CHAPTER 8
Atomic Physics

- 8.1 Atomic Structure and the Periodic Table
- 8.2 Total Angular Momentum

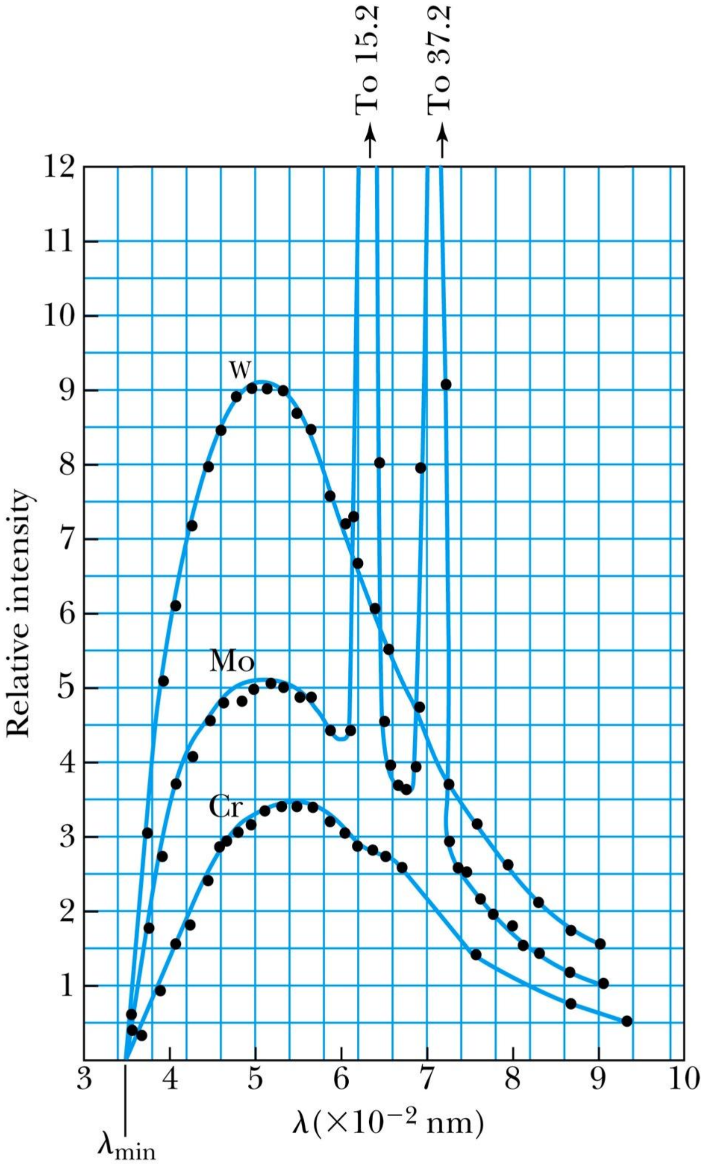
Atomic physics describes multi-electron atoms not only hydrogen-like one-electron atoms

Inverse Photoelectric Effect (slide from Chapter3).

- Conservation of energy requires that the electron kinetic energy equal the maximum photon energy where we neglect the work function because it is normally so small compared to the potential energy of the electron. This yields the **Duane-Hunt limit** which was first found experimentally. The photon wavelength depends only on the accelerating voltage and is the same for all targets.

$$eV_0 = hf_{\max} = \frac{hc}{\lambda_{\min}}$$

$$\lambda_{\min} = \frac{hc}{e}\frac{1}{V_0} = \frac{1.240\times 10^{-6}\ \mathrm{V\cdot m}}{V_0}$$



4.6: Characteristic X-Ray Spectra and Atomic Number

- Shells have letter names:

  K shell for $n = 1$

  L shell for $n = 2$

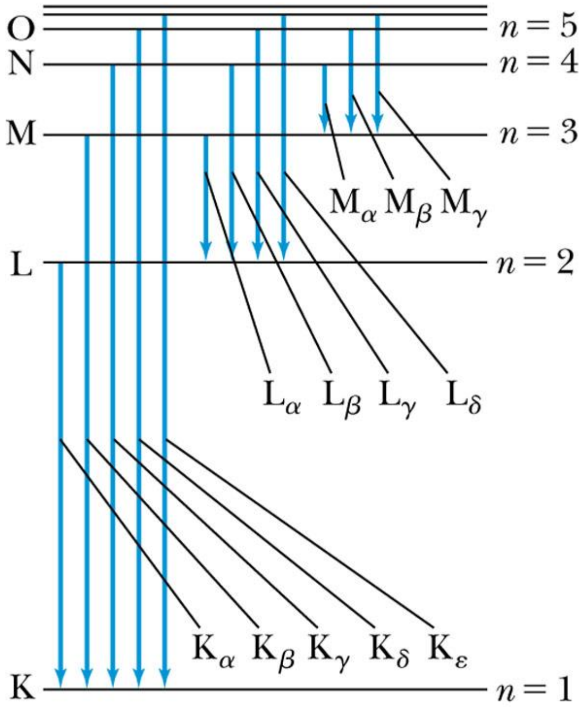
  ⋮

- The atom is most stable in its ground state.

→ An electron from higher shells will fill the inner-shell vacancy at lower energy.

- When it occurs in a heavy atom, the radiation emitted is an **x ray**.
- It has the energy E (x ray) $= E_u - E_\ell$.
- For this to happen an inner shell vacancy has to be produced(for instance by a high energy electron collision) in Roentgen’s discovery of X-rays

Atomic Number



L shell to K shell → K_α x ray

M shell to K shell → K_β x ray

- *Atomic number Z = number of protons in the nucleus*
- Moseley found a relationship between the frequencies of the characteristic x ray and Z.

  This holds for the K_α x ray

$$f K_\alpha = \frac{3cR}{4}(Z-1)^2$$

Moseley’s Empirical Results

- The x ray is produced from $n = 2$ to $n = 1$ transition.

- In general, the K series of x ray wavelengths are

$$\frac{1}{\lambda_K} = R(Z-1)^2\left(\frac{1}{1^2} - \frac{1}{n^2}\right) = R(Z-1)^2\left(1 - \frac{1}{n^2}\right)$$

Moseley’s research clarified the importance of the electron shells for all the elements, not just for hydrogen.

Atomic structure parameters

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

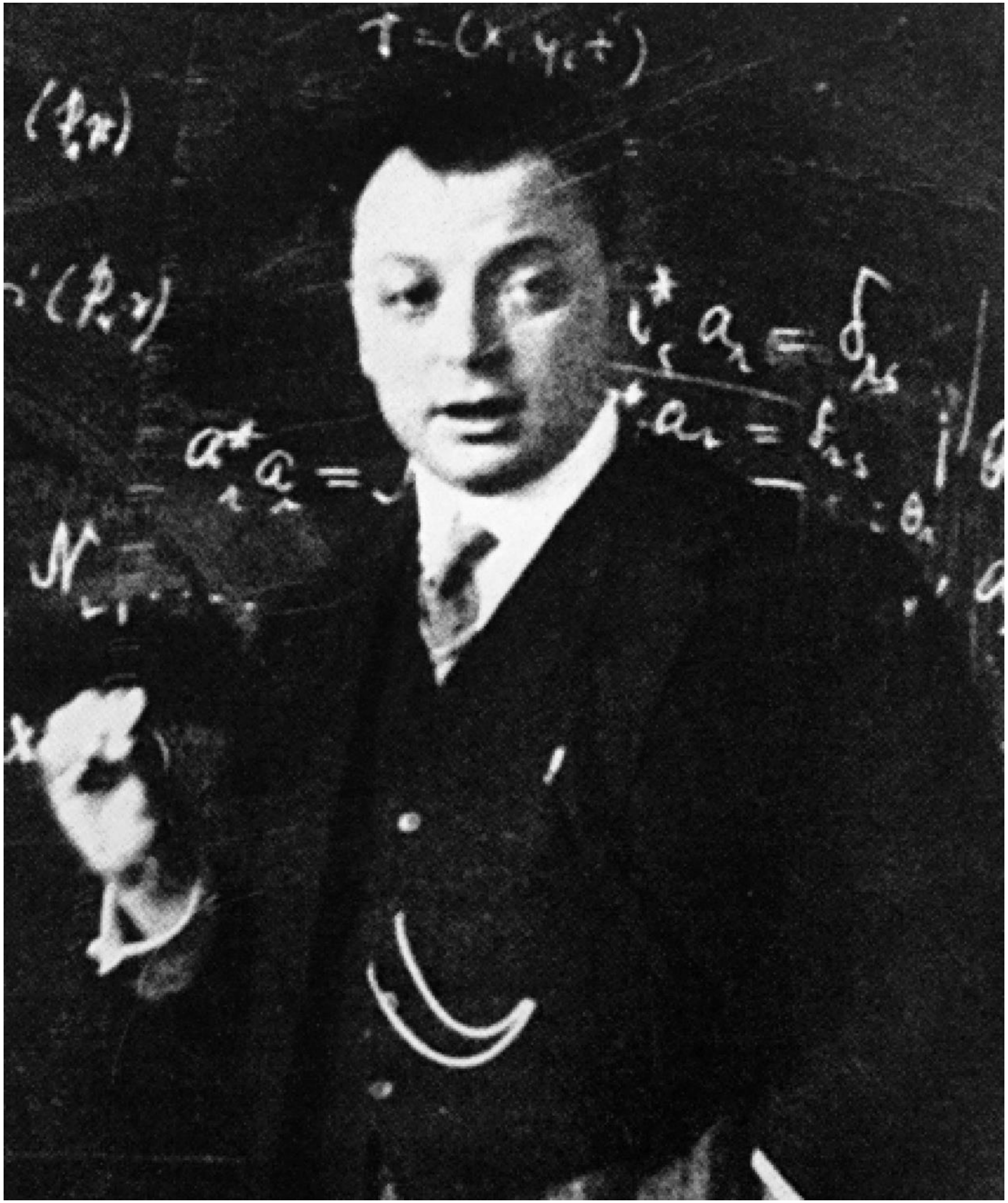
- To understand atomic spectroscopic data for optical frequencies, Wolfgang Pauli proposed an exclusion principle:

  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) Only one electron can be in a state with a given (complete) set of quantum numbers (Pauli exclusion principle).



Wolfgang Pauli (1900–1958) was born in Austria, studied at Munich under Arnold Sommerfeld, and spent brief periods at Göttingen (with Max Born), Copenhagen (with Niels Bohr), and Hamburg before accepting an appointment at Zurich in 1925 where he remained, except for brief periods at American universities including Princeton University during World War II. Pauli was a brilliant theoretical physicist who formulated the Pauli exclusion principle named after him, proposed a quantum spin number for the electron, and recognized the existence of the neutrino to explain nuclear beta decay. He received the Nobel Prize in 1945 for discovering the exclusion principle.

7.3: Quantum Numbers

The three quantum numbers:

n	Principal quantum number
ℓ	Orbital angular momentum quantum number
m_ℓ	Magnetic quantum number

The boundary conditions:

$n = 1, 2, 3, 4, \ldots$	Integer
$\ell = 0, 1, 2, 3, \ldots, n - 1$	Integer
$m_\ell = -\ell, -\ell + 1, \ldots, 0, 1, \ldots, \ell - 1, \ell$	Integer

The restrictions for quantum numbers:

- $n > 0$
- $\ell < n$
- $|m_\ell| \leq \ell$

Atomic Structure

Hydrogen: $(n, \ell, m_\ell, m_s) = (1, 0, 0, \pm\frac{1}{2})$ in ground state

In the absence of a magnetic field, the state $m_s = \frac{1}{2}$ is degenerate with the $m_s = -\frac{1}{2}$ state.

Helium: $(1, 0, 0, \frac{1}{2})$ for the first electron

$(1, 0, 0, -\frac{1}{2})$ for the second electron

Electrons have antialigned ($m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$) 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*^{1} or 1*s*
He: 1*s*^{2}

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

Pauli added a fourth quantum number ms

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

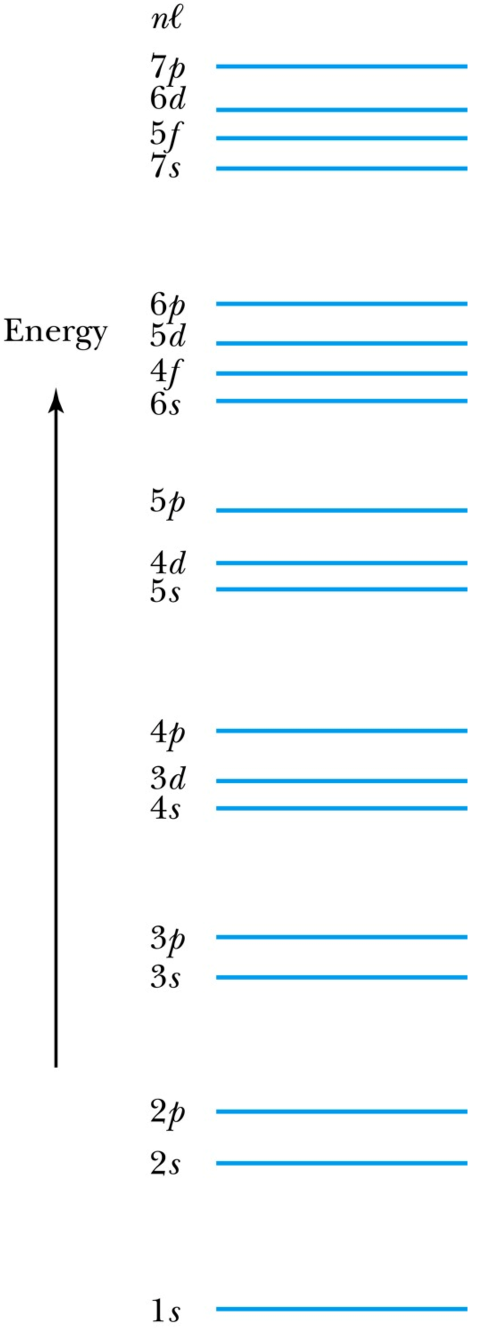
$\ell = 1$, (*p* state) can have six electrons, and so on

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

→ the shielding is so pronounced that the 4s fills before 3d even though it has a larger n



Order of Electron Filling in Atomic Subshells

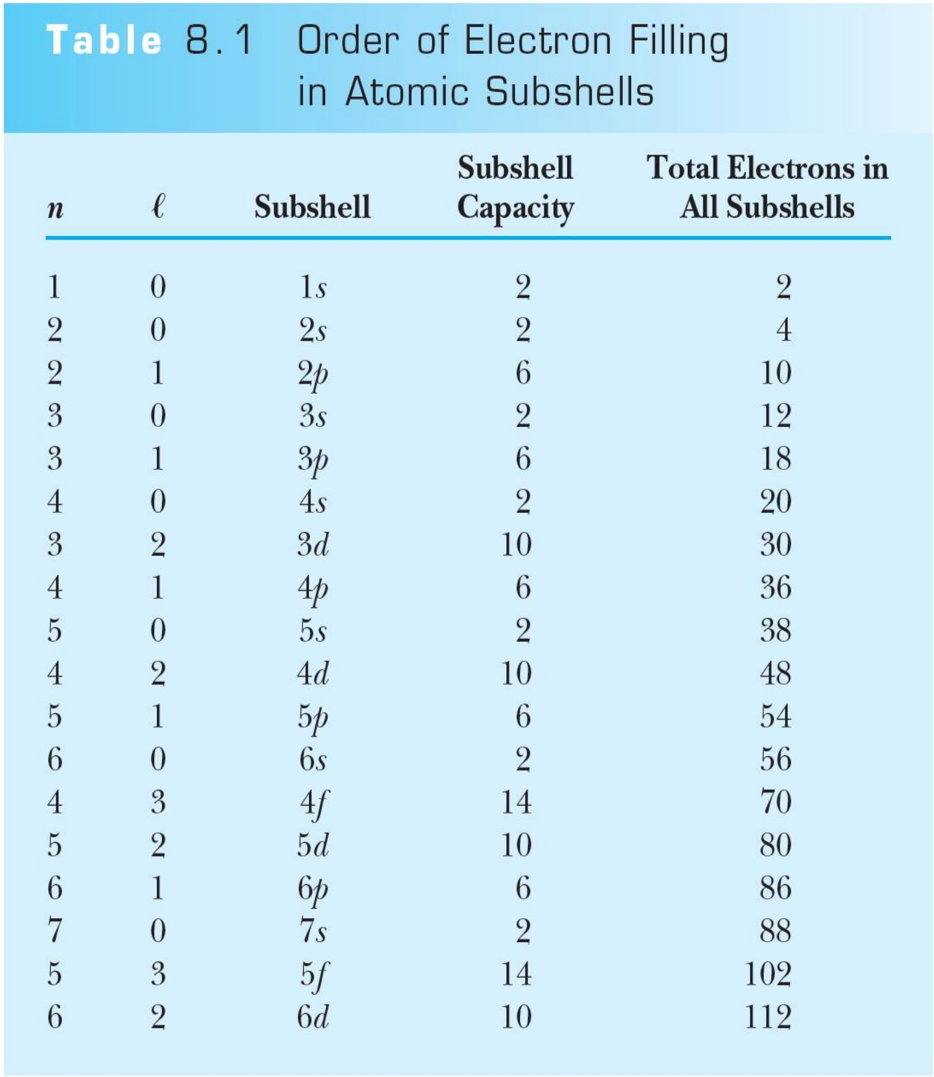
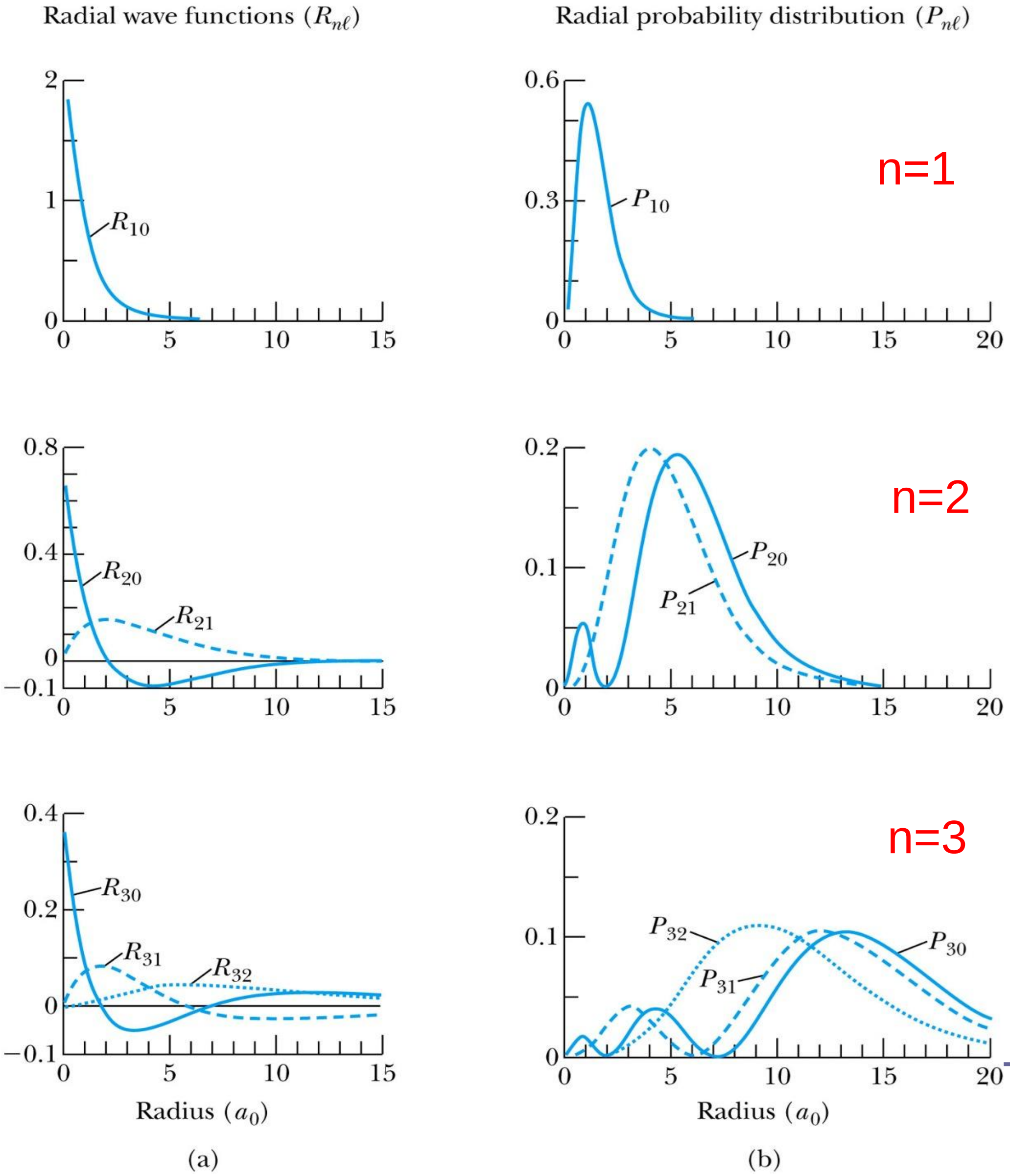


Table 8.1 Order of Electron Filling in Atomic Subshells

n	ℓ	Subshell	Subshell Capacity	Total Electrons in All Subshells
1	0	1*s*	2	2
2	0	2*s*	2	4
2	1	2*p*	6	10
3	0	3*s*	2	12
3	1	3*p*	6	18
4	0	4*s*	2	20
3	2	3*d*	10	30
4	1	4*p*	6	36
5	0	5*s*	2	38
4	2	4*d*	10	48
5	1	5*p*	6	54
6	0	6*s*	2	56
4	3	4*f*	14	70
5	2	5*d*	10	80
6	1	6*p*	6	86
7	0	7*s*	2	88
5	3	5*f*	14	102
6	2	6*d*	10	112

Due to shielding 4s shell fills before 3d

Radial Probability Distribution Functions



(a)

(b)

- $R(r)$ and $P(r)$ for the lowest-lying states of the hydrogen atom

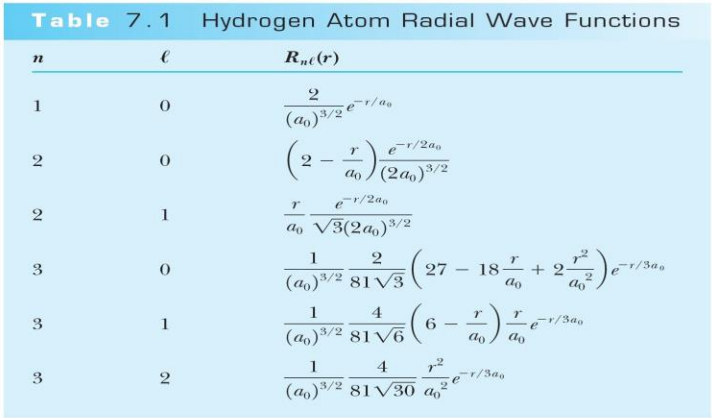


Table 7.1 Hydrogen Atom Radial Wave Functions

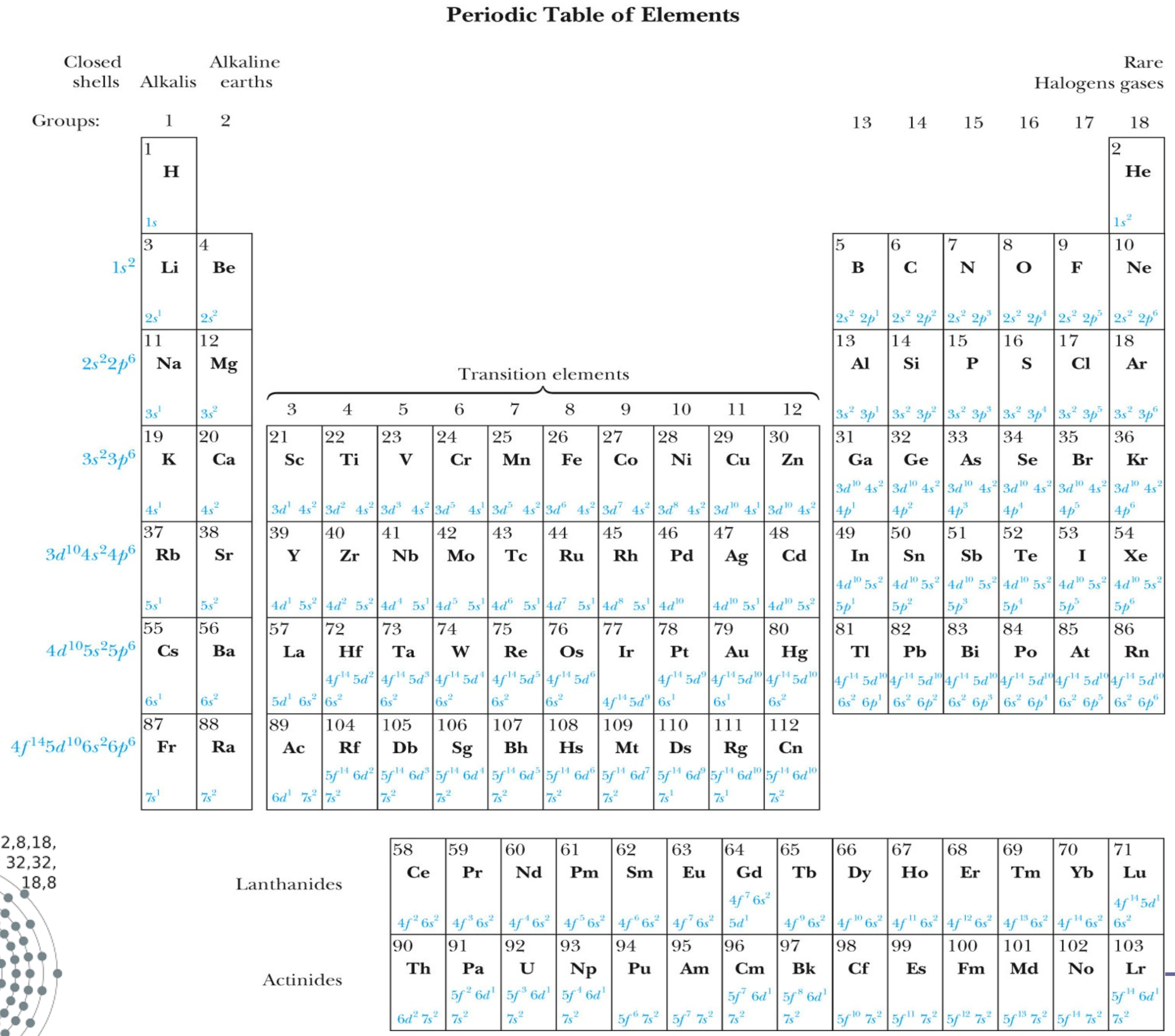
n	ℓ	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right) \frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0} \frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}} \frac{2}{81\sqrt{3}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0{}^2}\right) e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{6}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{30}} \frac{r^2}{a_0{}^2} e^{-r/3a_0}$

Horizontal axis in units of the Bohr radius

Shielding: high l electrons shield more than low l electrons and see a smaller nuclear charge Z

The Periodic Table

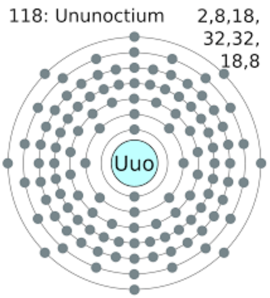
Horizontal groupings are according to separate subshells



Periodic Table of Elements

Closed shells	Alkalis	Alkaline earths	Transition elements														Halogens	Rare gases
Groups:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	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** $2s^2\ 2p^6$
$2s^22p^6$	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** $3s^2\ 3p^6$
$3s^23p^6$	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** $3d^{10}\ 4s^2\ 4p^6$
$3d^{10}4s^24p^6$	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** $4d^{10}\ 5s^2\ 5p^6$
$4d^{10}5s^25p^6$	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** $4f^{14}\ 5d^9$	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** $4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$
$4f^{14}5d^{10}6s^26p^6$	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 **Cn** $5f^{14}\ 6d^{10}\ 7s^2$						

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** $5f^{14}\ 6d^1\ 7s^2$



Vertical columns are Groups : similar chemical and physical properties

Groups and Periods in the Periodic Table

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

Filling of inner: d-levels for the transition elements, f-levels for Lanthanides an Actinides

Problem8.8

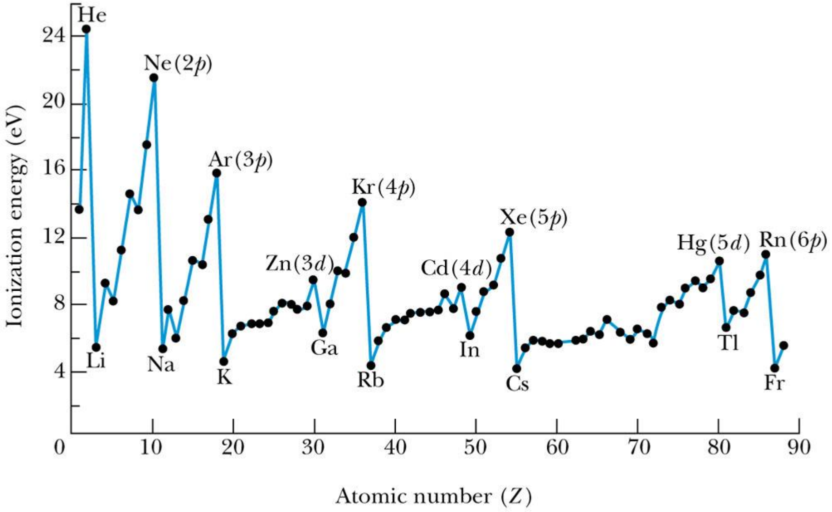
Use figure 8.2 to list all the (a) inert gases, (b) alkalis, (c) halogens, and (d) alkaline earths.

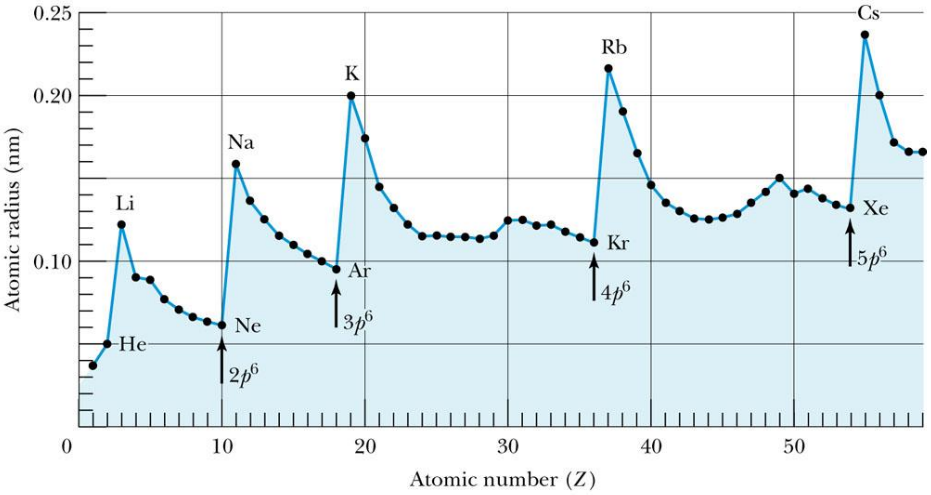
(a) He, Ne, Ar, Kr, Xe, Rn
(b) Li, Na, K, Rb, Cs, Fr
(c) F, Cl, Br, I, At

(d) Be, Mg, Ca, Sr, Ba, Ra

Ionization Energies of Elements and **Atomic Radii**

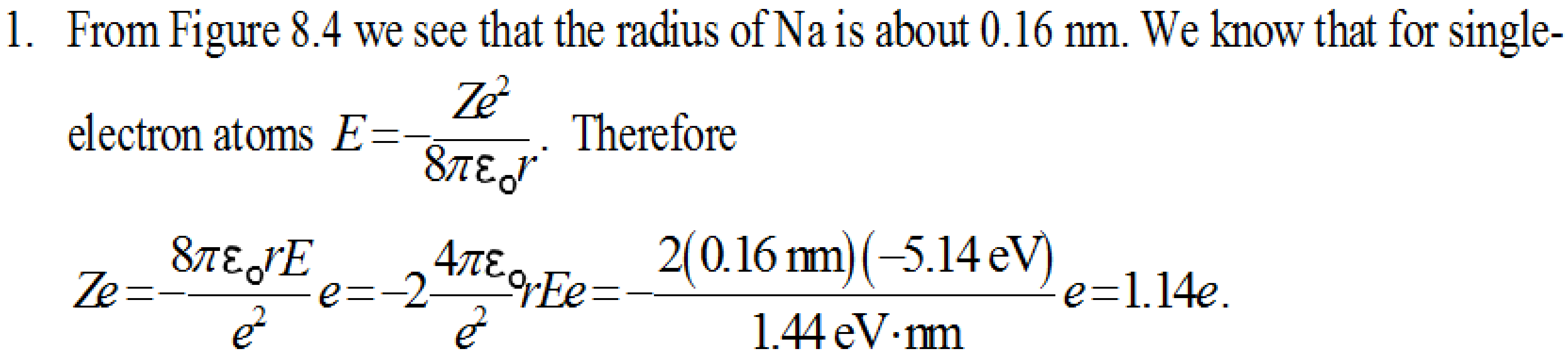
Some properties of elements are compared by the **ionization energies of elements** and **atomic radii**:





Problem 8.7

The 3s state of Na has an energy of -5.14eV. Determine the effective nuclear charge.



1. From Figure 8.4 we see that the radius of Na is about 0.16 nm. We know that for single-electron atoms $E = -\frac{Ze^2}{8\pi\varepsilon_0 r}$. Therefore

$$Ze = -\frac{8\pi\varepsilon_0 rE}{e^2}e = -2\frac{4\pi\varepsilon_0}{e^2}rEe = -\frac{2(0.16\text{ nm})(-5.14\text{ eV})}{1.44\text{ eV}\cdot\text{nm}}e = 1.14e.$$

$$\frac{e^2}{4\pi\epsilon_0} = 1.44 \text{ eV nm}$$

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

SS

Table 8.5 Spectroscopic Notation for Atomic Shells and Subhells

n	Shell Symbol	ℓ	Shell Symbol
1	K	0	s
2	L	1	p
3	M	2	d
4	N	3	f
5	O	4	g
6	P	5	h
. . .		. . .	

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Problem 8.2

What electron configuration would you expect (nl) for the first excited state of neon and xenon?

1. In the first excited state, go to the next higher level. In neon one of the $2p$ electrons is promoted to $3s$, so the configuration is $2p^5 3s^1$. By the same reasoning the first excited state of xenon is $5p^5 6s^1$.

Clicker - Questions

Indicate which statement is **not** true in the ordering of the periodic table ?

a) The electrons tend to occupy the lowest energy levels available to them

b) No two electrons in an atom can have the same set of quantum numbers (n , l , m_e , m_s)

c) Electrons with higher l values go earlier into unfilled shells than those with lower l values, because they are less shielded from the nuclear charge.

d) Electrons with higher l values go later into unfilled shell than those with lower l values, because they are more shielded from the nuclear charge.

Clicker - Questions

Consider the periodic table and select the statement which is true.

a) The electron configuration for each element is specified by n , l , and the projection of L namely m_l , and the projection of S namely m_s

b) The electron configuration for each element is specified by the principal quantum number n , and the angular quantum number l (s, p, d or f)

c) The electron configuration for each element is specified by n , l , and the spin quantum number s

d) The electron configuration for each element is specified by the principal quantum number n , and the angular quantum number l (s, p, d , f…….) and the number of electrons relevant for this element in each shell.

Clicker - Questions

2) Why the Alkali metals have the lowest ionization energies?

a) they have a single electron outside an inert noble gas core.

b) they have one valence electron which is strongly bound.

c) they have an electron missing in the outer shell.

d) They have the smallest atomic radii.

Problem 8.10

What are the electronic configurations for the ground states of the elements Ag, Hf, and Sb?

1. Ag: $\left[\mathrm{Kr}\right]4d^{10}5s^{1}$, Hf: $\left[\mathrm{Xe}\right]4f^{14}5d^{2}6s^{2}$, Sb: $\left[\mathrm{Kr}\right]4d^{10}5s^{2}5p^{3}$ where the bracket represents a closed inner shell. For example, $\left[\mathrm{Kr}\right]$ represents $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}3d^{10}4p^{6}$.

Problem 8.11

What atoms have the configuration (a) $1s^22s^22p^5$, (b) $1s^22s^22p^63s^2$, (c) $3s^23p^6$? Explain.

1. (a) count the number of electrons, 9; F, or use Table 8.2

(b) count the number of electrons, 12: Mg

(c) filled 3*p* shell: Ar

Clicker - Questions

1) Which is the correct electron configuration of ${}^{40}_{20}Ca$?

a) $1s^2\ 2s^2\ 2p^6\ 3p^6$

b) $1s^2\ 2s^2\ 2p^6\ 3s^2$

c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

d) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s$

Clicker - Questions

Which of the following is NOT a general selection rule for the filling of electron shells?

a)For a particular n, the subshells fill in the order s, p, d, f, ...

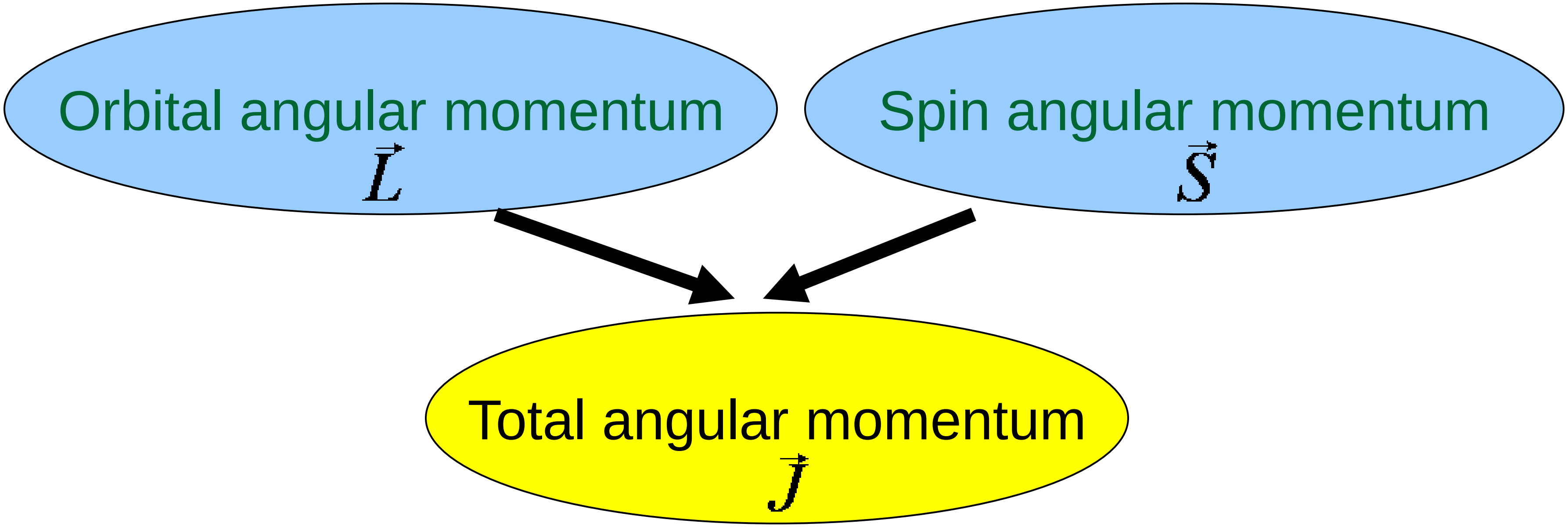
b)Shielding affects the ordering of energy levels as described by n and l.

c)The orbital and spin angular momentum in each shell and subshell are restricted by Hund's rules.

d)Electrons usually completely fill a subshell before starting another shell.

e)For the s shell there are 2 electrons, for the p shell 6, for the d shell 10, and for the f shell 16.

8.2: Total Angular Momentum



Orbital angular momentum $\vec{L}$

Spin angular momentum $\vec{S}$

Total angular momentum $\vec{J}$

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

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

Total Angular Momentum for single electron

Atoms outside an inert core

- 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

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

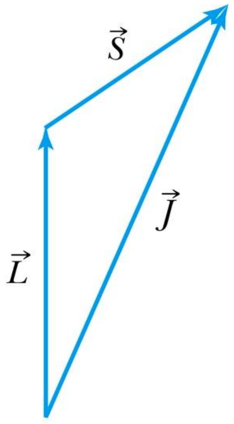
$$S = \sqrt{s(s+1)}\hbar$$

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

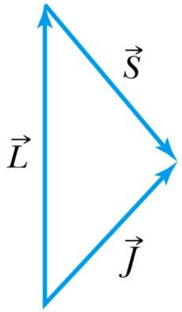
- The total angular momentum quantum number for the single electron can only have the values

$$j = \ell \pm s$$

The Total Angular Momentum Diagram



$$j = \ell + s$$
$$= 1 + \frac{1}{2} = \frac{3}{2}$$



$$j = \ell - s$$
$$= 1 - \frac{1}{2} = \frac{1}{2}$$

Figure 8.5 When forming the total angular momentum from the orbital and spin angular momenta, the addition must be done vectorially, $j = \ell + s$.

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 $\vec{L}$

Clicker - Questions

Which of the following statements is true about the spin-orbit coupling effects on the transitions of an atom such as sodium? Assume sodium is modeled by a single electron atom.

a)The difference in the energy of a split state does not depend on the electron's angular momentum, but instead the angular momentum of the nucleus.

b)The differences in energy level transitions are significant enough to change the order of filling of the subshells.

c)Electrons with a state of $l = 0$ never have split energy levels.

d)For single electron atoms (or atoms with one electron outside a filled shell) each nl state is made a doublet

Spin-orbit coupling

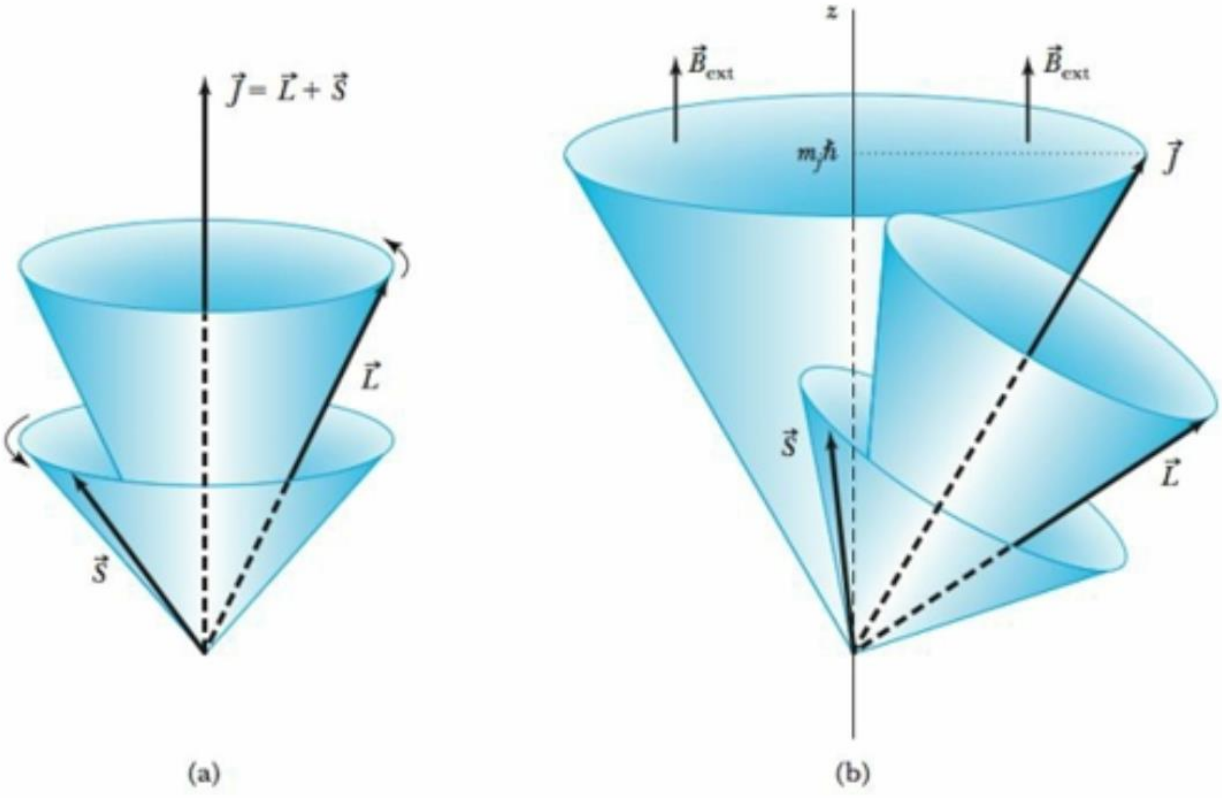


Figure 8.6 (a) The vectors $\vec{L}$ and $\vec{S}$ precess around $\vec{J}$. The total angular momentum $\vec{J}$ can have a fixed value in only one direction in space—not shown in this figure. (b) However, with an external magnetic field $\vec{B}_{\text{ext}}$ along the z axis, $\vec{J}$ will precess around the z direction (J_z is fixed), and both $\vec{L}$ and $\vec{S}$ precess around $\vec{J}$. We have shown the case where $\vec{L}$ and $\vec{S}$ are aligned.

Clicker - Questions

The energy levels of a single-electron atom (or the approximation for one electron outside of a filled shell) can be split due to a relationship between the spin and the orbital angular momentum. Choose the statement that best explains why this occurs.

a) The electron is affected by the magnetic field of the proton, which in the rest frame of the electron is seen as orbiting the electron.
b)There is a state with lesser energy when the spin magnetic moment of the electron and internal magnetic field of the atom are aligned.
c)Only in an external magnetic field do the energy levels split due to spin-orbit coupling.
d)Only in an external electric field do the energy levels split due to spin-orbit coupling.
e)The total angular momentum component in the z-direction is not quantized and can take on any value as a sum of orbital and spin angular momentum.

Doublet splitting of the Balmer line

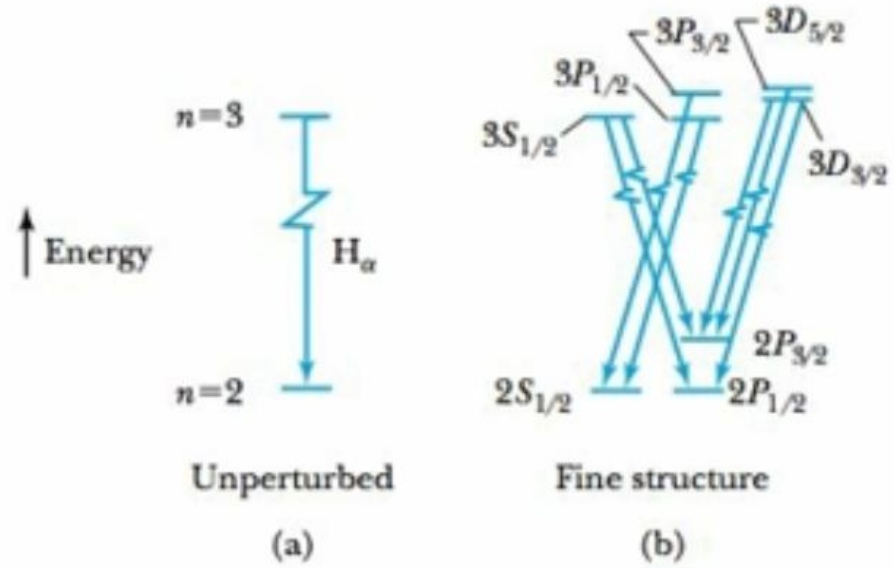


Figure 8.7 (a) The unperturbed H_α line is shown due to a transition between the $n = 3$ and $n = 2$ shells of the hydrogen atom. (b) The more detailed leve structure (not to scale) of the hydrogen atom leads to optical fine structure. The spin-orbit interaction splits each of the $\ell \neq 0$ states

Selection rules for single electron atom transitions

$$\Delta n = \text{anything} \qquad \Delta \ell = \pm 1$$

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

Comparison between sodium and hydrogen spectrum

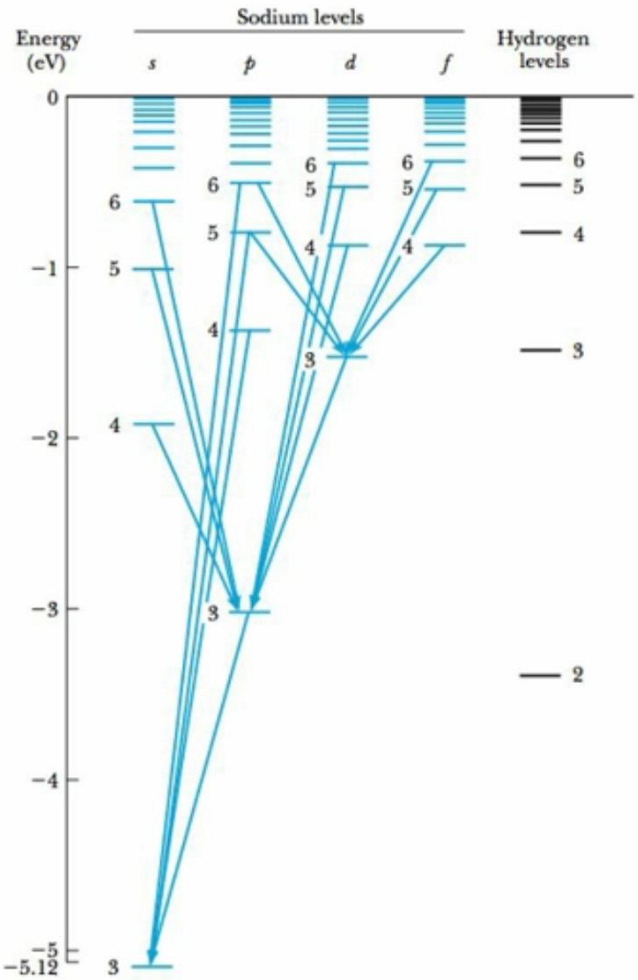


Figure 8.8 The energy-level diagram of sodium (a single electron outside an inert core) is compared to that of hydrogen. Coulomb effects cause the lower ℓ states of sodium to be lower than the corresponding levels of hydrogen. Several allowed transitions are shown for sodium.

Many-Electron Atoms

Consider 2- electron atoms: helium and the alkali 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*.

***In jj* coupling L+S=J for each electron**

LS Coupling

Many-Electron Atoms

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

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

- 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

Table 8.2 Spectroscopic Symbols for Two Electrons: One in 4*p* and One in 4*d*

S	*L*	*J*	Spectroscopic Symbol
0 (singlet)	1	1	4^1P_1
	2	2	4^1D_2
	3	3	4^1F_3
1 (triplet)	1	2	4^3P_2
		1	4^3P_1
		0	4^3P_0
1 (triplet)	2	3	4^3D_3
		2	4^3D_2
		1	4^3D_1
1 (triplet)	3	4	4^3F_4
		3	4^3F_3
		2	4^3F_2

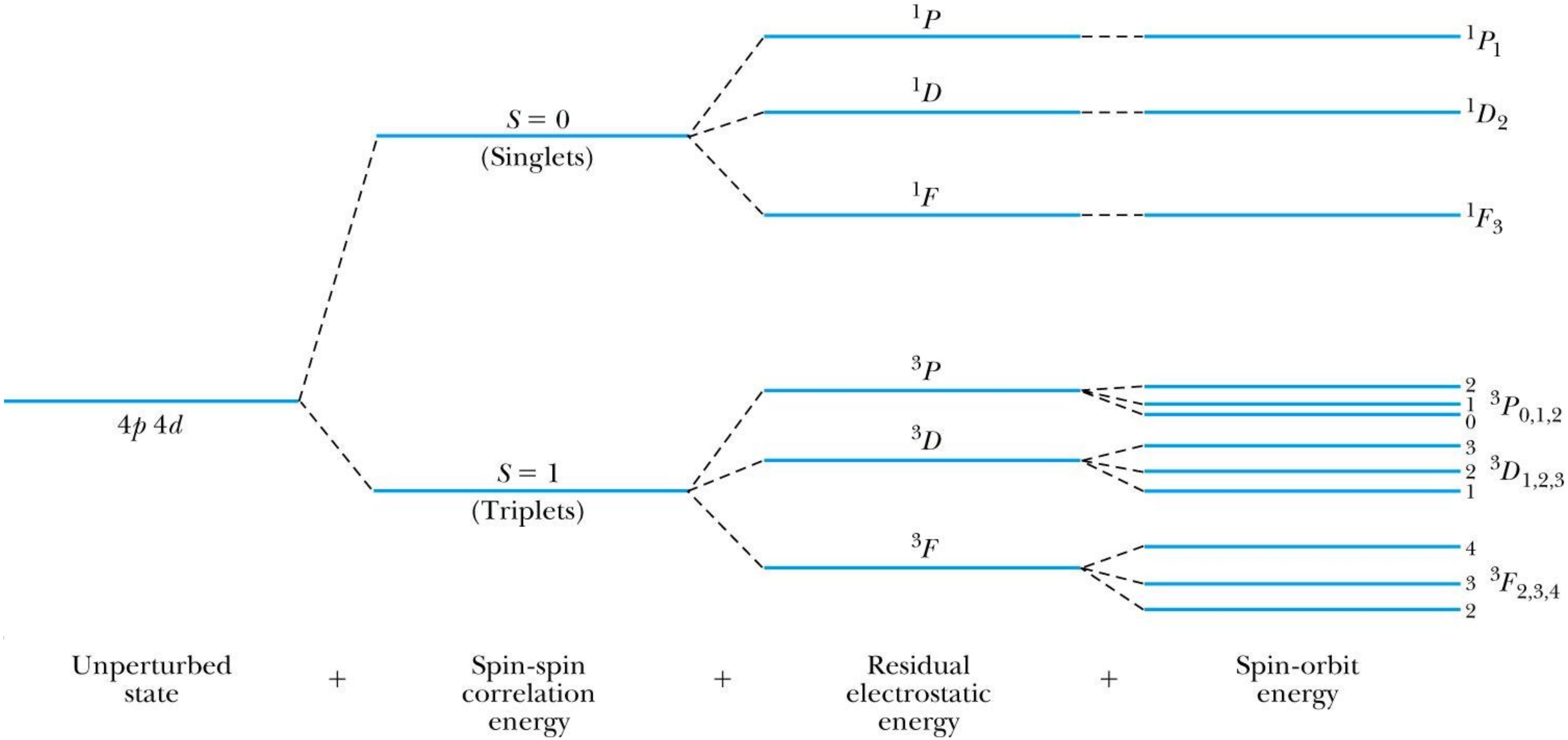
Table 8-2 p287

LS Coupling

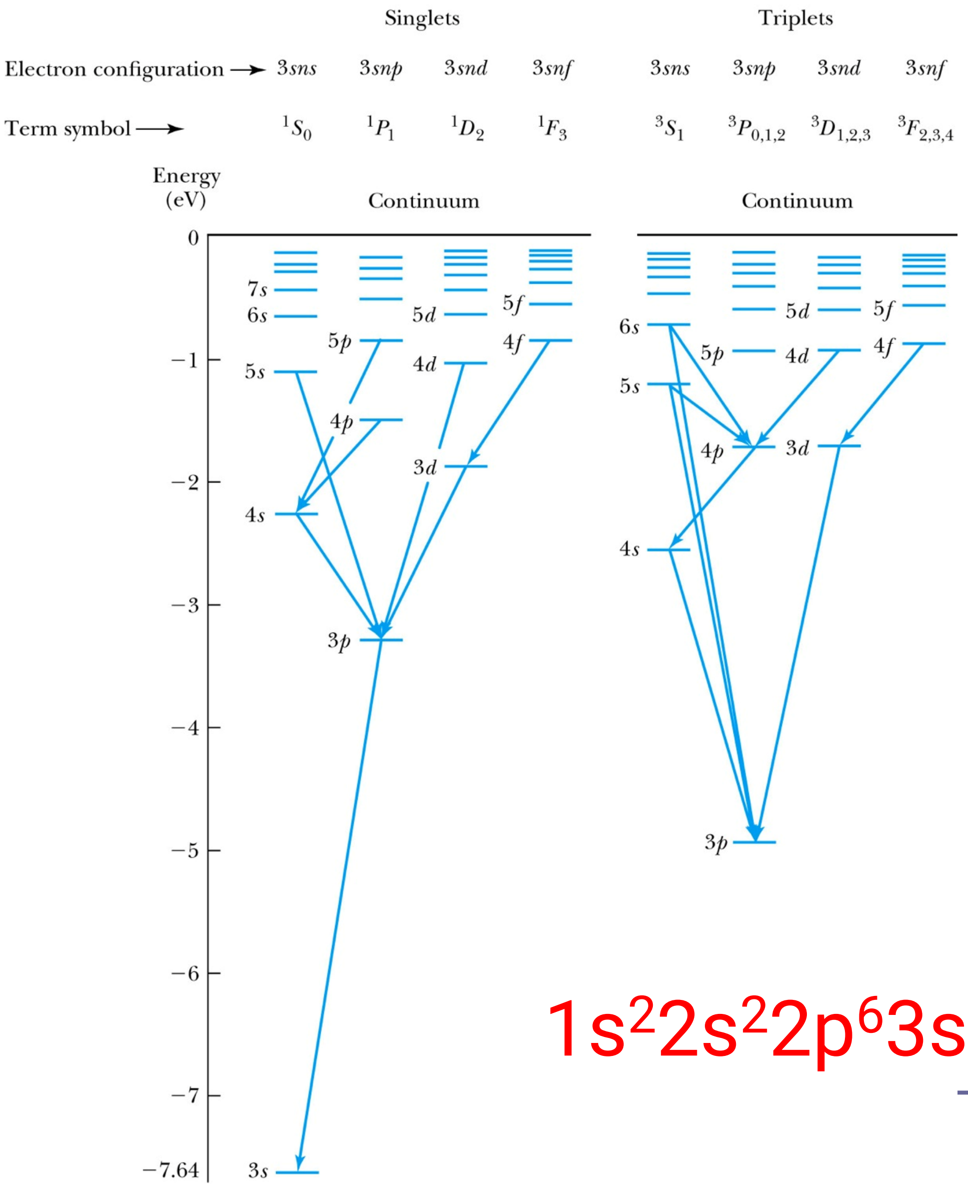
- The notation for a single-electron atom becomes

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

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



LS Coupling for the magnesium atom



- 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

$1s^22s^22p^63s^2$

3p state is metastable

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.

3s3p - lifetime of 2050 seconds, which corresponds to approximately ½ hour used in research with ultra-precise atomic clocks

jj coupling

In heavier atoms the situation is different. In atoms with bigger nuclear charges, spin–orbit interactions are frequently as large as or larger than spin–spin interactions or orbit–orbit interactions.

In this situation, each orbital angular momentum $\boldsymbol{\ell}_i$ tends to combine with the corresponding individual spin angular momentum $\mathbf{s}_i$, originating an individual total angular momentum $\mathbf{j}_i$.

These then couple up to form the total angular momentum **J**

***In jj* coupling L+S=J for each electron**

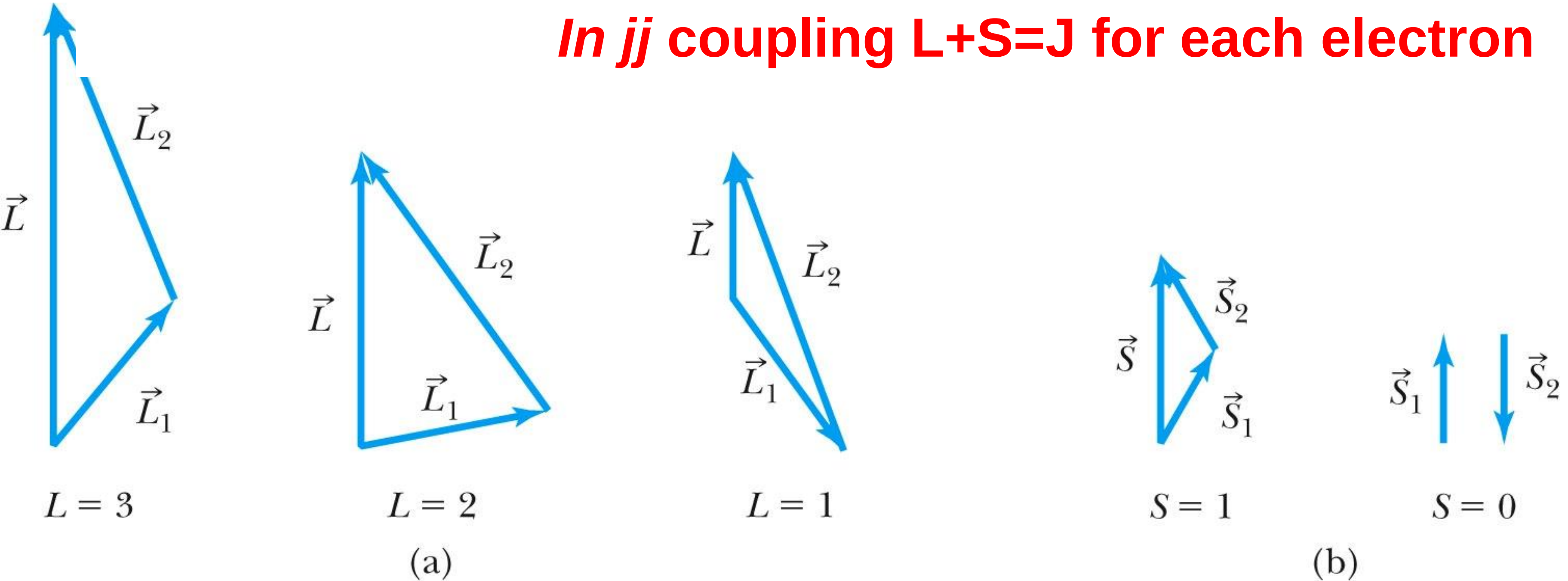


Figure 8.11 (a) Two electrons having orbital angular momentum quantum numbers of 1 and 2 combine to form L values of 1, 2, 3. (b) Two electrons having spin angular quantum numbers of 1/2 and 1/2 form S values of 0 and 1.

Figure 8-11 p290

The Normal Zeeman Effect: line splitting in a magnetic field

- A transition from *2p* to 1*s*

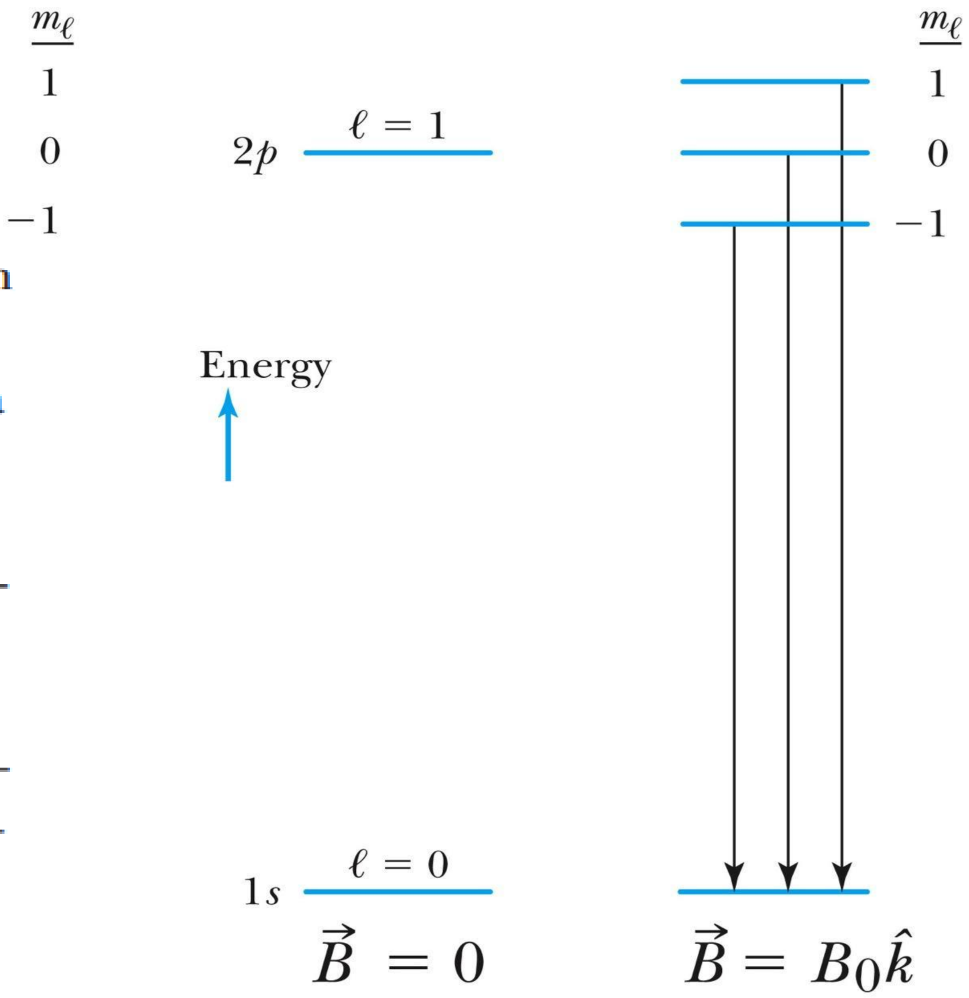


Figure 7.6 The normal Zeeman effect. (a) An external magnetic field removes the degeneracy of a $2p$ level and reveals the three different energy states. (b) There are now transitions with three different energies between an excited $2p$ level and the $1s$ ground state in atomic hydrogen. The energy ΔE has been grossly exaggerated along the energy scale.

From lecture10b

From lecture10b

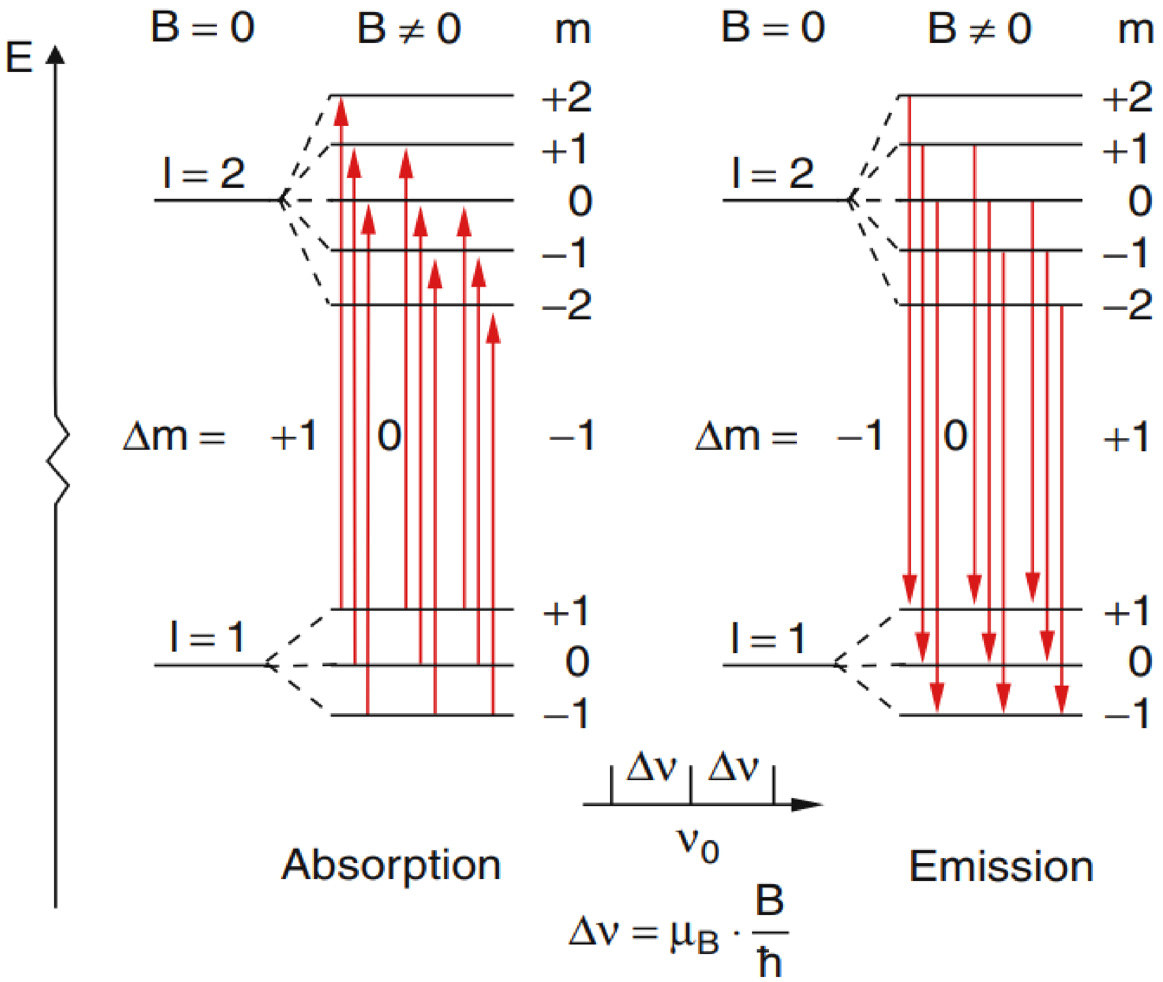


Fig. 5.12. Level scheme and transitions $\Delta m = 0, \pm 1$ between Zeeman level in absorption and emission for the normal Zeeman effect

3 spectral lines are detected for normal Zeeman effect

Level scheme and transitions beween excited states l = 2 l =1

W. Demtroeder. Atoms, Molecules and Photons: An Introduction to Atomic, Molecular and Quantum Physics, 2006.

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 $\vec{\mu}_\ell$

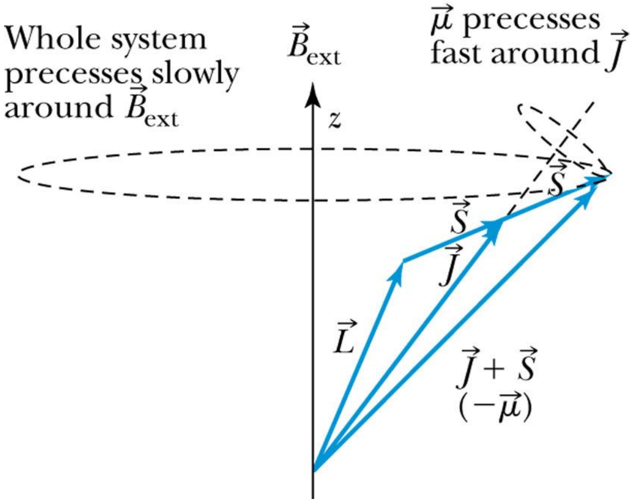
  and

  Spin magnetic moment $\vec{\mu}_s$
- The 2*J* + 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

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



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

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.
- $\vec{B}_{\text{ext}}$ splits each state *J* into 2*J* + 1 equally spaced levels separated Δ*E* = *V*.
- For photon transitions between energy levels

  Δm_J = ±1, 0 but $m_{J_1} = 0 \to m_{J_2} = 0$ is forbidden when Δ*J* = 0.

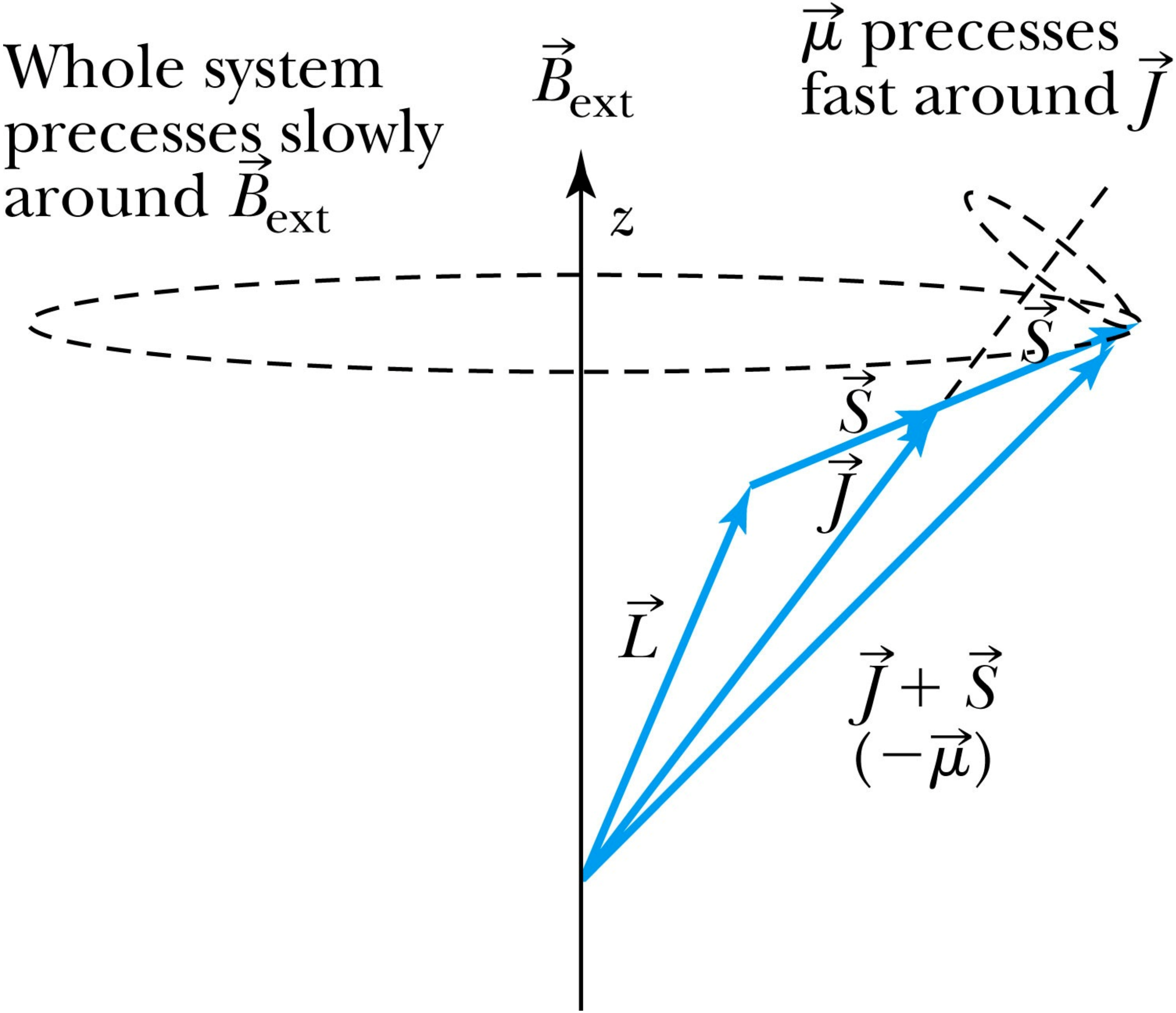


Figure 8-14 p293

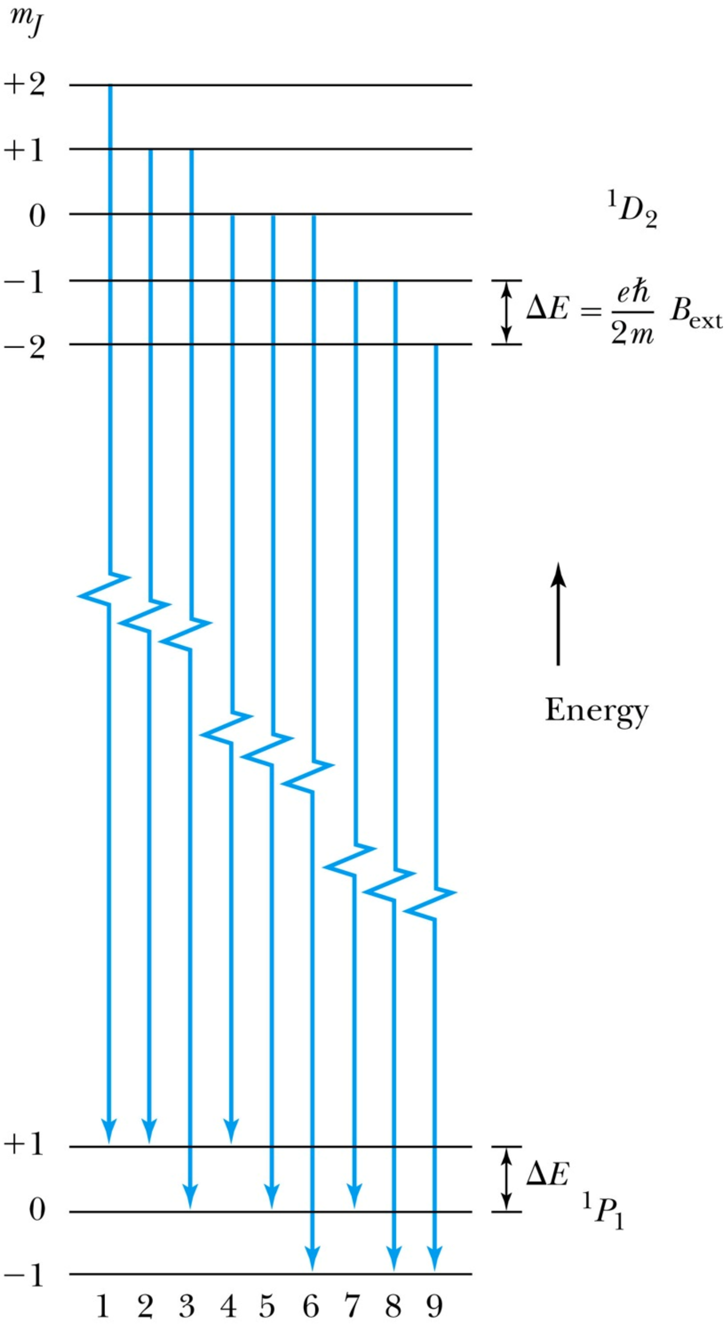
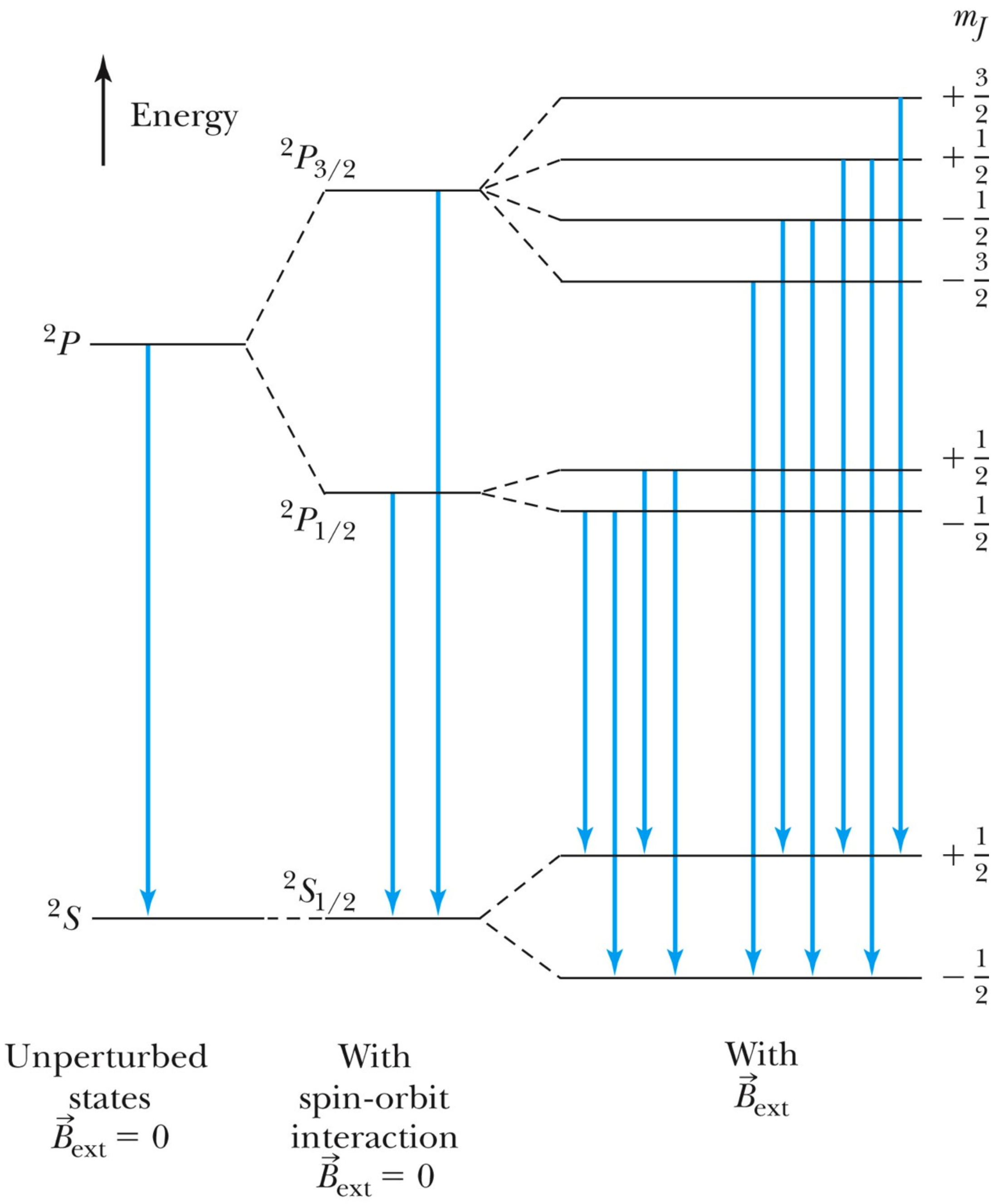


Figure 8-15 p293



Lande g-factors

$^2S_{1/2}$ $$g = 1 + \frac{\frac{1}{2}(\frac{1}{2}+1) + \frac{1}{2}(\frac{1}{2}+1)}{2 \cdot \frac{1}{2}(\frac{1}{2}+1)} = 2$$

$^2P_{1/2}$ $$g = 1 + \frac{\frac{1}{2}(\frac{1}{2}+1) + \frac{1}{2}(\frac{1}{2}+1) - 1(1+1)}{2 \cdot \frac{1}{2}(\frac{1}{2}+1)} = 0.67$$

$^2P_{3/2}$ $$g = 1 + \frac{\frac{3}{2}(\frac{3}{2}+1) + \frac{1}{2}(\frac{1}{2}+1) - 1(1+1)}{2 \cdot \frac{3}{2}(\frac{3}{2}+1)} = 1.33$$

Figure 8-16 p294

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. This is occasionally called the "bus seat rule" since it is analogous to the behaviour of bus passengers who tend to occupy all double seats singly before double occupation occurs.)
2) Insofar as rule 1 is not violated, *L* should also be maximized. This rule deals with reducing the repulsion between electrons. It can be understood from the classical picture that if all electrons are orbiting in the same direction (higher orbital angular momentum) they meet less often than if some of them orbit in opposite directions. In the latter case the repulsive force increases, which separates electrons. This adds potential energy to them, so their energy level is higher.
3) For atoms having subshells less than half full, *J* should be minimized. This rule considers the energy shifts due to spin–orbit coupling. In the case where the spin–orbit coupling is weak compared to the residual electrostatic interaction, L and S are still good quantum numbers and the splitting is given by minimizing J

- For labeled two-electron atom

In jj **coupling L+S=J for each electron**

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

Hund's rules

Select all of the following which are possible sets of quantum numbers (n, ℓ, mℓ, ms) for the 2 electrons in the unfilled shell of the ground state of a carbon atom.

a. (2, −1, 1, 1/2), (2, −1, 0, 1/2)
b. (2, 1, −1, −1/2), (2, 1, 0, 1/2)
c. (2, 1, −1, 1/2), (2, 1, 0, 1/2)
d. (2, 1, 1, 1/2), (2, 1, 0, 1/2)

See EXAMPLE 8.9

Born 4 February 1896
Karlsruhe
Died 31 March 1997 (aged
101)
Göttingen
Nationality German
Awards Max Planck Medal
(1943)
Otto Hahn Prize for Chemistry
and Physics (1974)
Scientific career
Fields Physics
Doctoral advisor Max Born
Doctoral students Harry
Lehmann
Carl Friedrich von Weizsäcker
Jürgen Schnakenberg
Edward Teller

What are *S*, *L*, and *J* for the following states?

	S	*L*	*J*
$^1S_0$	0	0	0
$^2P_{1/2}$	1/2	1	1/2
$^2G_{7/2}$	1/2	4	7/2
$^5F_1$	2	3	1

Select all of the following which are possible sets of quantum numbers (n, ℓ, m_ℓ, m_s) for the 2 electrons in the unfilled shell of the ground state of a zirconium atom.

correct (4, 2, -2, 1/2), (4, 2, -1, 1/2)

(4, -2, 2, -1/2), (4, -2, 1, -1/2)

correct (4, 2, 2, -1/2), (4, 2, 1, -1/2)

(4, 2, 2, 1/2), (4, 2, 1, 1/2)

[Kr] $4d^2$ $5s^2$

Apply the periodic table

What is the number of electrons in zirconium?

40 electrons

Zirconium has **40** electrons and **40** protons, so this picture has **40** electrons separated into the different levels.

Hund’s rules

Select all of the following which are possible sets of quantum numbers (n, ℓ, m_ℓ, m_s) for the 1 electron in the unfilled shell of the ground state of an aluminum atom.

Al

correct (3, 1,1, -1/2)

Not correct(3, 1, -1, -1/2),

Not correct (3, 1, 1, 1/2)

correct (3, 1, -1, 1/2

Hund’s rules

- Select all of the following which are possible sets of quantum numbers (n, ℓ, mℓ, ms) for the 3 electrons in the unfilled shell of the ground state of a vanadium atom.

- (2, 2, 2, 1/2), (2, 2, 1, 1/2), (2, 2, 0, 1/2)
- (3, -2, 2, -1/2), (3, -2, 1, -1/2), (3, -2, 0, -1/2)
- correct (3, 2, 2, -1/2), (3, 2, 1, -1/2), (3, 2, 0, -1/2)
- correct (3, 2, -2, 1/2), (3, 2, -1, 1/2), (3, 2, 0, 1/2)

Hund’s rules

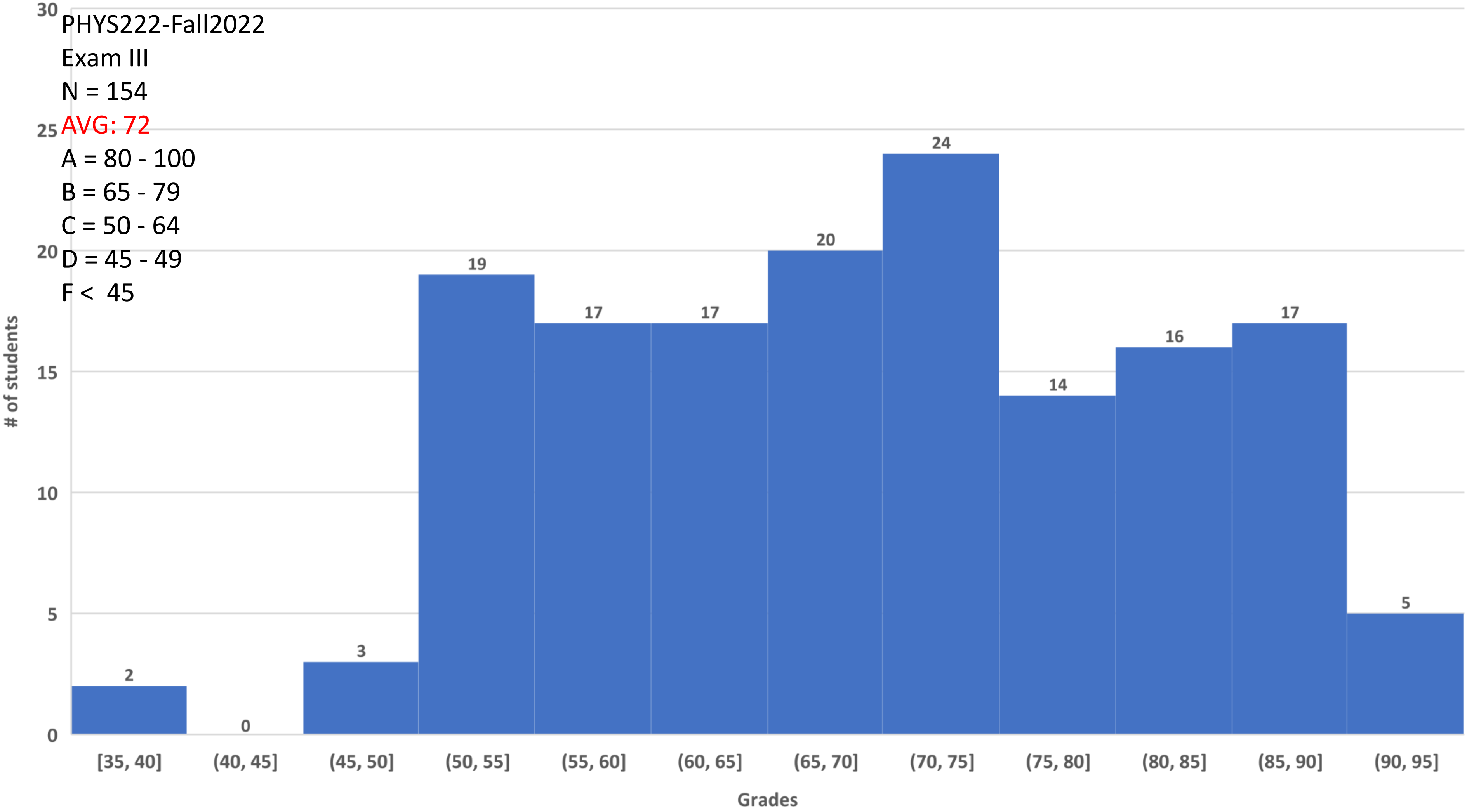
- Select all of the following which are possible quantum numbers (n, ℓ, mℓ, ms) for the electron in the unfilled shell of the ground state of a scandium atom.

- correct (3, 2, -2, 1/2)
- (3, -2, 2, -1/2)
- (3, -2, 2, 1/2)
- (3, 2, -2, -1/2)

Hund's rules

- Select all of the following which are possible sets of quantum numbers (n, ℓ, mℓ, ms) for the 3 electrons in the unfilled shell of the ground state of a phosphorus atom.

- (2, 1, 1, 1/2), (2, 1, 0, 1/2), (2, 1, -1, 1/2)
- correct (3, 1, -1, 1/2), (3, 1, 0, 1/2), (3, 1, 1, 1/2)
- correct (3, 1, 1, -1/2), (3, 1, 0, -1/2), (3, 1, -1, -1/2)
- (3, -1, 1, -1/2), (3, -1, 0, -1/2), (3, -1, -1, -1/2)



PHYS222-Fall2022
Exam III
N = 154
AVG: 72
A = 80 - 100
B = 65 - 79
C = 50 - 64
D = 45 - 49
F < 45