Atomic magnetism

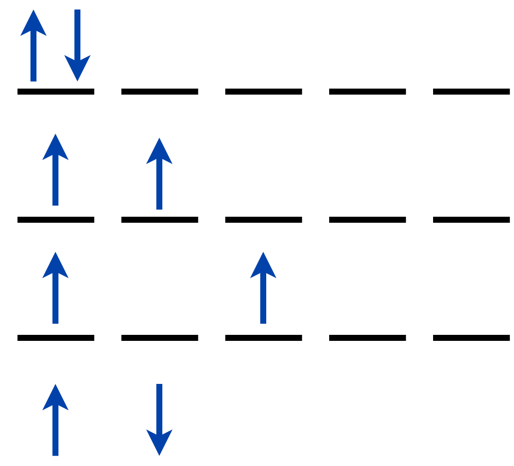
- Splitting of these degeneracies by Coulomb interactions between electrons is a hard, many-electron problem!
- For *isolated atoms*, i.e. with spherical symmetry, some general rules apply. These are called "Hund's rules" (Hund was German so I guess these are actually "dog's rules")
- In a crystal, the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



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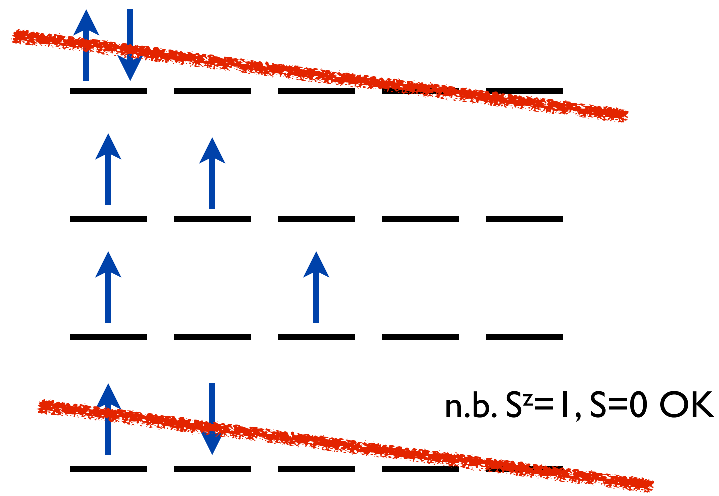
25+2*5*4/2=45 states

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



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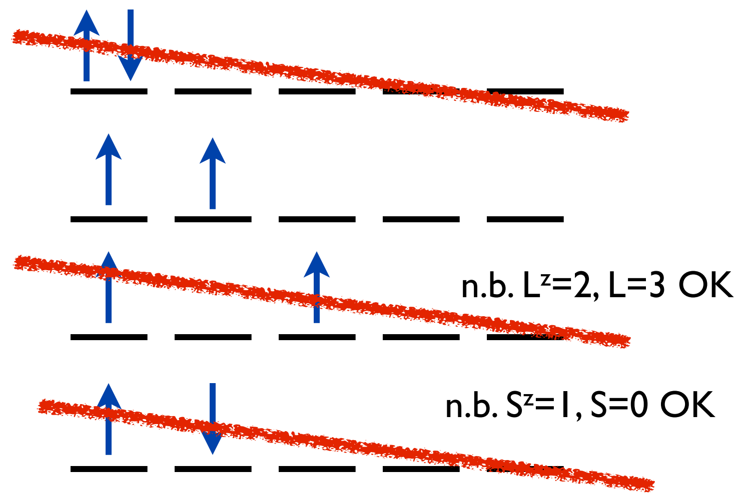
3*5*4/2=30 states

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!

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



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

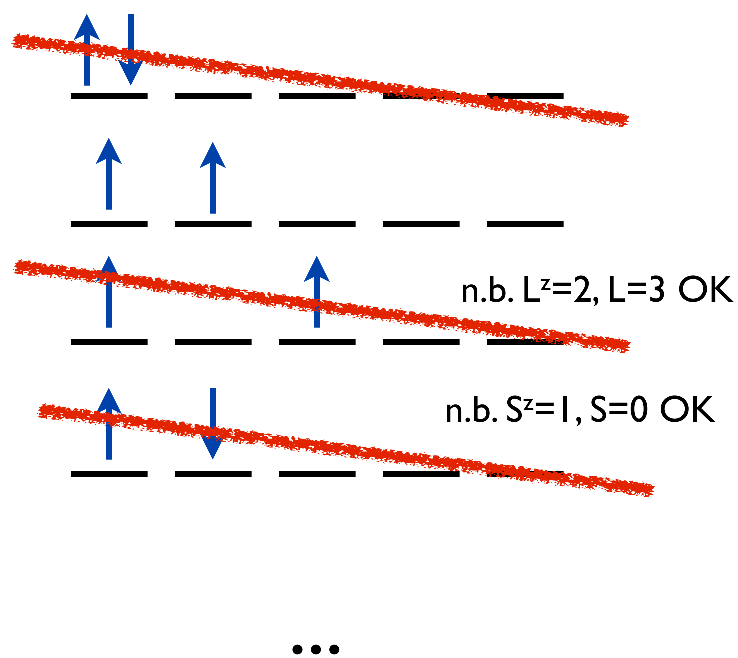
Hund 3

- 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

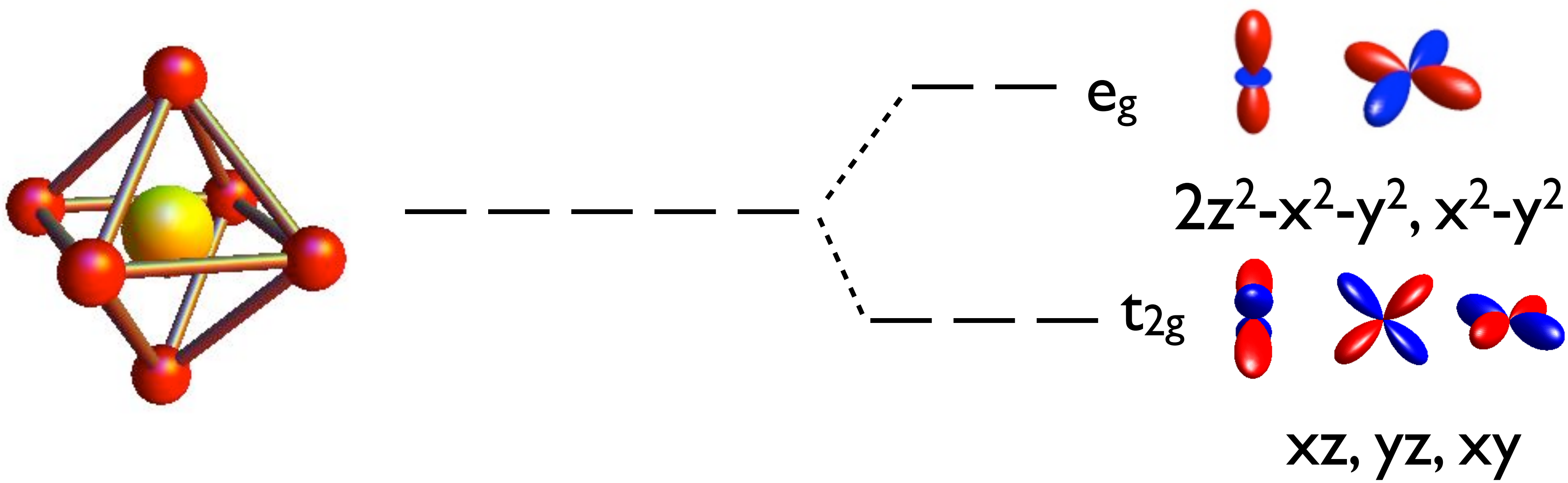
- Both Hund's 1 and 2 rule favor large angular momentum: magnetism!
  - These "rules" are due to atomic-scale Coulomb forces, so that the characteristic energies are ~ eV
  - Such "local moments" are already formed at those temperatures. This is one reason why magnetism can be a high temperature phenomena
- 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.

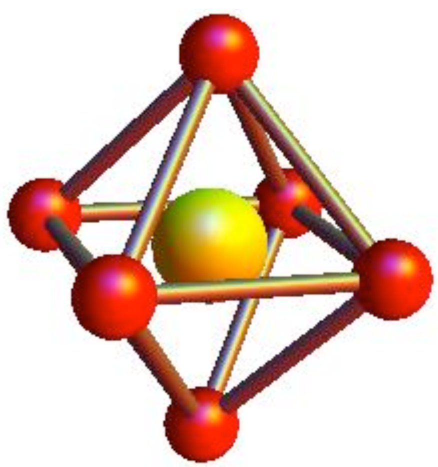
Moments in Solids

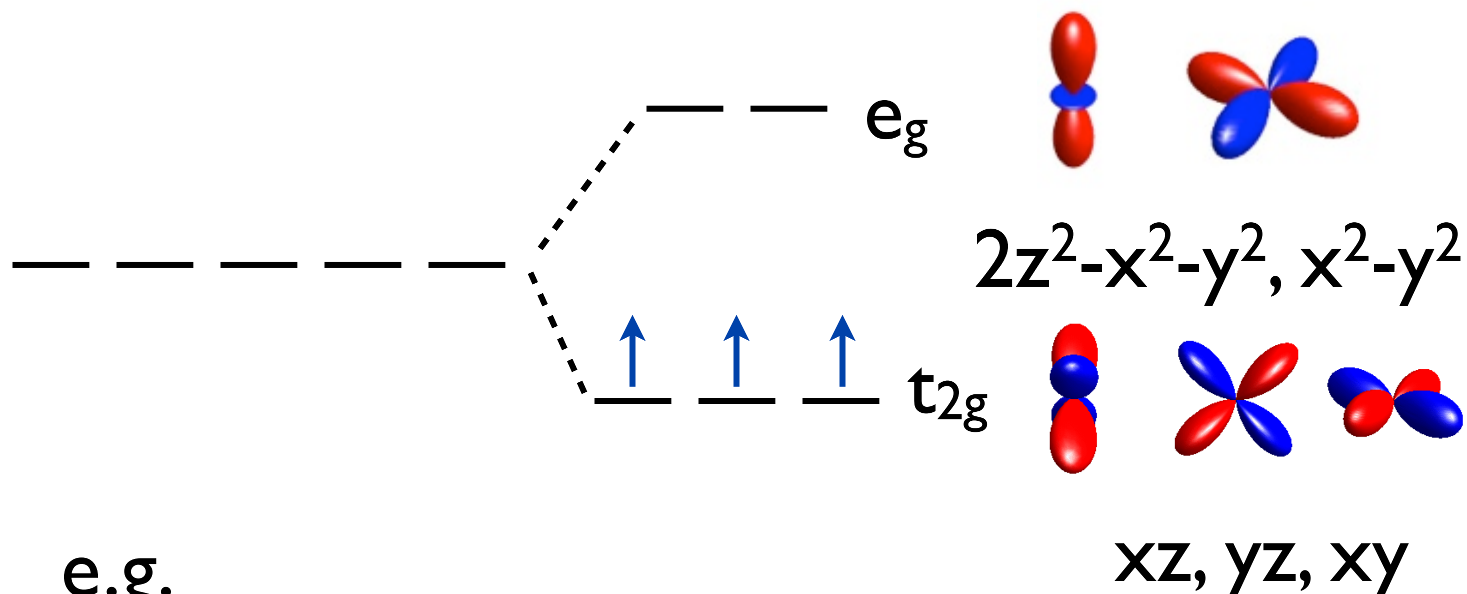
- Example: cubic crystal field for a metal atom in an oxygen octahedron



Moments in Solids

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





e.g.
$Cr^{3+}=3d^3$

S=3/2, L=0

Moments in Solids

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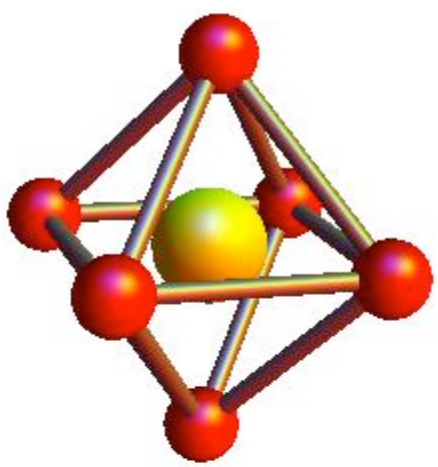

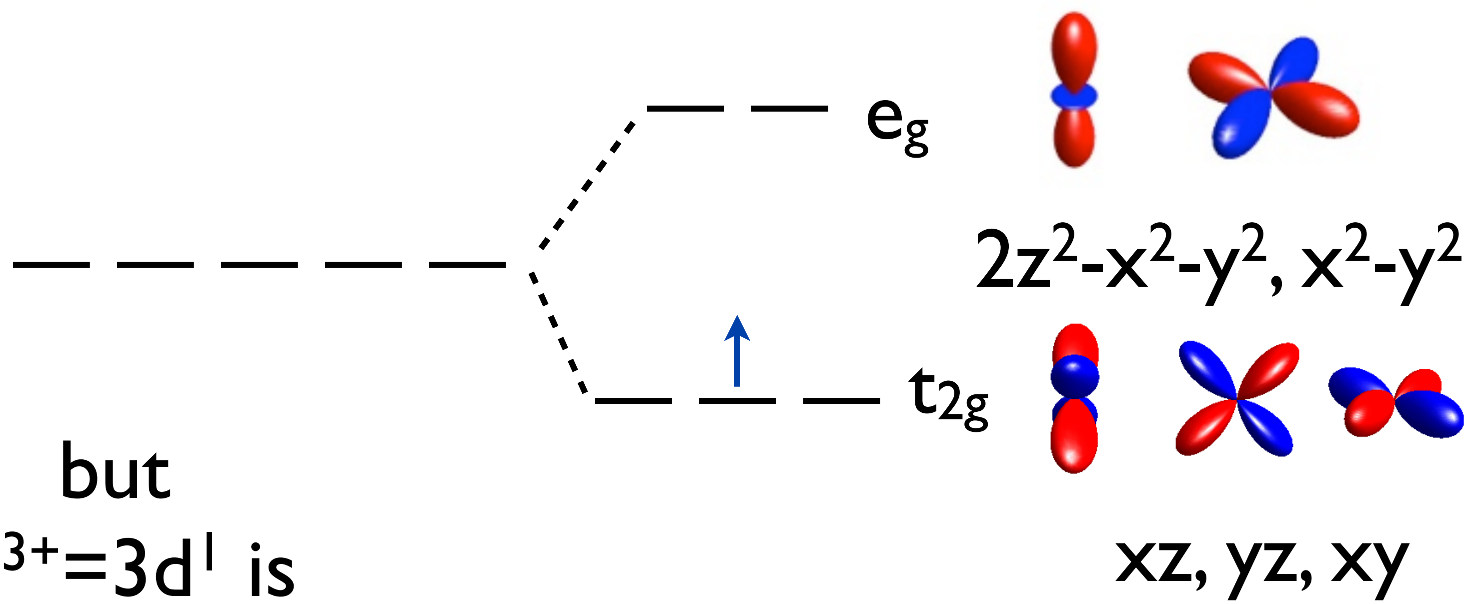

but
Ti^{3+}=$3d^1$ is
more
complicated

$S=1/2$, $L_{eff}=1$
"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 $\chi = \partial M / \partial H|_{H=0}$