Relativistic effects
&
magnetism
in WIEN2k

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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
  Schwerdtfeger, 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:**
\[ \hbar = m_e = e = 1 \]

\[ c \approx 137 \text{ au} \]
Few words about Special Theory of Relativity

**Light**

- Composed of photons (no mass)
- Speed of light = constant
- Atomic units:
  \[ \frac{\hbar}{m_e} = e = 1 \]
- \( c \approx 137 \text{ au} \)

**Matter**

- Composed of atoms (mass)
- Speed of matter:
  \[ v = f(\text{mass}) \]
- Mass:
  \[ \text{mass} = f(v) \]
Light

Composed of photons (no mass)

Speed of light = constant

Atomic units:
\( \hbar = m_e = e = 1 \)

c \approx 137 \text{ au}

Lorentz Factor (measure of the relativistic effects)

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

Matter

Composed of atoms (mass)

Speed of matter

\( v = f(\text{mass}) \)

mass = \( f(v) \)

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

Momentum: \( p = \gamma mv = Mv \)

Total energy: \( E^2 = p^2c^2 + m^2c^4 \)

\( E = \gamma mc^2 = Mc^2 \)
Definition of a relativistic particle (Bohr model)

Lorentz factor ($\gamma$)

« Non-relativistic » particle: $\gamma = 1$

- $H(1s)$
- $Au(1s)$

$c \approx 137$ au

Speed of the 1s electron (Bohr model):

- $e^-$
- $+Ze$

$\nu_e \propto \frac{Z}{n}$

\[
\gamma = \frac{1}{\sqrt{1 - \left(\frac{\nu_e}{c}\right)^2}} = \frac{1}{\sqrt{1 - (0.58)^2}} = 1.22
\]

Details for Au atom:

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

1s electron of Au atom = relativistic particle

$M_e(1s-Au) = 1.22m_e$
Relativistic effects

1) The mass-velocity correction

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

1) The mass-velocity correction

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

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.
Relativistic effects

1) The mass-velocity correction
Relativistic increase in the mass of an electron with its velocity (when $v_e \to c$)

2) The Darwin term
It has no classical relativistic analogue
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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)
Relativistic effects

1) The mass-velocity correction
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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
One electron radial Schrödinger equation

**HARTREE ATOMIC UNITS**

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

**INTERNATIONAL UNITS**

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

**Atomic units:**
\[\hbar = m_e = e = 1\]
\[1/(4\pi\varepsilon_0) = 1\]
\[c = 1/\alpha \approx 137 \text{ au}\]
One electron radial Schrödinger equation

**HARTREE ATOMIC UNITS**

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

\[
V = -\frac{Z}{r}
\]

**INTERNATIONAL UNITS**

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

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

**In a spherically symmetric potential**

\[
\Psi_{n,l,m} = R_{n,l}(r)Y_{l,m}(\theta, \phi)
\]

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

**Atomic units:**

\[
\hbar = m_e = e = 1
\]

\[
\frac{1}{4\pi\varepsilon_0} = 1
\]

\[
c = \frac{1}{\alpha} \approx 137 \text{ au}
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One electron radial Schrödinger equation

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

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

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

\[ -\frac{\hbar^2}{2m_e} \frac{1}{\rho^2} \frac{d}{d\rho} \left( \rho^2 \frac{dR_{n,l}}{d\rho} \right) + \left[ V + \frac{\hbar^2}{2m_e} \frac{l(l+1)}{\rho^2} \right] R_{n,l} = \varepsilon R_{n,l} \]
Dirac relativistic Hamiltonian provides a quantum mechanical description of electrons, consistent with the theory of special relativity.

\[ E^2 = p^2 c^2 + m^2 c^4 \]

\[ H_D \Psi = \varepsilon \Psi \quad \text{with} \quad H_D = c \vec{\alpha} \cdot \vec{p} + \beta m_e c^2 + V \]
Dirac relativistic Hamiltonian provides a quantum mechanical description of electrons, consistent with the theory of special relativity.

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

\[ \alpha_k = \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix} \quad \beta_k = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \]

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

\[ E^2 = p^2 c^2 + m^2 c^4 \]
Dirac equation: $H_D$ and $\Psi$ are 4-dimensional

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

$\Phi$ and $\chi$ are time-independent two-component spinors describing the spatial and spin-1/2 degrees of freedom

Leads to a set of coupled equations for $\Phi$ and $\chi$:

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

$$c(\sigma \cdot \vec{p}) \phi = (\varepsilon - V + m_e c^2) \chi$$
Dirac equation: $H_D$ and $\Psi$ are 4-dimensional

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

Solution in the slow particle limit (p=0)

Particles: up & down

Non-relativistic limit decouples $\Psi_1$ from $\Psi_2$ and $\Psi_3$ from $\Psi_4$

Antiparticles: up & down
For a free particle (i.e. \( V = 0 \)):

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

Solution in the slow particle limit (p=0)

Particles: up & down

\[
\begin{pmatrix}
\phi^i \\
m_e c^2 & 0 & 0 & 0 \\
0 & m_e c^2 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}
\]

Antiparticles: up & down

\[
\begin{pmatrix}
0 \\
0 & -m_e c^2 & 0 & 0 \\
\chi^\dagger & -m_e c^2 & 0 & 0 \\
0 & 0 & 0 & \chi^\dagger
\end{pmatrix}
\]

Non-relativistic limit decouples \( \Psi_1 \) from \( \Psi_2 \) and \( \Psi_3 \) from \( \Psi_4 \)

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

\[
\begin{align*}
j &= l + s/2 \\
\kappa &= -s(j + 1/2) \\
s &= +1, -1
\end{align*}
\]
For a spherical potential $V(r)$:

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

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

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

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

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

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

One electron radial Schrödinger equation in a spherical potential

Note that: \( \kappa (\kappa + 1) = l(l+1) \)
The resulting equations for the radial functions ($g_{nk}$ and $f_{nk}$) are simplified if we define:

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

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

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

and

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

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

Instead the good quantum numbers are $j$ and $\kappa$

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

No approximation has been made so far
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:

\[ g_{nk} \rightarrow \tilde{g}_{nl}, \quad f_{nk} \rightarrow \tilde{f}_{nl} \]

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

and

\[
\tilde{f}_{nl} = \frac{\hbar}{2M_e c} \frac{d\tilde{g}_{nl}}{dr}
\]

with the normalization condition:

\[
\int \left( \tilde{g}_{nl}^2 + \tilde{f}_{nl}^2 \right) r^2 dr = 1
\]
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:
\[ g_{nk} \to \tilde{g}_{nl} \quad f_{nk} \to \tilde{f}_{nl} \]

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

and
\[ \tilde{f}_{nl} = \frac{\hbar}{2M_e c} \frac{d\tilde{g}_{nl}}{dr} \]

with the normalization condition:
\[
\int \left( \tilde{g}_{nl}^2 + \tilde{f}_{nl}^2 \right) r^2 dr = 1
\]

The four-component wave function is now written as:

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

\[ H\tilde{\Psi} = \varepsilon\tilde{\Psi} + H_{SO}\tilde{\Psi} \]

with
\[
H_{SO} = \frac{\hbar^2}{4M_e^2 c^2} \frac{1}{r} \frac{dV}{dr} \begin{pmatrix} \tilde{\phi} & 0 \\ 0 & 0 \end{pmatrix}
\]

\( \tilde{\Phi} \) 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 (2\textsuperscript{nd} 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)

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.

case.inc for Au atom

<table>
<thead>
<tr>
<th>l</th>
<th>s=-1</th>
<th>s=+1</th>
<th>s=-1</th>
<th>s=+1</th>
<th>occupation</th>
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<td>-1</td>
<td>2</td>
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<tr>
<td>p</td>
<td>1</td>
<td>3/2</td>
<td>1</td>
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<td>f</td>
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<td>( n,κ,occup)</td>
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<td>( n,κ,occup)</td>
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<td>2,-2,4</td>
<td>( n,κ,occup)</td>
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</tbody>
</table>
Implementation in WIEN2k: core electrons

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

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.

<table>
<thead>
<tr>
<th>l</th>
<th>j=1+s/2</th>
<th>\kappa=-s(j+1/2)</th>
<th>occupation</th>
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</thead>
<tbody>
<tr>
<td>s</td>
<td>0</td>
<td>1/2</td>
<td>-1</td>
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<td>p</td>
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<td>1/2, 3/2</td>
<td>1, -2</td>
</tr>
<tr>
<td>d</td>
<td>2</td>
<td>3/2, 5/2</td>
<td>2, -3</td>
</tr>
<tr>
<td>f</td>
<td>3</td>
<td>5/2, 7/2</td>
<td>3, -4</td>
</tr>
</tbody>
</table>

\begin{align*}
1s^{1/2} & \rightarrow 1,-1,2 \quad (n, \kappa, \text{occu}) \\
2s^{1/2} & \rightarrow 2,-1,2 \quad (n, \kappa, \text{occu}) \\
2p^{1/2} & \rightarrow 2, 1,2 \quad (n, \kappa, \text{occu}) \\
2p^{3/2} & \rightarrow 2,-2,4 \quad (n, \kappa, \text{occu}) \\
3s^{1/2} & \rightarrow 3, 1,2 \quad (n, \kappa, \text{occu}) \\
3p^{1/2} & \rightarrow 3,-2,4 \quad (n, \kappa, \text{occu}) \\
3p^{3/2} & \rightarrow 3, 2,4 \quad (n, \kappa, \text{occu}) \\
3d^{3/2} & \rightarrow 3,-3,6 \quad (n, \kappa, \text{occu}) \\
3d^{5/2} & \rightarrow 4, 1,2 \quad (n, \kappa, \text{occu}) \\
4s^{1/2} & \rightarrow 4,-2,4 \quad (n, \kappa, \text{occu}) \\
4p^{1/2} & \rightarrow 4, 2,4 \quad (n, \kappa, \text{occu}) \\
4p^{3/2} & \rightarrow 4,-3,6 \quad (n, \kappa, \text{occu}) \\
4d^{5/2} & \rightarrow 5, 1,2 \quad (n, \kappa, \text{occu}) \\
5s^{1/2} & \rightarrow 4, 3,6 \quad (n, \kappa, \text{occu}) \\
4f^{5/2} & \rightarrow 4,-4,8 \quad (n, \kappa, \text{occu}) \\
4f^{7/2} & \rightarrow 0
\end{align*}
Valence electrons INSIDE atomic spheres are treated within scalar relativistic approximation [1] if RELA is specified in case.struct file (by default).

- 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 »

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 \( (\Psi_1) \)

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

sum include both up/down spin states

\( \rightarrow N \) is much smaller than the basis size in lapw1
**Implementation in WIEN2k: valence electrons**

→ **SOC is added in a second variation (lapwso):**

- First diagonalization (lapw1):
  \[ H_1 \Psi_1 = \epsilon_1 \Psi_1 \]

- Second diagonalization (lapwso):
  \[ \left( H_1 + H_{SO} \right) \Psi = \epsilon \Psi \]

The second equation is expanded in the basis of first eigenvectors \((\Psi_1)\)

\[
\sum_i^N \left( \delta_{ij} \epsilon_1^j + \langle \Psi_1^j | H_{SO} | \Psi_1^i \rangle \right) \langle \Psi_1^i | \Psi \rangle = \epsilon \langle \Psi_1^j | \Psi \rangle
\]

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
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 RLO is added
  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
The w2web interface is helping you

Non-spin polarized case
Controlling spin-orbit coupling in WIEN2k

The w2web interface is helping you

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.
- x symmetso Determines symmetry in spin-polarized 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, oclsumup/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

Spin polarized case
**Relativistic effects in the solid: Illustration**

- **LDA overbinding (7%)**
- **No difference NREL/SREL**

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

**hcp-Be**  
\[ Z = 4 \]
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

**hcp-Os**
- \( Z = 76 \)

**LDA overbinding (2%)**
- Clear difference NREL/SREL

**Bulk modulus:**
- NREL: 344 GPa
- SREL: 447 GPa
- Exp.: 462 GPa
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) The mass-velocity correction

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

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
(1) Relativistic orbital contraction

Radius of the 1s orbit (Bohr model):

\[ r(1s) = \frac{n^2a_0}{Z} \]

\[ a_0 = \frac{\hbar}{m_e c \alpha} = 1 \text{ bohr} \]

\[ r(1s) = \frac{1}{79} = 0.013 \text{ bohr} \]

Atomic units:
\[ \hbar = m_e = e = 1 \]
\[ c = 1/\alpha \sim 137 \text{ au} \]
(1) Relativistic orbital contraction

Radius of the 1s orbit (Bohr model):

\[ r(1s) = \frac{n^2 a_0}{Z} \quad \text{AND} \quad a_0 = \frac{\hbar}{m c \alpha} = 1 \text{ bohr} \]

\[ r(1s) = \frac{1}{79} = 0.013 \text{ bohr} \]

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

\[ M = \gamma \cdot m_e = 1.22 m_e \]

\[ a_0[\text{REL}A] = \frac{\hbar}{M_e c \alpha} = \frac{a_0}{\gamma} \]
(1) Relativistic orbital contraction

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

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

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

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

\[ n = 0, 1, 2 \ldots \]

\[ \text{Non relativistic (l=0)} \]

\[ \text{Relativistic (κ=-1)} \]

Orbital contraction

Au 6s

ns orbitals (with n > 1) contract due to orthogonality to 1s
(1) Orbital Contraction: Effect on the energy

Relativistic correction (%)
\[
\left( \frac{E_{\text{RELA}} - E_{\text{NRELA}}}{E_{\text{NRELA}}} \right)
\]

Orbital contraction

Non relativistic (l=0)  
Relativistic (κ=-1)

Au 1s

Au 6s

r^2ρ (e/bohr)

r (bohr)

1s 2s 3s 4s 5s 6s

0 10 20 30 40

-10 -20 -30 -40
(2) Spin-Orbit splitting of p states

---

Non-relativistic ($l=1$)

Au 5p
(2) Spin-Orbit splitting of p states

Spin-orbit splitting of l-quantum number

Non-relativistic (l=1)
Relativistic (κ = -2)

Au 5p

$p_{3/2}$ (κ = -2): nearly same behavior than non-relativistic p-state
(2) Spin-Orbit splitting of p states

- Spin-orbit splitting of l-quantum number

- $p_{1/2}$ ($\kappa=1$): 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

$p_{1/2} (\kappa=1)$: markedly different behavior than non-relativistic p-state $g_{\kappa=1}$ is non-zero at nucleus
Relativistic correction (%)\[\frac{(E_{\text{RELA}} - E_{\text{NRELA}})}{E_{\text{NRELA}}}\]

Scalar-relativistic p-orbital is similar to p\(^{3/2}\) wave function, but \(\Psi\) does not contain p\(^{1/2}\) radial basis function.

*Non relativistic (l=1)*

*Relativistic (\(\kappa=-2\))*

*Relativistic (\(\kappa=1\))*

---

(2) Spin-Orbit splitting of p states

**Au 5p**

\[r^2 \rho (\text{a/bohr})\]
Higher l-quantum number states expand due to better shielding of nucleus charge from contracted s-states.
Higher l-quantum number states expand due to better shielding of nucleus charge from contracted s-states

Non-relativistic (NREL)

\[ Z_{\text{eff1}} = Z - \sigma(\text{NREL}) \]
Higher l-quantum number states expand due to better shielding of nucleus charge from contracted s-states.

Non-relativistic (NREL): \[ Z_{\text{eff}1} = Z - \sigma(\text{NREL}) \]

Relativistic (REL): \[ Z_{\text{eff}2} = Z - \sigma(\text{REL}) \]

\[ Z_{\text{eff}1} > Z_{\text{eff}2} \]
Higher $l$-quantum number states expand due to better shielding of nucleus charge from contracted $s$-states.

**Non-relativistic (NREL)**

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

$Z_{\text{eff1}} > Z_{\text{eff2}}$

$+Z_{\text{eff1}}e$

**Relativistic (REL)**

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

$+Z_{\text{eff2}}e$

*Indirect relativistic effect*
(3) Orbital expansion: Au(d) states

Relativistic correction (%)

\[
\frac{E_{\text{RELA}} - E_{\text{NRELA}}}{E_{\text{NRELA}}}
\]

Orbital expansion: Au(d) states

- 3d\(^{3/2}\) 3d\(^{5/2}\) \(\kappa=2\) \(\kappa=-3\)
- 4d\(^{3/2}\) 4d\(^{5/2}\)
- 5d\(^{3/2}\) 5d\(^{5/2}\) \(\kappa=3\) \(\kappa=-4\)

Au 3d

Au 5d

Orbital expansion

Non relativistic (l=2)
Relativistic (\(\kappa=2\))
Relativistic (\(\kappa=-3\))
Relativistic effects on the Au energy levels

\[
\frac{E_{\text{RELA}} - E_{\text{NRELA}}}{E_{\text{NRELA}}}
\]
Atomic spectra of gold

Non-relativistic
Ry

6s  -0.33
5d  -0.60
5p  -3.98
5s  -6.20

Relativistic
Ry

6s  -0.45
5d_{5/2}  -0.47
5d_{3/2}  -0.58
5p_{3/2}  -4.07
5p_{1/2}  -5.28
5s  -7.94

Orbital contraction
Orbital expansion
SO splitting
SO splitting
Ag – Au: the differences (DOS & optical prop.)
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 $p^{1/2}$

**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 k-list)
> - initso_lapw (must be executed) detects new symmetry setting

<table>
<thead>
<tr>
<th></th>
<th>Direction of magnetization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[100]</td>
</tr>
<tr>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>(m_x)</td>
<td>A</td>
</tr>
<tr>
<td>(m_y)</td>
<td>B</td>
</tr>
<tr>
<td>(2_z)</td>
<td>B</td>
</tr>
</tbody>
</table>
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*
Magnetic coupling
&
Magnetic anisotropy

Xavier Rocquefelte
Institut des Sciences Chimiques de Rennes
(UMR 6226) Université de Rennes 1, FRANCE
Magnetic properties:

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

Spin-State  Long-range order  Magnetic exchange  Magnetic anisotropy

Energy scale (eV)

$10^0$  $10^{-3}$  $10^{-6}$
INTRODUCTION

Paramagnetic (PM) order

Ferrimagnetic order

Ferromagnetic (FM) order

Antiferromagnetic (AFM) order
Magnetic susceptibility of a ferromagnetic (FM) compound

\[
\chi_{\text{mol}}(\text{emu/mol})
\]

PM without long range interaction

T(K)
Magnetic susceptibility of a ferromagnetic (FM) compound

\[ \chi_{\text{mol}}(\text{emu/mol}) \]

PM without long range interaction

T(K)

0

0.1

0.2

0.3

0.4
Magnetic susceptibility of a ferromagnetic (FM) compound
Magnetic susceptibility of a ferromagnetic (FM) compound
Magnetic susceptibility of a ferromagnetic (FM) compound
Magnetic susceptibility of an antiferromagnetic (AFM) compound
Magnetic susceptibility of an antiferromagnetic (AFM) compound

Graph showing the magnetic susceptibility ($\chi_{\text{mol}}$ in emu/mol) against temperature (T in K) for PM without long-range interactions.
Magnetic susceptibility of an antiferromagnetic (AFM) compound

\[ \chi_{\text{mol}}(\text{emu/mol}) \]

AFM without long-range interactions

PM without long-range interactions

\( J_{\text{AF}} \)
COLLINEAR MAGNETISM

**Ferromagnetic**

- Curie temperature: $T_C$
- $\chi_{\text{mol}}$ (emu/mol) graph showing $\chi_{\text{mol}}$ decreasing with $T$.
- Ferromagnetic order ↑ when $kT$ ↓
- Ferromagnetic exchange: $J_F < 0$

**Antiferromagnetic**

- Néel temperature: $T_N$
- $\chi_{\text{mol}}$ (emu/mol) graph showing $\chi_{\text{mol}}$ increasing with $T$ and then decreasing.
- Antiferromagnetic exchange: $J_{AF} > 0$
AFM with 2 subnetworks having different magnetization directions

Frustrated AFM

Topologic frustration

⇒ weak ferromagnetism

FM-AFM competition

\[ J_1 : \text{FM} \quad J_2 : \text{AFM} \]
NON-COLLINEAR MAGNETISM

AFM with 2 subnetworks having different magnetization directions

Frustrated AFM

Topologic frustration  
FM-AFM competition

Magnetic moment has a direction in space

⇒ spin-orbit coupling

J_1: FM  J_2: AFM
Estimation of magnetic coupling parameters

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

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

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

$J_{ij} > 0 \Rightarrow$ AFM  

$J_{ij} < 0 \Rightarrow$ FM

Long-range order
Estimation of magnetic coupling parameters

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

$H = H_0 + \sum_{i<j} J_{ij} \vec{S}_i \cdot \vec{S}_j$

$J_{ij} > 0 \Rightarrow$ AFM

$J_{ij} < 0 \Rightarrow$ FM

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

$S$: Spin held by the magnetic center

$\sigma_i = \pm 1$ (up or down spin)

$J_{ij}$: spin exchange parameter between the spin sites $i$ and $j$
Estimation of magnetic coupling parameters

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

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

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

$J_{ij} > 0 \Rightarrow \text{AFM}$

$J_{ij} < 0 \Rightarrow \text{FM}$

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 ($S = \frac{1}{2}$)

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

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

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

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

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

$J_{12} = 2 \left( E_{\text{FM}} - E_{\text{AFM}} \right)$
Estimation of magnetic coupling parameters

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

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

\(\text{Ni}^{2+} \rightarrow S = 1\)
Estimation of magnetic coupling parameters

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

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

\( \text{Ni}^{2+} \rightarrow S = 1 \)

2 inequivalent Ni sites in the rhombohedral unit cell (S.G. R-3m)

\( J \): magnetic coupling defined by \( \text{Ni}_1-O-\text{Ni}_2 \) path (angle: 180°)

12J / unit cell

2J / f.u.
Estimation of magnetic coupling parameters

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

$\text{Ni}^{2+} \rightarrow S = 1$

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

2 inequivalent Ni sites in the rhombohedral unit cell (S.G. R-3m)

$J$: magnetic coupling defined by Ni$_1$-O-Ni$_2$ path (angle: 180°)

$E_{FM} = E_0 + 2J$

$E_{AFM} = E_0 - 2J$

$J = (E_{FM} - E_{AFM}) / 4$
Magnetic structure of NiO - GGA+U calculations

PRB 62, 16392 (2000)

$Ni \text{ M.M. (exp.)} = 1.64 - 1.9 \mu_B$
Magnetic structure of NiO - GGA+U calculations

$E_g (\text{exp.}) = 3 - 4.4 \text{ eV}$

PRB 62, 16392 (2000)
Magnetic structure of NiO - GGA+U calculations

-6 383.9
-6 383.95
-6 384
-6 384.05
-6 384.1
-6 384.15
-6 384.2
-6 384.25
-6 384.3
-6 384.35
-6 384.4
-6 384.45
-6 384.5
-6 384.55
-6 384.6
-6 384.65
-6 384.7
-6 384.75
-6 384.8
-6 384.85
-6 384.9
-6 384.95
-6 385

$U_{\text{eff}}$ (eV)

TOTAL ENERGY (Ry)

Exp. Ground State: AFM

AFM (more stable)

FM
Magnetic structure of NiO - GGA+U calculations

$J_{(exp.)} = 19 \text{ meV}$

PRB 6, 3447 (1972)
Estimation of the magnetic anisotropy

♦ 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
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:

$$\text{MAE} = E[uvw] - E[\text{easy axis}]$$

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

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

Estimation of the magnetic anisotropy allows to define the magnetization easy and hard axes.

Here we have considered the following expression:

$$MAE = E[u \, v \, w] - E[\text{easy axis}]$$

$E[u \, v \, w]$ is the energy deduced from spin-orbit calculations with the magnetization along the $[u \, v \, w]$ crystallographic direction.

Relativistic effects & Non-collinear magnetism

(WIEN2k / WIENncm)

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Institut des Sciences Chimiques de Rennes (UMR 6226) Université de Rennes 1, FRANCE
Pauli Hamiltonian for magnetic systems

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

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

(2x2) Pauli spin matrices
Pauli Hamiltonian for magnetic systems

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

\[
H_P = -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}} + \mu_B \vec{\sigma} \cdot \vec{B}_{\text{eff}} + \zeta (\vec{\sigma} \cdot \vec{l}) + ... 
\]

\[
\begin{pmatrix}
\sigma_1 & \frac{1}{2} \\
\frac{1}{2} & \sigma_2
\end{pmatrix}
\]

(2x2) 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

\[
H_P = -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}} + \mu_B \vec{\sigma} \cdot \vec{B}_{\text{eff}} + \xi (\vec{\sigma} \cdot \vec{l}) + \ldots
\]

Effective electrostatic potential

\[
V_{\text{eff}} = V_{\text{ext}} + V_H + V_{\text{xc}}
\]

Effective magnetic field

\[
B_{\text{eff}} = B_{\text{ext}} + B_{\text{xc}}
\]

Exchange-correlation potential

Exchange-correlation field
Pauli Hamiltonian for magnetic systems

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

- Effective electrostatic potential:
  \[ V_{\text{eff}} = V_{\text{ext}} + V_H + V_{\text{xc}} \]
- Effective magnetic field:
  \[ B_{\text{eff}} = B_{\text{ext}} + B_{\text{xc}} \]
- Spin-orbit coupling:
  \[ \zeta = \frac{\hbar^2}{2M_e^2c^2} \frac{1}{r} \frac{dV}{dr} \]

Many-body effects which are defined within DFT LDA or GGA.
Exchange and correlation

From DFT exchange correlation energy:

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

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

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

\[
V_{xc} = \frac{\partial E_{xc}(\rho, \bar{m})}{\partial \rho} \quad \quad \quad \hat{B}_{xc} = \frac{\partial E_{xc}(\rho, \bar{m})}{\partial \bar{m}}
\]

LDA expression for \(V_{xc}\) and \(B_{xc}\):

\[
V_{xc} = \varepsilon_{xc}^{hom}(\rho, \bar{m}) + \rho \frac{\partial \varepsilon_{xc}^{hom}(\rho, \bar{m})}{\partial \rho} \quad \quad \quad \hat{B}_{xc} = \rho \frac{\partial \varepsilon_{xc}^{hom}(\rho, \bar{m})}{\partial \bar{m}} \hat{m}
\]

\(B_{xc}\) is parallel to the magnetization density vector \((\hat{m})\)
Non-collinear magnetism

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

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

\[
\begin{pmatrix}
-\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}} + \mu_B B_z + \ldots \\
\mu_B (B_x - iB_y) \\
\mu_B (B_x + iB_y) \\
-\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}} - \mu_B B_z + \ldots
\end{pmatrix}
\psi = \varepsilon \psi
\]

\[ \psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \]  
\[ \psi_1 \text{ and } \psi_2 \text{ are non-zero} \]

♦ Solutions are non-pure spinors
♦ Non-collinear magnetic moments
Collinear magnetism

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

\[ H_P = -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}} + \mu_B \vec{\sigma} \cdot \vec{B}_{\text{eff}} + \xi (\vec{\sigma} \cdot \vec{l}) + \ldots \]

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

\[
\psi^\uparrow = \begin{pmatrix} \psi_1 \\ 0 \end{pmatrix}, \quad \psi^\downarrow = \begin{pmatrix} 0 \\ \psi_2 \end{pmatrix}
\]

\[ \varepsilon^\uparrow \neq \varepsilon^\downarrow \]

- 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

$$H_P = -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}} + \mu_B \mathbf{\vec{B}}_{\text{eff}} + \xi (\mathbf{\vec{e}} \cdot \mathbf{l}) + \ldots$$

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

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

- Solutions are pure spinors
- Degenerate spin solutions
Magnetism and WIEN2k

Wien2k can only handle collinear or non-magnetic cases

**non-magnetic case**

\[ m = n_↑ - n_↓ = 0 \]

**run_lapw script:**

- \( x \) lapw0
- \( x \) lapw1
- \( x \) lapw2
- \( x \) lcore
- \( x \) mixer

**magnetic case**

\[ m = n_↑ - n_↓ \neq 0 \]

**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
**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 !!!
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.

Relation between spin density matrix and magnetization

\[
\begin{align*}
    m_z &= n_{\uparrow\uparrow} - n_{\downarrow\downarrow} \\
    m_x &= \frac{1}{2}(n_{\uparrow\downarrow} + n_{\downarrow\uparrow}) \\
    m_y &= i\frac{1}{2}(n_{\uparrow\downarrow} - n_{\downarrow\uparrow})
\end{align*}
\]

runncm_lapw script:

- xncm_lapw0
- xncm_lapw1
- xncm_lapw2
- xncm_lcore
- xncm.mixer

DOS

E_F
\[ \alpha = \vec{R} \cdot \vec{q} \]

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

- Spin-spiral is defined by a vector \( q \) given in reciprocal space and an angle \( \theta \) between magnetic moment and rotation axis.

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

\[ \Rightarrow \text{Translational symmetry is lost!} \]

\[ \Rightarrow \text{But WIENncm is using the generalized Bloch theorem. The calculation of spin waves only requires one unit cell for even incommensurate modulation q vector.} \]
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)

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