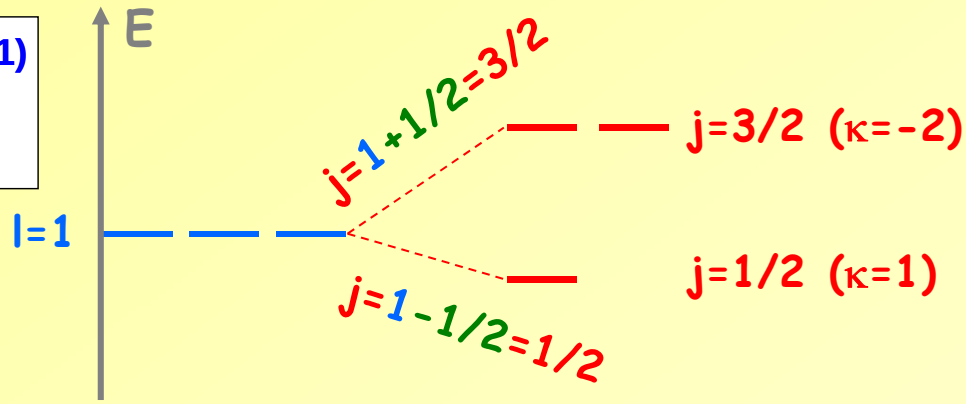
♦ $p_{1/2}$ (κ=1): markedly different behavior than non-relativistic p-state

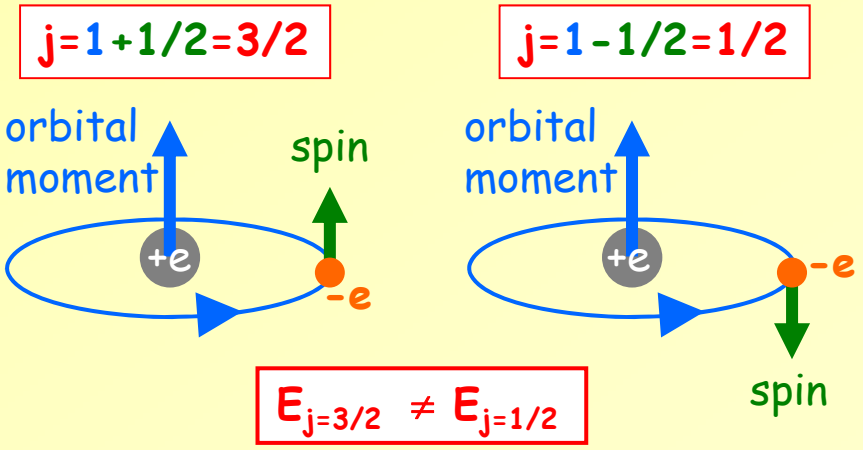
$g_{\kappa=1}$ is non-zero at nucleus

(2) Spin-Orbit splitting of p states

♦ Spin-orbit splitting of l-quantum number







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

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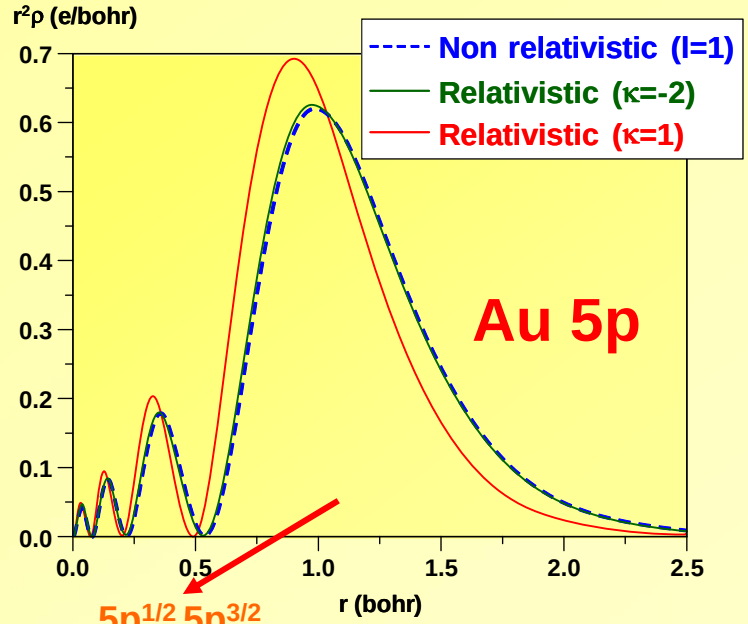
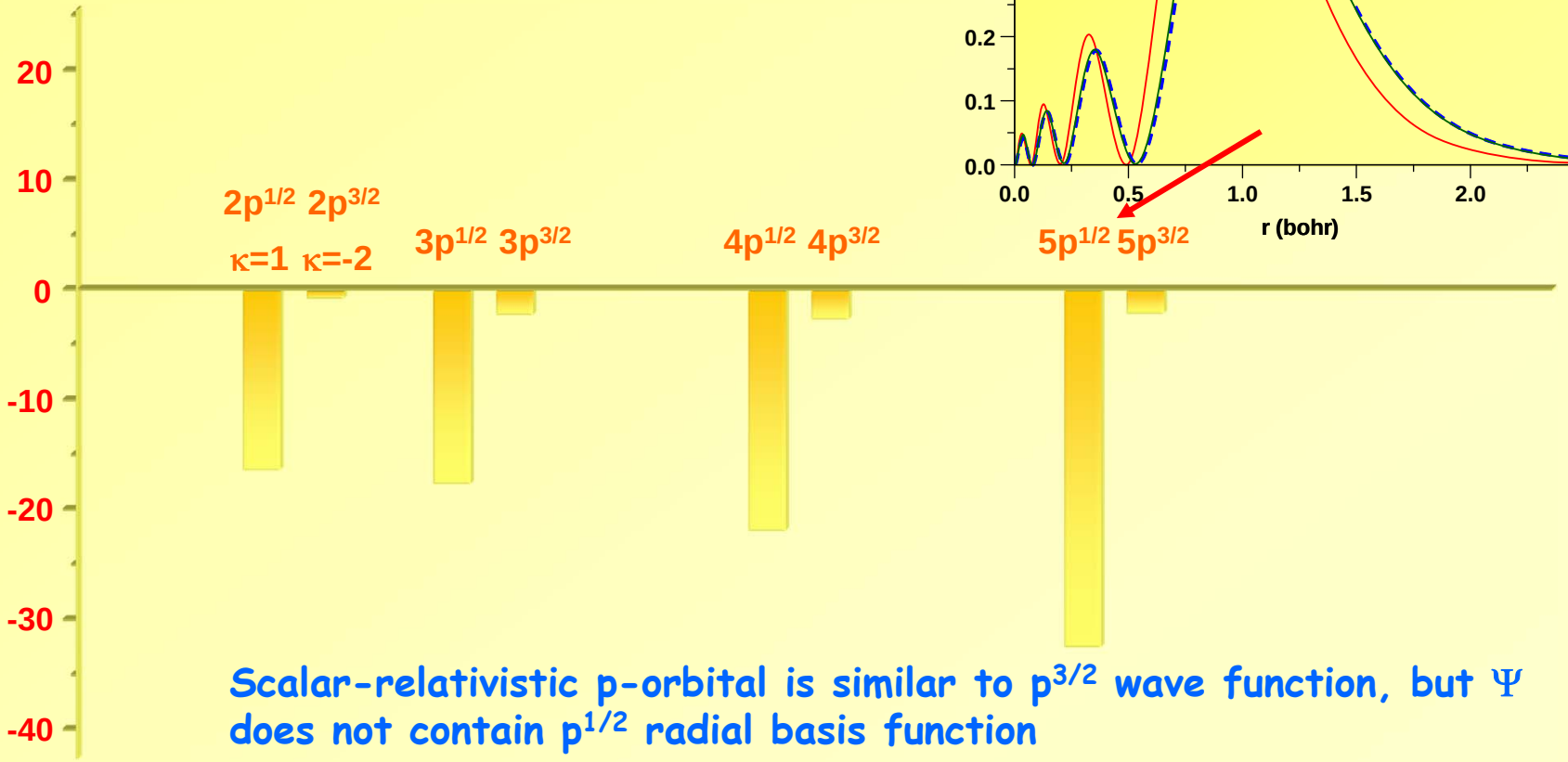
$g_{\kappa=1}$ is non-zero at nucleus

(2) Spin-Orbit splitting of p states



Relativistic correction (%)

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

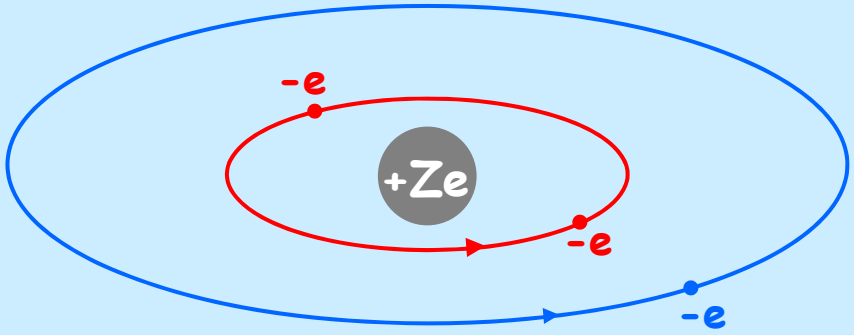


Scalar-relativistic p-orbital is similar to $p^{3/2}$ wave function, but Ψ does not contain $p^{1/2}$ radial basis function

(3) Orbital expansion: Au(d) states

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

Non-relativistic (NREL)



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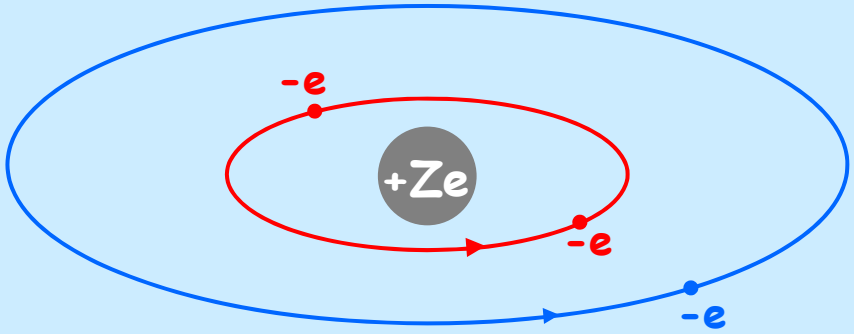
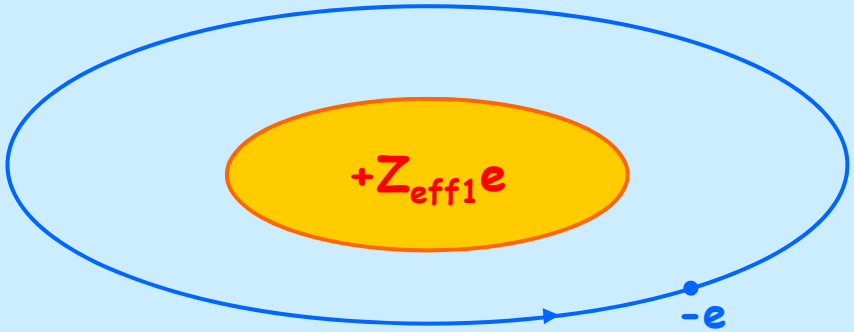


$Z_{eff1} = Z - \sigma(NREL)$



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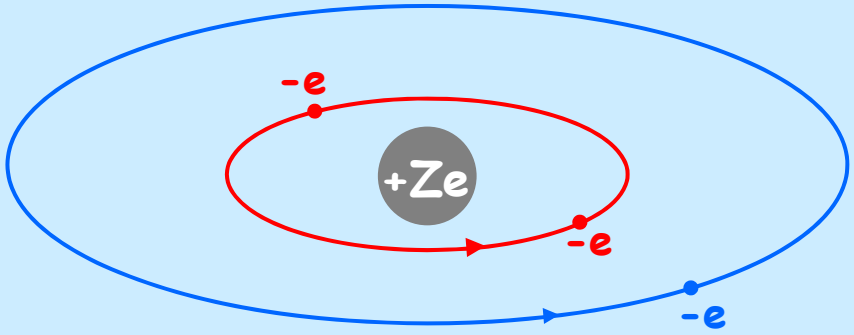
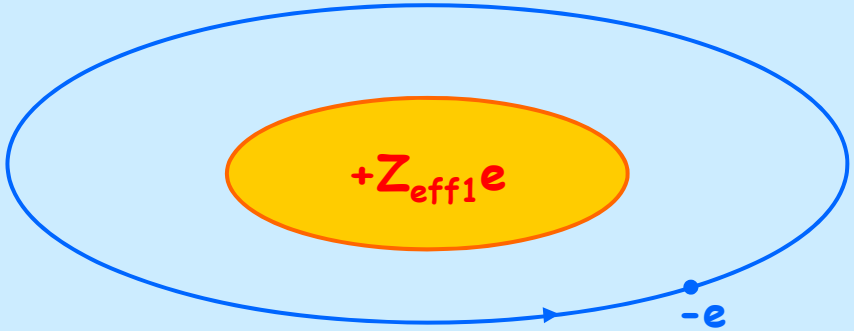
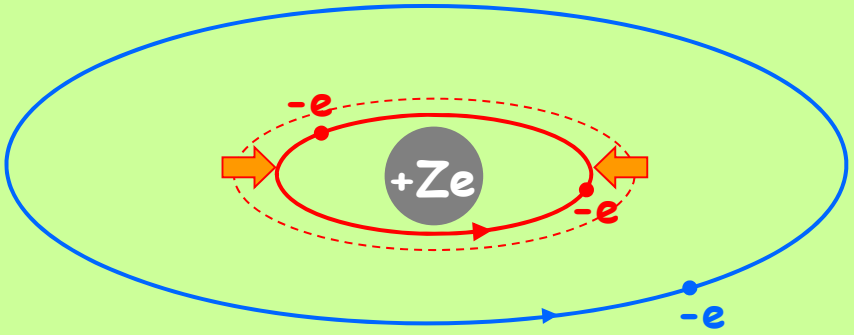


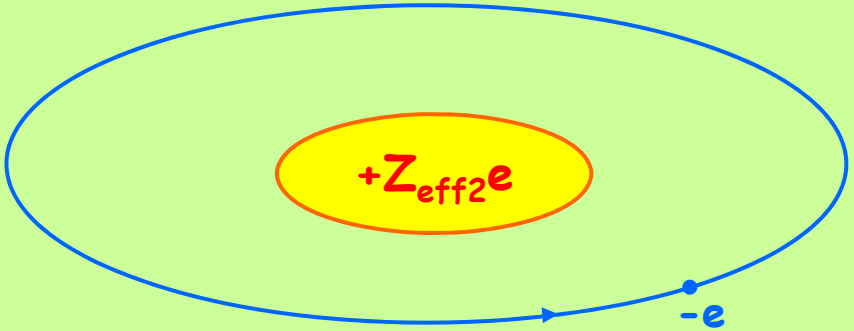
$Z_{eff1} = Z - \sigma(NREL)$



Relativistic (REL)



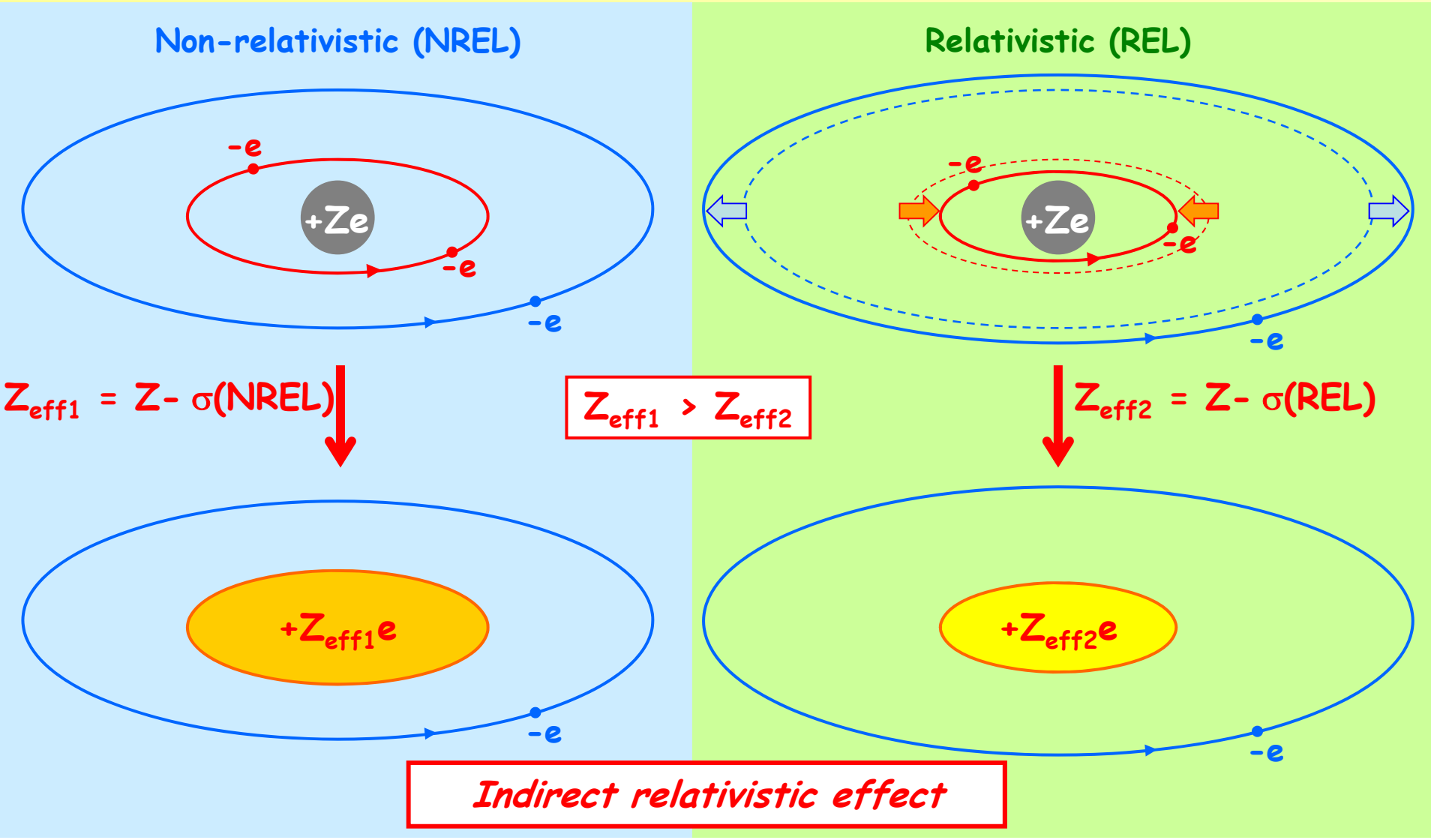
$Z_{eff2} = Z - \sigma(REL)$



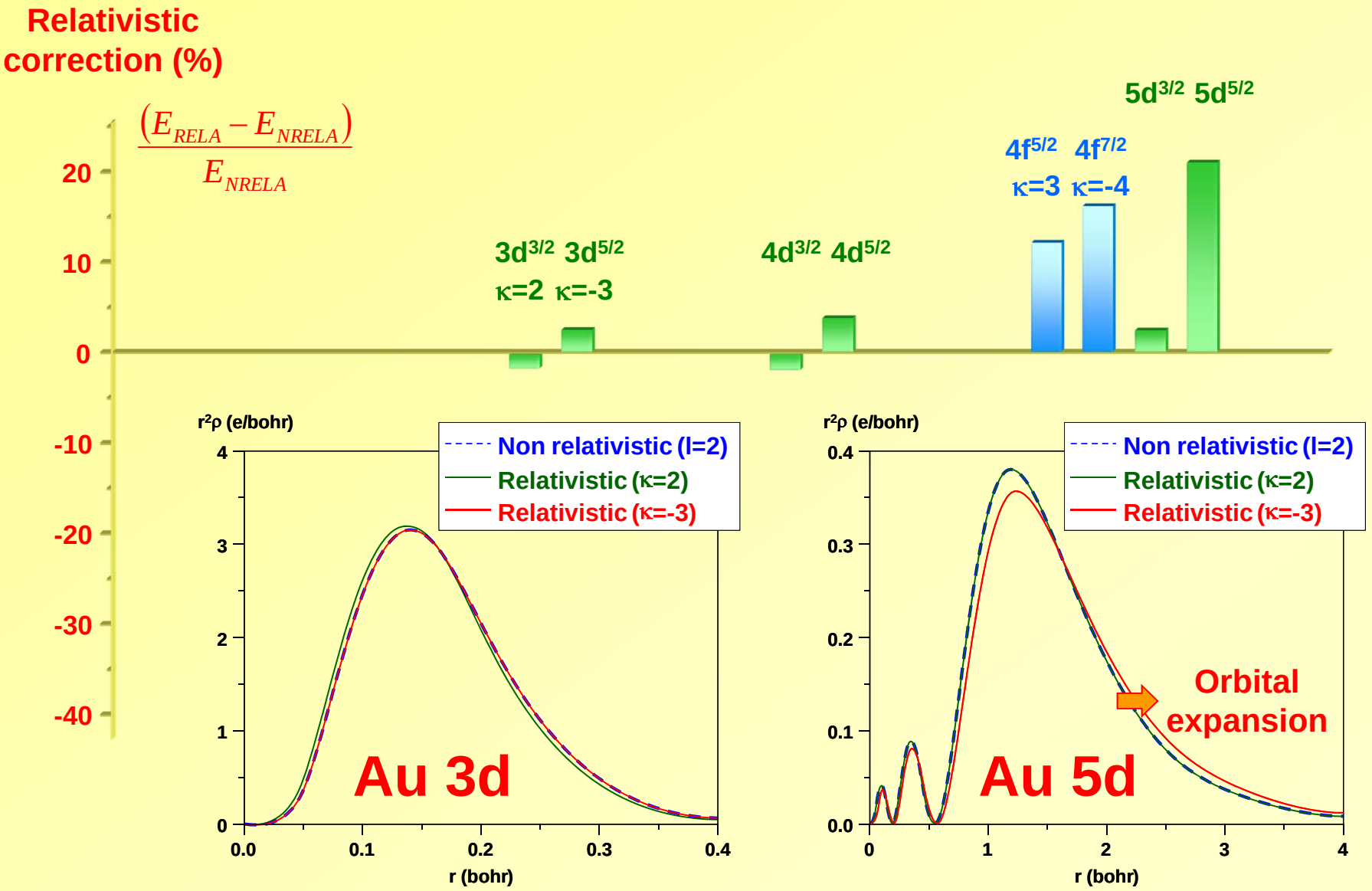
$Z_{eff1} > Z_{eff2}$

(3) Orbital expansion: Au(d) states

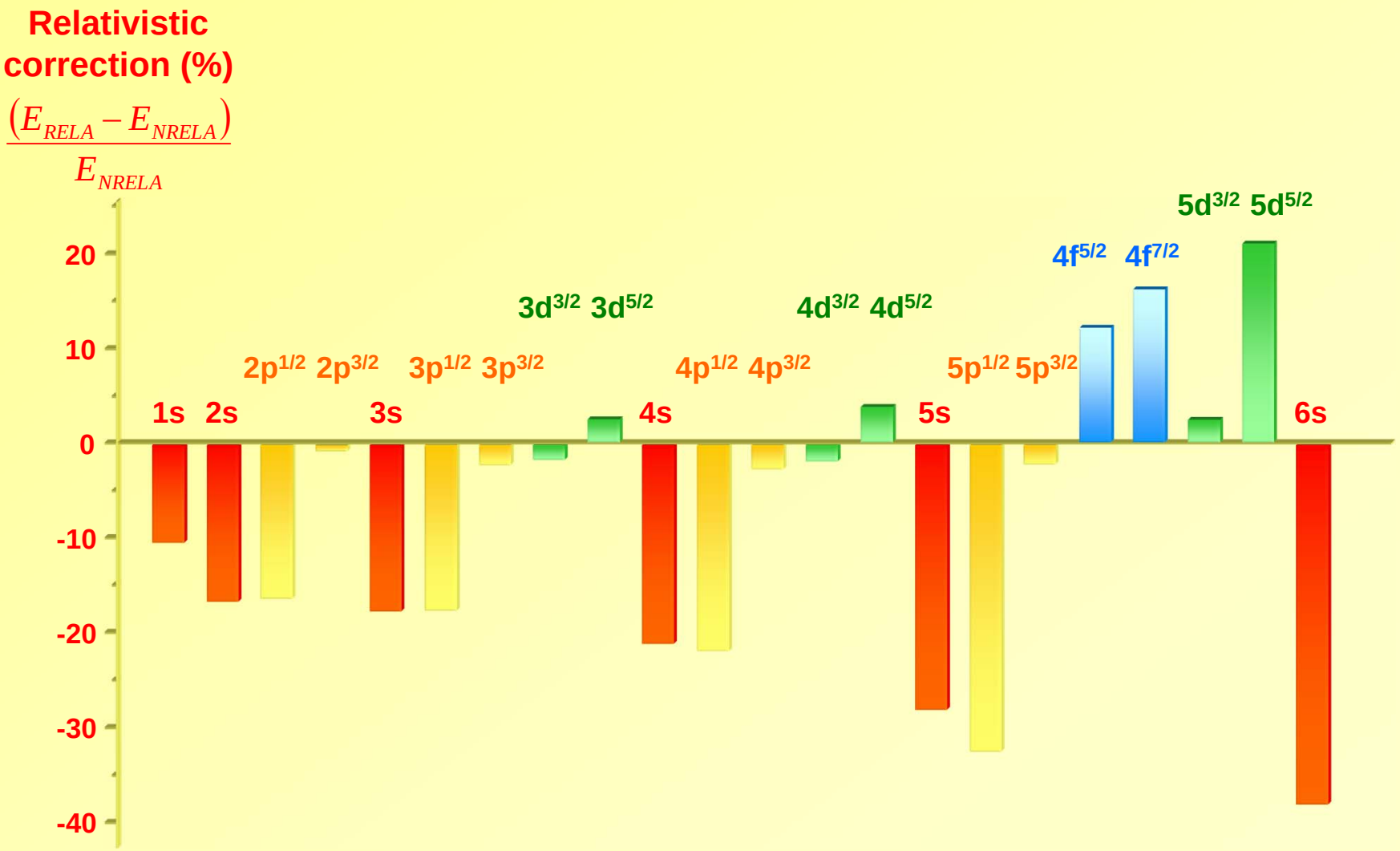
Higher l-quantum number states expand due to **better shielding** of nucleus charge from contracted s-states



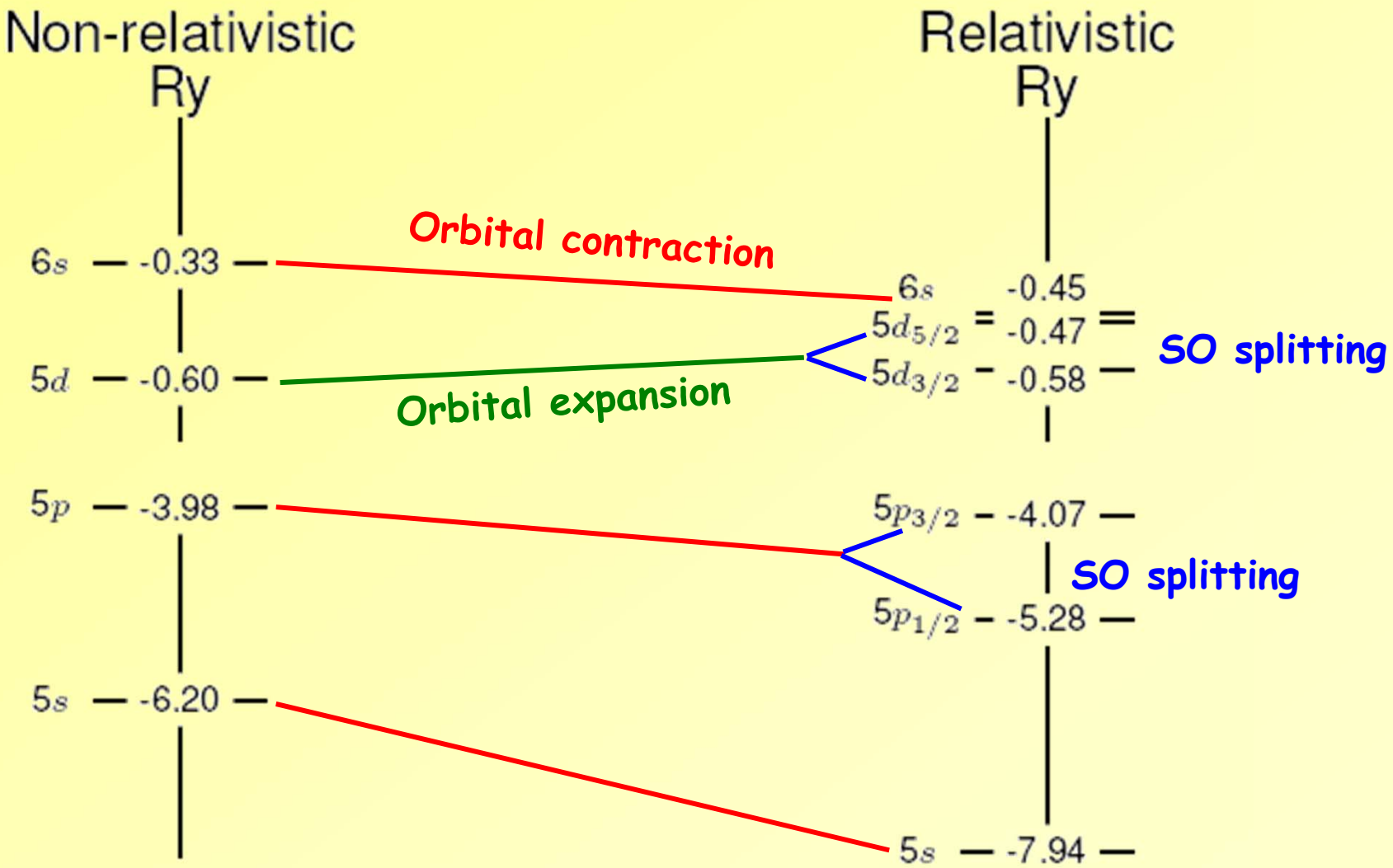
(3) Orbital expansion: Au(d) states



Relativistic effects on the Au energy levels

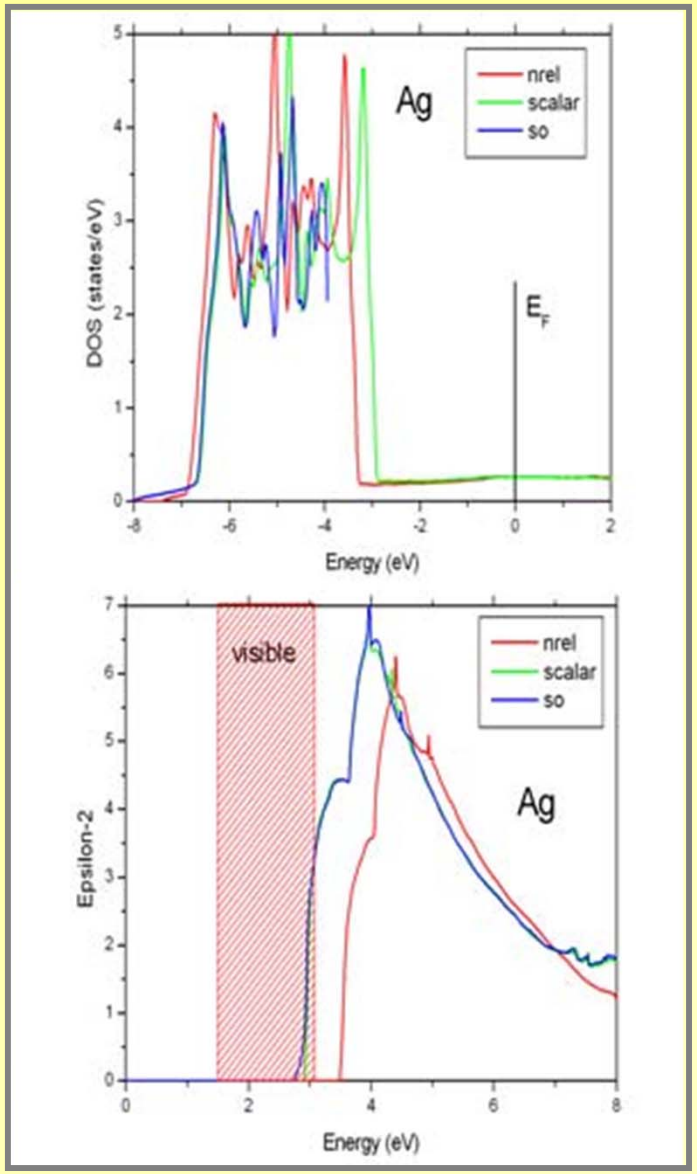


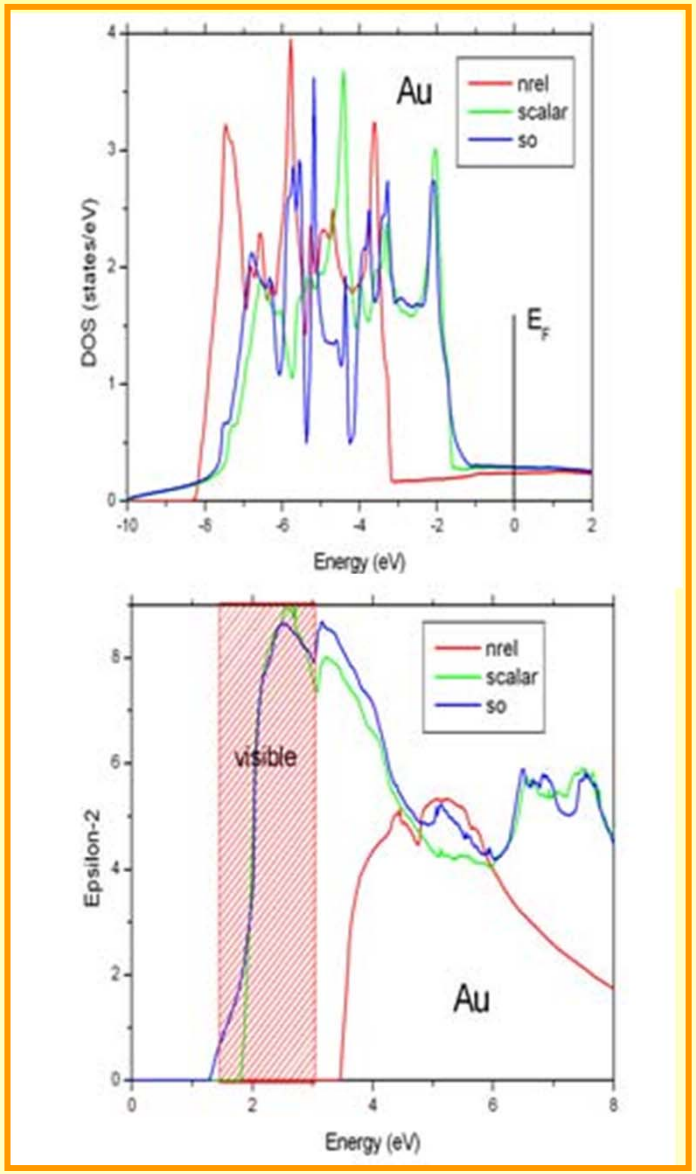
Atomic spectra of gold



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

Ag



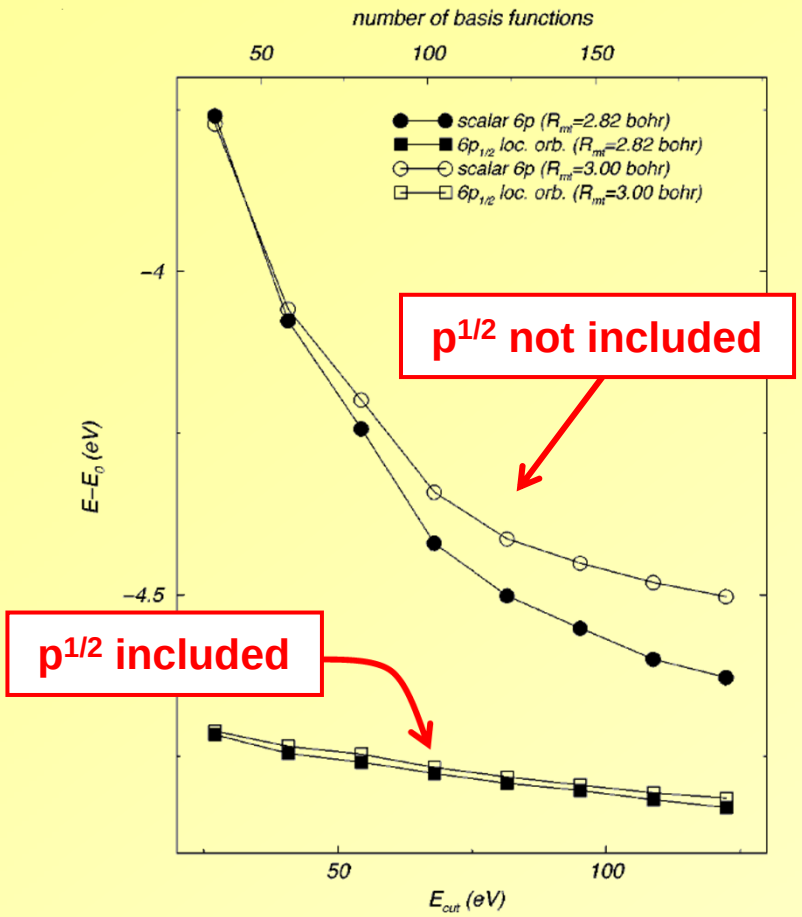


Au

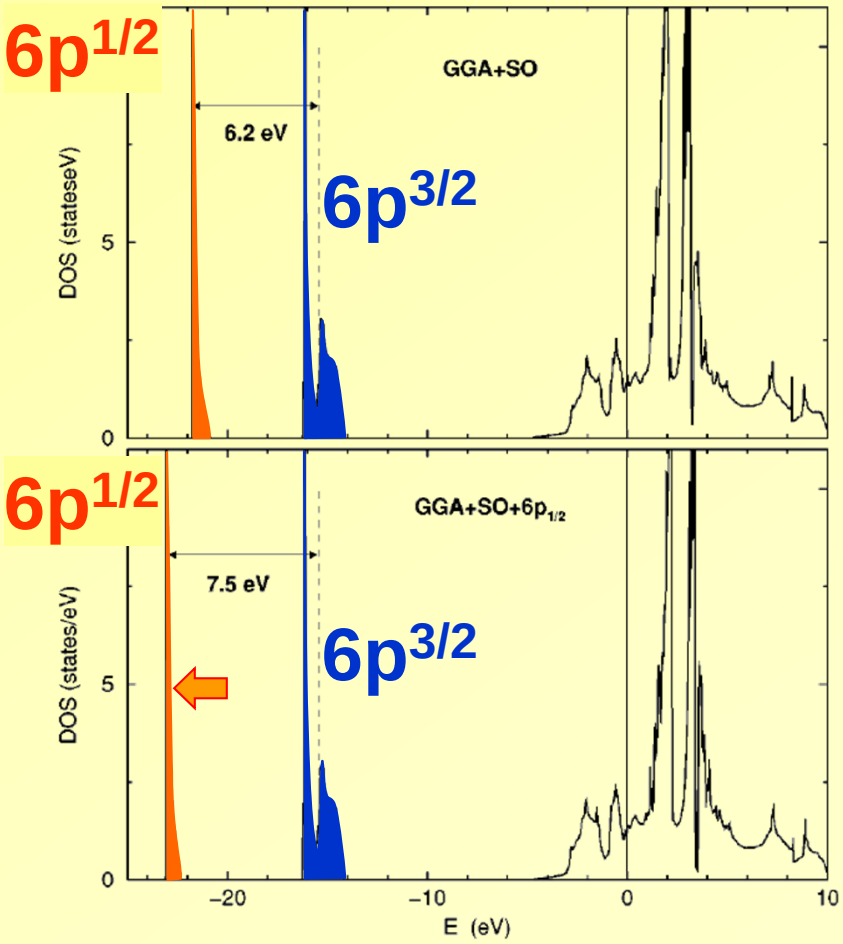
Relativistic semicore states: $p^{1/2}$ orbitals

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 in magnetic systems

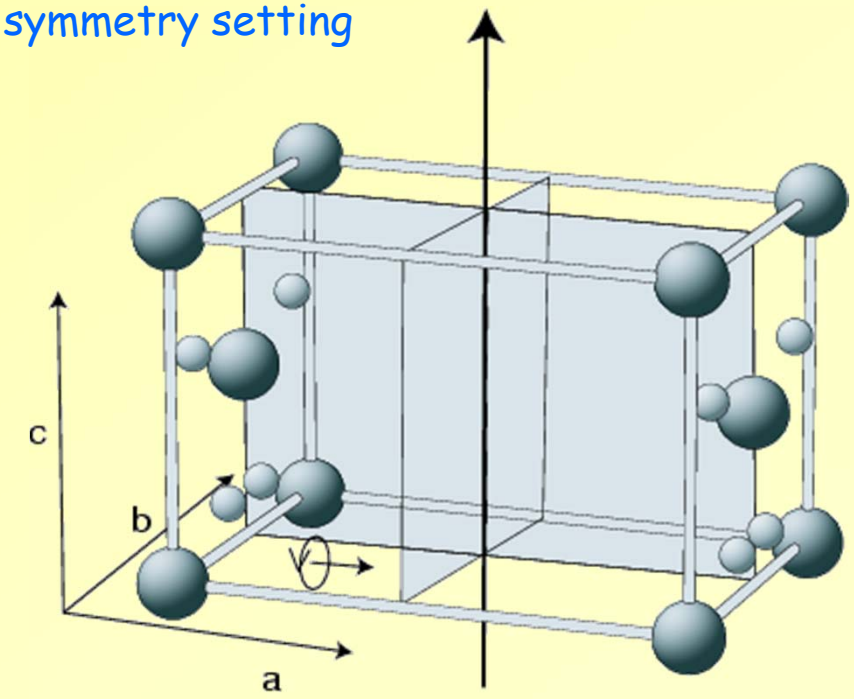
SOC couples magnetic moment to the lattice

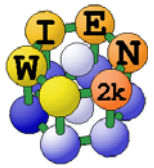
- direction of the exchange field matters (input in case.inso)

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!!!)

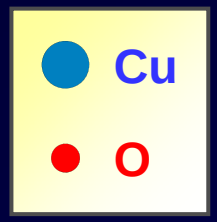
  x lapw1 (increase E-max for more eigenvalues, to have
  x lapwso basis for lapwso)
  x lapw2 -so -c SO **ALWAYS** needs **complex lapw2** version
- **Non-magnetic systems:**

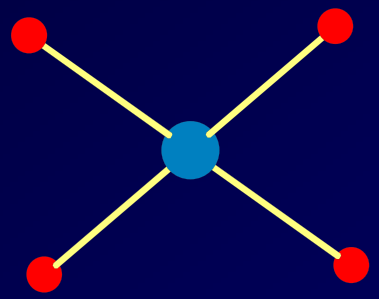
  SO does NOT reduce symmetry. initso_lapw just generates case.inso and case.in2c.
- **Magnetic systems:**

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

CuO interlude

ATOMIC STRUCTURE OF CuO

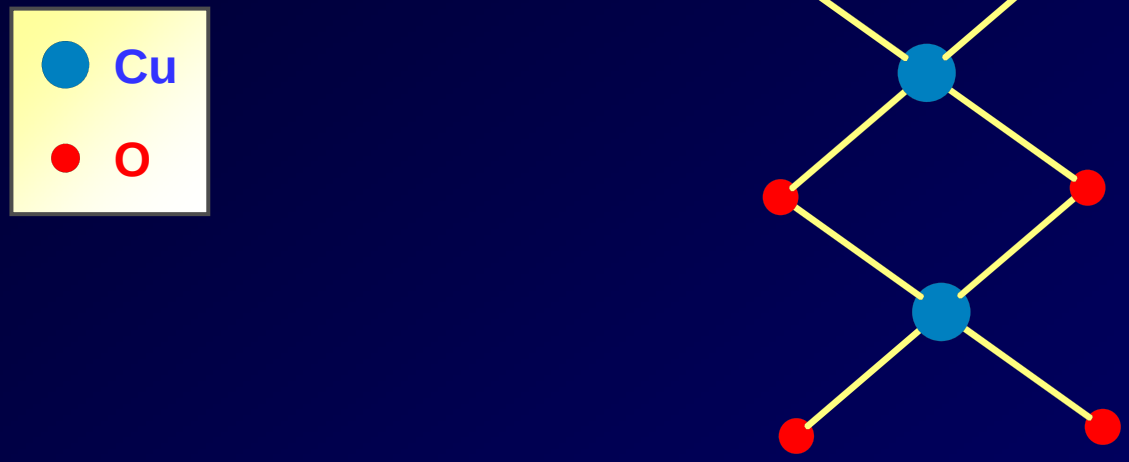




CuO_4 square planar

CuO interlude

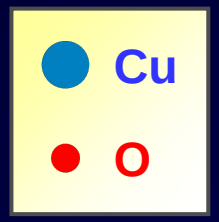
ATOMIC STRUCTURE OF CuO

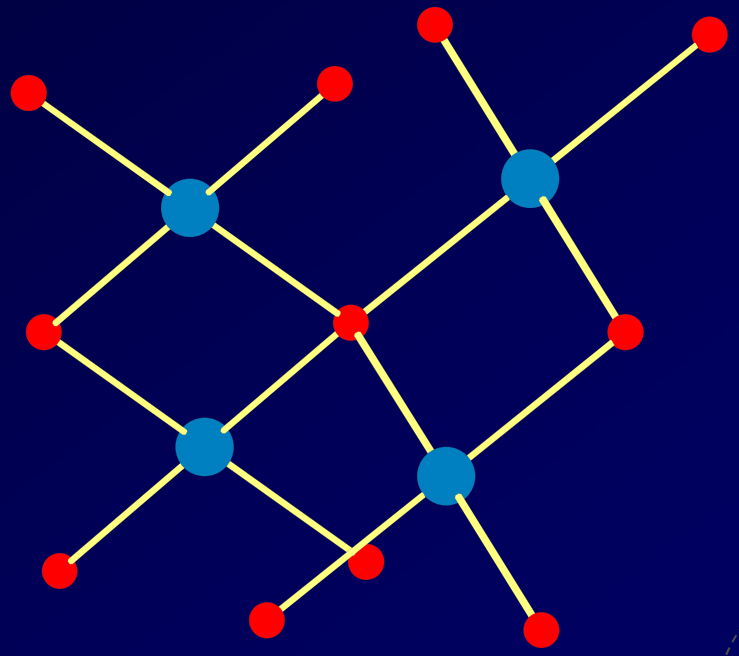


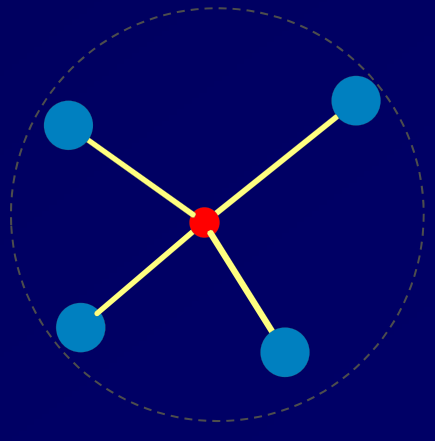
CuO_2 ribbons

CuO interlude

ATOMIC STRUCTURE OF CuO



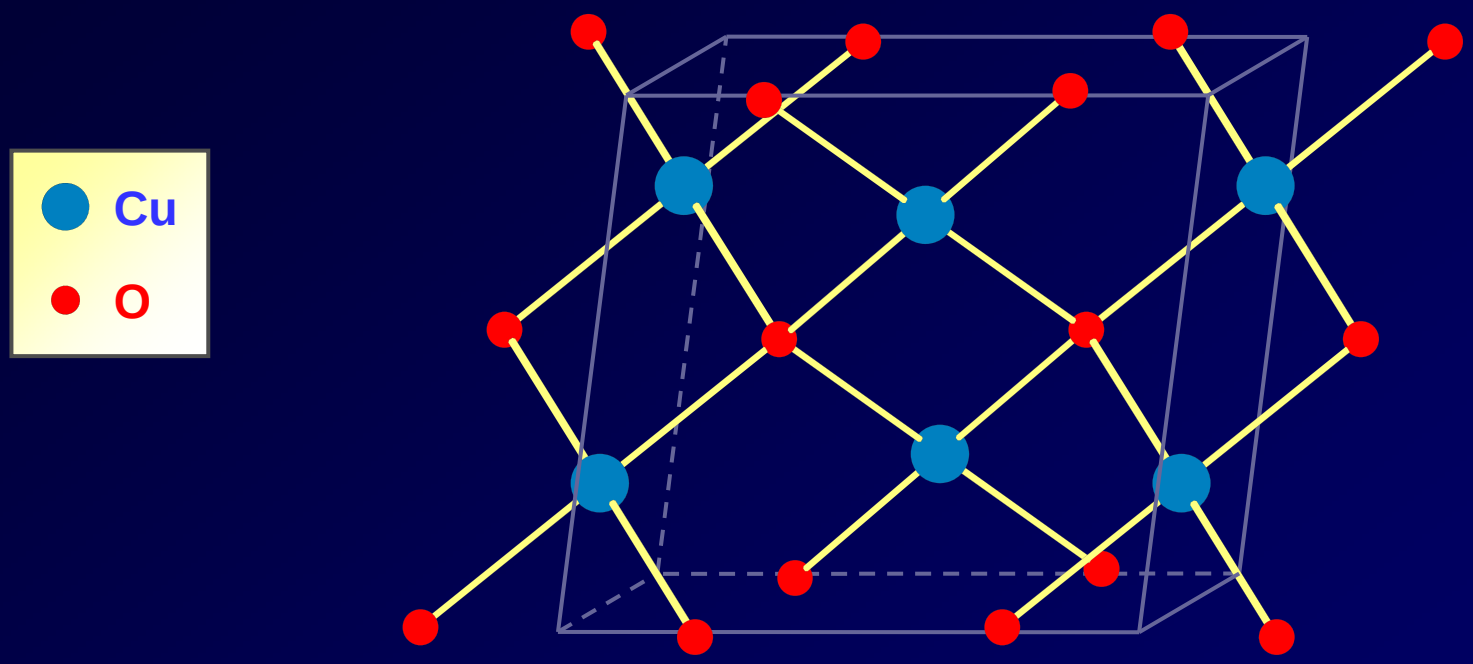




Oxygen 4-fold coordinated

CuO interlude

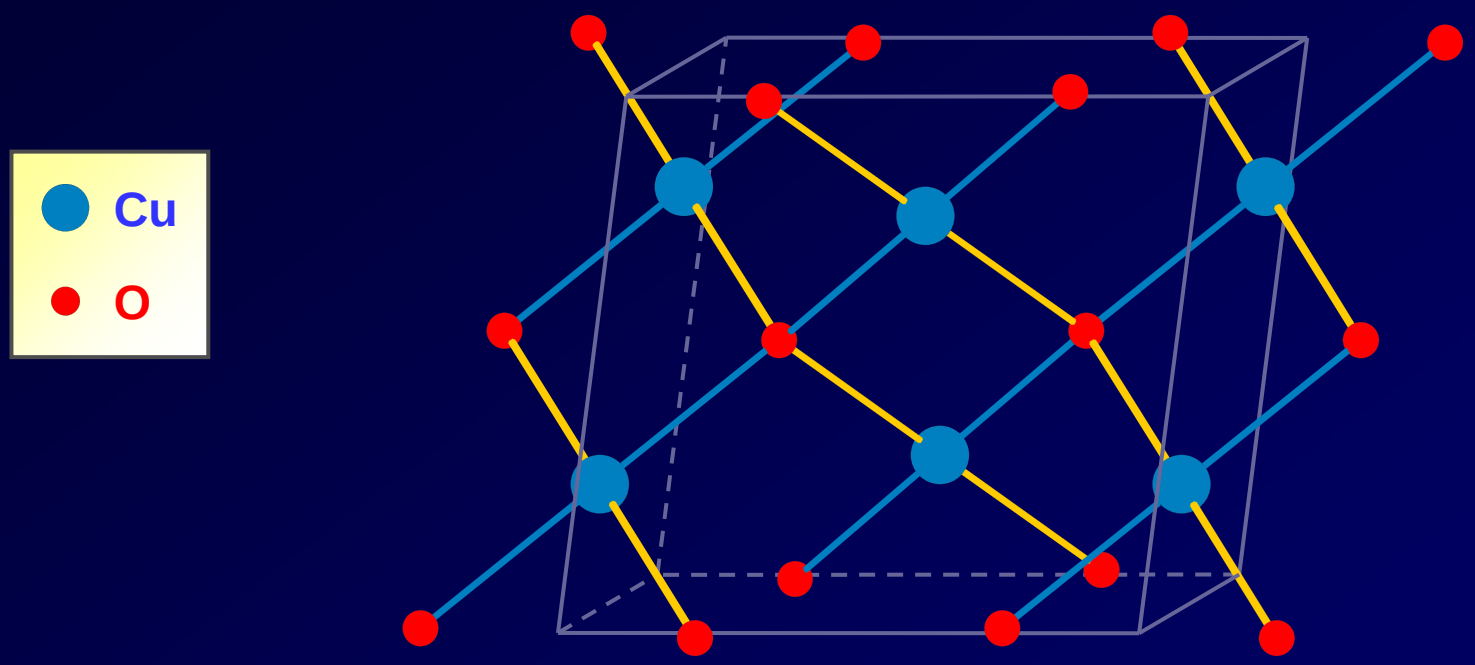
ATOMIC STRUCTURE OF CuO



Monoclinic 3D atomic structure

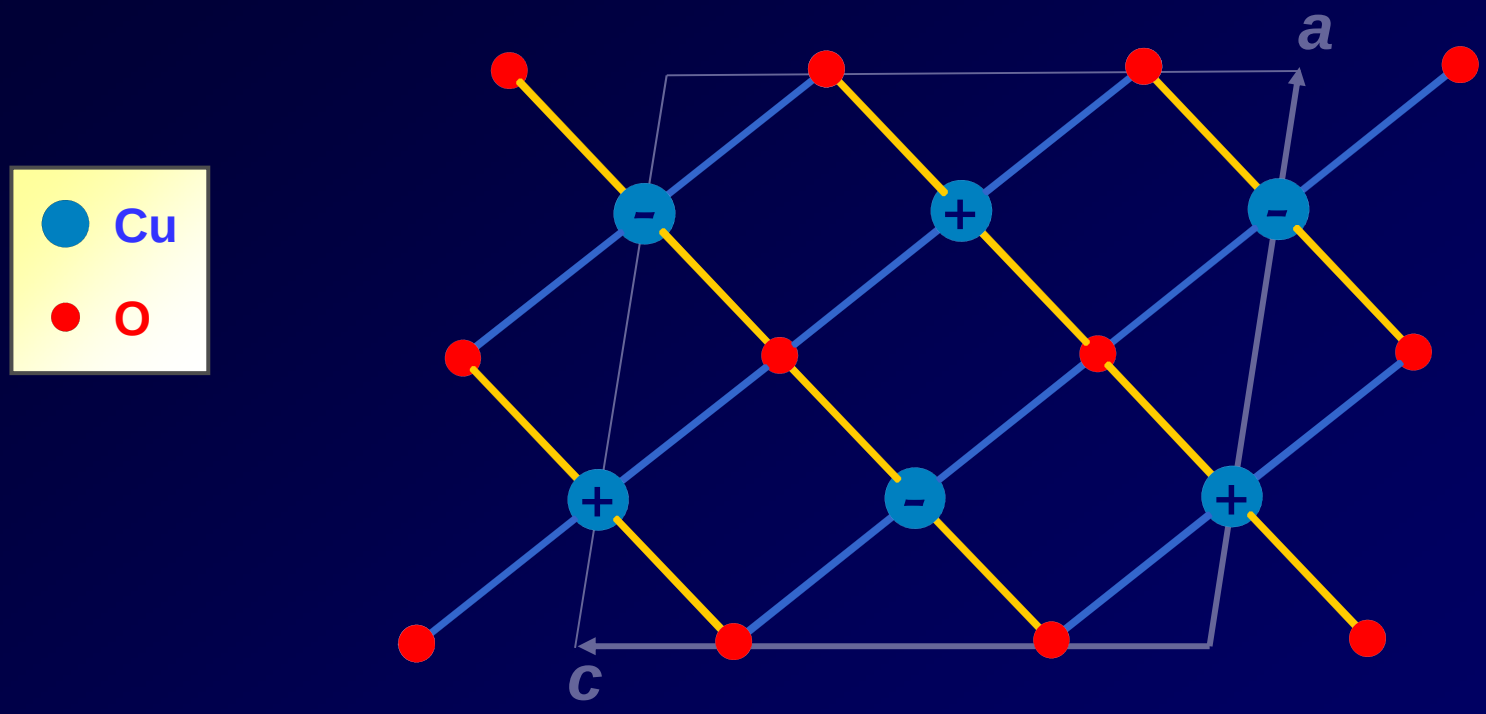
CuO interlude

MAGNETIC STRUCTURE OF CuO



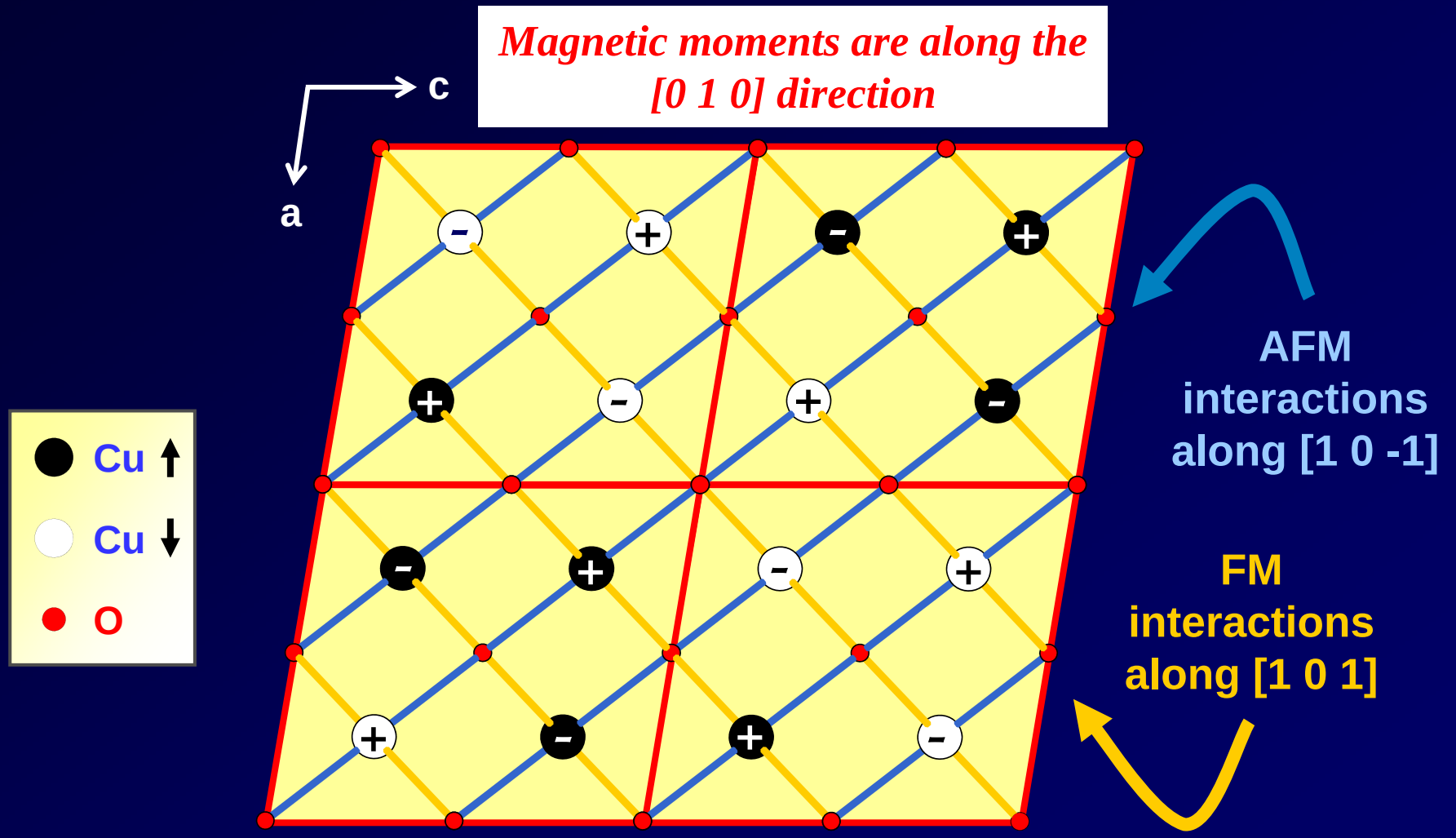
CuO interlude

MAGNETIC STRUCTURE OF CuO



CuO interlude

LOW-TEMPERATURE MAGNETIC STRUCTURE OF CuO FROM SINGLE-CRYSTAL NEUTRON DIFFRACTION[1]



[1] J.B. Forsyth et al., J. Phys. C: Solid State Phys. 21 (1988) 2917

CuO interlude

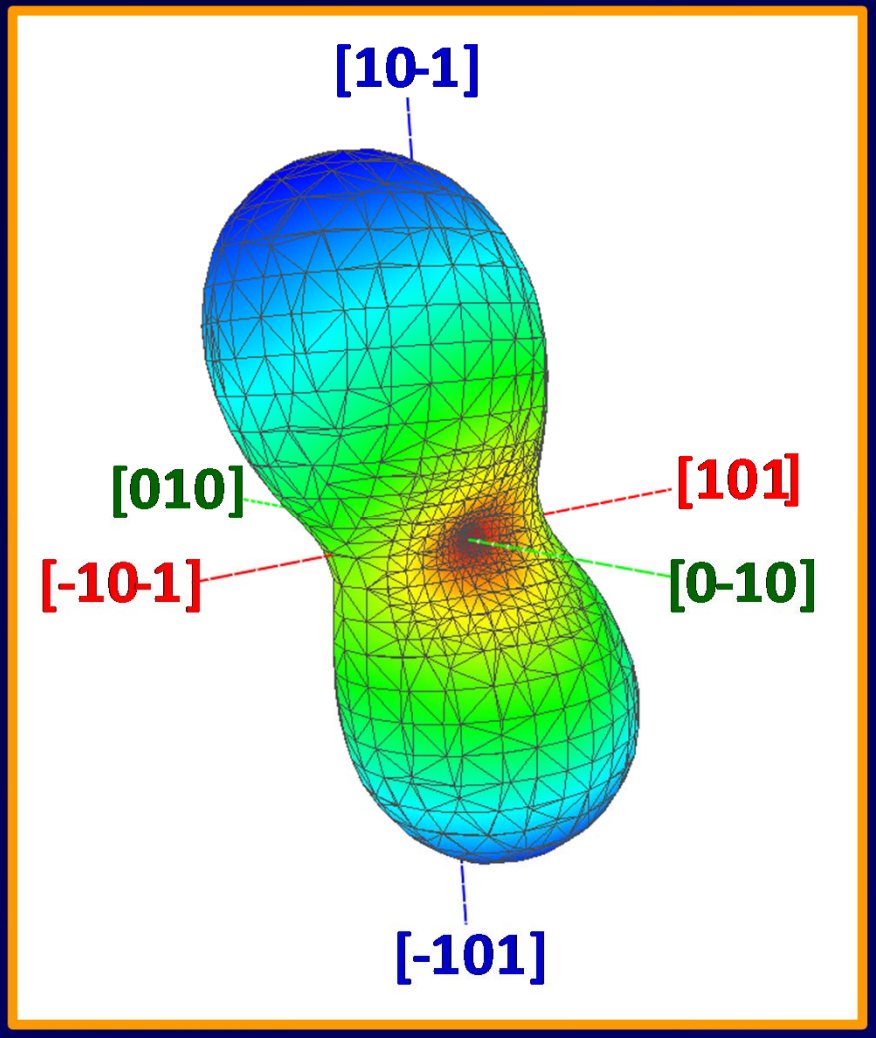
Estimation of the Magneto-crystalline Anisotropy Energy (MAE) of CuO

Allows to define the magnetization easy and hard axes

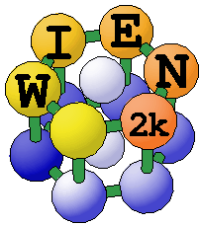
Here we have considered the following expression:

$$MAE = E[u\ v\ w] - E[0\ 1\ 0]$$

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., Accepted



20th WIEN2k Workshop
PennStateUniversity – 2013

TU WIEN

Relativistic effects
&
Non-collinear magnetism

(WIEN2k / WIENncm)

Xavier Rocquefelte
Institut des Matériaux Jean-Rouxel (UMR 6502)
Université de Nantes, FRANCE

UNIVERSITÉ DE NANTES

Pauli Hamiltonian for magnetic systems

⇨ *2x2 matrix in spin space, due to Pauli spin operators*

$$H_P = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff} + \mu_B \vec{\sigma}\cdot\vec{B}_{eff} + \zeta\left(\vec{\sigma}\cdot\vec{l}\right) + \ldots$$

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

(2×2) Pauli spin matrices

Pauli Hamiltonian for magnetic systems

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(2×2) Pauli spin matrices

⇨ *Wave function is a 2-component vector (spinor) – It corresponds to the large components of the dirac wave function (small components are neglected)*

$$H_P \begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix} = \varepsilon \begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix}$$

spin up

spin down

Pauli Hamiltonian for magnetic systems

⇨ *2x2 matrix in spin space, due to Pauli spin operators*

$$H_P = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff} + \mu_B \vec{\sigma}\cdot\vec{B}_{eff} + \zeta\left(\vec{\sigma}\cdot\vec{l}\right) + \ldots$$

Effective electrostatic potential

$$V_{eff} = V_{ext} + V_H + V_{xc}$$

Exchange-correlation potential

Effective magnetic field

$$B_{eff} = B_{ext} + B_{xc}$$

Exchange-correlation field

Pauli Hamiltonian for magnetic systems

⇨ *2x2 matrix in spin space, due to Pauli spin operators*

$$H_P = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff} + \mu_B \vec{\sigma}\cdot\vec{B}_{eff} + \zeta\left(\vec{\sigma}\cdot\vec{l}\right) + \ldots$$

Effective electrostatic potential

$$V_{eff} = V_{ext} + V_H + V_{xc}$$

Effective magnetic field

$$B_{eff} = B_{ext} + B_{xc}$$

Spin-orbit coupling

$$\zeta = \frac{\hbar^2}{2M_e^2 c^2}\frac{1}{r}\frac{dV}{dr}$$

Exchange-correlation potential

Exchange-correlation field

Many-body effects which are defined within DFT LDA or GGA

Exchange and correlation

⇨ *From DFT exchange correlation energy:*

$$E_{xc}(\rho(r),\vec{m}) = \int \rho(r)\, \varepsilon_{xc}^{hom}\left[\rho(r),\vec{m}\right] dr^3$$

Local function of the electronic density (ρ) and the magnetic moment (m)

⇨ *Definition of V_{xc} and B_{xc} (functional derivatives):*

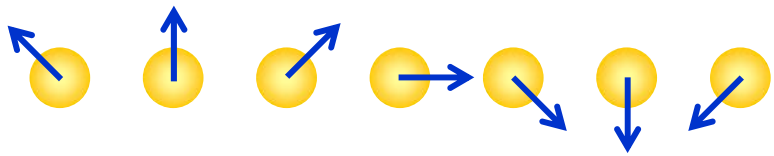
$$V_{xc} = \frac{\partial E_{xc}(\rho,\vec{m})}{\partial \rho} \qquad \vec{B}_{xc} = \frac{\partial E_{xc}(\rho,\vec{m})}{\partial \vec{m}}$$

⇨ *LDA expression for V_{xc} and B_{xc}:*

$$V_{xc} = \varepsilon_{xc}^{hom}(\rho,\vec{m}) + \rho \frac{\partial \varepsilon_{xc}^{hom}(\rho,\vec{m})}{\partial \rho} \qquad \vec{B}_{xc} = \rho \frac{\partial \varepsilon_{xc}^{hom}(\rho,\vec{m})}{\partial m} \hat{m}$$

B_{xc} is parallel to the magnetization density vector ($\hat{m}$)

Non-collinear magnetism



⇨ *Direction of magnetization vary in space, thus spin-orbit term is present*

$$H_P = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff} + \mu_B \vec{\sigma}\cdot\vec{B}_{eff} + \zeta\left(\vec{\sigma}\cdot\vec{l}\right) + \ldots$$

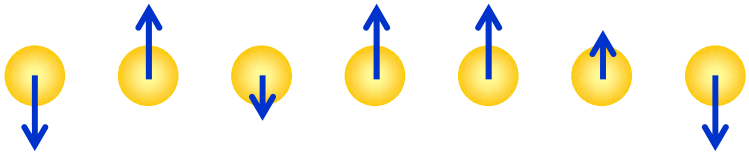
$$\begin{pmatrix} -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff} + \mu_B B_z + \ldots & \mu_B\left(B_x - iB_y\right) \\ \mu_B\left(B_x + iB_y\right) & -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff} - \mu_B B_z + \ldots \end{pmatrix} \psi = \varepsilon\psi$$

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

Ψ_1 and Ψ_2 are non-zero

- *Solutions are non-pure spinors*
- *Non-collinear magnetic moments*

Collinear magnetism



⇨ *Magnetization in z-direction / spin-orbit is not present*

$$H_P = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff} + \mu_B \vec{\sigma}\cdot\vec{B}_{eff} + \zeta\cancel{\left(\vec{\sigma}\cdot\vec{l}\right)} + \ldots$$

$$\begin{pmatrix} -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff} + \mu_B B_z + \ldots & 0 \\ 0 & -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff} - \mu_B B_z + \ldots \end{pmatrix} \psi = \varepsilon\psi$$

$$\psi_\uparrow = \begin{pmatrix} \psi_1 \\ 0 \end{pmatrix} \qquad \psi_\downarrow = \begin{pmatrix} 0 \\ \psi_2 \end{pmatrix}$$

$$\varepsilon_\uparrow \neq \varepsilon_\downarrow$$

- *Solutions are pure spinors*
- *Collinear magnetic moments*
- *Non-degenerate energies*

Non-magnetic calculation

⇨ *No magnetization present, $B_x = B_y = B_z = 0$ and no spin-orbit coupling*

$$H_P = -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff} + \mu_B \vec{\sigma} \vec{B}_{eff} + \zeta\left(\vec{\sigma}\cdot\vec{l}\right) + \ldots$$

$$\begin{pmatrix} -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff} & 0 \\ 0 & -\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff} \end{pmatrix} \psi = \varepsilon\psi$$

$$\psi_\uparrow = \begin{pmatrix} \psi \\ 0 \end{pmatrix} \qquad \psi_\downarrow = \begin{pmatrix} 0 \\ \psi \end{pmatrix}$$

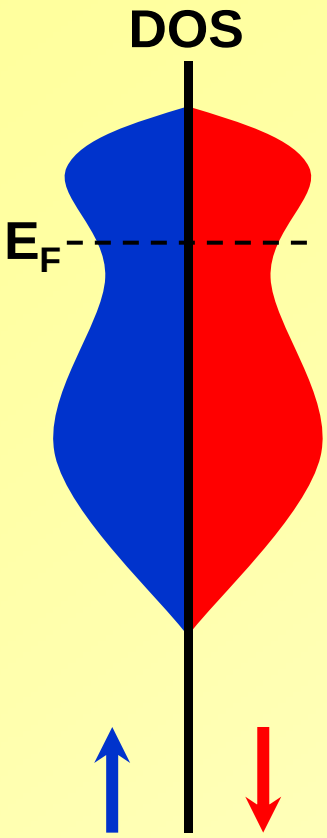
$$\varepsilon_\uparrow = \varepsilon_\downarrow$$

- *Solutions are pure spinors*
- *Degenerate spin solutions*

Magnetism and WIEN2k

⇨ *Wien2k can only handle collinear or non-magnetic cases*

non-magnetic case



$m = n_\uparrow - n_\downarrow = 0$

run_lapw script:

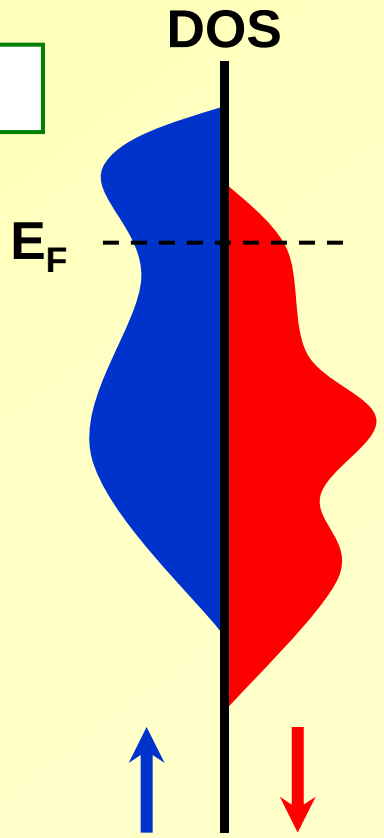
x lapw0
x lapw1
x lapw2
x lcore
x mixer

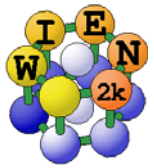
magnetic case

$m = n_\uparrow - n_\downarrow \neq 0$

run_lapw script:

x lapw0
x lapw1 -up
x lapw1 -dn
x lapw2 -up
x lapw2 -dn
x lcore -up
x lcore -dn
x mixer





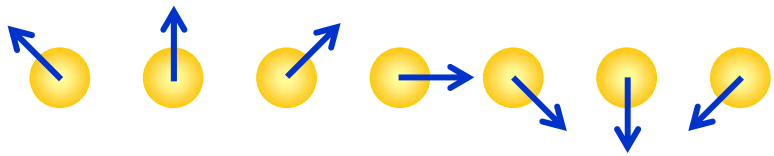
Magnetism and WIEN2k

⇨ *Spin-polarized calculations*

- runsp_lapw script (unconstrained magnetic calc.)
- runfsm_lapw -m value (constrained moment calc.)
- runafm_lapw (constrained anti-ferromagnetic calculation)

- spin-orbit coupling can be included in second variational step
- never mix polarized and non-polarized calculations in one case directory !!!

Non-collinear magnetism



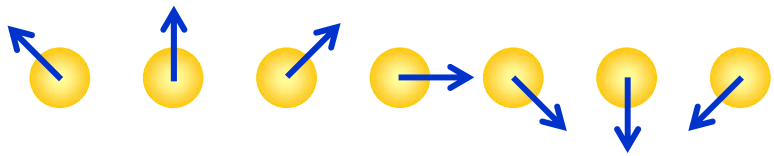
In case of non-collinear spin arrangements WIENncm (WIEN2k clone) has to be used:

- code based on Wien2k (available for Wien2k users)
- structure and usage philosophy similar to Wien2k
- independent source tree, independent installation

WIENncm properties:

- real and spin symmetry (simplifies SCF, less k-points)
- constrained or unconstrained calculations (optimizes magnetic moments)
- SOC in first variational step, LDA+U
- Spin spirals

Non-collinear magnetism



⇨ *For non-collinear magnetic systems, both spin channels have to be considered simultaneously*

runncm_lapw script:

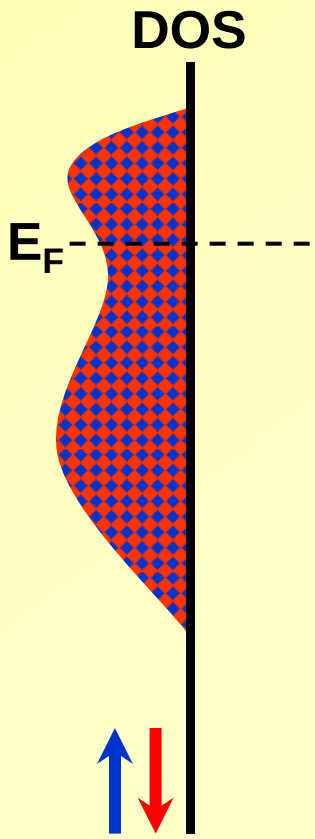
xncm lapw0
xncm lapw1
xncm lapw2
xncm lcore
xncm mixer

Relation between spin density matrix and magnetization

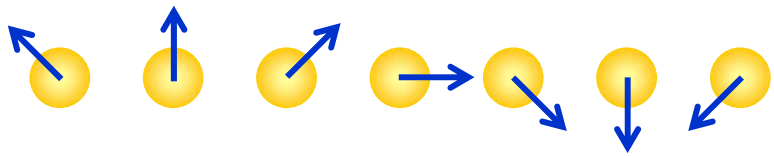
$$m_z = n_{\uparrow\uparrow} - n_{\downarrow\downarrow} \neq 0$$

$$m_x = \tfrac{1}{2}(n_{\uparrow\downarrow} + n_{\downarrow\uparrow}) \neq 0$$

$$m_y = i\tfrac{1}{2}(n_{\uparrow\downarrow} - n_{\downarrow\uparrow}) \neq 0$$

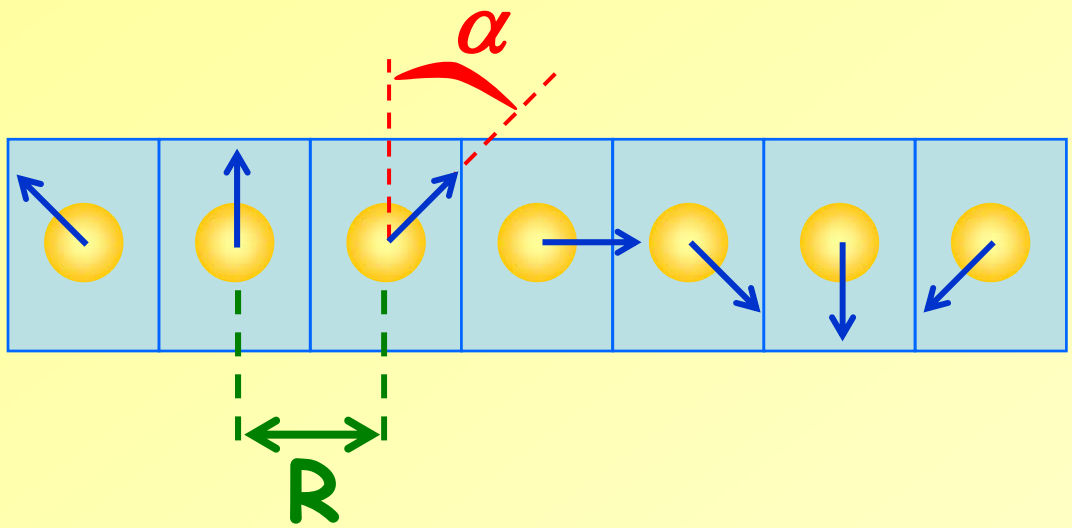


WienNCM: Spin spirals



⇨ *Transverse spin wave*

$$\alpha = \vec{R} \cdot \vec{q}$$



$$\vec{m}^n = m\left(\cos\left(\vec{q}\cdot\vec{R}^n\right), \sin\left(\vec{q}\cdot\vec{R}^n\right)\sin\theta\,, \cos\theta\right)$$

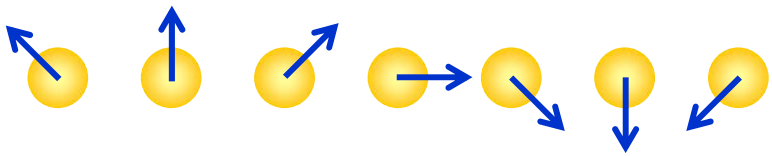
♦ spin-spiral is defined by a vector q given in reciprocal space and an angle θ between magnetic moment and rotation axis.

♦ Rotation axis is arbitrary (no SOC) – fixed as z-axis in WIENNCM

⇒ **Translational symmetry is lost !**

⇒ But WIENncm is using the generalized Bloch theorem. The calculation of spin waves only requires **one unit cell** for even incommensurate modulation q vector.

WienNCM: Usage



1. **Generate the atomic and magnetic structures**
   - Create atomic structure
   - Create magnetic structure

   See utility programs: ncmsymmetry, polarangles, …

2. **Run initncm (initialization script)**

3. **Run the NCM calculation:**
   - **xncm** (WIENncm version of **x** script)
   - **runncm** (WIENncm version of **run** script)

More information on the manual (Robert Laskowski)

rolask@theochem.tuwien.ac.at