Magnetism, relativistic effects strongly correlated solids

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"Spin-polarized calculations"
- runsp_lapw (for magnetic cases, case.clmup/dn)
  - runs lapw1/2 for both spins independently
- case.scf contains additional information:
  - MMT total moment
  - MMJ001 moment within 1st atomic sphere
  - HFF001 contact hyperfine field
- runfsm_lapw –m Moment (fixed-spin-moment calc.)
  - for difficult to converge magnetic cases or simply to constrain a moment
- runafm_lapw (Antiferromagnetic, use with care)
  - calculates only spin-up, uses symmetry to generate spin-dn
  - faster, more stable convergence
  - afminput requires "original" struct file or a symmetry operation which transforms the AFM-atoms into each other. The AFM subgroup can be "klassengleich" (bcc Cr) or "translatengleich" (same lattice, less symmetry)

Stoner-Magnetism

non-magnetic DOS
magnetic DOS

spin-dn states shift upwards by exchange-splitting

m_{UB} = n_{up} - n_{dn}

FSM curves

high-spin/low-spin
magnetic moment
Relativistic effects

Dirac equation in central field (spherical symmetry):

\[
\left\{ \frac{p^2}{2m} + V - \frac{p^4}{8m^2c^2} - \frac{\hbar^2}{4m^2c^2} \frac{dV}{dr} r + \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} (\vec{l} \cdot \vec{s}) \right\} \Phi = \epsilon \Phi
\]

Non-rel. SE, mass + Darwin, spin-orbit

Due to SO spin \( s \) and orbital angular momentum \( l \) are no longer good quantum numbers. Instead use total angular momentum \( j = l \pm s \).

<table>
<thead>
<tr>
<th>j = l ± s/2</th>
<th>( l = s \pm \frac{1}{2} )</th>
<th>occupation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>s = -1</td>
<td>1</td>
</tr>
<tr>
<td>s</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>p</td>
<td>1/2</td>
<td>2</td>
</tr>
<tr>
<td>d</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>f</td>
<td>3</td>
<td>6</td>
</tr>
</tbody>
</table>

Thorium

<table>
<thead>
<tr>
<th>n = 6</th>
<th>Energy (Ry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6d_{3/2}</td>
<td>-0.24</td>
</tr>
<tr>
<td>7s</td>
<td>-0.32</td>
</tr>
<tr>
<td>6p_{3/2}</td>
<td>-1.55</td>
</tr>
<tr>
<td>6p_{1/2}</td>
<td>-2.12</td>
</tr>
<tr>
<td>6s</td>
<td>-3.33</td>
</tr>
</tbody>
</table>

Relativistic orbital contraction

Au s orbital (no SOC)

- 1s contracts due to relativistic mass enhancement
- 2s - 6s contract due to orthogonality to 1s

\[ M = m/\sqrt{1 - (v/c)^2} \]  ν proportional Z: Gold: Z = 79; M = 1.2 m

SOC splitting: Au 5p state

- Spin Orbit splitting of l-quantum number.
- \( P_{1/2} (\kappa = 1) \): markedly different behavior than non-relativistic p-state
- \( g_\nu=1 \) : non-zero at nucleus
Orbital expansion: Au d states

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

Gold - atomic spectra

Scalar relativistic approximation

Drop all terms which depend on $\kappa$, keep Darwin and enhanced mass $M$ and modified large $\tilde{g}$ and small $\tilde{f}$ component of $\Phi$

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

with $M = m + \frac{\varepsilon - V}{2c^2}$ and $\tilde{f} = \frac{1}{2Mc} \frac{d\tilde{g}}{dr}$

Spin $s$ and $l$ are still good quantum numbers.
The four-component wave function $\tilde{\Psi}$ contains $\tilde{\Phi}$ as pure spin state

$$\tilde{\Psi} = \begin{pmatrix} \tilde{\Phi} \\ \tilde{\chi} \end{pmatrix}, \quad \tilde{\Phi} = \tilde{g} Y_{lm} \chi_s$$

Spin-orbit in second variation

Use the scalar-relativistic (pure-spin) eigenstates $\tilde{\Psi}_n$ (with $E_n < E_{cut}$) as basis and add Spin-orbit interaction:

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

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

SO mixes spin-up and dn states ("doubles matrixsize").

Scalar-relativistic p-orbital is similar to $p_{3/2}$ wave function, but $\tilde{\Psi}$ does not contain $p_{1/2}$ radial basis function:

Add "Local orbital" with $p_{1/2}$ radial function
Relativistic semi-core states in fcc Th

- additional local orbitals for 6p_{1/2} orbital in Th
- Spin-orbit (2nd variational method)


Spin-orbit coupling: magnetic systems

- Define direction of magnetism (coupled to the lattice only by SO, magneto crystalline anisotropy)
- Possible reduction of symmetry: magnetic field breaks time-inversion and spin transforms like a pseudovector (current due to magn.field)
  - number of symmetry operations reduced
  - Irreducible BZ enlarged (do NOT "add" Inversion!)
  - atoms may become non-equivalent, reduced local symmetry (more LM)

_initso_lapw (with symmetso) detects new symmetry and creates new files (case.struct, in*, clm*).
- Symmetry operations are classified into
  - A (preserves real space AND direction of spin)
  - B (preserves real space, inverts magnetic moment). Together with time-inversion this is still a valid symmetry operation.

Spin-orbit coupling: symmetry

<table>
<thead>
<tr>
<th>direction of magnetization</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
<tr>
<td>m_x</td>
</tr>
<tr>
<td>m_y</td>
</tr>
<tr>
<td>2_z</td>
</tr>
</tbody>
</table>

Spin-orbit coupling: symmetry

- 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 a better 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*
case.inso

WFFIL
4 1 0
-10.0000 1.50000
0 0 0 1
llmax,ipr,kpot
emin,emax (output energy window)
direction of magnetization (lattice vectors)
1
number of atoms for which RLO is added
2
atom number,e-lo,de (case.in1), repeat NX times
0 0 0 0
number of atoms for which SO is switched off, atoms

Ag – Au: the difference

Spin-orbit splitting of the $L$-gap surface state on Au-111 and Ag-111

G. Nicolay, F. Reinert, S. Hüfner, P. Blaha, PRB 65, 33407

Beyond LDA (GGA)

LDA+U
Success and failure of “standard” DFT in solids

- Standard LDA (GGA) gives good description of structural and electronic properties of most solids (lattice parameters within 1-2%, at least qualitatively correct bandstructure, metal-insulator, magnetism, …)
- Problems: “localized” (correlated) electrons
  - late 3d transition metal oxides/halides
    - metals instead of insulators (FeO, FeF₂, cuprates, …)
    - nonmagnetic instead of anti-ferromagnetic (La₃CuO₄, YBa₂Cu₃O₆)
  - 4f, 5f electrons
    - all f-states pinned at the Fermi energy, “always” metallic
    - orbital moments much too small
- “weakly” correlated metals
  - FeAl is ferromagnetic in theory, but nonmagnetic experimentally
  - 3d-band position, exchange splitting, …

FeO, Cu-oxides

- FeO

PBE-GGA

EV-GGA (splits bands with good “start”)

Cuprates (La₂CuO₄, YBa₂Cu₃O₆)

- LDA and GGA yields non-magnetic metals instead of AFM insulators

Can LSDA be improved?

- ab initio methods
- GGA: usually improvement, but often too small.
- Exact exchange: imbalance between exact X and approximate C
- Hybrid functionals: Hartree-Fock + LDA/GGA mix (adiabatic connection)
- GW: gaps in semiconductors, but groundstate? expensive!
- Quantum Monte-Carlo: very expensive
  - not fully ab initio
- Self-interaction-correction: vanishes for Bloch states
- Orbital polarization: Hund’s 2nd rule by atomic Slater-parameter
- LDA+U: strong Coulomb repulsion via external Hubbard U parameter
- DMFT: extension of LDA+U for weakly correlated systems

“Beyond-LDA” results for NiO

- LDA: tiny gap, Ni-d higher than O-p
- Beyond LDA:
  - gap: ok! (by design)
  - but:
  - bandwidth
  - position of Ni-d and O-p bands vary a lot

Massida etal., PRB55, 13494 (1997)
Szotec etal., PRB47, 4029 (1993)
Anisimov etal., PRB48, 16929 (1993)
**Beyond-LDA** results for NiO

I. Moreira et al., PRB65, 155102 (2002)

LDA, hybrid-DFT or Hartree-Fock:

- **gaps, bandstructure (spectra):** not groundstate properties
  - validity is difficult to judge
  - some properties (like gaps or magnetic moments) are obtained by "design"

- compare electron density (or "related" quantities)
  - X-ray diffraction has improved (synchrotrons, detectors), but only for Si it might be accurate enough to test DFT-methods

**Electric field gradients**

Fe-EFG in FeF₂:
- LSDA: 6.2
- GGA: 16.8
- exp: 16.5

**LDA+U method**

- Separation of electrons into two subsystems:
  - itinerant electrons (described by LSDA)
  - Localized d (f) electrons:
    \[
    E^{ee} = \frac{1}{2} U N^2 - \frac{1}{2} J \sum_{\sigma} N_{\sigma}^2 - \frac{1}{2} (U - J) \sum_{\sigma} n_{\sigma}^2
    \]
  - \(N\)...total number of e⁻, \(n_{\sigma,m}\)...orbital occupancies

- Hubbard U describes the coulomb energy cost to place two electrons at the same site:
  \[
  U = E(n + 1) + E(n - 1) - 2E(n) \quad \Rightarrow \quad n + \bullet + n + 1 + n - 1
  \]

- \(J\) is the averaged intraatomic exchange parameter

**LDA+U Functional**

- Define a new energy functional:
  \[
  F^{LDA+U} = F^{LDA} + E^{ee}(n) - F^{dc}(n)
  \]

- Double counting term \(F^{dc}\) can be approximated in several ways
  - **Fully localized limit** (Anisimov et al.): Assumes that the total number of d (f) electrons \(N = \sum n_m\) is given properly by LDA (but not the eigenvalues). Their energy is (SC free Hartree energy):
    \[
    E^{dc} = U/2 N(N - 1) - J/2 \sum_{\sigma} N_{\sigma}^2
    \]
    \[
    V_{m,m',\sigma} = (U - J)(n_{m',\sigma} - n_{m,\sigma})
    \]
    can shift center of bands

  - **Around mean field approximation** (Czyzyk&Sawatzky):
    \[
    E^{dc} = \frac{1}{2} U N^2 - \frac{1}{2} J \sum_{\sigma} N_{\sigma}^2 - \frac{1}{2} (U - J) \sum_{\sigma} n_{\sigma,\text{aver}}^2
    \]
    \[
    V_{m,m',\sigma} = (U - J)(n_{\text{aver},\sigma} - n_{m,\sigma})
    \]
    leaves center unchanged

- Orbitals with occupancies \(n_{m,\sigma}\) larger than \(1/2\) (or \(n_{\text{average}}\)) become more occupied, others become depopulated.
rotational invariant LDA+U

- In essence, LDA+U shifts occupied states \( n_i > ½ \) down in energy by \( U/2 \) (increasing the occupation \( n_i \)) and empty states up (decreasing their occupation).

- A generalization leads to the “rotational invariant LDA+U” method, which is independent of coordinate systems, uses the full density matrix \( n_{m,m'} \) and two parameters, Hubbard U and Stoner exchange J.

- U and J can be taken from experiment or estimated by constraint LDA calculations (see recipe on our website).

\( U \ldots 2-10 \text{ eV}, J \ldots 1-2 \text{ eV} \)

LDA+U in WIEN2k:

- cp $WIENROOT/SRC_templates/case.inorb .
- cp $WIENROOT/SRC_templates/case.indm .
- cp $WIENROOT/SRC_templates/case.indm .
  (done automatically in w2web)
- Specify atoms, orbitals, double counting correction (FLL) and U (J=0)
- runsp_lapw -orb
- for nonmagnetic cases use runsp_c_lapw -orb
- Note: Different solutions may be obtained when starting from different density matrices.

Cuprates

- \( \text{La}_2\text{CuO}_4 \): nonmagnetic metal instead of AFM insulator

LDA+U in weakly correlated metals: FeAl

- Experimentally
  - FeAl is nonmagnetic
- DFT
  - Conventional LSDA calculation
    - yields a ferromagnetic ground state
  - LDA+U(AFM)
    - nonmagnetic
    - \( \text{Fe-t}_{2g} \) and \( \text{Fe-e}_g \) affected differently