• For ions with spherical symmetry, have “Hund’s rules”

• In this case, total S, L commute with $H$ (neglecting SOC).

• Hund’s rule 1: Maximize S

• Hund’s rule 2: Maximize L (after applying 1)

• Hund’s rule 3: apply SOC
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

$n.b. S^z=1, S=0$ OK

$3 \times 5 \times 4 / 2 = 30$ 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

$(2S+1)(2L+1) = 3*7 = 21$ states
Hund 3

- Hund’s third rule includes the effect of spin-orbit coupling
- \( \lambda \mathbf{L} \cdot \mathbf{S} \) 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: $J = |L-S|=2$

$n.b. \ L_z=2, \ L=3$ OK
$n.b. \ S_z=1, \ S=0$ OK

$2J+1=5$ states

$45 \rightarrow 30 \rightarrow 21 \rightarrow 5$ states
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.
Local moments

• How do we know local moments exist?
  • Curie Susceptibility
  • Electron spin resonance
  • Specific heat (entropy)
Curie Susceptibility

• Magnetic moment in general is proportional to spin

\[ \mu = g \mu_B \frac{S}{\hbar} \]

- spin S quantum spin
- \( S^2 = S(S+1)\hbar^2 \)
- \( g \approx 2 \) for pure spin moment
- \( g \)-factor (could be a tensor)

- Bohr magneton

\[ \mu_B = \frac{e\hbar}{2m_e} = 9.3 \times 10^{-24} \text{ J/T} \]
\[ = 0.671 \text{ K/T} \]

• Magnetic dipole interaction

\[ \mathcal{H} = -\mu \cdot \mathbf{H} \]
Compare with metals

Curie Law

$$\chi = \frac{N(g\mu_B)^2}{3} \frac{S(S+1)}{kT}$$

Pauli paramagnetism

$$\chi = V \frac{(g\mu_B)^2}{4} D(\epsilon_F)$$

basically $kT \rightarrow \epsilon_F$

Much larger susceptibility than delocalized electrons
Magnetic cooling

- The large susceptibility of free spins at low temperature means they are easily aligned by small magnetic fields.

- This alignment corresponds to a drastic reduction of entropy. One can use this control over entropy to remove entropy from another system, thereby cooling it.
Magnetic Cooling

Heat bath

$T_i$, $H_i$

large entropy

$T_f < T_i$

increase $H$

Heat bath

$T_i$, $H_f$

small entropy

lower $H$
Magnetic Cooling

- A → B: isothermal step - raise field, lower entropy
- B → C: adiabatic step - lower field, same entropy: lower temperature
- For paramagnetic spins, $S = S(H/T)$
  - Hence $H_1/T_f = H_2/T_i$
Exchange

• How do spins interact?

• Magnetostatic dipole-dipole coupling

\[ H_{d-d} = - \frac{\mu_0}{4\pi r^3} [3(m \cdot r)(m' \cdot r) - m \cdot m'] \]

• This is rather weak, \( \approx 1 \text{K} \) for even large spins

• Electrostatic interaction usually dominates, just as it does inside atoms

• Indirectly leads to spin coupling through Pauli principle
Exchange

Lattice of spins has extensive degeneracy

\[ \Omega \ (2S+1)^N \text{ states} \]

\[ S = Nk_B \ (2S+1) \]

Must be released. (3rd law of thermo)

This is due to interaction.

Two kinds:
1. Magnetic dipole (\( S <_{\text{th}} 1K \))
2. Electrostatic origin
   - Already seen. Hund's rule. Is due to Coulomb in site alone.
   - Exchange interaction.

Generally have form like \( \mathbf{J}_{ij} S_i^a S_j^b \)

\( \Rightarrow \) decay rapidly with \( r_{ij} \).

\( \Rightarrow \) become related to Fermi statistics and spin.

\( \Rightarrow \) Can have various structures.

Typical Picture - Due to "virtual exchange" of \( e^- \) between atomic orbitals.
Hubbard Model

\[ H = \sum_i \varepsilon_i \hat{n}_i - \sum_{\langle i,j \rangle} t (\hat{c}_i^\dagger \hat{c}_j + h.c.) + U \sum_i \hat{n}_{i \sigma} \hat{n}_{i \bar{\sigma}} \]

\[ t << U \quad \text{exchange} \quad \text{interaction} \]

\[ \frac{\hbar}{U} = 0 \quad \text{isotopic} \quad \Rightarrow \text{spinless} \quad \text{fermion} \quad \text{here} \quad S = \cdot \]

\[ O(\hbar^2) : \text{exchange} \quad \text{interaction} \]

Use DPT

\[ H = H_0 + H' \]

\[ H_{\text{eff}} = -\frac{2 \hbar}{\hbar} (H_0 - E_0)^{-1} H' P_0 \]

\[ \left[ \text{Provided} \quad \text{D}, H' P_0 = 0 \quad \text{P}_0 = \text{Projector} + 6 \frac{s}{s} \text{Subspace} \right] \]

\[ H_{\text{eff}} = -\frac{t^2}{\hbar} \sum_{\langle i,j \rangle} \left( C_{i \alpha} C_{j \alpha} + h.c. \right) \left( H_0 - E_0 \right)^{-1} \left( \sum_{k \alpha} \frac{1}{\varepsilon_k} \right) \frac{1}{\varepsilon_k} \left( C_{k \beta} C_{k \beta} + h.c. \right) \]

\[ = -\frac{2 t^2}{\hbar} \sum_{\langle i,j \rangle} C_{i \alpha} C_{j \alpha} + C_{\beta \alpha} C_{\beta \beta} \]

\[ = \frac{2 t^2}{\hbar} \sum_{\langle i,j \rangle} \left( C_{i \alpha} C_{j \alpha} + C_{i \beta} C_{j \beta} - S_{i \alpha} S_{j \beta} \right) \]

\[ = \frac{2 t^2}{\hbar} \sum_{\langle i,j \rangle} \left( C_{i \alpha} C_{j \alpha} + C_{i \beta} C_{j \beta} - 1 \right) \]

\[ = \frac{2 t^2}{\hbar} \sum_{\langle i,j \rangle} \left( C_{i \alpha} C_{j \alpha} + C_{i \beta} C_{j \beta} - 1 \right) \]

\[ \left( \frac{1}{2} S_{i \alpha} + \frac{2}{5} \frac{S_i \cdot S_j}{S_i \cdot S_j} \right) \]

\[ = \frac{2 t^2}{\hbar} \left( \frac{7}{2} S_{i \alpha} + \frac{2}{5} \frac{S_i \cdot S_j}{S_i \cdot S_j} \right) \]

\[ = \frac{4 t^2}{\hbar} \sum \left( \frac{7}{2} S_{i \alpha} + \frac{2}{5} \frac{S_i \cdot S_j}{S_i \cdot S_j} - 1 \right) = \frac{4 t^2}{\hbar} \sum \left( \frac{5}{4} S_{i \alpha} - 1 \right) \]
$$H = \frac{1}{2} \sum \vec{S}_i \cdot \vec{S}_j$$

N.B. - $J > 0$ : Antiferro (usually)
- $\sum \vec{S}_i \cdot \vec{S}_j$ form due to $SU(2)$

This is not a true symmetry of H
But approx. sort. If SOC can be neglected,

General $H_{ij} = J \vec{S}_i \cdot \vec{S}_j + D \vec{S}_i \cdot \vec{S}_j + \vec{S}_i \cdot \vec{S}_j$

When SOC is "weak", $J > D >> T$ typically.

(1st elec. (3d) w/o orbital degeneracy)