Many-Electron Atoms

Thornton and Rex, Ch. 8

In principle, can now solve Sch. Eqn for any atom.

In practice, -> Complicated!

Goal--

To explain properties of elements from principles of quantum theory
(without exact solutions)

- Elements distinguished by nuclear charge Z (= number of electrons)
- To first approx., each electron moves in electric field of nucleus + remaining electrons:

electron state : (n, ℓ, m_ℓ, m_s)

shell (n) — subshell (ℓ)

$\left\{ \begin{array}{l} n \text{ labels energy, but no simple formula.} \\ \ell \text{ subshells no longer completely degenerate.} \end{array} \right\}$

- Principles for filling electron states:

1) Always fill lowest energy state first.

2) No two electrons can have same quantum numbers (n, ℓ, m_ℓ, m_s).

Pauli Exclusion Principle

No two electrons can occupy the same quantum state.

Building up atomic structure of atoms

	n	ℓ	m_ℓ	m_s
Hydrogen	1	0	0	$\pm 1/2$

Helium	1	0	0	$+1/2$
	1	0	0	$-1/2$

Helium has a <u>closed</u> shell.

For Lithium, now add $n=2$ electron,
but $\ell=0$ or $\ell=1$?

Smaller ℓ always has lower energy.

Lithium	1	0	0	$+1/2$
	1	0	0	$-1/2$
	2	0	0	$\pm 1/2$

	n	ℓ	m_ℓ	m_s
Hydrogen	1	0	0	+1/2
Helium	1	0	0	-1/2
Lithium	2	0	0	+1/2
Beryllium	2	0	0	-1/2
Boron	2	1	-1	+1/2
Carbon	2	1	0	+1/2
Nitrogen	2	1	+1	+1/2
Oxygen	2	1	-1	-1/2
Flourine	2	1	0	-1/2
Neon	2	1	+1	-1/2
Sodium	3	0	0	+1/2
Magnesium	3	0	0	-1/2
Aluminum	3	1	-1	+1/2
Silicon	3	1	0	+1/2
Phosporus	3	1	+1	+1/2
Sulfur	3	1	-1	-1/2
Chlorine	3	1	0	-1/2
Argon	3	1	+1	-1/2
Potassium	4	0	0	+1/2

(Last Electron Added)

Chemical properties of elements

Electrons in outermost, largest n orbits are most weakly bound. They determine the chemical properties of the elements. Elements with similar electron structure have similar properties.

- Inert or Noble Gases
  Closed p subshell (s for He).
  He ($1s^2$), Ne ($2s^22p^6$), Ar ($3s^23p^6$)

- Alkalis
  Have single electron electron outside closed shell.
  Li ($2s^1$), Na ($3s^1$), K ($4s^1$)

- Halogens
  Are one electron short of a closed shell.
  F ($2s^22p^5$), Cl ($3s^23p^5$)

Total Angular Momentum

Consider a 1-electron atom (or with just 1 electron outside closed shell).

It has Orbital Angular momentum $\vec{L}$ and Spin Angular momentum $\vec{S}$.

These can be combined to give Total Angular momentum $\vec{J} = \vec{L} + \vec{S}$.

J is quantized with

$$J = \sqrt{j(j+1)}\ \hbar$$

and

$$J_z = m_j \hbar$$

where $j = \ell \pm s$

or $j = \ell \pm 1/2$ (since $s = 1/2$)

j will be half-integral (1/2, 3/2, 5/2, ...)
m_j will also be half-integral, ranging from
$-j$ to j.

Example: $\ell = 1$, $s = 1/2$

$m_\ell = (1, 0, -1)$ $\quad$ $m_s = (-1/2, +1/2)$

$3 \cdot 2 = 6$ states

Can combine into

$j = 3/2 = 1 + 1/2$
$m_j = (-3/2, -1/2, +1/2, +3/2)$ (4 states)

or

$j = 1/2 = 1 - 1/2$
$m_j = (-1/2, +1/2)$ (2 states)

Total number of j-states is $6 = 4 + 2$.

Spectroscopic notation

$$nL_j$$

Principle Quantum Number

Orbital Angular Momentum Letter

Total Angular Momentum Number

Examples: $2S_{1/2}$ $3P_{3/2}$ etc.

Spin-Orbit Coupling

- Recall, coupling of spin to a magnetic field shifts the energy ($V_B = -\vec{\mu}_s \cdot \vec{B}$).

- Motion of electron produces an "internal" magnetic field.

So there is an additional contribution to the energy:

$$V_{SL} = -\vec{\mu}_s \cdot \vec{B}_{int}$$

Proportional to -S

Proportional to L

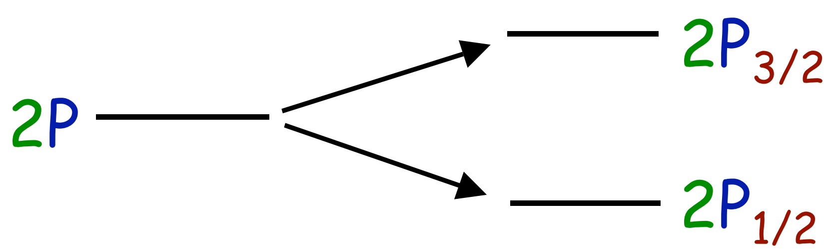
$$V_{SL} \mu \ \vec{S} \cdot \vec{L}$$

This is the Spin-Orbit Coupling:

$$V_{SL} \mu \ \vec{S} \cdot \vec{L}$$

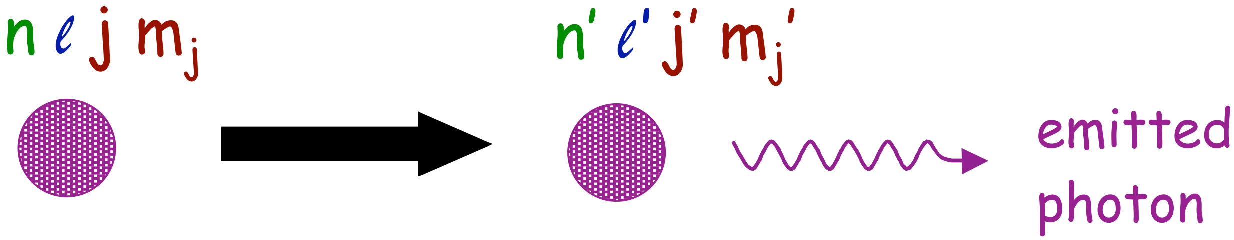
Now states with definite energy do not have unique L and S quantum numbers (m_ℓ, m_s). We must use J quantum numbers (j, m_j).

States with $j = \ell - 1/2$ have slightly less energy than states with $j = \ell + 1/2$.



(States with different m_j are still degenerate for each j.)

Selection Rules



Allowed transitions:

- lifetimes $\tau \sim 10^{-9}$ sec

Δn = anything, $\Delta \ell = \pm 1$,

$\Delta j = 0, \pm 1$, $\Delta m_j = 0, \pm 1$

Forbidden transitions:

- lifetimes much longer

Ex. $2s \rightarrow 1s$, $\tau \sim 1/7$ sec

Many-Electron Atoms

A careful analysis involving $\vec{L}$ and $\vec{S}$ in multi-electron atoms is very complicated.

Hund's Rules

(Empirical rules for filling a subshell, while minimizing the energy)

1) The total Spin should be maximized (without violating Pauli Exclusion Principle).

2) Without violating Rule 1, the Orbital Angular momentum should also be maximized.

Handwaving explanation:

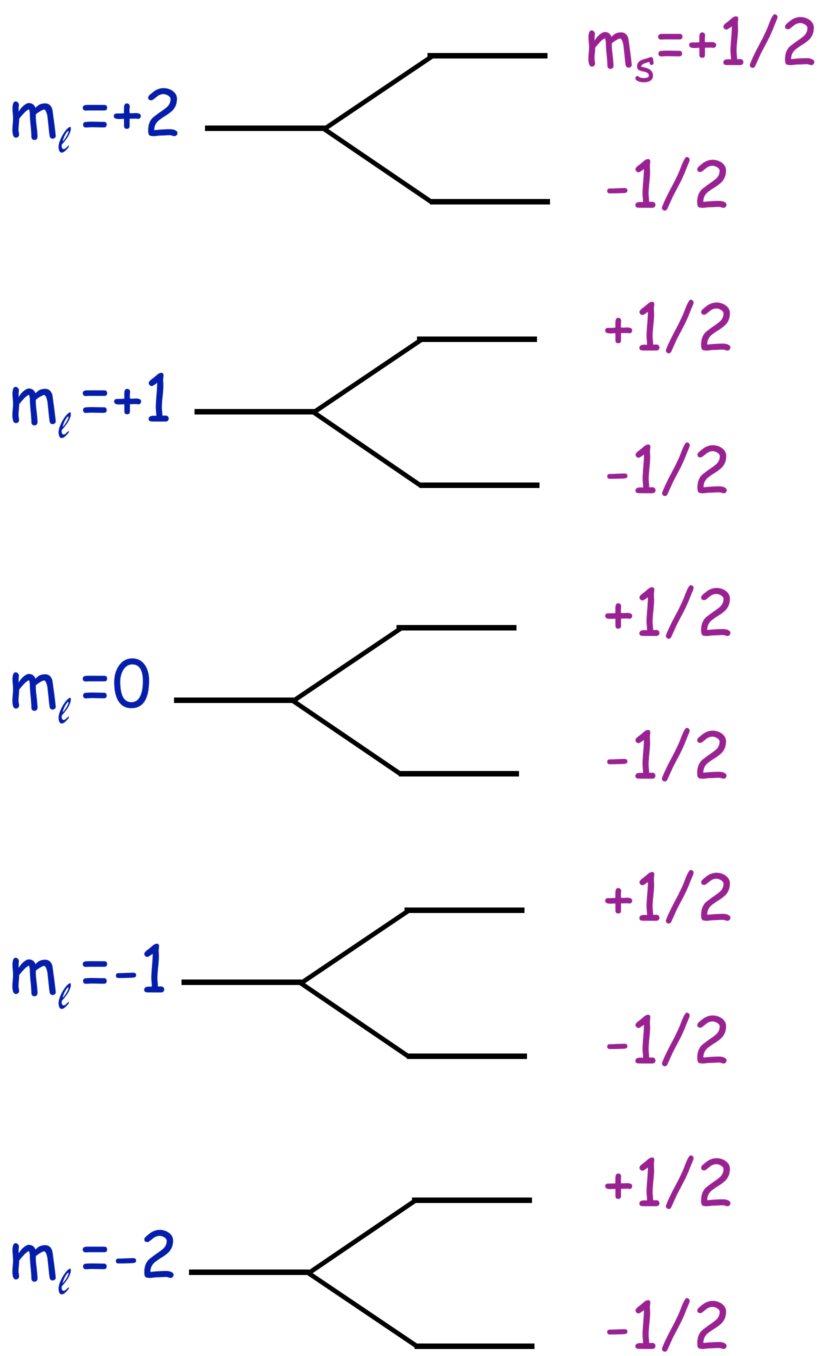
Electrons repel each other, so we want them as far from each other as possible.

1) If spins of two electrons are aligned (for maximum $\vec{S}$), then Pauli Exclusion Principle says they must have different $\vec{L}$ orbits. They will tend to be farther apart.

2) If the $\vec{L}$ orbits are aligned (although with different magnitudes), then the electrons will travel around the nucleus in the same direction, so they don't pass each other as often.

Example:

A d subshell ($\ell=2$) can contain 10 electrons.



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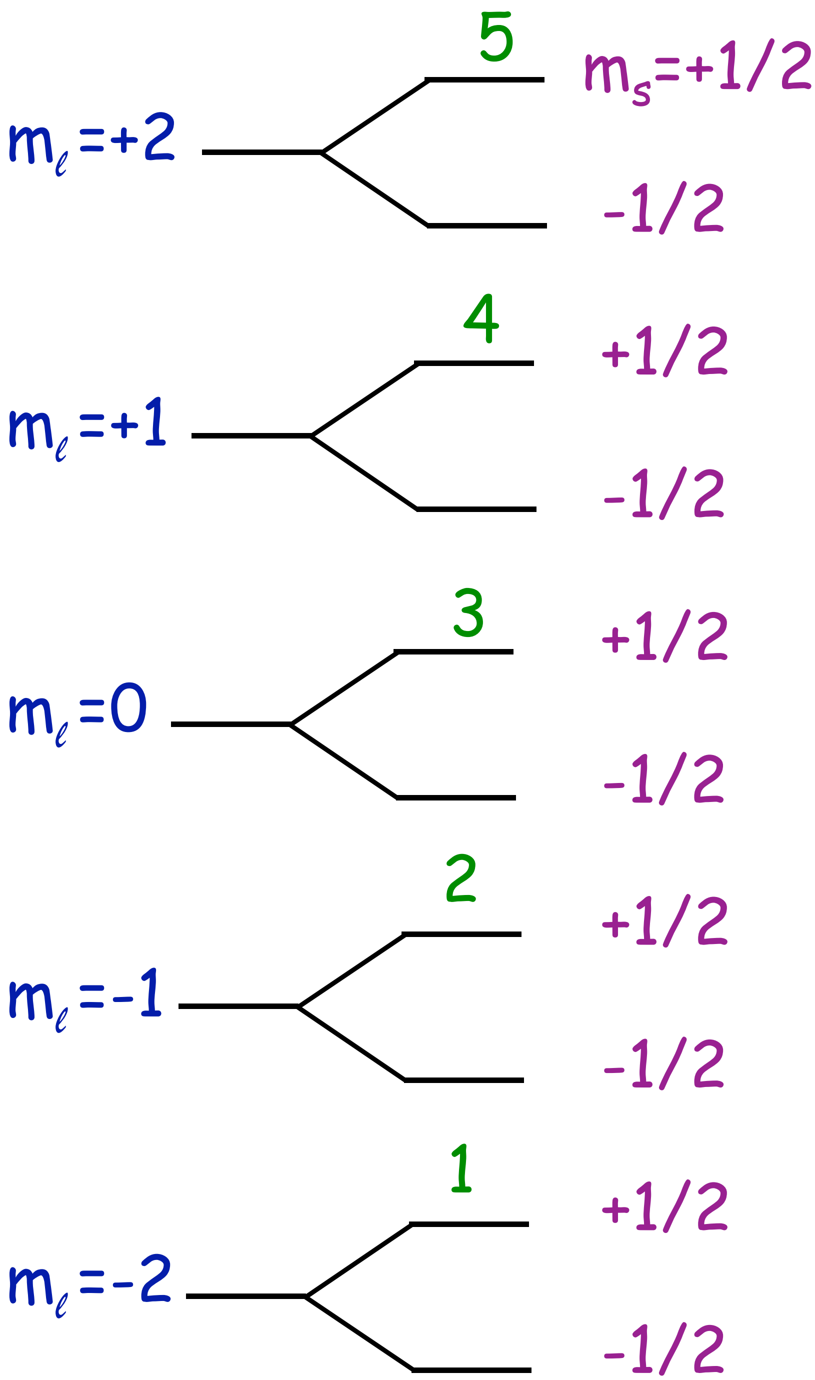
A d subshell ($\ell=2$) can contain 10 electrons.



Put first 5 electrons all with spin in same direction.

First 2 electrons have $m_\ell=-2$ and -1, etc.

Many-Electron Atoms

For many-electron atoms there is now orbit-orbit and spin-spin interactions, in addition to spin-orbit interactions.

Consider simplest case of 2 electrons with $\vec{L}_1$, $\vec{S}_1$ and $\vec{L}_2$, $\vec{S}_2$.

Only "good" quantum number is associated with total angular momentum

$$\vec{J} = \vec{L}_1+\vec{L}_2+\vec{S}_1+\vec{S}_2 \ .$$

(By "good", I mean states with definite energy have definite j and m_j.)

How can we describe atom to best understand energy levels?

LS, or Russell-Saunders, Coupling

For most atoms the spin-orbit coupling is relatively weak. Then it makes sense to add the angular momentum in steps:

First, $\vec{L} = \vec{L}_1 + \vec{L}_2$
$\vec{S} = \vec{S}_1 + \vec{S}_2$

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

For 2 electrons the Total Spin Quantum Number S is $= 0$ (spins anti-parallel)
or $= 1$ (spins parallel).

The Total Orbital Angular Momentum Quantum Number L is an integer in the range between $|\ell_1 - \ell_2|$ and $|\ell_1 + \ell_2|$.

The Total Angular Momentum Quantum Number J is an integer in the range between $|L - S|$ and $|L + S|$.

Note that for $S=0$, there is 1 value of J, given by $J=L$. This state is called a Singlet.

For $S=1$, there are 3 values of J, given by $J=L-1$, $J=L$, $J=L+1$. These states are called a Triplet.

In general, the multiplicity of the states is given by $(2S+1)$.

The Spectroscopic notation is

$$n^{(2S+1)}L_J$$

Example:

2 electrons, one in 4p, other in 4d.

I.e., $n=4$, $\ell_1=1$, $s_1=1/2$
$\ell_2=2$, $s_2=1/2$

Possible values of S:

$S=0$ or $S=1$

Possible values of L:

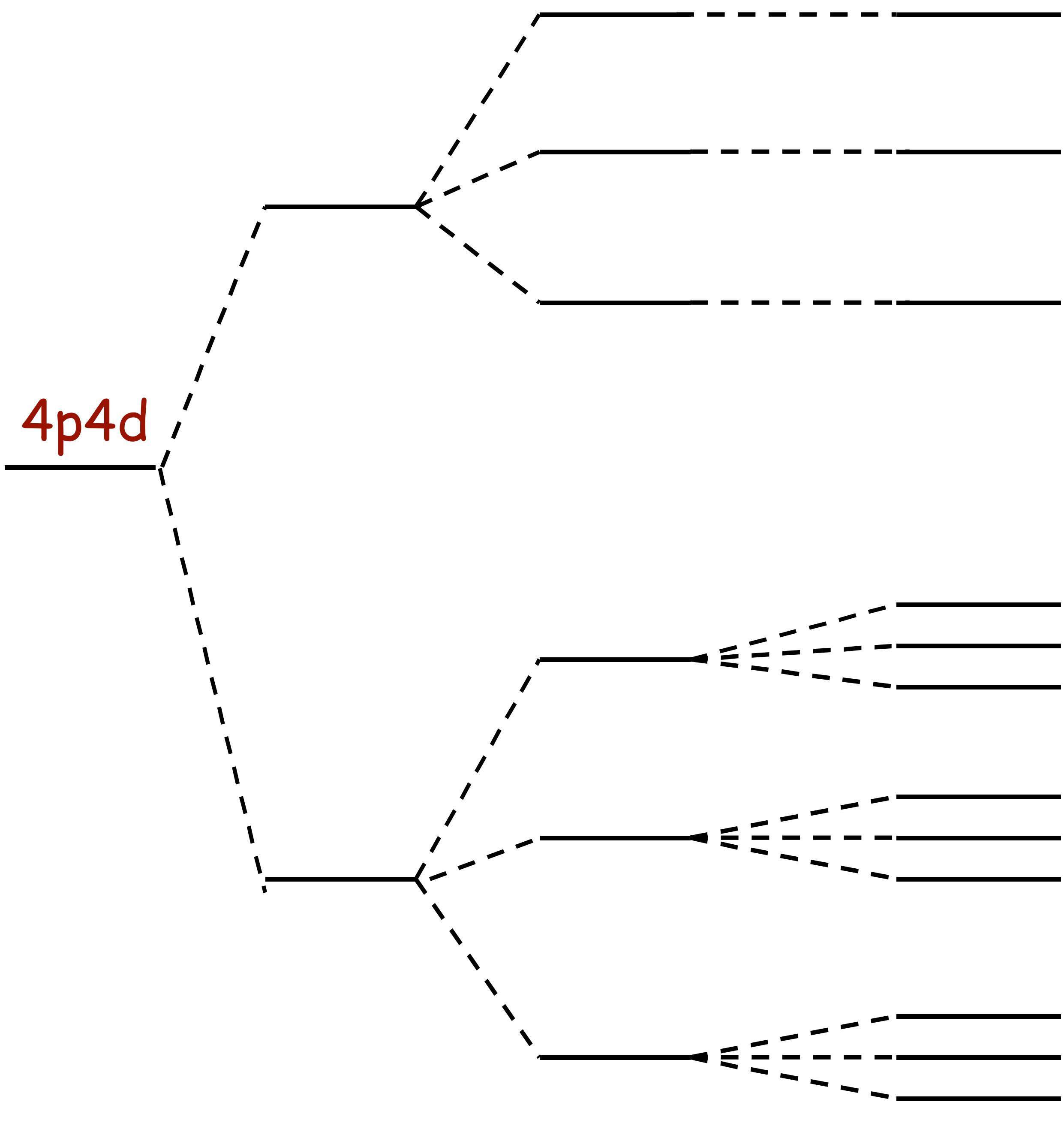
$L=1$, 2, or 3

Possible values of J:

for singlet ($S=0$): $J=L$

for triplet ($S=1$): $J=L-1$
or $J=L$
or $J=L+1$

Use Hund's rules to order the energies.



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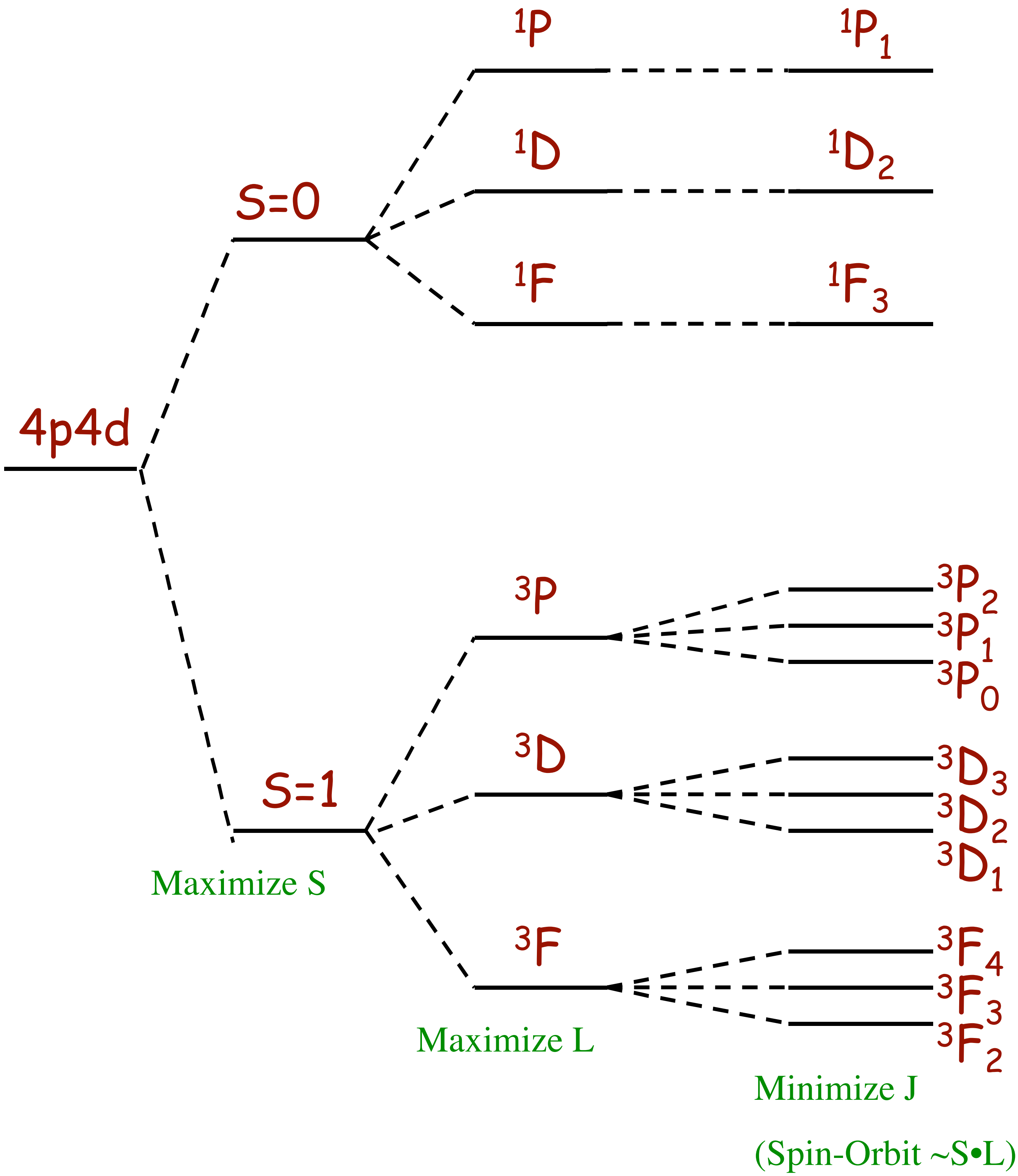


Example:

Helium $1s^2$

$\ell_1 = 0$, $s_1 = 1/2$
$\ell_2 = 0$, $s_2 = 1/2$

Possible values of $S = 0, 1$

Possible values of $L = 0$

Possible values of $J = 0, 1$

States: ${}^1S_0$, $\cancel{{}^3S_1}$

not allowed by Pauli Exclusion
(requires both electrons all same QN's)

If one electron is excited to $2s$, so the state is $1s2s$, then

both ${}^1S_0$, ${}^3S_1$ are allowed.

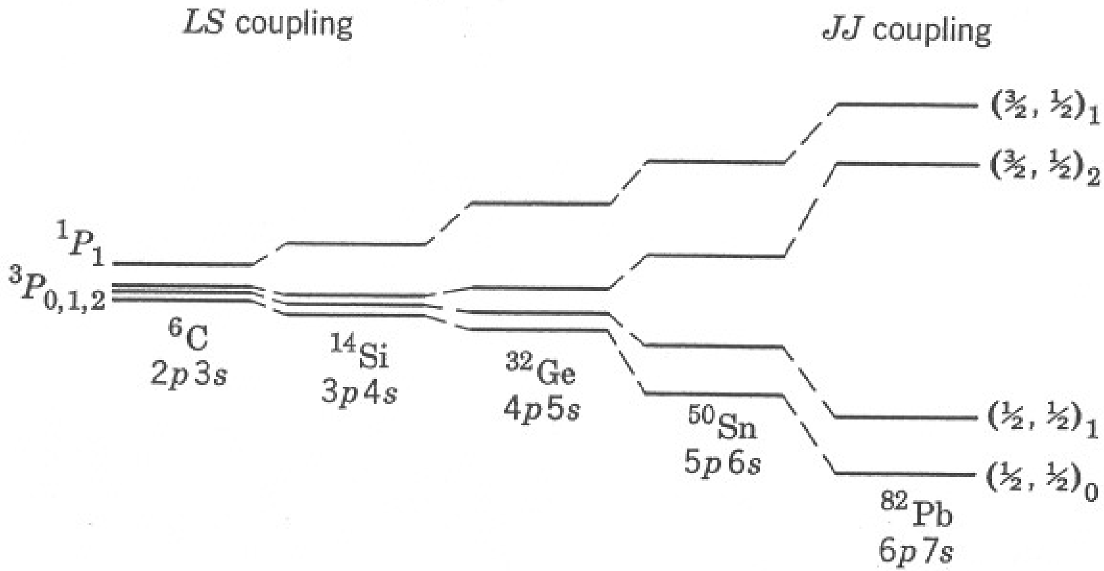
jj Coupling

For high-Z elements the spin-orbit coupling is large for each electron. Now add the angular momentum:

First, $\vec{J}_1 = \vec{L}_1 + \vec{S}_1$

$$\vec{J}_2 = \vec{L}_2 + \vec{S}_2$$

Then $\vec{J} = \vec{J}_1 + \vec{J}_2$


LS coupling
JJ coupling
$^1P_1$
$^3P_{0,1,2}$
^{6}C
2p 3s
^{14}Si
3p 4s
^{32}Ge
4p 5s
^{50}Sn
5p 6s
^{82}Pb
6p 7s
$(\frac{3}{2}, \frac{1}{2})_1$
$(\frac{3}{2}, \frac{1}{2})_2$
$(\frac{1}{2}, \frac{1}{2})_1$
$(\frac{1}{2}, \frac{1}{2})_0$

Anomalous Zeeman Effect

Recall, energy shift in external magnetic field:

$$V_B = -\vec{\mu} \cdot \vec{B}$$

The magnetic moment gets both orbital and spin contributions:

$$\vec{\mu} = \vec{\mu}_L + \vec{\mu}_S = \frac{-e}{2m}\left[\vec{L} + 2\vec{S}\right]$$

If $S=0$, this is simple. It is just the Normal Zeeman effect. Energy levels split according to m_ℓ values:

$$V_B = m_\ell \mu_B B$$

But. . . . . . . most atoms are not "Normal".

If both S and L are nonzero, the spin-orbit coupling requires us to use J-states. Projecting $\vec{\mu}$ onto $\vec{J}$ gives

$$V_B = \frac{e}{2m}\, g\ \vec{J} \cdot \vec{B}$$

$$= \mu_B\, g\, m_J\, B$$

where the projection factor (called the Landé g factor) is

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

This is the Anomalous Zeeman Effect.