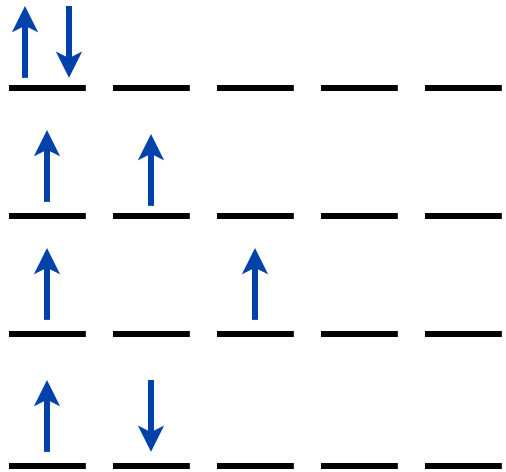
- For ions with spherical symmetry, have “Hund’s rules”
- In this case, total S, L commute with H (neglecting SOC).
- Hund’s rule 1: Maximize S
- Hund’s rule 2: Maximize L (after applying 1)
- Hund’s rule 3: apply SOC

Hund's rules

- Example: 2 electrons

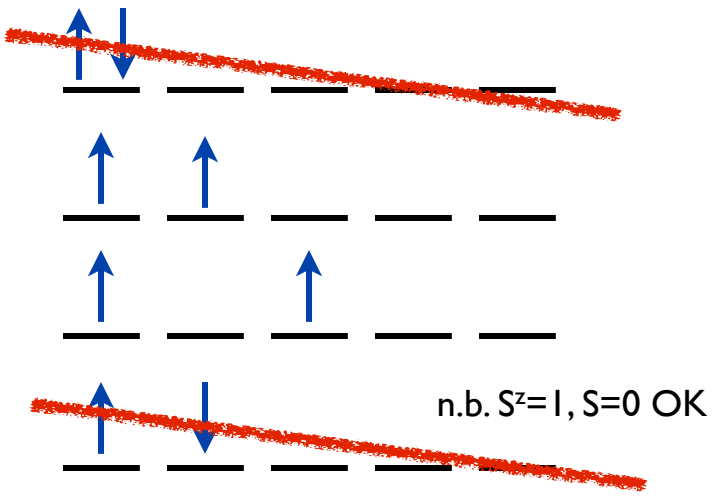


...

25+2*5*4/2=45 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

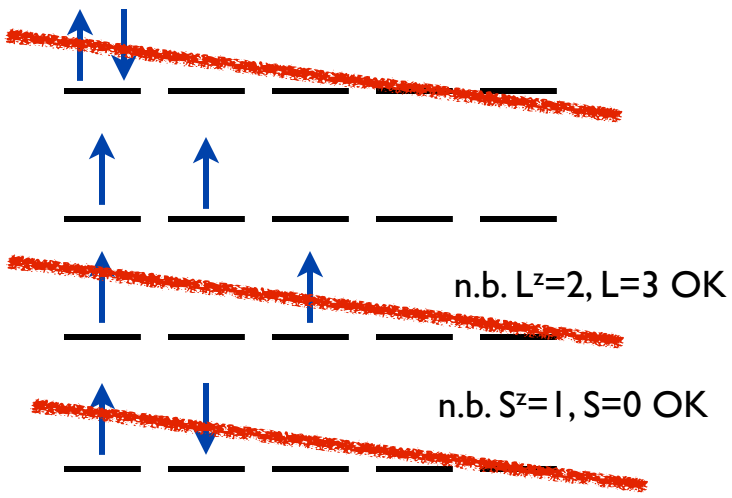


...

3*5*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!



...

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

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

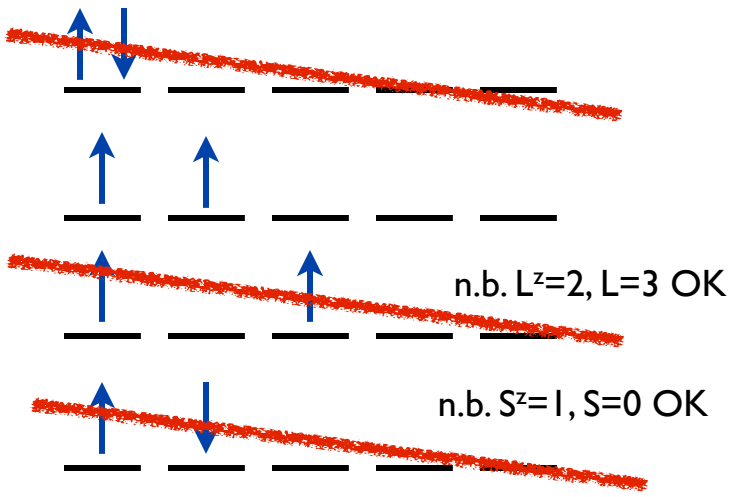
Hund 3

- 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

Moments in solids

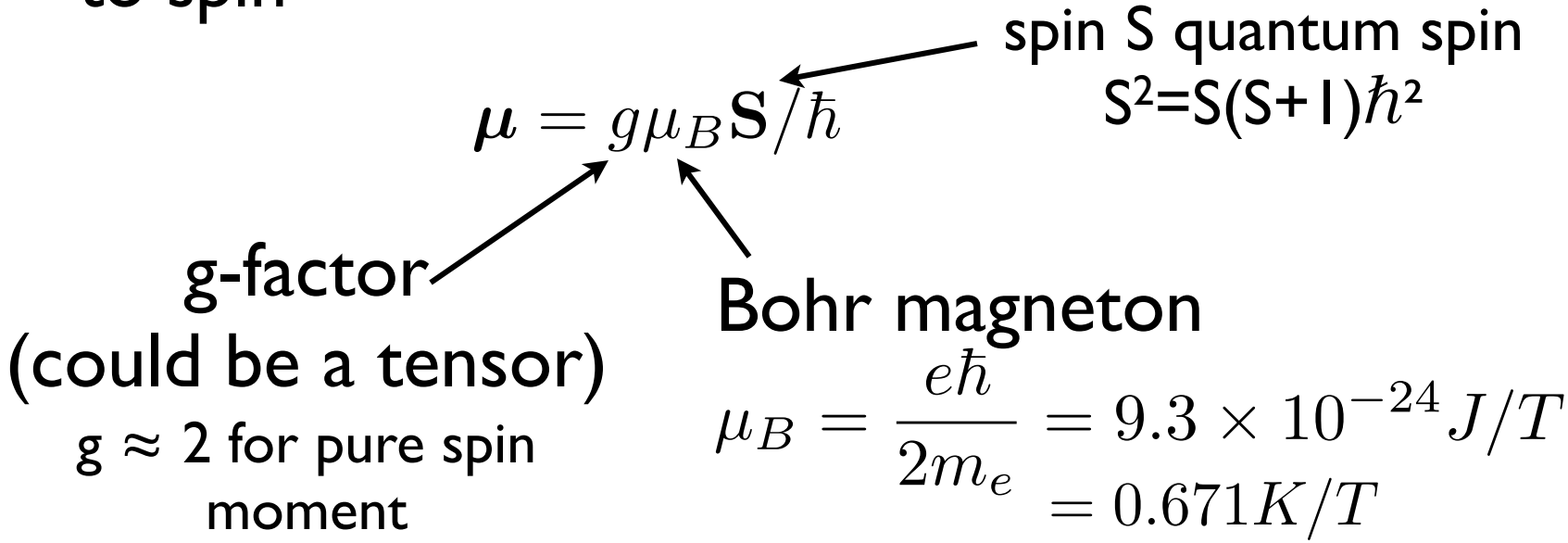
- An ion in a solid is subjected to *crystal fields*, which lower the symmetry from spherical, and hence split the atomic multiplets
- Typically this reduces the orbital angular momentum which is possible
  - an extreme case (low symmetry): effectively L=0 because no orbital degeneracy
- Those crystal 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



- Magnetic dipole interaction

$$\mathcal{H} = -\boldsymbol{\mu} \cdot \mathbf{H}$$

Compare with metals

Curie Law

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

Pauli paramagnetism

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

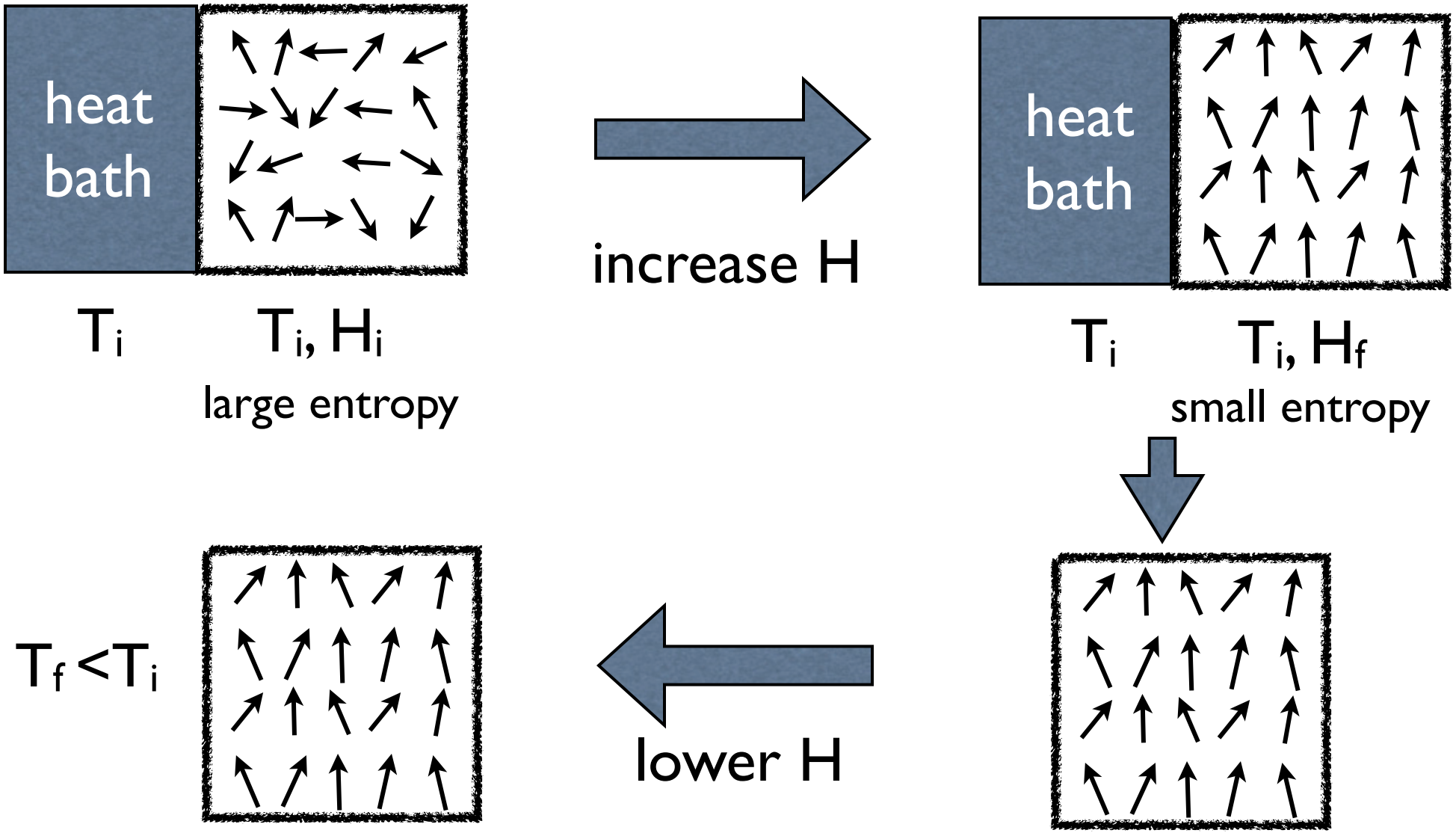
basically kT → ε_F

Much larger susceptibility than delocalized electrons

Magnetic cooling

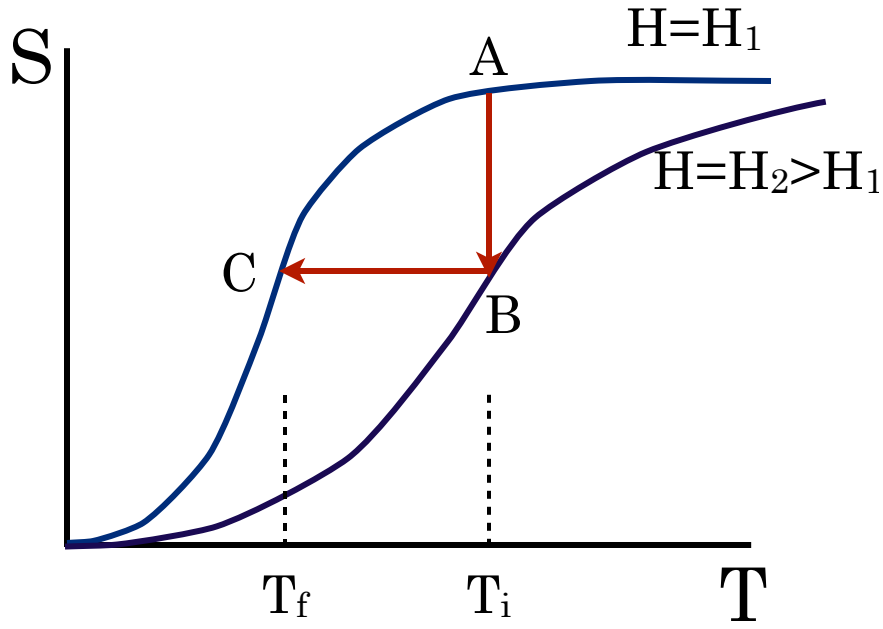
- The large susceptibility of free spins at low temperature means they are easily aligned by small magnetic fields
- This alignment corresponds to a drastic reduction of entropy. One can use this control over entropy to remove entropy from another system, thereby cooling it.

Magnetic Cooling



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

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

    - This is rather weak, $\lesssim$ 1K 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

$(2S+1)^N$ states

$S = N k_B \ln(2S+1)$

Must be released. (3^{rd} law of thermo)

This is due to interactions.

Two kinds: ① Magnetic dipole (Strength $\leq 1K$)

② Electrostatic origin

- Already saw Hund's Rule J_H due to Coulomb in single atom.

↓

Exchange Interaction

Generally have form like $J_{ij}^{ab} S_i^a S_j^b$

↳ decay rapidly with $|i-j|$ because related to Fermi statistics and overlap

↳ Can have varied structure in spin space.

Typical Picture: Due to "virtual exchange" of e^- between atomic orbitals.

Ken

Hubbard Model

$$H = \sum_i \varepsilon_0 \hat{n}_i \underbrace{- \sum_{\langle ij \rangle} t (c_{i\alpha}^\dagger c_{j\alpha} + h.c.)}_{H'} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

$t \ll U$: ~~exchange interaction~~

$t/U = 0$: Isolated atoms → spins (here $S = \frac{1}{2}$)

$\mathcal{O}((t/U)^2)$: exchange interaction

Use DPT $\quad H = H_0 + H'$

$$H_{eff} = -\mathcal{P} H' (H_0 - E_0)^{-1} H' P_0$$

[Provided $\quad P_0 H' P_0 = 0$

P_0 = Projection to GS Subspace]

$$H_{eff} = -t^2 \mathcal{P} \sum_{\langle ij \rangle} (c_{i\alpha}^\dagger c_{j\alpha} + h.c.) (H_0 - E_0)^{-1} \Big(\sum_{k\rho} c_{k\rho}^\dagger c_{k\rho} + h.c. \Big) P$$

$\Longleftarrow$ intermediate shell $\neq 0$

$$= -\frac{2t^2}{U} \sum_{\langle ij \rangle} c_{i\alpha}^\dagger c_{j\alpha} \; c_{j\beta}^\dagger c_{i\beta}$$

$$= \frac{2t^2}{U} \sum_{\langle ij \rangle} c_{i\alpha}^\dagger c_{i\beta} \left(c_{j\beta}^\dagger c_{j\alpha} - \delta_{\alpha\beta} \right)$$

$$= \frac{2t^2}{U} \sum_{\langle ij \rangle} \left(c_{i\alpha}^\dagger c_{i\beta} \; c_{j\beta}^\dagger c_{j\alpha} - 1 \right)$$

$$\left(\frac{n_i}{2} \delta_{\alpha\beta} + \vec{S}_i \cdot \vec{\sigma}_{\beta\alpha} \right) \left(\frac{n_j}{2} \delta_{\beta\alpha} + \vec{S}_j \cdot \vec{\sigma}_{\alpha\beta} \right)$$

$$= \frac{2t^2}{U} \sum_{\langle ij \rangle} \left(\frac{n_i n_j}{2} + 2 \vec{S}_i \cdot \vec{S}_j - 1 \right) = \frac{4t^2}{U} \sum_{\langle ij \rangle} \left(\vec{S}_i \cdot \vec{S}_j - \frac{1}{4} \right)$$

Up to cubic, we get $H = J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j$

N.B. - $J > 0$: Antiferro (usually)

- $\vec{S}_i \cdot \vec{S}_j$ form: due to SU(2) spin-rotation symmetry.

This is not a true symmetry of nature. But approx sometimes. If SOC can be neglected.

In general $H_{ij} = J\, \vec{S}_i \cdot \vec{S}_j + \vec{D} \cdot \vec{S}_i \times \vec{S}_j + S_i \underline{\Gamma} S_j$

- $\vec{D} \cdot \vec{S}_i \times \vec{S}_j$: Dzyaloshinskii-Moriya (DM)
- $S_i \underline{\Gamma} S_j$: tensor symmetric exchange anisotropy

*When SOC is "weak" $J \gg D \gg \Gamma$ typically.

(light elements (3d) w/o orbital degeneracy)