Atomic Physics

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

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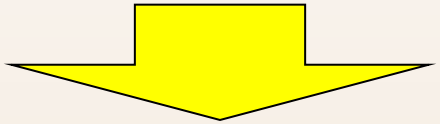
Atomic Structure and the Periodic Table

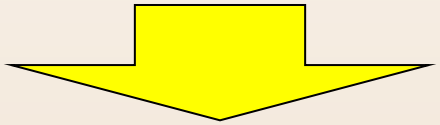
- What would happen if there are *more than one electron*?

  ⟶ 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: $(n, \ell, m_\ell, m_s) = (1, 0, 0, \pm ½)$ 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…

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

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

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* …

ℓ = 0, (*s* state) can have two electrons.

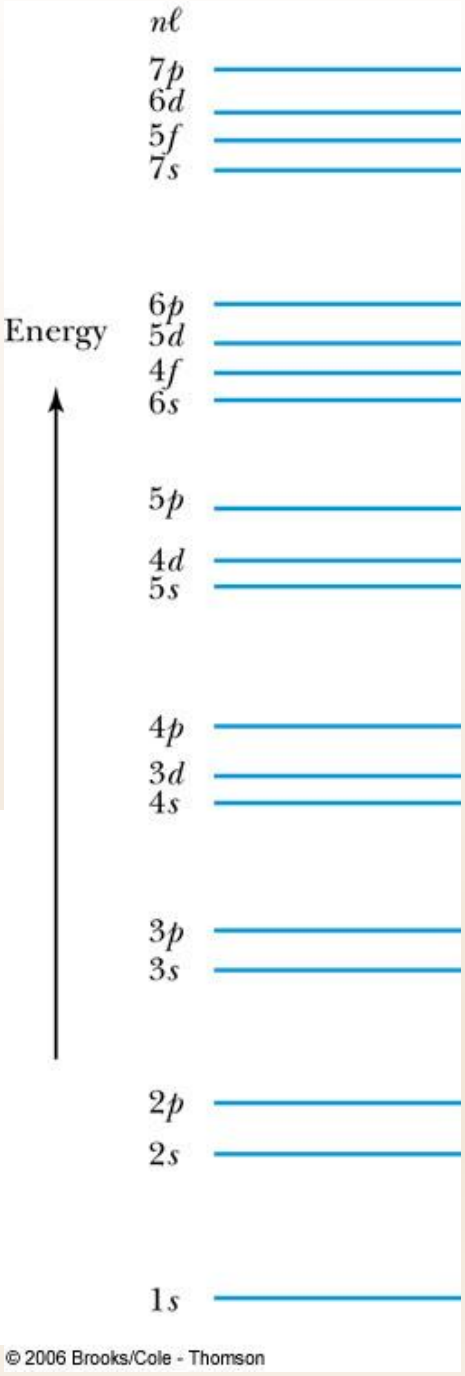
ℓ = 1, (*p* state) can have six electrons, and so on.

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

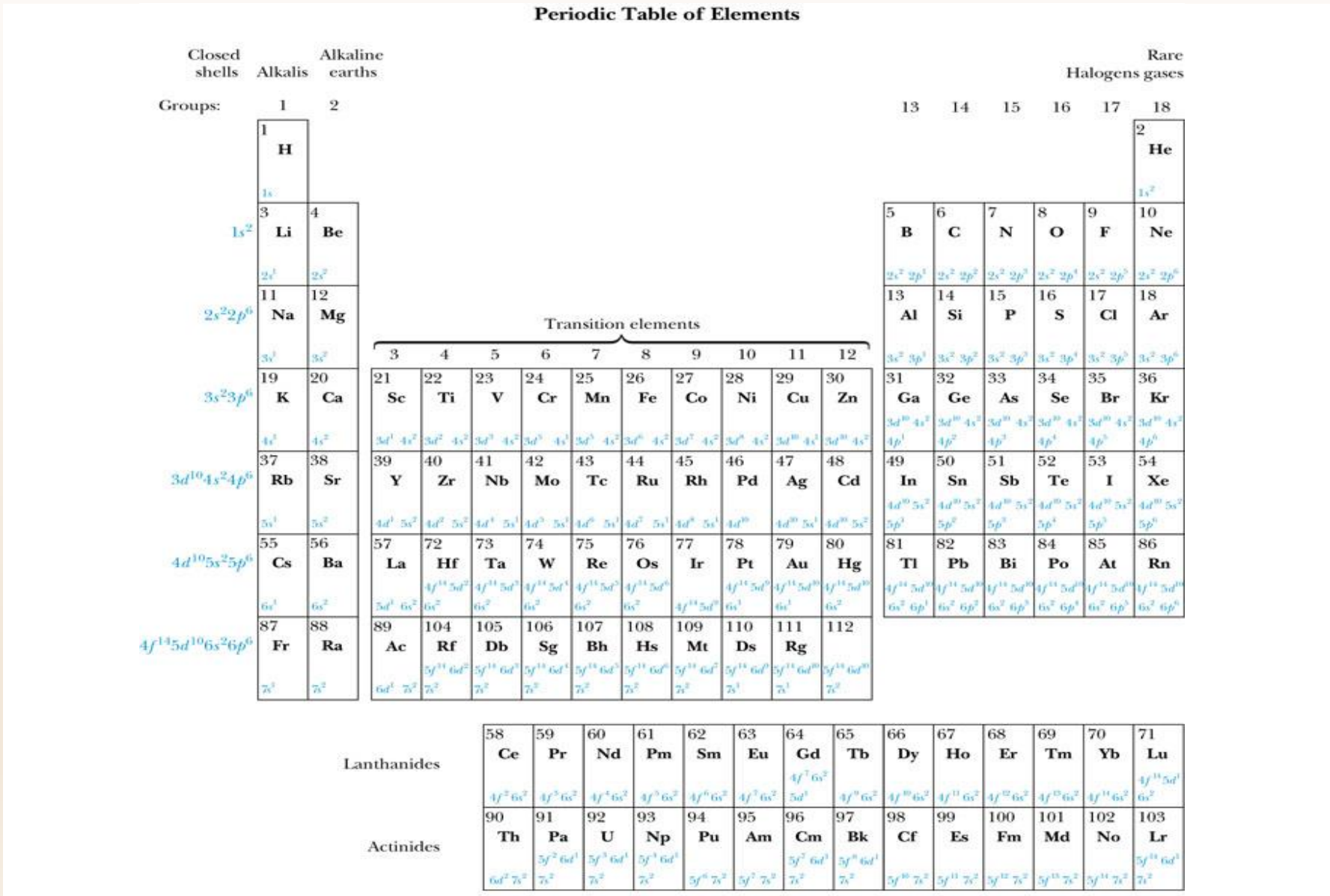
→ Electrons with higher ℓ values are more shielded from the nuclear charge.

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

→ 4*s* fills before 3*d*.



The Periodic Table



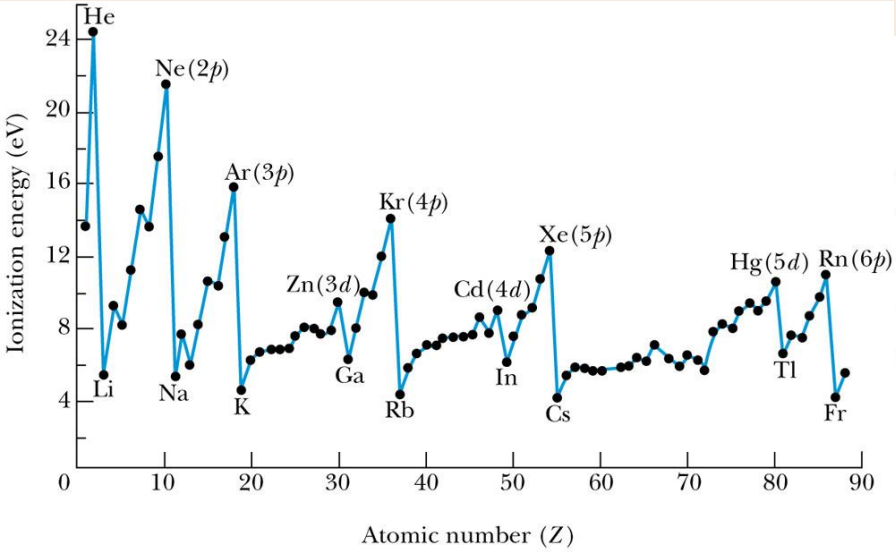
Groups and Periods

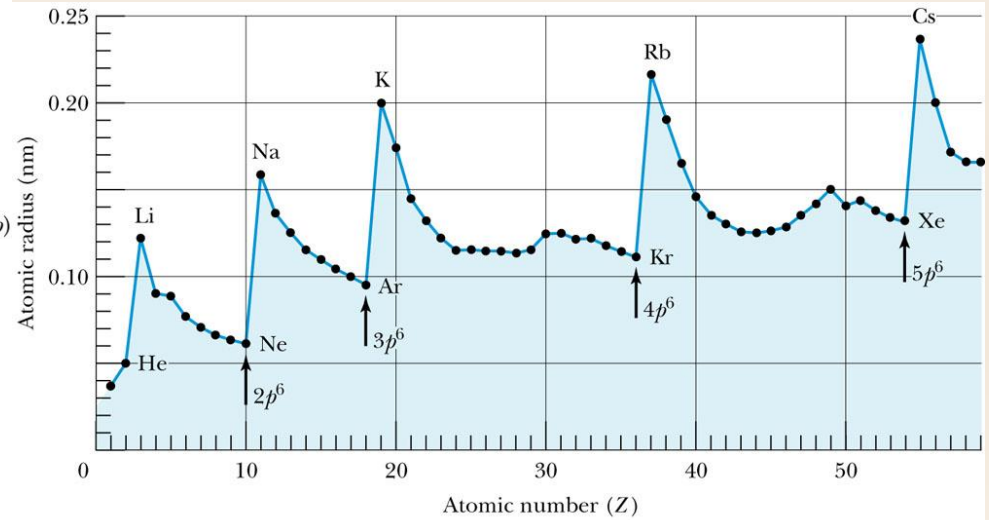
Groups:

- 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

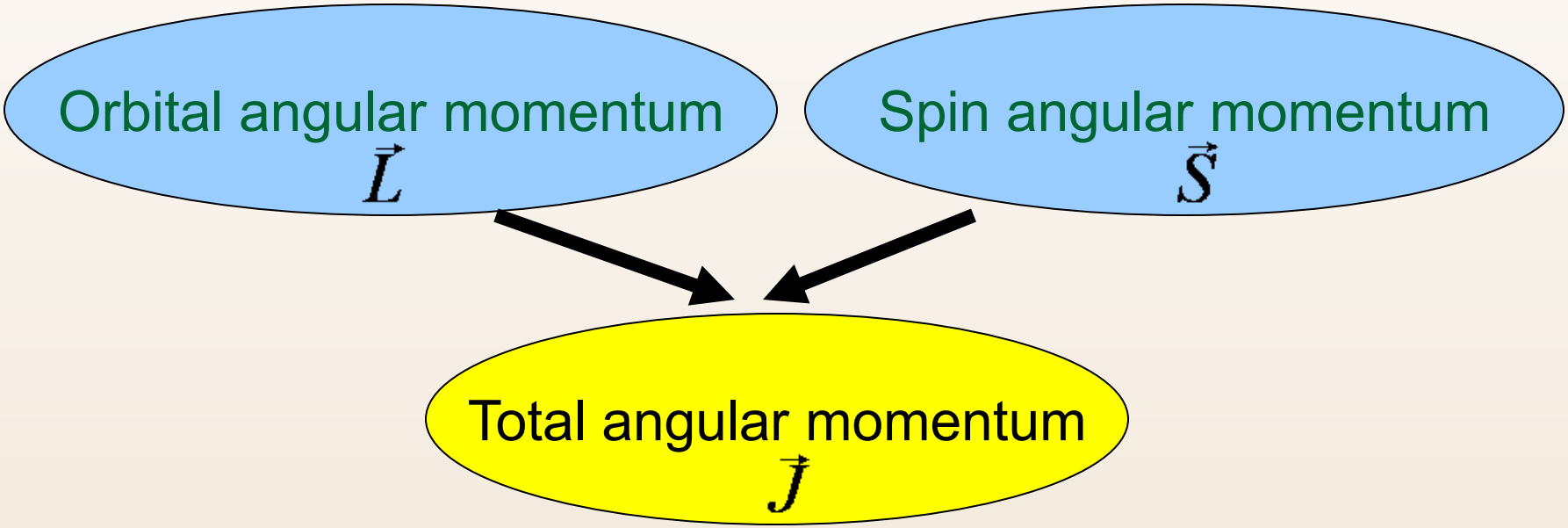
Lanthanides (*rare earths*):

- Have the outside $6s^2$ subshell completed
- As occurs in the 3*d* subshell, the electrons in the 4*f* 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

Total Angular Momentum



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

L, L_z, S, S_zJ 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.

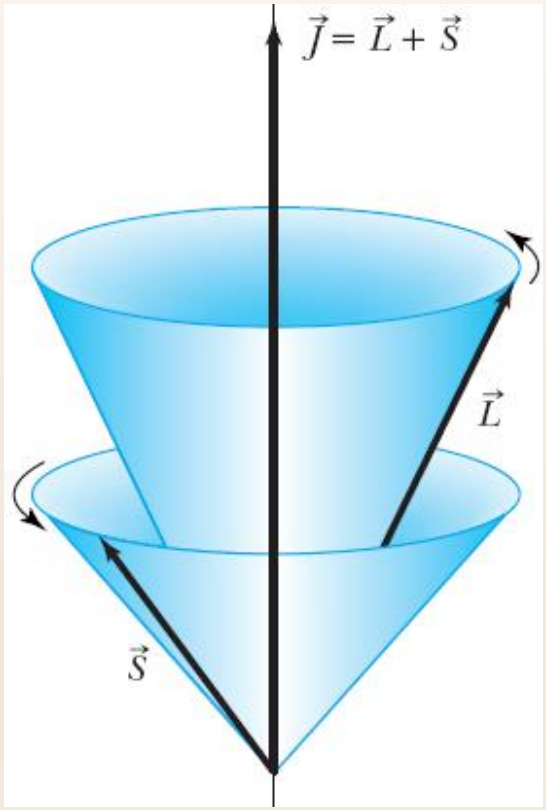
$$Vs\ \ell \sim \vec{S} \times \vec{L} = SL\cos\alpha$$

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

Total Angular Momentum

No external magnetic field:

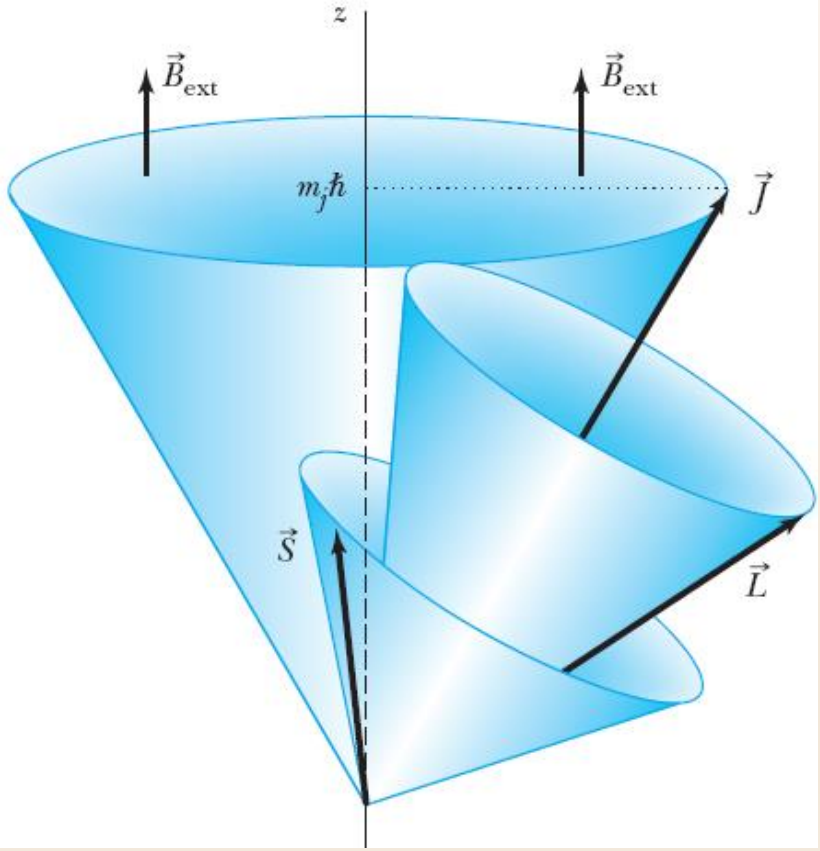
- Only J_z can be known because the uncertainty principle forbids J_x or J_y from being known at the same time as J_z.



Total Angular Momentum

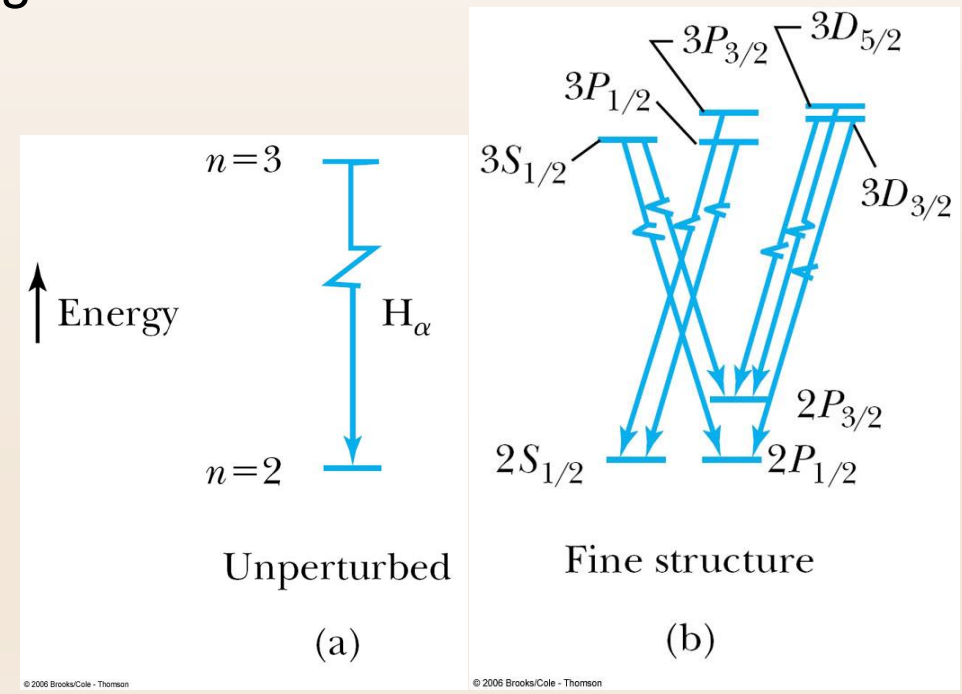
With an internal magnetic field:

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



Total Angular Momentum

- Now the selection rules for a single-electron atom become
  - Δn = anything $\Delta \ell = \pm 1$
  - $\Delta mj = 0, \pm 1$ $\Delta j = 0, \pm 1$
- 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.

$$\left.\begin{aligned}\vec{L} &= \vec{L}_1 + \vec{L}_2 \\ \vec{S} &= \vec{S}_1 + \vec{S}_2\end{aligned}\right\} \longrightarrow \vec{J} = \vec{L} + \vec{S}$$

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

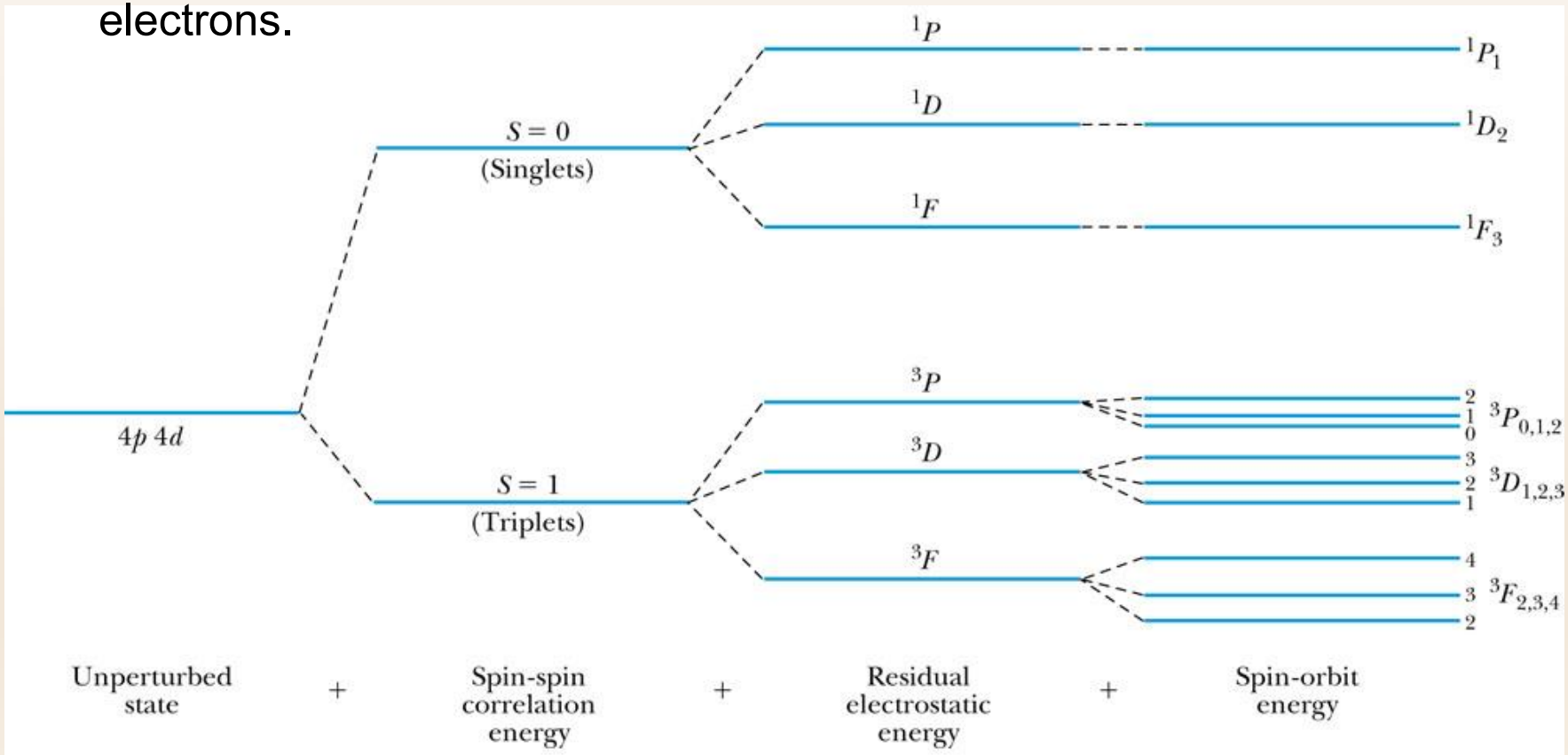
- For given L, there are $2S + 1$ values of J.
- For $L > S$, J goes from $L - S$ to $L + S$.
- For $L < S$, there are fewer than $2S + 1$ possible J values.
- The value of $2S + 1$ is the **multiplicity** of the state.

LS Coupling

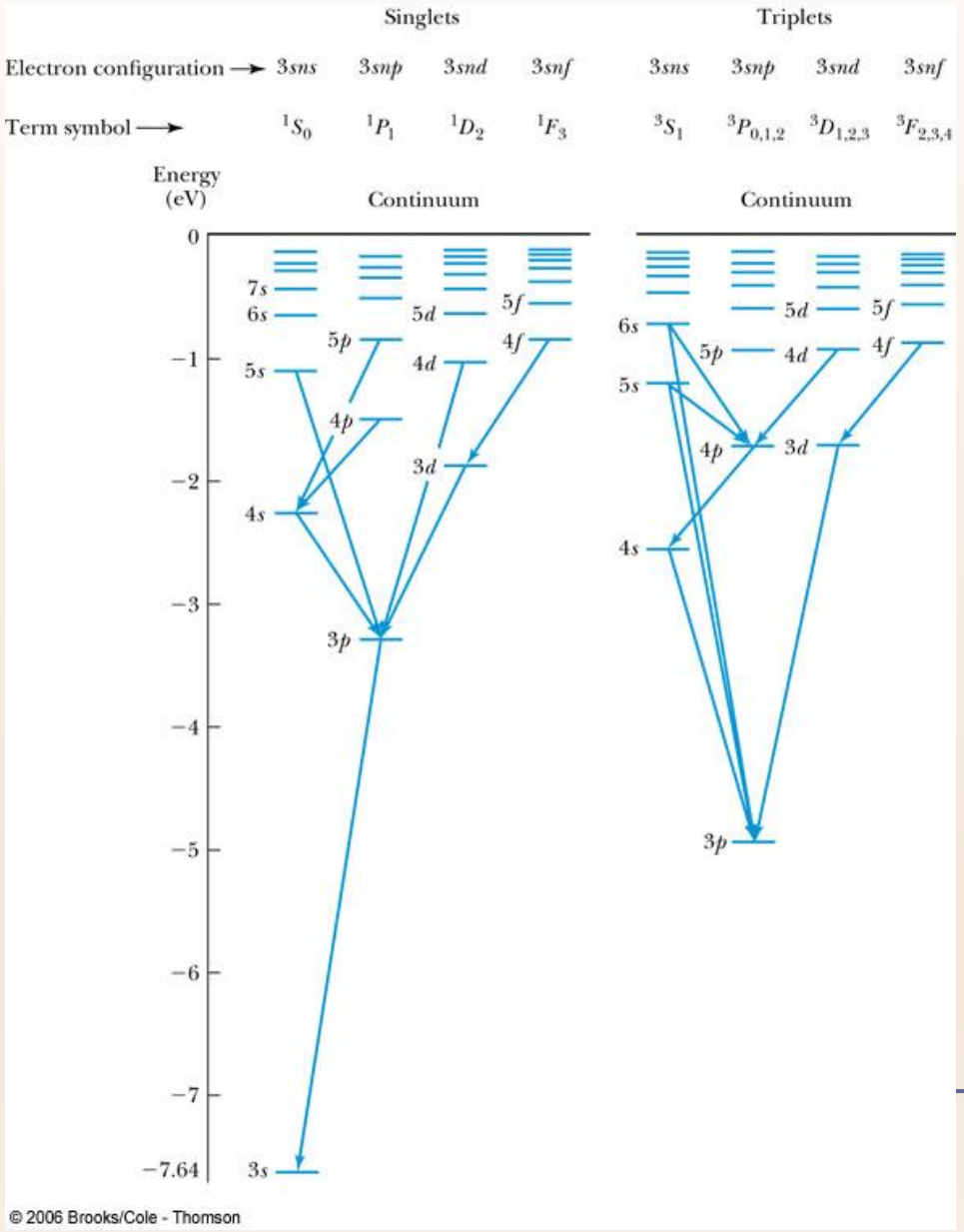
- The notation for a single-electron atom becomes

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

- 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
  - $\Delta L = \pm 1$ $\quad\quad$ $\Delta S = 0$
  - $\Delta J = 0, \pm 1$ $\quad\quad$ ($J = 0 \rightarrow J = 0$ 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 $\vec{L}_i$.

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

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

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

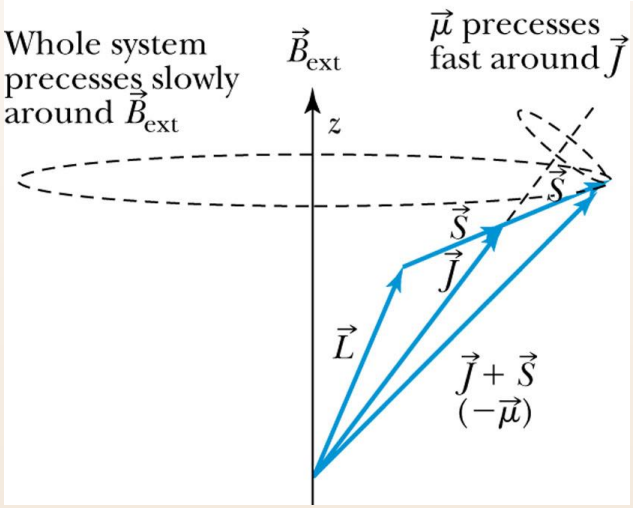
Anomalous Zeeman Effect

- 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 $\Delta J = 0$.