Two Asides (Optional)

(1) Many electrons ⇒ many orbital AM's and many spin AM's

How to add them up? Spin-Orbit Interaction?

(2) What are the Hund's rules?

Aside 1: How about Spin-Orbit Interaction in other atoms?

- It is important! Many electrons ⇒ many $\vec{L}_i$ and many $\vec{S}_i$ (i labels electrons)

LS coupling

1/. Form Total $\vec{L}$ first

$$\vec{L} = \sum_i \vec{L}_i$$

2/. Form Total $\vec{S}$ first

$$\vec{S} = \sum_i \vec{S}_i$$

3/. Then $\vec{L}$ and $\vec{S}$ interact

JJ coupling

1/. Form $\vec{J}_i$ (total angular momentum of particle i)

$$\vec{J}_i = \vec{L}_i + \vec{S}_i$$

2/. $\vec{J}_i$ interacts with $\vec{J}_j$

- Which mechanism is more important?
  - Depends on which element
- Exp't: features in spectrum

Aside 2: Hund's Rules

- E.g. $1s^2\ 2s^2\ 2p^2$
  - There are 6 2p-states
  - How to fill two electrons for ground state?
- Each atom is a separate QM problem [each filling is a QM calculation]
- Frederick Hund gave three empirical rules

  [student of Born]

Friedrich Hund (b. 1896) received his Ph.D. in physics from the University of Göttingen in 1922. In 1926 he and Robert Mulliken worked together at Göttingen on the theory of molecular orbitals. Although Hund was not mentioned by the Nobel Prize committee, Mulliken has stated that he would have been glad to share the Nobel Prize with Hund. Hund was professor of theoretical physics at Rostock, Leipzig, Jena, Frankfurt, and Göttingen.

- Values of L, S, J for the states of lowest energy are determined by Hund's rules (HRs). These rules are applied one by one in the order of HR1, HR2, HR3.

HR1   S takes the maximum value allowed by the Pauli Exclusion principle [meaning: as many as possible of electrons have parallel spins]

Practically, each electron, up to half the number of states in the shell, gives +½ to S. Beyond half-fill, each electron gives −½ to S.

[HR1 goes first and determines S]

HR2 L takes the maximum value that is consistent with S

[meaning: electrons have their orbital angular momenta as well aligned as possible, after fixing S]

[HR2 goes second to fix L]

- HR1 and HR2 are robust [always hold] (∵ due to Coulomb interaction)
- Work for isolated atoms and ions

HR3 $J = |L-S|$ for a shell less than half-fill

$J = L+S$ for a shell more than half-fill

- HR3 is less robust (∵ associated with spin-orbit interaction)
- may fail due to influence of neighboring ions (in solids) and/or applied B_{ext}

Examples

			l_z	
	Number of 3d electrons	2 V^{3+} ion		6 Fe^{2+} ion
	Occupancy of states as given by Hund's rules	↑	2	↑ ↓
		↑	1	↑
			0	↑
			−1	↑
			−2	↑
HR1	Hund's rule 1: determination of S. Make as many spins parallel as possible	$S=\frac{1}{2}+\frac{1}{2}$ $=1$		$S=\frac{1}{2}+\frac{1}{2}+\frac{1}{2}+\frac{1}{2}+\frac{1}{2}-\frac{1}{2}$ $=2$
HR2	Hund's rule 2: determination of L. Make $\sum l_z$ as large as possible	$L=\sum l_z$ $=2+1=3$		$L=2+1+0-1-2+2$ $=2$
HR3	Hund's rule 3: determination of J.	Shell less than half-full $J=\lvert L-S\rvert=2$		Shell more than half-full $J=L+S=4$
	Spectroscopic notation, $^{2S+1}L_J$	$^3F_2$		$^5D_4$

$^{2S+1}L_J$

Use of Hund's rules to calculate the quantum numbers S, L and J of the ground states of the V^{3+} and Fe^{2+} ions. The 3d shell has $l=2$ so there are $2l+1$ sublevels corresponding to $l_z=-2,-1,0,1,2$ as indicated. In the spectroscopic notation, values of L of 0, 1, 2, 3, 4, 5, 6,... are indicated by letters S, P, D, F, G, H, I,..