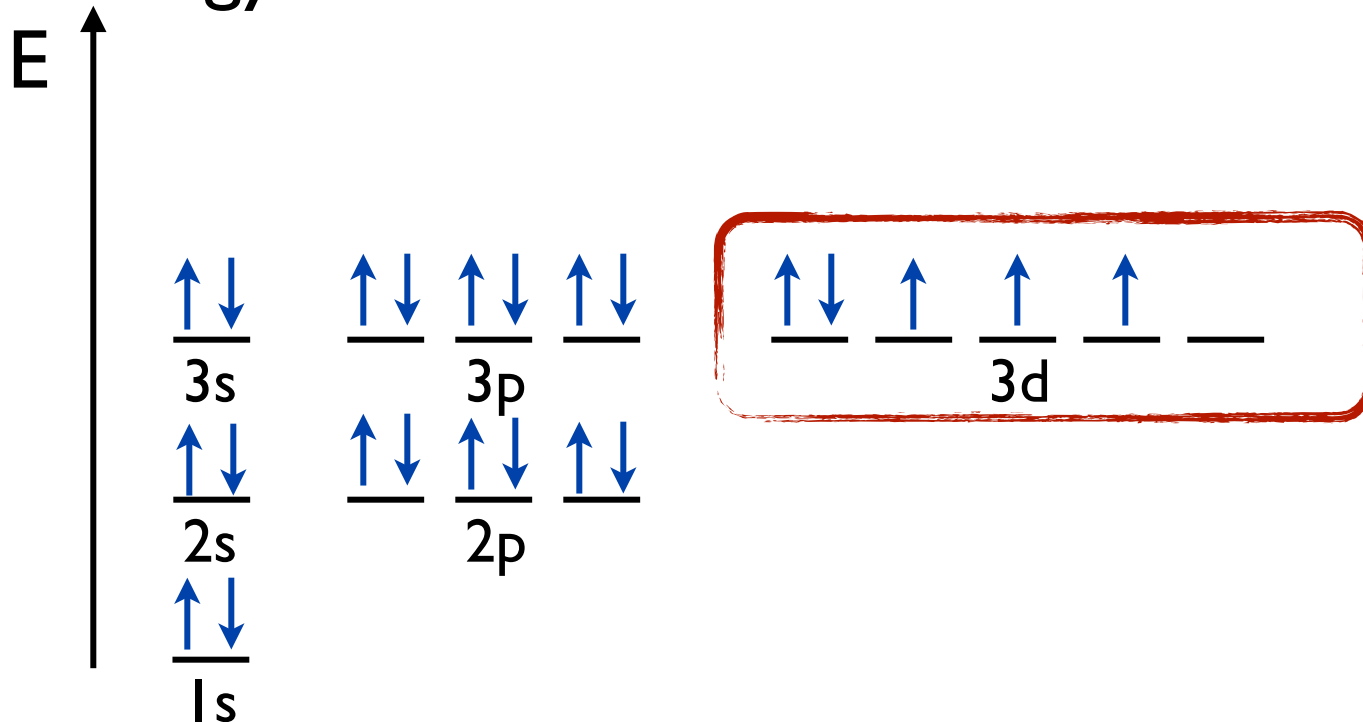


Atomic magnetism

- Since magnetism requires small kinetic energy, it is strongest when electrons are approximately localized to atoms
 - Many “isolated” atoms are magnetic
 - Most magnetism has some atomic origins

Atomic magnetism

- Hydrogen atom $E_n = -\frac{Ry}{n^2}$
- Level degeneracy: magnetism w/o kinetic energy cost



Atomic magnetism

- In principle, many-electron atom is a many-particle quantum problem

$$H = \sum_i -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} + \sum_{i>j} \frac{e^2}{r_{ij}} + H_{SOC}$$

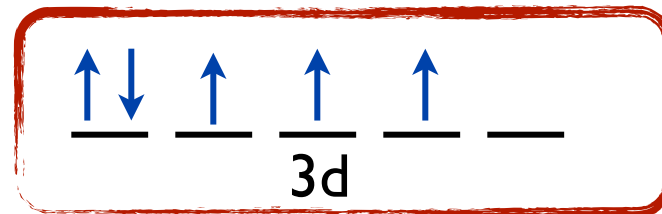
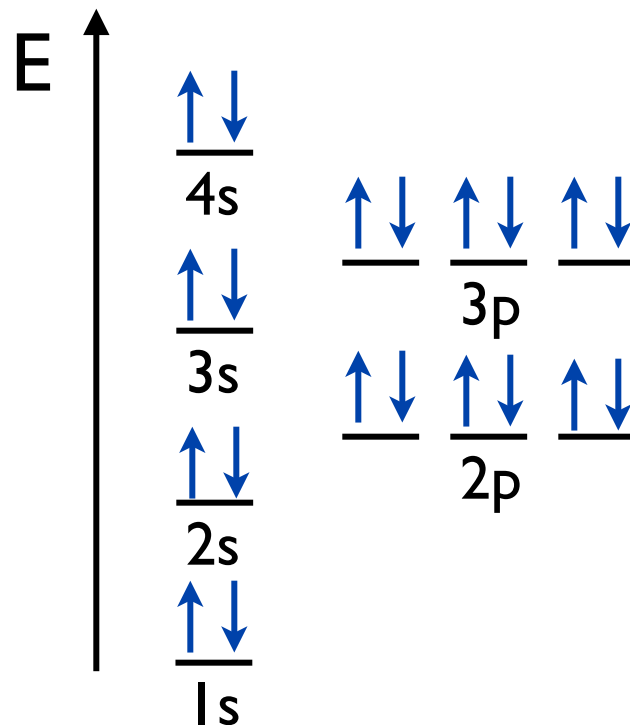
- This requires solving for an N-particle wavefunction

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N; \sigma_1, \dots, \sigma_N)$$

- Very hard and complex! We can get some intuition by thinking of l-electron levels for the “outer” electrons only

Atomic magnetism

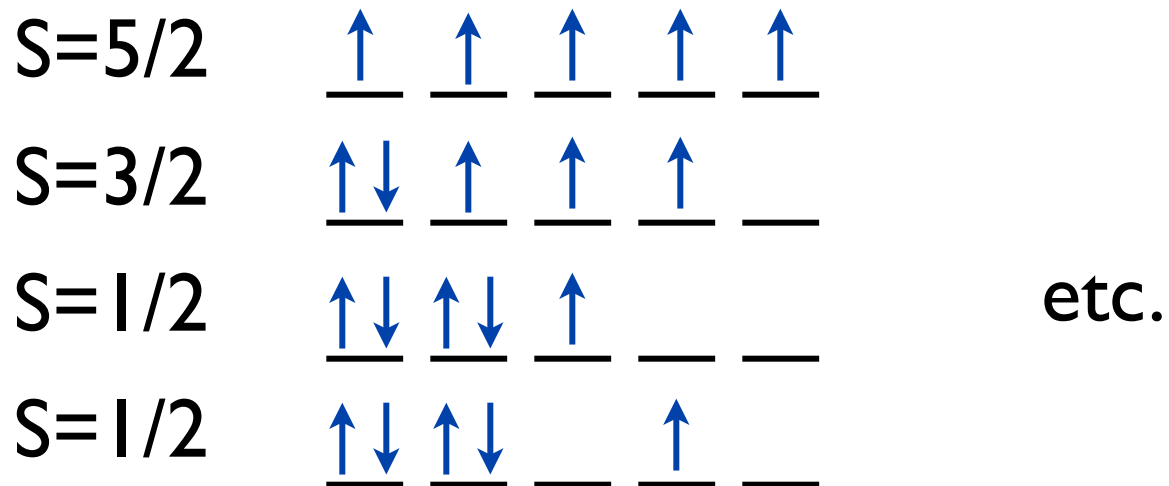
- In larger atoms, accidental degeneracy is lifted, and $E_{2s} < E_{2p}$, $E_{3s} < E_{3p} < E_{3d}$ etc



- $2L+1$ degeneracy is required by spherical symmetry
- Generally d and f electrons are most isolated - more localized - from other atoms because they are “protected” inside higher shell s states
- Most magnetism involves *transition metals* or *rare earths*

Atomic magnetism

- A partially filled shell has a lot of possible states



- Without considering interactions *between* electrons in these shells, all are degenerate

Atomic magnetism

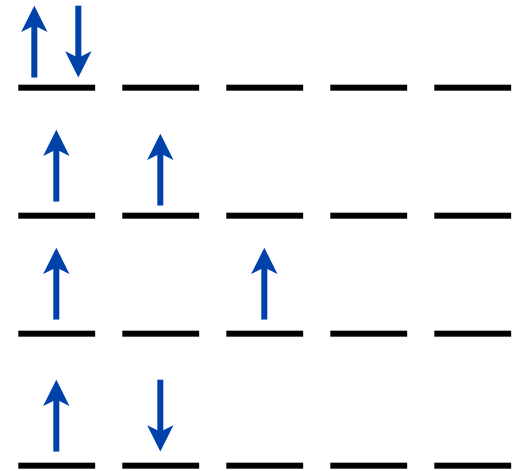
- Splitting of these degeneracies by Coulomb interactions between electrons is a hard, many-electron problem!
- For *isolated atoms*, i.e. with spherical symmetry, some general rules apply. These are called “Hund’s rules” (Hund was German so I guess these are actually “dog’s rules”)
- In a crystal, the 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

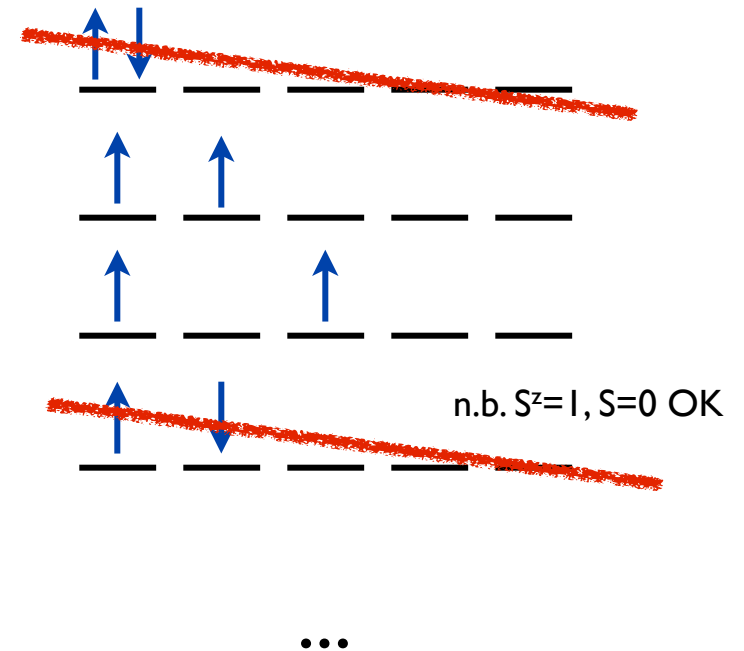


...

$$25 + 2 * 5 * 4 / 2 = 45 \text{ states}$$

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

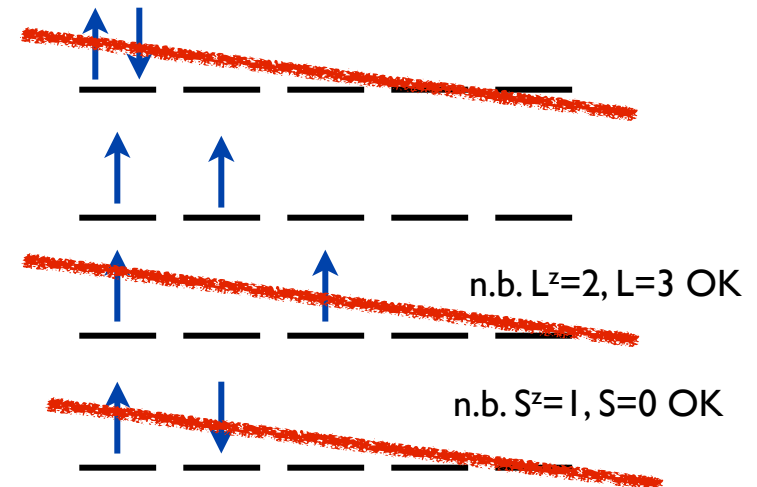


$$3 \cdot 5 \cdot 4 / 2 = 30 \text{ states}$$

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



...

$$(2S+1)(2L+1) = 3*7 = 21 \text{ states}$$

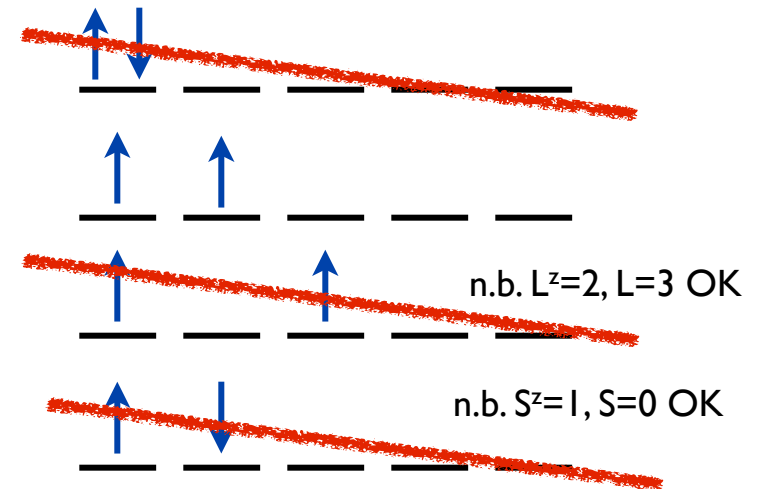
Hund 3

- 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: $J = |L-S|=2$



...

$2J+1=5$ 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 $\sim eV$
- 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.