Atomic magnetism

- Splitting of these degeneracies by Coulomb interactions between electrons is a hard, many-electron problem!

- For isolated atoms, i.e. with spherical symmetry, some general rules apply. These are called “Hund’s rules” (Hund was German so I guess these are actually “dog’s rules”)

- In a crystal, the electrons also experience a “crystal field” from other atoms, which lowers symmetry and makes the situation more complex
Hund’s rules

• An isolated atom has spherical symmetry
  • Means total orbital angular momentum \( L \) is conserved

• If spin-orbit coupling is neglected, it also has separate spin-rotation (spin conservation) symmetry
  • Means total spin \( S \) is conserved

• This is a good starting point, since SOC is small.

• Note: this means there is, even with interactions a \((2S+1) \times (2L+1)\) atomic degeneracy
Hund’s rules

• Example: 2 electrons

\[ 25 + 2 \times 5 \times 4 / 2 = 45 \text{ states} \]
Hund’s rules

• Example: 2 electrons

• Rule 1: maximize spin

• Forces $S=1$

• Reason: Pauli exclusion: electrons are kept further apart, which minimizes $1/r$ Coulomb energy

\[3 \times 5 \times 4 / 2 = 30 \text{ states}\]
Hund’s rules

- Example: 2 electrons
  - Rule 1: maximize spin
    - S=1
  - Rule 2: maximize L
    - L=3
- This is also to minimize Coulomb repulsion but it is less obvious!

One picture - but I am not sure it is the right one!
- is that electrons orbiting in the same direction are less likely to meet

\[(2S+1)(2L+1)\]

=\(3 \times 7 = 21\) states
Hund 3

- Hund’s third rule includes the effect of spin-orbit coupling
- $\lambda L \cdot S$ implies states with different $J = L + S$ have different energy
- quantum mechanics: $|L-S| \leq J \leq L+S$

- **Hund 3:**
  - For a less than half-filled shell, $J = |L-S|$
  - For a more than half-filled shell, $J = L+S$

This is basically just SOC applied to holes
Hund’s rules

• Example: 2 electrons
  • Rule 1: maximize spin
    • $S=1$
  • Rule 2: maximize $L$
    • $L=3$
  • Rule 3: $J = |L - S| = 2$

$2J + 1 = 5$ states

45 → 30 → 21 → 5 states
Remarks

• Both Hund’s 1 and 2 rule favor large angular momentum: magnetism!

• These “rules” are due to atomic-scale Coulomb forces, so that the characteristic energies are ~ eV

• Such “local moments” are already formed at those temperatures. This is one reason why magnetism can be a high temperature phenomena

• Any isolated ion with J > 1/2 has atomic magnetism, and a degenerate ground state
Moments in solids

- An ion in a solid is subjected to *crystal fields*, which lower the symmetry from spherical, and hence split the atomic multiplets.

- Typically this reduces the orbital angular momentum which is possible.

- An extreme case (low symmetry): effectively $L=0$ because no orbital degeneracy.

- Those crystal fields may be comparable to the atomic Coulomb energies, and hence compete with Hund’s rules 1+2. They are often larger than Hund 3.
Moments in Solids

- Example: cubic crystal field for a metal atom in an oxygen octahedron

\[ t_{2g} = \{2z^2-x^2-y^2, x^2-y^2, xz, yz, xy\} \]

\[ e_g = \{\text{not applicable}\} \]
Moments in Solids

- Example: cubic crystal field for a metal atom in an oxygen octahedron

\[ \begin{align*}
\text{e.g.} & \quad \text{Cr}^{3+}=3d^3 \quad S=3/2, \quad L=0 \\
\text{e.g.} & \quad 2z^2-x^2-y^2, \quad x^2-y^2, \quad xz, \quad yz, \quad xy
\end{align*} \]
Moments in Solids

• Example: cubic crystal field for a metal atom in an oxygen octahedron

\[ e_g \]
\[ 2z^2-x^2-y^2, x^2-y^2 \]
\[ t_{2g} \]
\[ xz, yz, xy \]

but

\[ \text{Ti}^{3+}=3d^1 \] is more complicated

\[ S=1/2, L_{\text{eff}}=1 \]

“orbital degeneracy”
Local moments

• Local moments are *not* part of band theory

• Works in materials where electrons are localized to atoms, and delocalization is prevented somehow -- insulators

• Such materials, which have partially filled shells but are insulating, are called Mott insulators

• How do we know they exist?
Curie Susceptibility

• Existence of local moments means degenerate states

• By application of a small magnetic field, this degeneracy is split and a particular spin state is selected

• Expect large susceptibility $\chi = \frac{\partial M}{\partial H}|_{H=0}$