CHAPTER 8
Atomic Physics

- 8.1 Atomic Structure and the Periodic Table
- 8.2 Total Angular Momentum
- 8.3 Anomalous Zeeman Effect

What distinguished Mendeleev was not only genius, but a passion for the elements. They became his personal friends; he knew every quirk and detail of their behavior.

- J. Bronowski

8.1: Atomic Structure and the Periodic Table

- What would happen if there are *more than one electron*?

  → a nucleus with charge +2e attracting two electrons.

  → the two electrons repelling one another.

- Can not solve problems exactly with the Schrödinger equation because of the complex potential interactions.

- Can understand experimental results without computing the wave functions of many-electron atoms by applying the boundary conditions and selection rules.

Pauli Exclusion Principle

- To understand atomic spectroscopic data for optical frequencies, Pauli proposed an exclusion principle:

  No two electrons in an atom may have the same set of quantum numbers (n, ℓ, m_ℓ, m_s).

- It applies to all particles of half-integer spin, which are called *fermions*, and particles in the nucleus are fermions.

The periodic table can be understood by two rules:

1) The electrons in an atom tend to occupy the lowest energy levels available to them.
2) Pauli exclusion principle.

Atomic Structure

Hydrogen: (n, ℓ, m_ℓ, m_s) = (1, 0, 0, ±½) in ground state.

- In the absence of a magnetic field, the state m_s = ½ is degenerate with the m_s = −½ state.

Helium: (1, 0, 0, ½) for the first electron.

(1, 0, 0, −½) for the second electron.

- Electrons have antialigned (m_s = +½ and m_s = −½) spins as being *paired*. → Supports Pauli exclusion principle.

- The principle quantum number also has letter codes.
  - *n* = 1 2 3 4...
  - Letter = K L M N…

Electrons for H and He atoms are in the K shell.
H: 1*s*^{2}
He: 1*s*^{1} or 1*s*

- *n* = **shells** (eg: K shell, L shell, etc.)
- *n*ℓ = **subshells** (eg: 1*s*, 2*p*, 3*d*)

Atomic Structure

How many electrons may be in each subshell?

	Total
For each m_ℓ: two values of m_s	2
For each ℓ: $(2\ell + 1)$ values of m_ℓ	$2(2\ell + 1)$

Recall: ℓ = 0 1 2 3 4 5 …

letter = *s* *p* *d* *f* *g* *h* …

$\ell = 0$, (*s* state) can have two electrons.

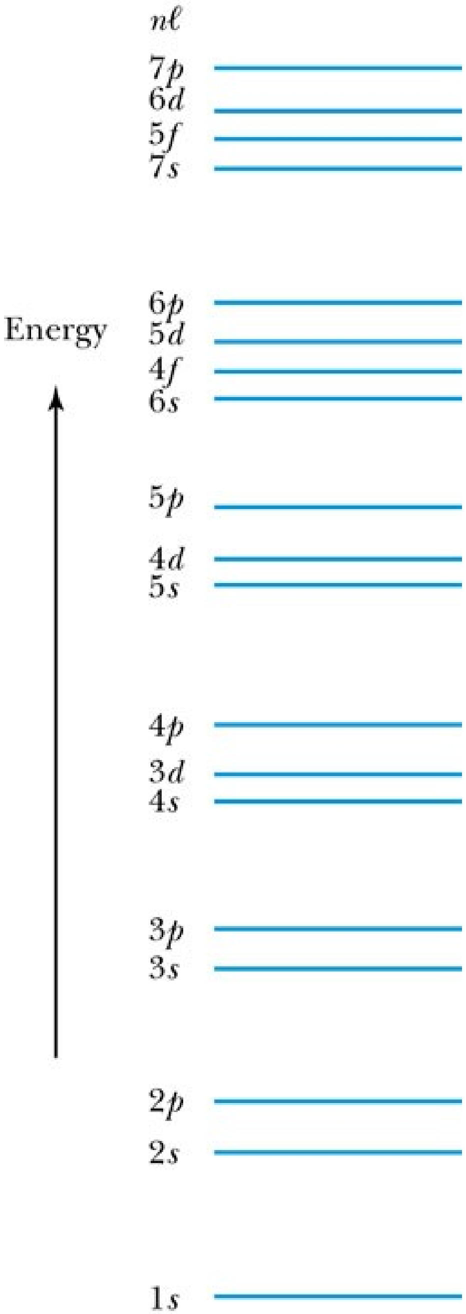
$\ell = 1$, (*p* state) can have six electrons, and so on.

The lower ℓ values have more elliptical orbits than the higher ℓ values.

→ Electrons with higher ℓ values are more shielded from the nuclear charge.

→ Electrons lie higher in energy than those with lower ℓ values.

→ 4*s* fills before 3*d*.



The Periodic Table

Periodic Table of Elements

Groups:	1 (Alkalis)	2 (Alkaline earths)	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17 (Halogens)	18 (Rare gases)
Closed shells			Transition elements															
	1 H $1s$																	2 He $1s^2$
$1s^2$	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^2 2p^1$	6 C $2s^2 2p^2$	7 N $2s^2 2p^3$	8 O $2s^2 2p^4$	9 F $2s^2 2p^5$	10 Ne $2s^2 2p^6$
$2s^2 2p^6$	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$
$3s^2 3p^6$	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^1 4s^2$	22 Ti $3d^2 4s^2$	23 V $3d^3 4s^2$	24 Cr $3d^5 4s^1$	25 Mn $3d^5 4s^2$	26 Fe $3d^6 4s^2$	27 Co $3d^7 4s^2$	28 Ni $3d^8 4s^2$	29 Cu $3d^{10} 4s^1$	30 Zn $3d^{10} 4s^2$	31 Ga $3d^{10} 4s^2 4p^1$	32 Ge $3d^{10} 4s^2 4p^2$	33 As $3d^{10} 4s^2 4p^3$	34 Se $3d^{10} 4s^2 4p^4$	35 Br $3d^{10} 4s^2 4p^5$	36 Kr $3d^{10} 4s^2 4p^6$
$3d^{10} 4s^2 4p^6$	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^1 5s^2$	40 Zr $4d^2 5s^2$	41 Nb $4d^4 5s^1$	42 Mo $4d^5 5s^1$	43 Tc $4d^6 5s^1$	44 Ru $4d^7 5s^1$	45 Rh $4d^8 5s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10} 5s^1$	48 Cd $4d^{10} 5s^2$	49 In $4d^{10} 5s^2 5p^1$	50 Sn $4d^{10} 5s^2 5p^2$	51 Sb $4d^{10} 5s^2 5p^3$	52 Te $4d^{10} 5s^2 5p^4$	53 I $4d^{10} 5s^2 5p^5$	54 Xe $4d^{10} 5s^2 5p^6$
$4d^{10} 5s^2 5p^6$	55 Cs $6s^1$	56 Ba $6s^2$	57 La $5d^1 6s^2$	72 Hf $4f^{14} 5d^2 6s^2$	73 Ta $4f^{14} 5d^3 6s^2$	74 W $4f^{14} 5d^4 6s^2$	75 Re $4f^{14} 5d^5 6s^2$	76 Os $4f^{14} 5d^6 6s^2$	77 Ir $4f^{14} 5d^7 6s^2$	78 Pt $4f^{14} 5d^9 6s^1$	79 Au $4f^{14} 5d^{10} 6s^1$	80 Hg $4f^{14} 5d^{10} 6s^2$	81 Tl $4f^{14} 5d^{10} 6s^2 6p^1$	82 Pb $4f^{14} 5d^{10} 6s^2 6p^2$	83 Bi $4f^{14} 5d^{10} 6s^2 6p^3$	84 Po $4f^{14} 5d^{10} 6s^2 6p^4$	85 At $4f^{14} 5d^{10} 6s^2 6p^5$	86 Rn $4f^{14} 5d^{10} 6s^2 6p^6$
$4f^{14} 5d^{10} 6s^2 6p^6$	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac $6d^1 7s^2$	104 Rf $5f^{14} 6d^2 7s^2$	105 Db $5f^{14} 6d^3 7s^2$	106 Sg $5f^{14} 6d^4 7s^2$	107 Bh $5f^{14} 6d^5 7s^2$	108 Hs $5f^{14} 6d^6 7s^2$	109 Mt $5f^{14} 6d^7 7s^2$	110 Ds $5f^{14} 6d^9 7s^1$	111 Rg $5f^{14} 6d^{10} 7s^1$	112 $5f^{14} 6d^{10} 7s^2$						

Lanthanides	58 Ce $4f^2 6s^2$	59 Pr $4f^3 6s^2$	60 Nd $4f^4 6s^2$	61 Pm $4f^5 6s^2$	62 Sm $4f^6 6s^2$	63 Eu $4f^7 6s^2$	64 Gd $4f^7 6s^2 5d^1$	65 Tb $4f^9 6s^2$	66 Dy $4f^{10} 6s^2$	67 Ho $4f^{11} 6s^2$	68 Er $4f^{12} 6s^2$	69 Tm $4f^{13} 6s^2$	70 Yb $4f^{14} 6s^2$	71 Lu $4f^{14} 5d^1 6s^2$
Actinides	90 Th $6d^2 7s^2$	91 Pa $5f^2 6d^1 7s^2$	92 U $5f^3 6d^1 7s^2$	93 Np $5f^4 6d^1 7s^2$	94 Pu $5f^6 7s^2$	95 Am $5f^7 7s^2$	96 Cm $5f^7 6d^1 7s^2$	97 Bk $5f^8 6d^1 7s^2$	98 Cf $5f^{10} 7s^2$	99 Es $5f^{11} 7s^2$	100 Fm $5f^{12} 7s^2$	101 Md $5f^{13} 7s^2$	102 No $5f^{14} 7s^2$	103 Lr $5f^{14} 6d^1 7s^2$

Groups and Periods

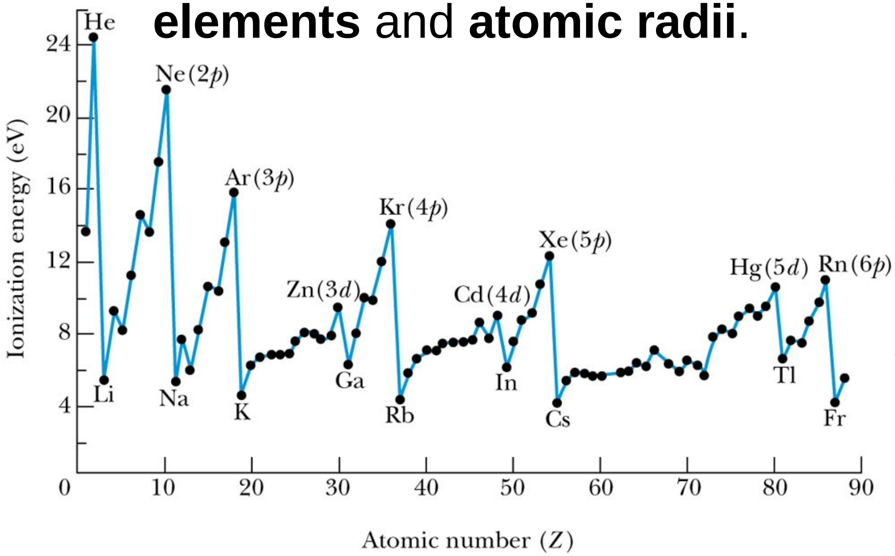
Groups:

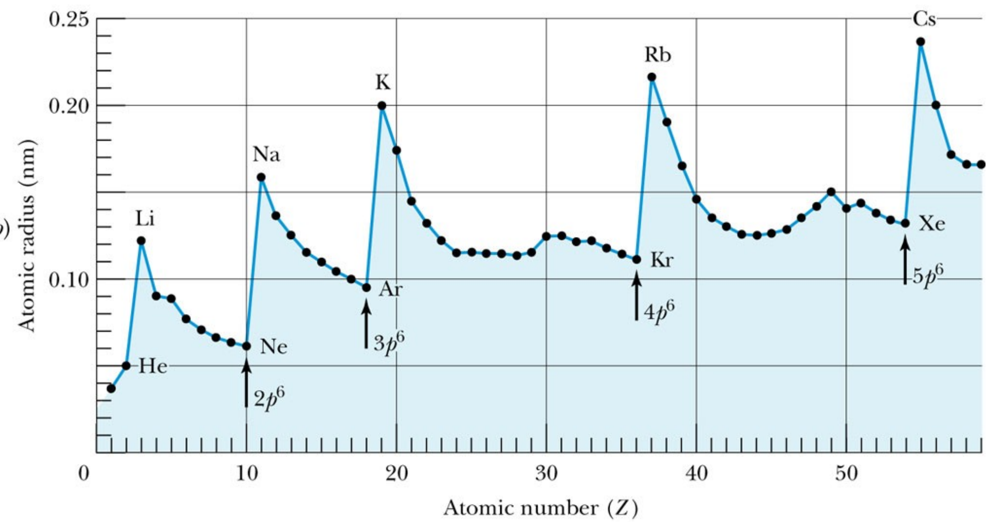
- Vertical columns.
- Same number of electrons in an ℓ orbit.
- Can form similar chemical bonds.

Periods:

- Horizontal rows.
- Correspond to filling of the subshells.

- Some properties of elements are compared by the **ionization energies of elements** and **atomic radii**.





The Periodic Table

Inert Gases:

- Last group of the periodic table
- Closed *p* subshell except helium
- Zero net spin and large ionization energy
- Their atoms interact weakly with each other

Alkalis:

- Single *s* electron outside an inner core
- Easily form positive ions with a charge +1e
- Lowest ionization energies
- Electrical conductivity is relatively good

Alkaline Earths:

- Two *s* electrons in outer subshell
- Largest atomic radii
- High electrical conductivity

The Periodic Table

Halogens:

- Need one more electron to fill outermost subshell
- Form strong ionic bonds with the alkalis
- More stable configurations occur as the *p* subshell is filled

Transition Metals:

- Three rows of elements in which the 3*d*, 4*d*, and 5*d* are being filled
- Properties primarily determined by the *s* electrons, rather than by the *d* subshell being filled
- Have *d*-shell electrons with unpaired spins
- As the *d* subshell is filled, the magnetic moments, and the tendency for neighboring atoms to align spins are reduced

The Periodic Table

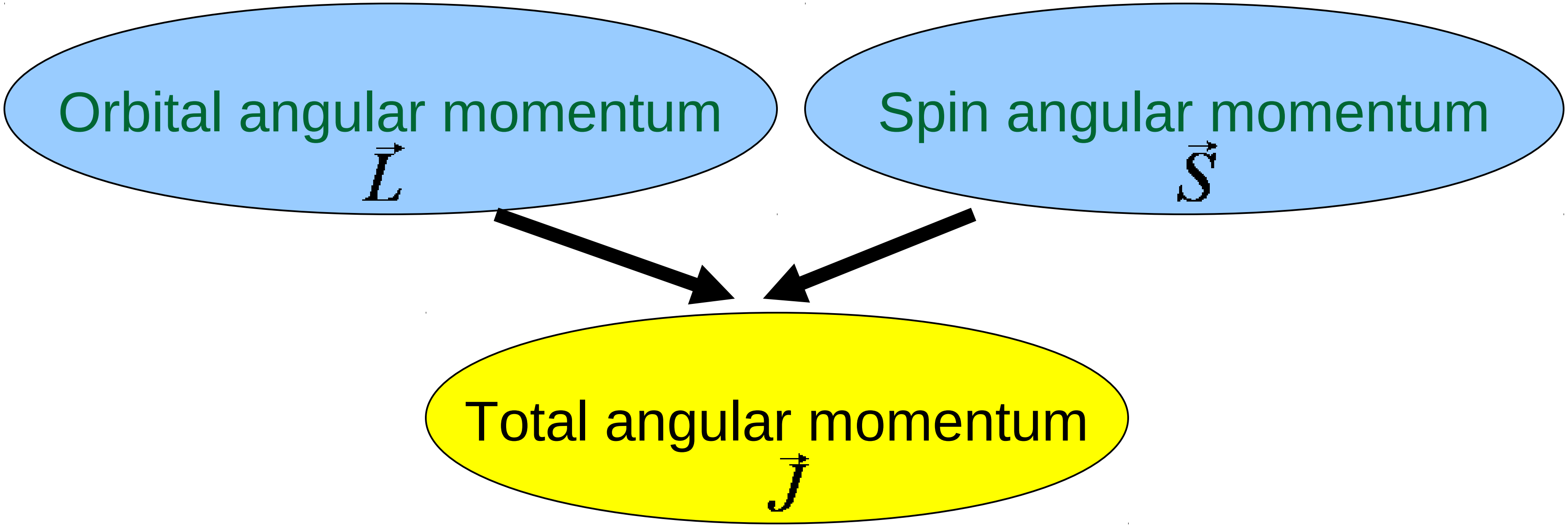
Lanthanides (*rare earths*):

- Have the outside $6s^2$ subshell completed
- As occurs in the $3d$ subshell, the electrons in the $4f$ subshell have unpaired electrons that align themselves
- The large orbital angular momentum contributes to the large ferromagnetic effects

Actinides:

- Inner subshells are being filled while the $7s^2$ subshell is complete
- Difficult to obtain chemical data because they are all radioactive
- Have longer half-lives

8.2: Total Angular Momentum



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

L, L_z, S, $S_z J$ and J_z are quantized.

Total Angular Momentum

- If j and m_j are quantum numbers for the single electron (hydrogen atom).

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

$$J_z = m_j \hbar$$

- Quantization of the magnitudes.

$$L = \sqrt{\ell(\ell+1)}\hbar$$

$$S = \sqrt{s(s+1)}\hbar$$

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

- The total angular momentum quantum number for the single electron can only have the values

$$j = \ell \pm s$$

Spin-Orbit Coupling

- An effect of the spins of the electron and the orbital angular momentum interaction is called **spin-orbit coupling**.

> - The dipole potential energy $V_{s\ell} = -\vec{\mu}_s \cdot \vec{B}_{\text{internal}}$.
> - The spin magnetic moment $\propto -\vec{S}$.
> - $\vec{B}_{\text{internal}} \propto \vec{L}$.

- $\vec{B}_{\text{internal}}$ is the magnetic field due to the proton.

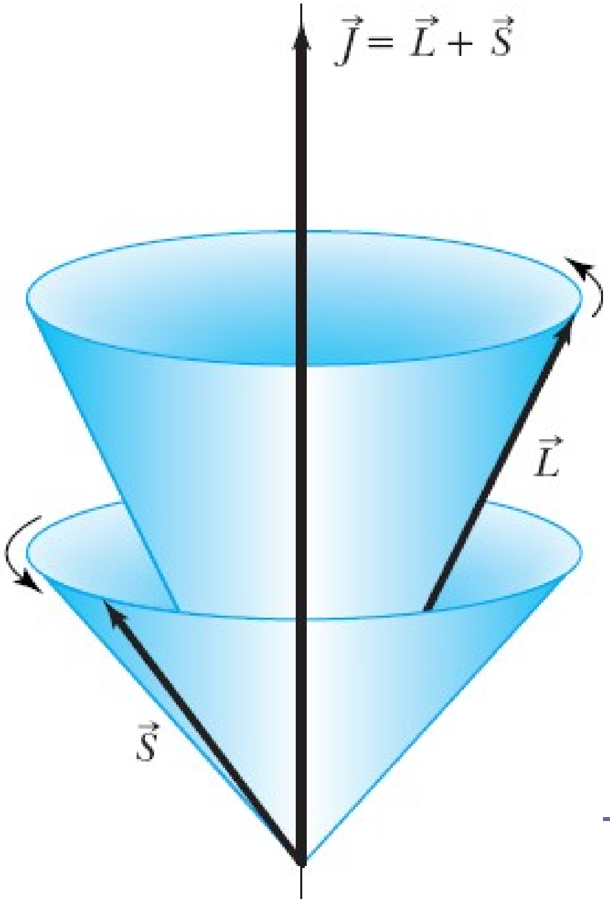
$$V_{s\ell} \sim \vec{S} \times \vec{L} = SL\cos\alpha$$

where cos α is the angle between $\vec{S}$ and $\vec{L}$.

Total Angular Momentum

No external magnetic field:

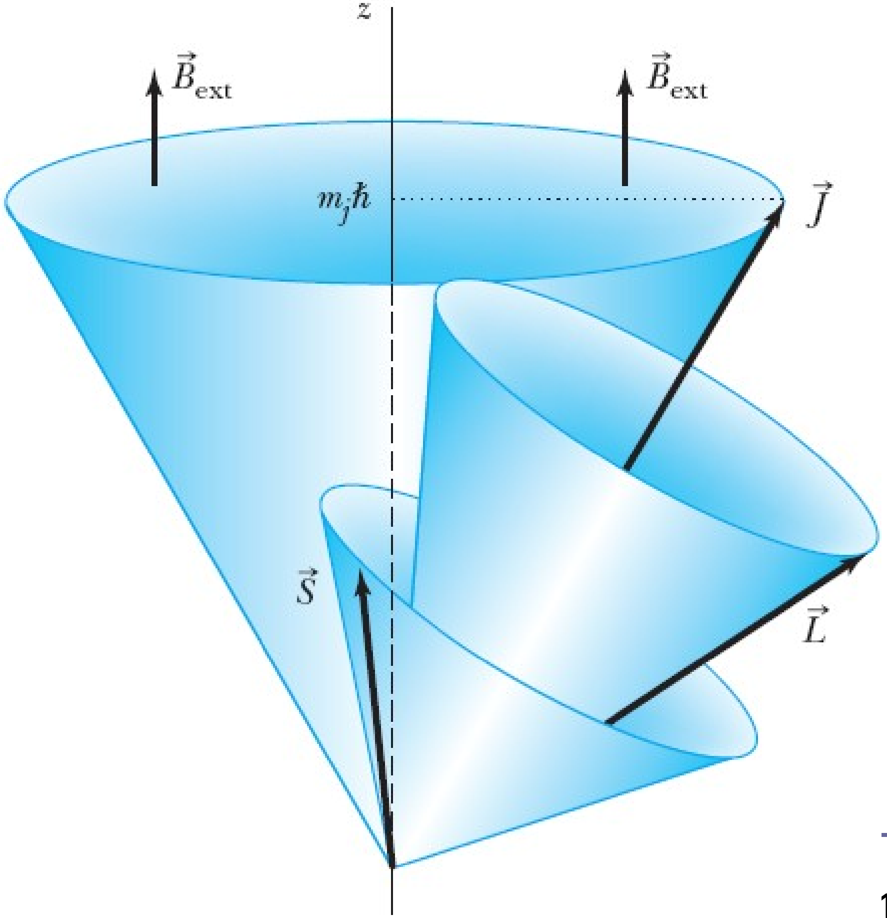
- Only J_z can be known because the uncertainty principle forbids J_x or J_y from being known at the same time as J_z.



Total Angular Momentum

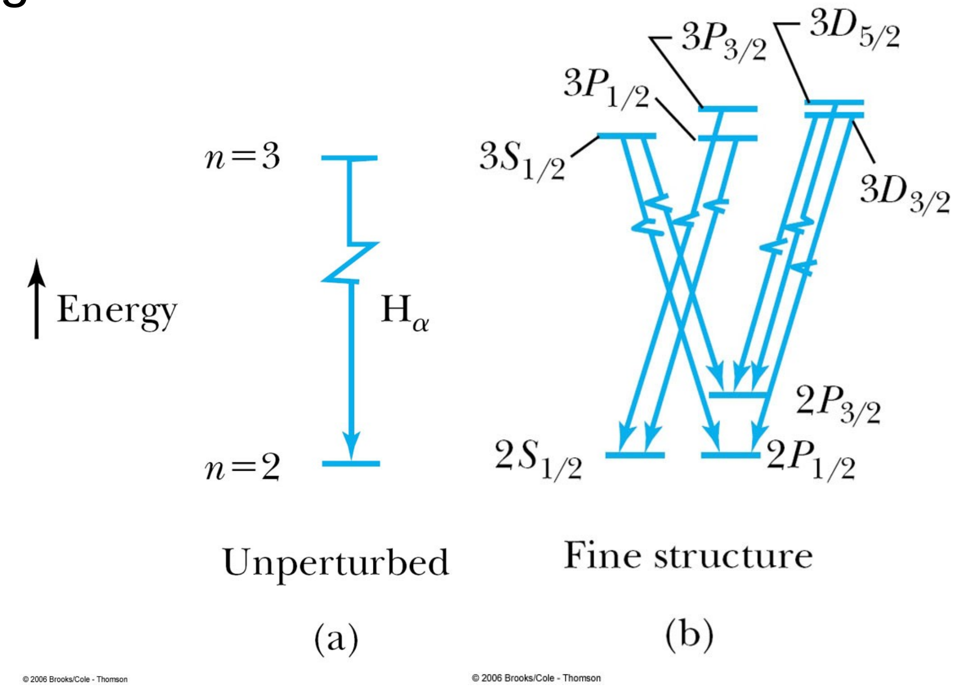
With an internal magnetic field:

- $\vec{J}$ will precess about $\vec{B}_{\text{ext}}$.



Total Angular Momentum

- Now the selection rules for a single-electron atom become
  - Δ*n* = anything   Δℓ = ±1
  - Δ*mj* = 0, ±1   Δ*j* = 0, ±1
- Hydrogen energy-level diagram for *n* = 2 and *n* = 3 with the spin-orbit splitting.



Many-Electron Atoms

Hund's rules:

1) The total spin angular momentum *S* should be maximized to the extent possible without violating the Pauli exclusion principle.
2) Insofar as rule 1 is not violated, *L* should also be maximized.
3) For atoms having subshells less than half full, *J* should be minimized.

- For labeled two-electron atom

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

- There are ***LS* coupling** and ***jj* coupling** to combine four angular momenta *J*.

LS Coupling

- This is used for most atoms when the magnetic field is weak.

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

- If two electrons are single subshell, *S* = 0 or 1 depending on whether the spins are antiparallel or parallel.

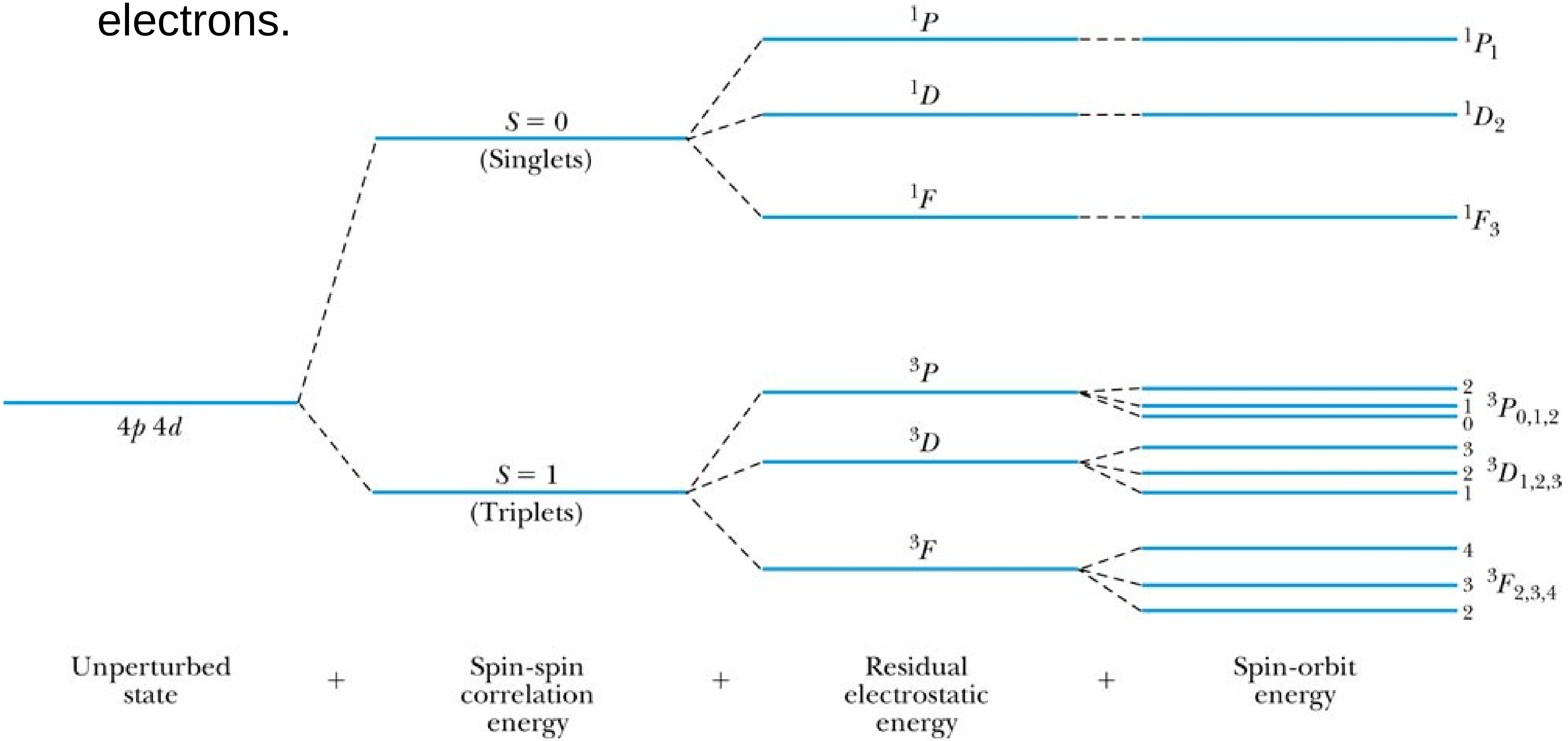
- For given *L*, there are 2*S* + 1 values of *J*.
- For *L* > *S*, *J* goes from *L* − *S* to *L* + *S*.
- For *L* < *S*, there are fewer than 2*S* + 1 possible *J* values.
- The value of 2*S* + 1 is the **multiplicity** of the state.

LS Coupling

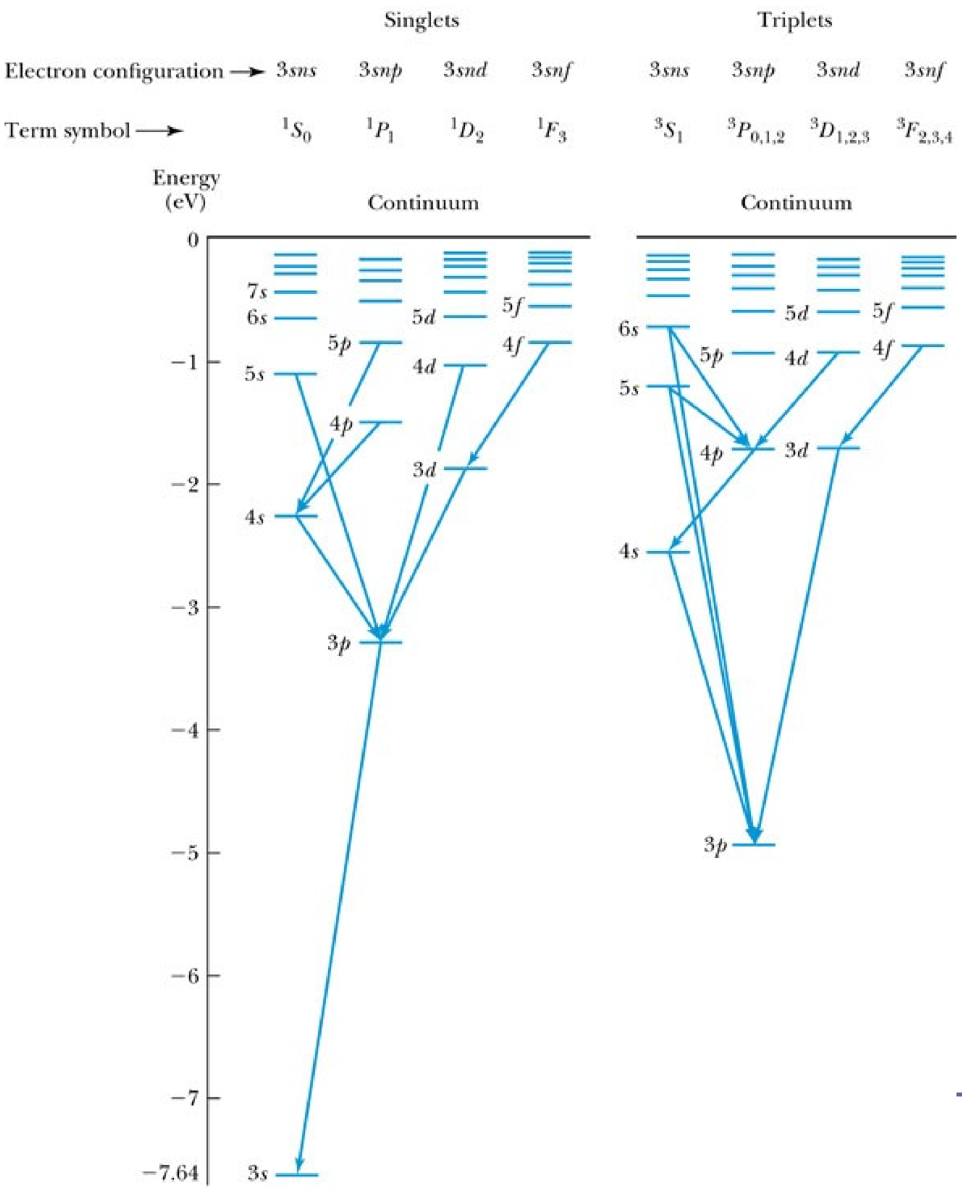
- The notation for a single-electron atom becomes

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

- The letters and numbers are called **spectroscopic symbols**.
- There are **singlet** states (S = 0) and **triplet** states (S = 1) for two electrons.



LS Coupling



- There are separated energy levels according to whether they are $S = 0$ or 1.
- **Allowed** transitions must have $\Delta S = 0$.
- No allowed (**forbidden**) transitions are possible between singlet and triplet states with much lower probability.

LS Coupling

- The allowed transitions for the *LS* coupling scheme are
  - $\Delta L = \pm 1$ $\Delta S = 0$
  - $\Delta J = 0, \pm 1$ ($J = 0 \rightarrow J = 0$ is forbidden)
- A magnesium atom excited to the 3*s*3*p* triplet state has no lower triplet state to which it can decay.
- It is called **metastable**, because it lives for such a long time on the atomic scale.

jj Coupling

- It is for the heavier elements, where the nuclear charge causes the spin-orbit interactions to be as strong as the force between the individual $\vec{S}_i$ and $\vec{L}_i$.

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

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

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

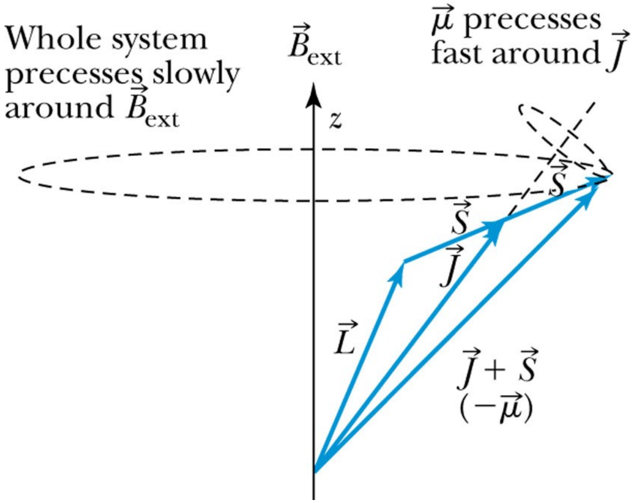
8.3: Anomalous Zeeman Effect

- More than three closely spaced optical lines were observed.
- The interaction that splits the energy levels in an external magnetic field $\vec{B}_{\text{ext}}$ is caused by $\vec{\mu} \cdot \vec{B}$ interaction.
- The magnetic moment depends on → Orbital contribution $\vec{\mu}_\ell$ and → Spin magnetic moment $\vec{\mu}_s$
- The $2J + 1$ degeneracy for a given total angular momentum state J is removed by the effect of the $\vec{B}_{\text{ext}}$.
- If the $\vec{B}_{\text{ext}}$ is small compared to internal magnetic field, then $\vec{L}$ and $\vec{S}$ precess about $\vec{J}$ while $\vec{J}$ precesses *slowly* about $\vec{B}_{\text{ext}}$.

Anomalous Zeeman Effect

- The total magnetic moment is

$$\vec{\mu} = \vec{\mu}_\ell + \vec{\mu}_s = -\frac{e}{2m}\vec{L} - \frac{e}{m}\vec{S} = -\frac{e}{2m}(\vec{J} + \vec{S})$$



$$V = \frac{e\hbar B_{ext}}{2m} g m_J = \mu_B B_{ext} g m_J$$

μ_B is the Bohr magneton and

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

it is called the **Landé *g* factor**.

- The magnetic total angular momentum numbers m_J from $-J$ to J in integral steps.
- $\vec{B}_{ext}$ splits each state J into $2J + 1$ equally spaced levels separated $\Delta E = V$.
- For photon transitions between energy levels $\Delta m_J = \pm 1, 0$ but $m_{J_1} = 0 \rightarrow m_{J_2} = 0$ is forbidden when $\Delta J = 0$.