The Role of Relativity in Magnetism:
Calculating Magnetic Moments in Solids

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Background: Magnetism and Relativity
- Localized and itinerant models of magnetism (Hund’s rules and band model)
- Dirac equation and associated quantities important for magnetism

Survey of Phenomena that Affect Magnetic Moments
- Relativistic mass shifts orbitals and broadens bands
- Spin polarization produces a spin moment
- Orbital polarization produces an orbital moment
- Spin-orbit induces an orbital moment

Method: Electronic Structure and Experiment
- An introduction to non-magnetic DFT(LDA): Non-relativistic
- “Spin-only” relativistic DFT(LSDA) calculates spin moments
- Orbital polarization and spin-orbit corrections for orbital moments
- Magnetic neutron scattering measures spin and orbital moments

Results: Calculated Magnetic Moments Compared with Neutron Measurements
- Transition metals (3d)
- Lanthanides (4f)
- Actinides (5f)

Concluding Remarks
Localized Magnetism

- In localized model, electrons and their moments are confined to a non-interacting atom.
- Applies to free ions, insulators, or localized atomic state.

Moments are well described by Hund’s rules:

1. Maximize S (Spin Polarization)
2. Maximize L (Orbital Polarization)
3. $J = |L - S|$ for less than half filled
   $J = |L + S|$ for more than half filled
   (Minimize $H_{SO} = \xi(L \cdot S)$)

- Spin and orbital moments of single electrons being
  
  $\mu_{\text{spin}} = 2 \mu_B [S(S + 1)]^{1/2}$ \text{ and } $\mu_{\text{orbital}} = \mu_B [L(L + 1)]^{1/2}$

- Atomic magnetic moment is given by
  
  $\mu_{\text{atom}} = g_J \mu_B [J(J + 1)]^{1/2}$ with $g_J = 1 + \frac{J(J+1)-L(L+1)+S(S+1)}{2J(J+1)}$
- Band picture: atomic orbitals overlap and form energy bands.
- Delocalized electrons become responsible for magnetic properties.
- Stoner model: Favorable to spend KE for a gain in exchange energy \( I g(E_f) > 1 \)
  \( \rightarrow \) Spin-up and -down bands spontaneously spin split.
  \( \rightarrow \) Requires narrow bands with large DOS at the Fermi Energy.
Magnetism from Relativity: Dirac Equation

- Dirac equation: relativistic, quantum mechanical description of the electron.
  → Naturally incorporates spin and fine structure

\[
i\hbar \frac{\partial \Psi}{\partial t} = (c\alpha \cdot (p - \frac{qA}{c}) + \beta mc^2 + qV)\Psi
\]

\[
\begin{pmatrix}
0 & \sigma \\
\sigma & 0
\end{pmatrix}
\quad \text{and} \quad
\begin{pmatrix}
I & 0 \\
0 & -I
\end{pmatrix}, \quad \Psi = \begin{pmatrix} \Phi \\ \chi \end{pmatrix}
\]

- Leads to two coupled equations: two positive and two negative energy solutions.

- Equation in \( \Phi \) (\( E > 0 \)): (Expand to order \((v/c)^4\) for \( V(r) \) only)

\[
\left[ \frac{p^2}{2m} + V(r) - mc^2 \left( \frac{1}{8} \left( \frac{p}{mc} \right)^4 \right) + \frac{1}{2m^2c^2r} \frac{1}{dr} \frac{dV}{dr} (\boldsymbol{S} \cdot \boldsymbol{L}) - \frac{\hbar^2}{4m^2c^2} \frac{dV}{dr} \frac{\partial}{\partial r} \right] \Phi = E\Phi
\]

- Spin-orbit energy scales as \( \sim Z^4 \) to \( Z^2 \)
**Effects of Relativistic Mass Correction**

**Consequences of the relativistic mass increase**
- **Contraction of the s and p orbitals:**
  \[ a_{Bohr} \sim \frac{n^2}{mZ} = \frac{n^2}{m_0Z} = a^0_B \sqrt{1 - \frac{v^2}{c^2}} \]
- Screening causes d and f orbitals to expand
- Results in a change in band width:
  \[ Z=29 \text{ Cu}, \, Z=47 \text{ Ag}, \, Z=79 \text{ Au} \]
  \[ \rightarrow \text{shift in d-band edge of Cu, Ag, and Au} \]
  - Effect grows with \( Z \) (\(~1.5 \text{ eV for Au}\))

**Typical shifts**
- 3d metals: 0.1-0.5 eV
- 4f metals: 1-6 eV
- 5f metals: 6-10 eV
Spin Polarization (Hund’s First Rule))

- Itinerant states (e.g., 3d, 5f), bands spin-split.
- Localized 4f state is free-ion-like

**Typical energy gain**
- 3d metals 0.04-0.4 eV
- 4f metals: 0.5-10 eV
- 5f metals: 3d<E<4f

Plot shows spin-pairing energy gain for free-ion 4f states.
Orbital Polarization (Hund’s Second Rule)

- Plot shows orbital-polarization energy gain for free-ion 4f states.

- In itinerant systems, the orbital polarization is more complex and largely quenched by crystal fields.

**Typical energy gain**
- 3d metals 0.0001-0.002 eV
- 4f metals: 0.5-1.7 eV
- 5f metals: 3d<E<4f
Spin-orbit (Hund’s Third Rule)

**SO in localized states**
- SO coupling energies for free-ion 4f states:

**SO in the itinerant picture:**
- Small effect on band position and width
- Large d-state splitting in interior of DOS (0.19, 0.40, 1.2 eV)

**Typical SO coupling energies**
- 3d metals 0.003-0.01 eV
- 4f metals: 0.1-0.9 eV
- 5f metals: 0.3-2 eV
Spin Polarization + Spin-Orbit Induces Orbital Moment

Model DOS for Fe, Co, and Ni:

- SO coupling lifts degeneracy between $m_l$ and $-m_l$ states.
- Orbital moment develops.
Basics of Density Functional Theory

Non-relativistic DFT


- Hohenberg-Kohn: $E_{\text{tot}}$ is a unique functional of electron density, $n(r) = \sum_{i}^{\text{occ.}} |\psi_{i}(r)|^2$.

- $E_{\text{tot}}[n(r)]$ is a minimum for the ground state density.

- Construct the functional:

  \[
  E_{\text{tot}}[n(r)] = T[n(r)] + E_{e-e}[n(r)] + E_{xc}[n(r)] + \int V_{\text{ext}}(r)n(r)dr
  \]

- Minimize $E_{\text{tot}}[n(r)]$ wrt $n(r)$, to yield single particle “Kohn-Sham” equation:

  \[
  \left\{-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}}[n(r)]\right\} \psi_{i}(r) = \epsilon_{i}\psi_{i}(r)
  \]

  \[
  V_{\text{eff}}[n(r)] = V_{\text{ext}}[n(r)] + V_{e-e}[n(r)] + \frac{\delta E_{xc}[n(r)]}{\delta n(r)}
  \]

- Use Local Density Approximation for unknown $E_{xc}[n]$

  \[
  E_{xc}^{LDA}[n(r)] = \int n(r)\epsilon_{xc}^{heg}[n]dr
  \]

- Solve the set of equations self-consistently
Spin-polarized, Relativistic DFT (LSDA)

In Relativistic DFT, the theorems are generalized for the analogue quantities

\[ n(r) \to J_\mu(r) = [n(r), J(r)] \]
\[ V_{\text{ext}}(r) \to A_{\mu}^{\text{ext}}(r) = [V_{\text{ext}}(r), A_{\text{ext}}(r)] \]

- A fully relativistic functional can be constructed

\[ E_{\text{rel}}^{tot}[J_\mu(r)] = T[J_\mu(r)] + E_{e-e}[J_\mu(r)] + E_{xc}[J_\mu(r)] + \int J_\mu(r)A_{\mu}^{\text{ext}}(r)dr \]

Simplification: Couple the magnetic field to the spin only → Use “spin-only” functional:

\[ E_{\text{tot}}[J_\mu(r)] = T[J_\mu(r)] + E_{e-e}[J_\mu(r)] + E_{xc}[J_\mu(r)] + \int (n(r)V_{\text{ext}}(r) - m(r) \cdot B_{\text{ext}}(r)) dr \]

- Minimize this functional wrt electron and magnetization densities (n and m)
→ obtain set of self-consistent spin-polarized (scalar) relativistic equations.
→ They will contain a \( V_{\text{eff}} \) and \( B_{\text{eff}} \).
- Use Local Spin Density Approximation for exchange correlations (Hund’s first):

\[ E_{xc}^{LSDA}[n(r), m(r)] = \int n(r)e_{xc}^{spheg}[n(r), m(r)]dr \]

→ XC of different spin states, but not orbital states.
Orbital Polarization Correction

- LSDA ignores orbital correlations ⇒ no chance for orbital polarization (Hund’s second)

- Solution: Make ad hoc correction to single-particle energies as follows:

- Correlate orbital states with a Hamiltonian of the form

\[-\frac{1}{2} \sum_{i \neq j} l_i \cdot l_j\]

- In a mean-field treatment, a term proportional to $L^2$ is added to $E_{xc}[n]$:

\[E_{OP}[n] = -\frac{1}{2} RL^2\]

- By the Kohn-Sham minimization, a one-electron eigenvalue shift is obtained:

\[\delta \epsilon_{ml} = -\frac{\partial E_{OP}}{\partial n_{ml}} = -RLm_l\]
Spin-Orbit Correction

• To include Hund’s third rule, add in SO Hamiltonian:

\[ H_{SO} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{\partial V(r)}{\partial r} S \cdot L \]

• S and L are no longer good quantum numbers. → Work with eigenstates of J.

• Doubling in size of basis to solve secular equation.

• Simplification: “Second variational treatment:”

1. Solve \((H^{SR} - \epsilon_N^{SR} S^{SR})C_N^{SR} = 0\) in a pure spin basis for N solutions \(C_N^{SR}\) and \(\epsilon_N^{SR}\).

2. Using the lowest N SR orbitals, form n eigenstates in J.

3. Solve the secular equation again with \(H = \epsilon^{SR}\delta_{ij} + H^{SO}\)
Measurement of Moments: Magnetic Neutron Scattering

• Incident neutron sees different spin and orbital magnetization distribution.

• Form factor is a direct measure of magnetization distribution in an atom.

\[ f_L(Q) = \int M_L(r) \exp(iQ \cdot r) \quad \text{and} \quad f_S(Q) = \int M_S(r) \exp(iQ \cdot r) \]

• Expand \( f \) in functions that describe radial and angular distribution of spin and orbital densities: \( C(\theta,\phi)_i < j_i(Q) > \Rightarrow f(Q) = \langle j_0 \rangle + C_2 \langle j_2 \rangle + C_4 \langle j_4 \rangle + \ldots \)

• Dipole approximation: \( f_S \approx \langle j_0 \rangle \) and \( f_L \approx \langle j_0 \rangle + \langle j_2 \rangle \)

• Magnetic amplitude, \( \mu_{tot} f(Q) \), is measured and written as

\[ \mu_{tot} f(Q) = \mu_S f_S(Q) + \mu_L f_L(Q) = \mu_{tot} [\langle j_0 \rangle + C_2 \langle j_2 \rangle] \]

• \( C_2 = \mu_L / \mu_{tot} \Rightarrow \) extract \( \mu_s \) and \( \mu_l \) by fitting data.
3d, 4f, and 5f Orbital Properties

- 4f most localized, most shielded
- 3d most extended, least shielded
- 5f lies in between
• **3d states**: small Z, large crystal field quenching.

• Spin moments agree very well with experiment.

• Total magnetic moment described by LSDA alone.

• Orbital magnetic moment is small due to quenching.

• SO induces small orbital moment; Orbital moment improves with OP.
Magnetic Moments: 4f Lanthanides

- **4f states**: large Z, no quenching
- Large orbital moments due to SO and OP.
- Total moment requires LSDA and SO+OP.
- Total moment agrees well with Hund’s rules for free ion.
Magnetic Moments: 5f Actinides

- **5f states**: large Z, partial quenching
- Orbital and spin moments are similar in size
- LSDA spin moments lie below experiment.
- Orbital roughly agree with experiment; worse for SO+OP.
- Errors cancel for total moment?

LSDA+SO+OP scheme needs improvement for very heavy actinide systems.
Conclusions

- Relativity plays a major role in magnetism.

- Mass correction, and Hund’s rules (spin polarization, spin-orbit, orbital-polarization) are essential for calculating accurate moments.

- Relativistic, spin-polarized DFT(LSDA) is flexible enough to handle both localized and itinerant systems.

- DFT(LSDA)+ corrections shows good agreement with neutron magnetic scatting experiments.