

Chapter 8: the Quantum Mechanical Atom

Motivation: Want to look more closely at the electronic structure of atoms to understand how compounds form and why the noble gases are so stable.

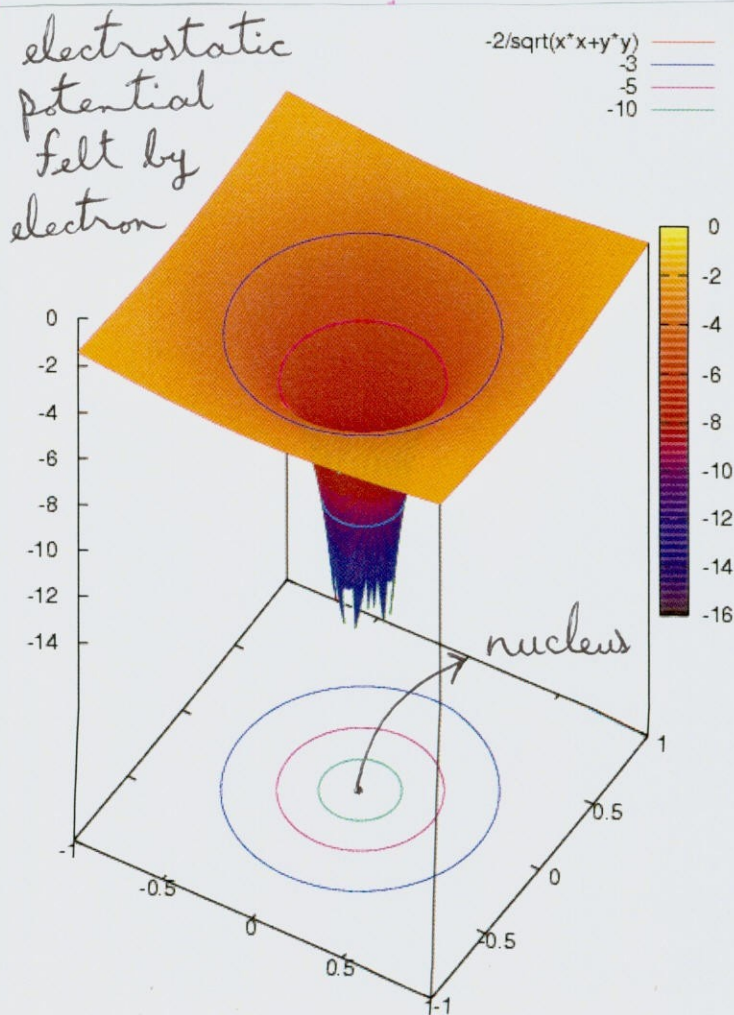
Conceptual problem: if we try to describe an atom with classical physics, we quickly get into trouble.

Think about an electron located at some distance d from the nucleus. What is its velocity?

Velocity is a vector quantity, so look at the components in the directions radial to and tangential to the nucleus.

radial \rightarrow will escape or collapse
BAD...

tangential \rightarrow can orbit (like Earth around Sun) but it is then accelerating because velocity is a vector quantity and an accelerating charge radiates energy: death spiral, collapse



This problem, along with many others, encouraged physicists to come up with a new description of matter at the atomic scale.

Bohr model of the hydrogen atom:

"planetary" model \rightarrow electron orbits the nucleus like the planets orbit the sun.

⊙ orbiting electron has an energy restricted to a value from a list $\{a, b, c, d, \dots\}$ ie only certain energies allowed

Let's see what the implications of this are. Thinking classically, how can we have only certain energies $\{a, b, c, d, \dots\}$?

$U \rightarrow$ electron orbits at select distances from the nucleus (like planets: no orbits between Earth and Venus)

$K \rightarrow$ kinetic energy needs to be restricted as well. If the electron could vary its speed during the orbit at a fixed distance from the nucleus, E would continuously change.

Bohr's solution: label the allowed orbits (in increasing distance from the nucleus) $n=1, 2, 3, \dots$ and restrict the angular momentum of the electron in orbit n to be $\frac{nh}{2\pi}$ where h is a constant (Planck's).

Lets work out the implications of this:

$$\text{angular momentum for circular motion} = mvr = \frac{nh}{2\pi}$$

m = electron mass

v = velocity

r = radius of orbit

What is E ?

$$E = K + U = \text{kinetic} + \text{potential}$$

$$K = \frac{1}{2}mv^2$$

U is electrostatic attraction between the orbiting electron (charge $-e$) and the nucleus (charge $+Ze$ where $Z = \#$ of protons).

$$U = \frac{(-e)(Ze)}{r} \cdot \frac{1}{4\pi\epsilon_0} \rightarrow \text{constant for SI units}$$

$$= -\frac{Ze^2}{4\pi\epsilon_0 r}$$

need to do some math

$$\text{Get } E = \frac{Z^2}{n^2} (-2.18 \times 10^{-18} \text{ J})$$

and $Z=1$ for hydrogen

Let's work out the implications of this:

$$\text{angular momentum for circular motion} = mvr = \frac{nh}{2\pi}$$

m = electron mass

v = velocity

r = radius of orbit

$$K = \frac{1}{2}mv^2$$

$$U = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

e = electron charge

Z = # of protons in nucleus

ϵ_0 = constant

Math details

What is E ? Need to do more physics (to find r)

$F = ma$ (Newton's 2nd Law) and

only force is electrostatic (Coulomb) and for circular motion $a = v^2/r$

$$\Rightarrow \frac{Ze^2}{4\pi\epsilon_0 r^2} = \frac{mv^2}{r} \quad (\text{force proportional to derivative of potential})$$

Use $r = \frac{nh}{2\pi mv}$ on left hand side to give

$$\frac{Ze^2 4\pi^2 m^2 v^2}{4\pi\epsilon_0 n^2 h^2} = \frac{mv^2}{r} \Rightarrow r = \frac{\epsilon_0 h^2 n^2}{Ze^2 \pi m} = \frac{n^2}{Z} \alpha_0$$

$$\alpha_0 = 0.529 \text{ \AA}$$

Now work out energy: $E = K + U = \frac{1}{2}mv^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$

Use $mvr = \frac{nh}{2\pi}$ to get $v = \frac{nh}{2\pi mr}$

$$E = \frac{1}{2} \frac{m n^2 h^2}{4\pi^2 m^2 r^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \quad \text{and plug in } r = \frac{n^2}{Z} \alpha_0 :$$

$$E = \frac{m n^2 h^2 Z^2}{8\pi^2 m^2 n^4 \alpha_0^2} - \frac{Ze^2}{4\pi\epsilon_0 n^2 \alpha_0} = \frac{Z^2}{n^2} (-2.18 \times 10^{-18} \text{ J})$$

and $Z=1$ for hydrogen

Chem 1311 | Bohr had one more part to his theory Ch 8-10 (4)

⊙ The laws of classical mechanics do not apply when electrons make a jump from one allowed orbit to another. The energy difference before and after the jump is carried off (or supplied by) a single quantum ("packet") of light called a photon.

Before we go into more detail, let us pause and ask what experimental data we have that could test Bohr's theory

Experimental data: When a glass tube filled with H_2 has an electric spark go through it, light is emitted. But only certain wavelengths of light are observed in this emission.

The observed wavelengths are named after different people

Lyman series: $\lambda = 122 \text{ nm}, 103 \text{ nm}, 97.2 \text{ nm}, \dots$ ultraviolet

Balmer series: $\lambda = 656 \text{ nm}, 486 \text{ nm}, 434 \text{ nm}, \dots$ visible
 red blue-green violet

Paschen series: $\lambda = 1870 \text{ nm}, 1280 \text{ nm}, 1090 \text{ nm}, \dots$ infrared

Brackett series: $\lambda = 4050 \text{ nm}, 2620 \text{ nm}, 2170 \text{ nm}, \dots$ infrared

Pfund series: $\lambda = 7460 \text{ nm}, 4650 \text{ nm}, 3740 \text{ nm}, \dots$ infrared

Humphreys series: $\lambda = 12372 \text{ nm}, 7503 \text{ nm}, 5129 \text{ nm}, \dots$ infrared

Does Bohr's model explain and/or agree with this data?

Yes light of wavelength λ can be thought of as consisting of photons ("packets" of light)

with energy $E = \frac{hc}{\lambda}$ $h = \text{Planck's constant}$
 $c = \text{speed of light}$

What wavelength should we expect to see if Bohr's model is correct?

$$\Delta E = E(n_2) - E(n_1) \quad \text{electron jumps from } n_2 \text{ to } n_1.$$

$$= (-2.18 \times 10^{-18} \text{ J}) \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \quad \text{If } n_2 > n_1 \text{ get } \Delta E > 0$$

Take $n_1 = 2$ and consider $n_2 = 3, 4, 5, \dots$

The emitted photon will have energy ΔE , or

$$\frac{hc}{\lambda} = (-2.18 \times 10^{-18} \text{ J}) \left(\frac{1}{n_2^2} - \frac{1}{4} \right)$$

$$\Rightarrow \frac{1}{\lambda} = \frac{-2.18 \times 10^{-18} \text{ J}}{hc} \left(\frac{1}{n_2^2} - \frac{1}{4} \right)$$

units: $\left(\frac{1}{n_2^2} - \frac{1}{4} \right)$ is dimensionless. Want $1/\lambda$ in $1/\text{nm}$:

$$\frac{-2.18 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ Js} \cdot 3.00 \times 10^8 \text{ ms}^{-1}} = -\frac{2.18}{(6.626)(3)} \times 10^8 \text{ m}^{-1}$$

$$= -0.110 \times 10^8 \text{ m}^{-1} \frac{\text{m}}{10^9 \text{ nm}} = -0.0110 \text{ nm}^{-1}$$

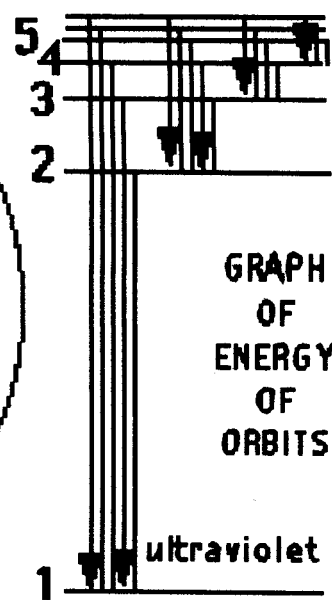
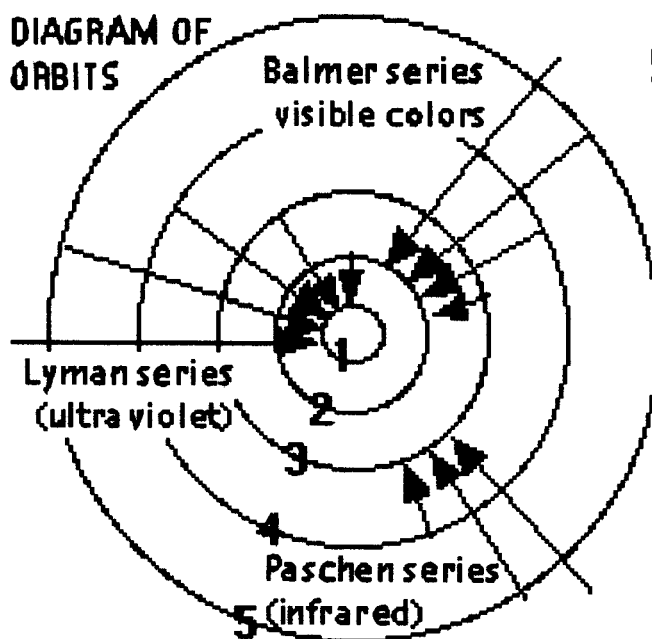
$$\left. \begin{array}{l} n_2 = 3 \Rightarrow \lambda = 655 \text{ nm} \\ n_2 = 4 \Rightarrow \lambda = 485 \text{ nm} \\ n_2 = 5 \Rightarrow \lambda = 433 \text{ nm} \end{array} \right\} \text{Balmer series}$$

so $1/\lambda = -0.0110 \text{ nm}^{-1} \left(\frac{1}{n_2^2} - \frac{1}{4} \right)$

In general,

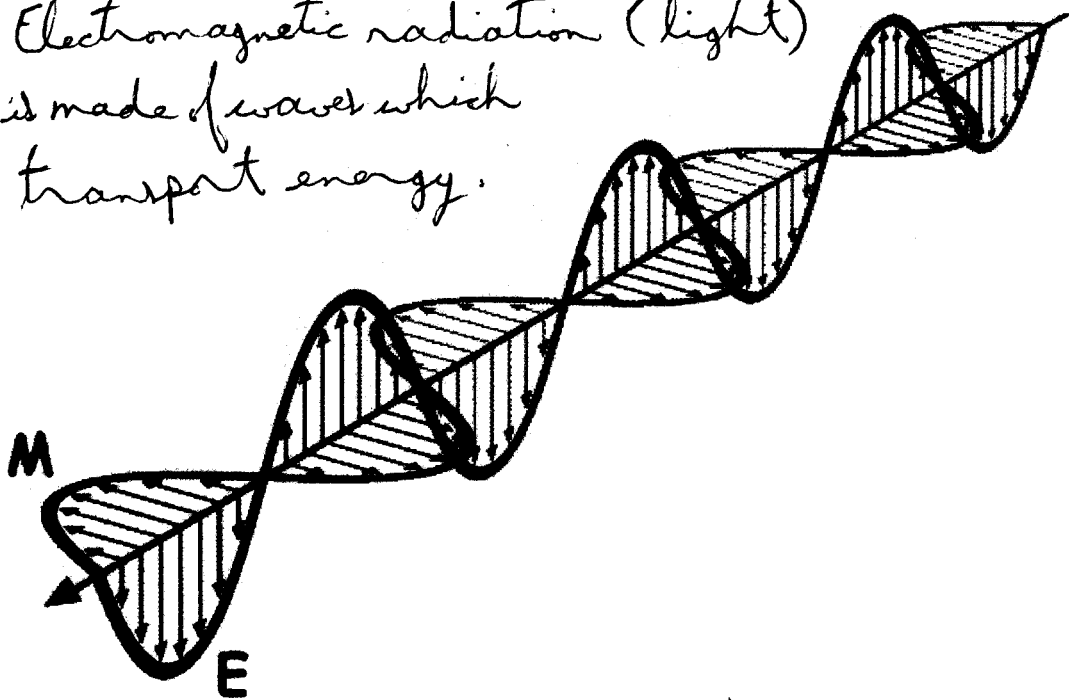
- $n_i = 1 \rightarrow$ Lyman series
- $n_i = 2 \rightarrow$ Balmer series
- $n_i = 3 \rightarrow$ Paschen series
- $n_i = 4 \rightarrow$ Brackett series
- $n_i = 5 \rightarrow$ Pfund series
- $n_i = 6 \rightarrow$ Humphreys series

DIAGRAM OF ORBITS



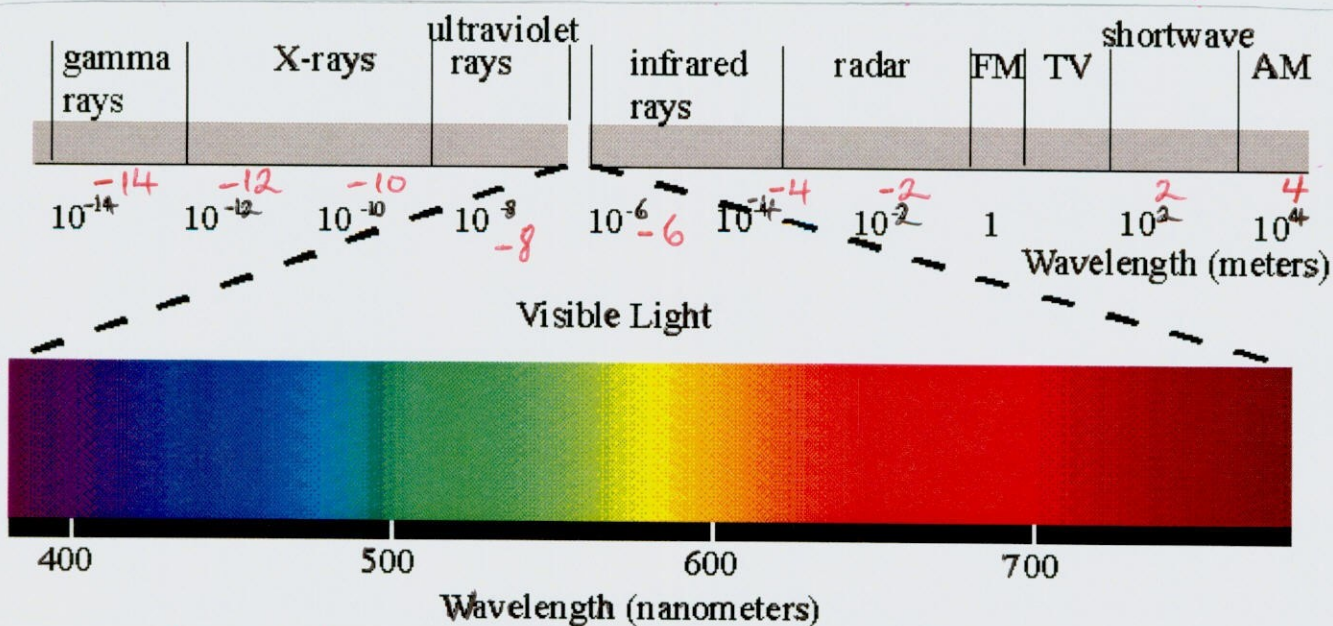
Look at light more closely

Electromagnetic radiation (light) is made of waves which transport energy.



The waves consist of electrical and magnetic components which are at 90° angles to each other and are at 90° angles to the direction of propagation.

The energy can also be thought of as traveling as photons -- packets with a particular wavelength and frequency at $c = 3.00 \times 10^8 \text{ m/s}$



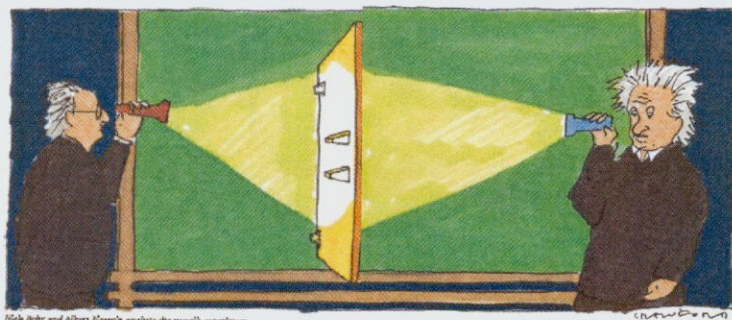
Wave / particle duality:

matter (ex electron, baseball) has the properties of a wave with wavelength $\lambda = \frac{h}{p} = \frac{h}{mv}$ ($p = \text{momentum} = \text{mass} \times \text{velocity}$)

where $h = \text{Planck's constant}$

This interpretation is due to de Broglie

If you are interested in learning more about this duality, see the Scientific American \rightarrow article on page 86 of the Dec. 1994 issue, which I have put on Web CT.



Niels Bohr and Albert Einstein analyze the two-slit experiment.

ex de Broglie wavelength of an electron moving with velocity $v = 1.0 \times 10^6 \text{ ms}^{-1}$

$$\lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{(9.11 \times 10^{-31} \text{ kg})(1.0 \times 10^6 \text{ ms}^{-1})} = 7.3 \times 10^{-10} \text{ m} = 7.3 \text{ \AA}$$

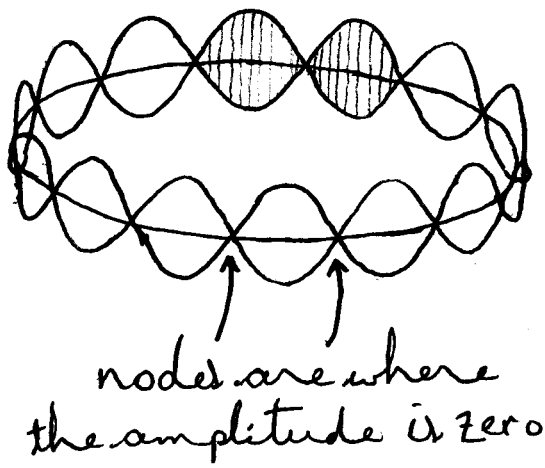
ex de Broglie wavelength of a baseball of mass 0.20 kg thrown with a velocity of 20 ms^{-1} (45 miles/hour)

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ Js}}{(0.20 \text{ kg})(20 \text{ ms}^{-1})} = 1.7 \times 10^{-34} \text{ m} = 1.7 \times 10^{-24} \text{ \AA}$$

Too small to be observed, so we never notice a baseball possessing wavelike properties.

But the electron's wavelength is large enough to affect properties at the molecular scale (ex C-C bond length $\sim 1.5 \text{ \AA}$)

How do the wavelike properties of an electron manifest themselves when the electron is orbiting the nucleus of an atom?



Standing waves:
wavelengths must be an integer fraction of the circumference (actually $3-d$, not $2d$, but too hard to draw).

Electron waves in atoms are called orbitals.

We need 3 quantum numbers to describe an orbital:

n, l, m_l (more complicated than Bohr's model)

n = principal quantum #

$n = 1, 2, 3, \dots, \infty$

↳ first shell
→ second shell

value of n related to the size of the orbital (distance from nucleus)

The energy also goes up as n increases

This is more or less Bohr's theory

l = secondary quantum #

• divides shells into subshells from $l=0$ to $l=n-1$

We assign a letter to each numerical value of l
so we don't confuse it with n .

$l=0$ called 's' (allowed for all n)

$l=1$ called 'p' (allowed for $n \geq 2$)

$l=2$ called 'd' (allowed for $n \geq 3$)

$l=3$ called 'f' (allowed for $n \geq 4$)

⋮

determines the shape of the orbital ('s' for spherical)
and also affects the energy a bit. Like n , the
higher the value of l , the higher the energy.

$m_l =$ magnetic quantum #

- divides the subshells into individual orbitals by their orientation.
- different m_l values have the same energy unless in the presence of an external magnetic field
- values go from $-l$ to l (including 0).

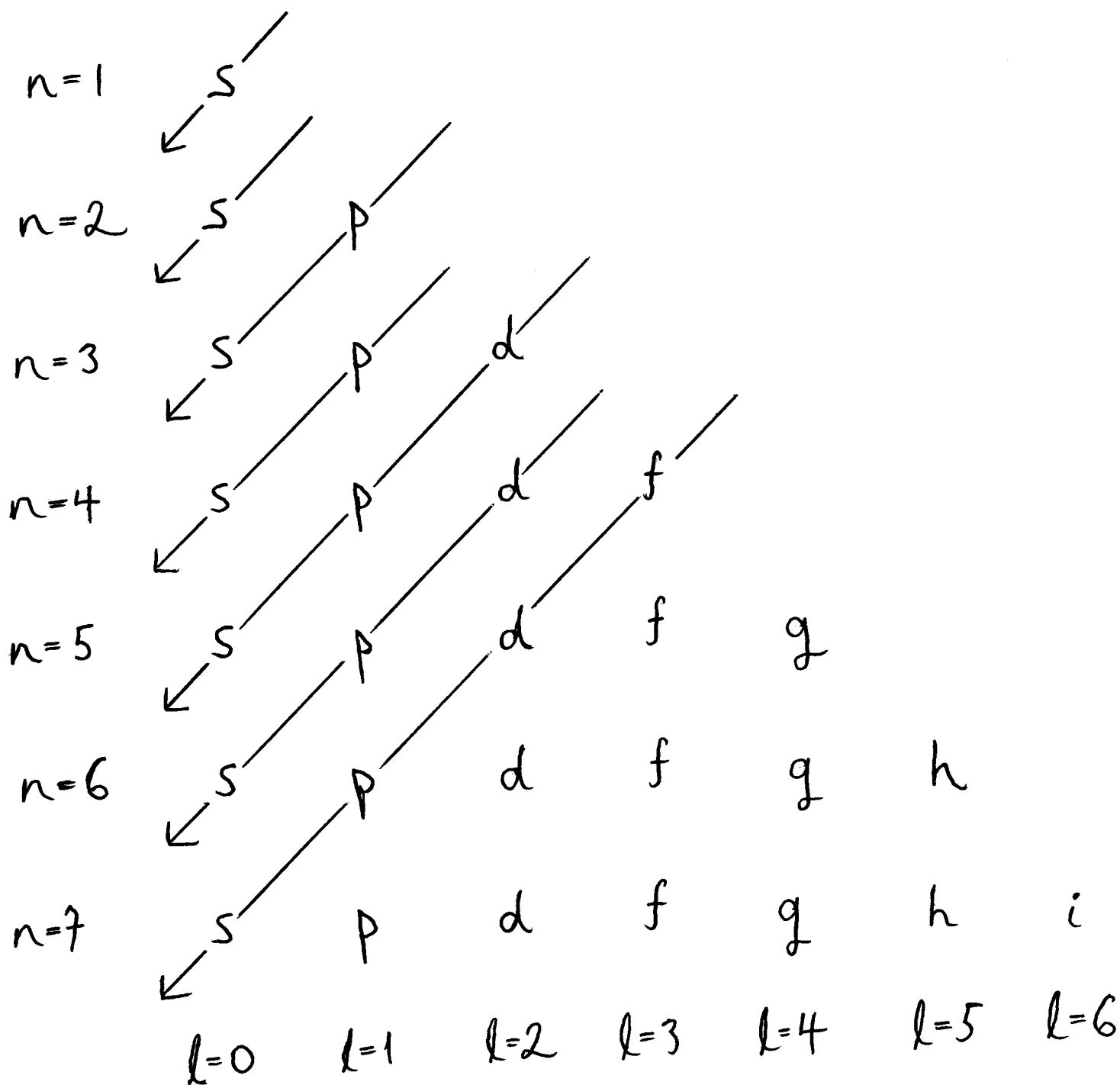
Putting this together gives Table 8.1 of the textbook

Value of n	Value of l	Values of m_l	Subshell	Number of Orbitals
1	0	0	1s	1
2	0	0	2s	1
	1	-1, 0, 1	2p	3
3	0	0	3s	1
	1	-1, 0, 1	3p	3
	2	-2, -1, 0, 1, 2	3d	5
4	0	0	4s	1
	1	-1, 0, 1	4p	3
	2	-2, -1, 0, 1, 2	4d	5
	3	-3, -2, -1, 0, 1, 2, 3	4f	7

$m_s =$ Spin quantum # : each electron can be spin up or spin down, $m_s = \pm 1/2$ (same energy)

This is a property of the electron and not of the orbital

Order of increasing energy and also the order in which electrons populate the orbitals in atoms.



The textbook has a different method. Read this.

Electronic configuration of atoms

Two more rules:

- each orbital (specific value of n, l, m_l) can hold 2 electrons (of different spin m_s)
- Hund's Rule: in orbitals of equal energy, electrons are spread out as much as possible, (electron repulsion) and the spins are aligned if possible.

ground electronic state of an atom: fill in electrons

H: only 1 electron ○ ○

He: 2 electrons ○ ○

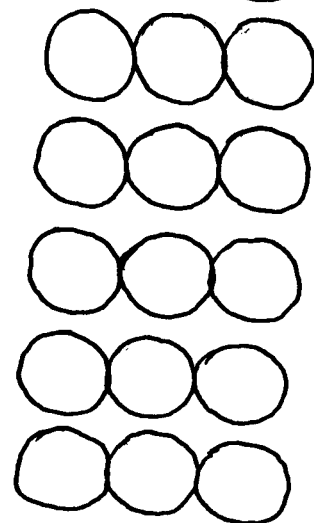
Li: 3 electrons ○ ○ ○ ○

Be: 4 electrons ○ ○ ○ ○

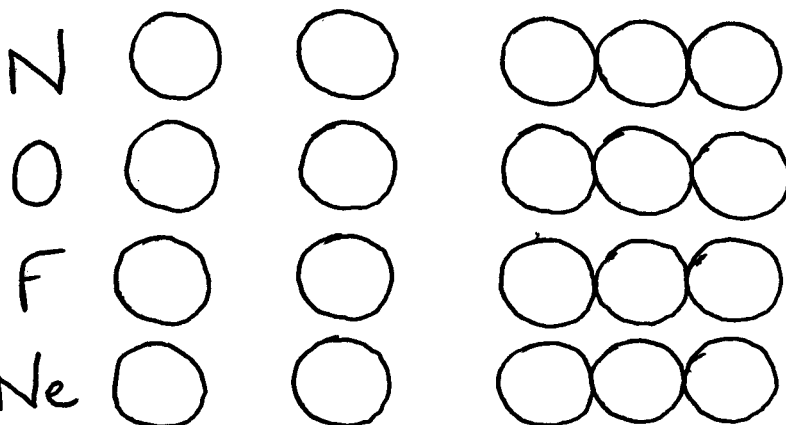
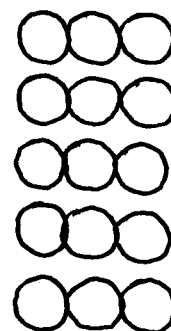
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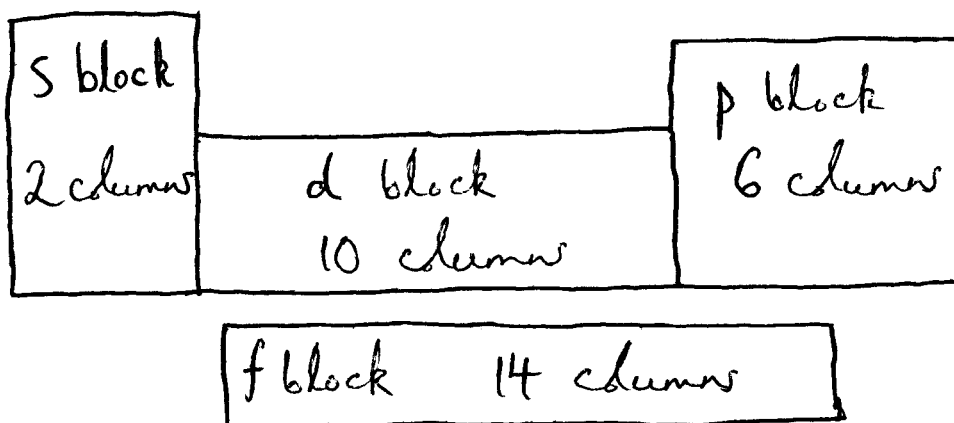
B: 5 electrons



C: 6 electrons



Periodic
Table

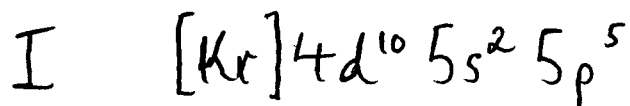
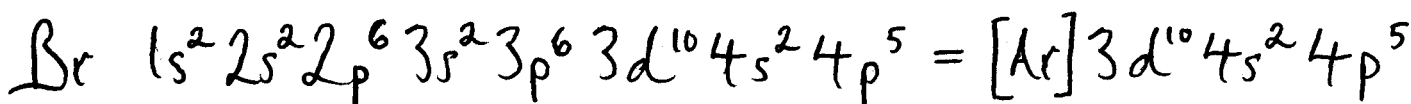
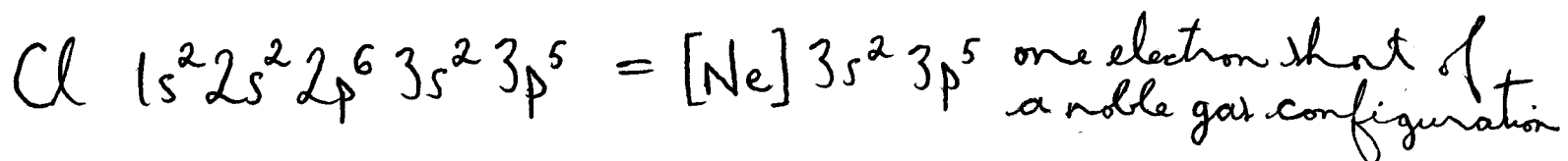
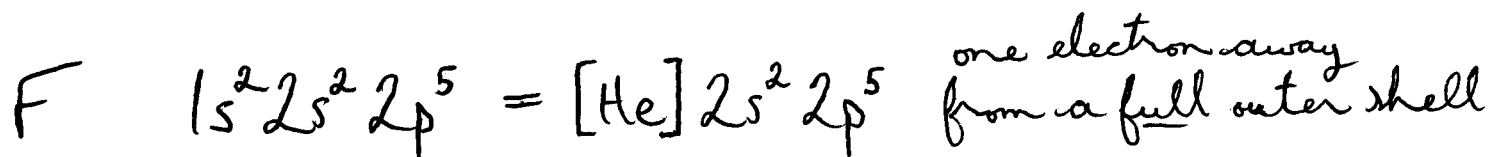


Chemistry has to do with electrons.

Specifically, it is the outer shell electrons (largest n) that determine interactions with other atoms (to form compounds).

This is because the electrons in the lower shells, called core electrons, are 'hidden' and don't play a role in chemical reactivity.

Now we can understand the periodicity of the reactivity of the elements. Look at the halogens



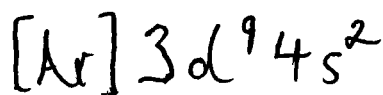
One short of full
s.p levels

Transition metals and rare earth elements can have unexpected electron configurations.

The reason is that the difference in energy between the subshells gets small as n (principal quantum #) gets large.

What would we predict for copper = Cu ?

$[\text{Ar}] 4s^2 3d^9$ except we always write the outer shell (outside noble gas core are the valence electrons), last, so



However, the actual electron configuration (experiment) ^(from)

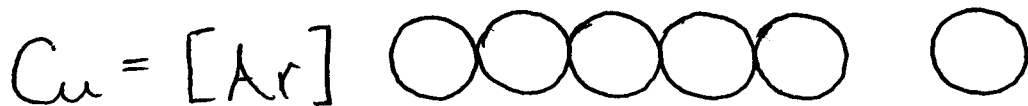


The 3d orbital "borrows" an electron from the 4s orbital to become full. This turns out to be more stable.

It turns out $1/2$ filled shells also have enhanced stability.

We would predict that Cr = $[\text{Ar}] 3d^4 4s^2$

but it is actually Cr = $[\text{Ar}] 3d^5 4s^1$

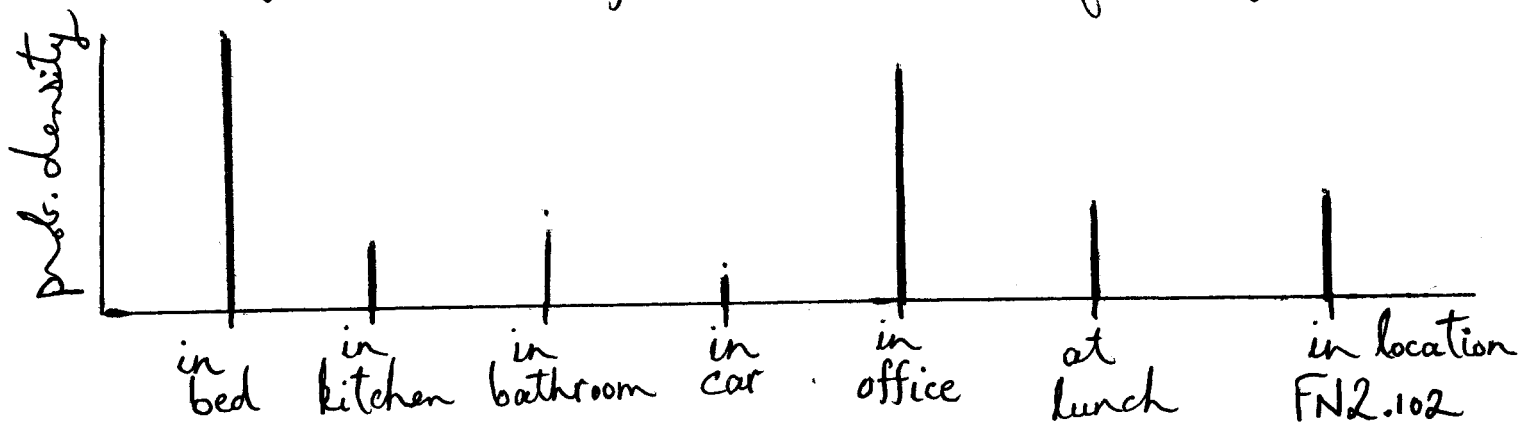


Look at the size and shape of the orbitals now.

For an electron living in an orbital, we describe its location in space by a function $\Psi(x, y, z)$, called the wavefunction, and we interpret the square of this function, $\Psi^2(x, y, z)$, as the probability density of the electron's location.

What is a probability density?

ex probability density of Dr. Nielsen's location from early this morning up to the end of today's class:



What does this tell us? If you were to pick a time at random from this morning up until now, you would be more likely to find me in my office than in my car.

Same with the electron. The prob. density $\Psi^2(x, y, z)$ tells you how likely the electron is to be found at position (x, y, z) around the nucleus.

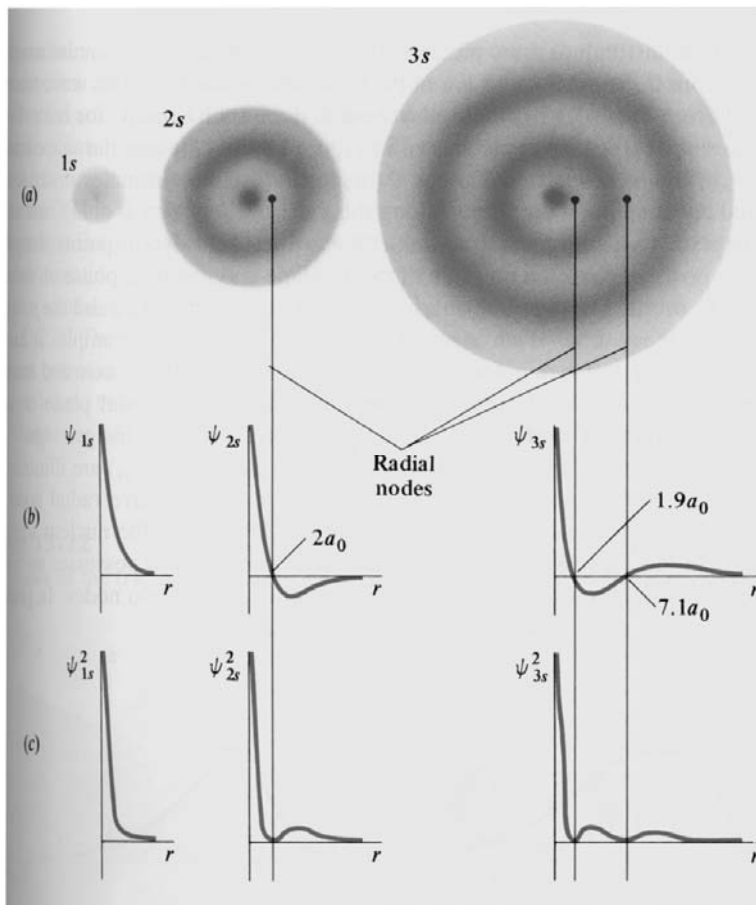
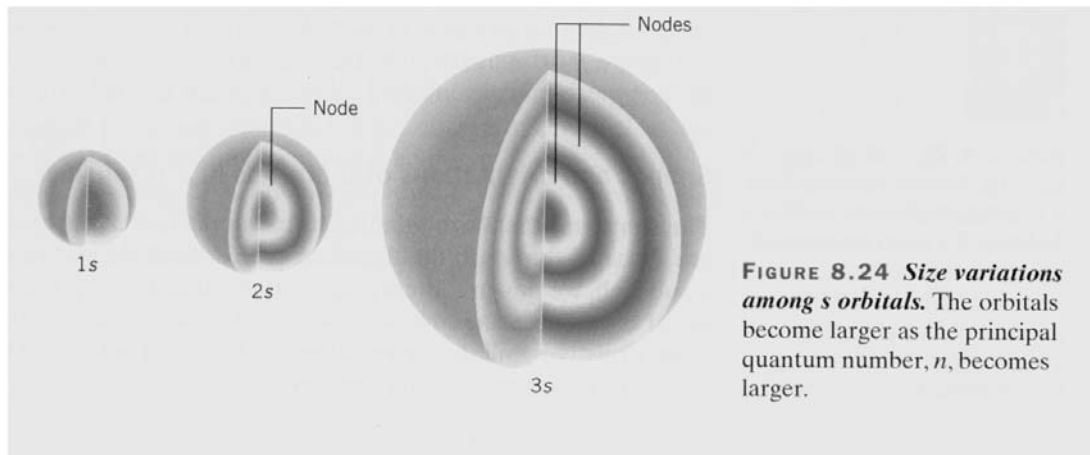


Figure 13-19

Three representations of hydrogen s orbitals. (a) An electron-density representation of a hydrogen atom in its $1s$, $2s$, and $3s$ states. The spheres are cut off at a radius that encloses 90% of the total electron density. (b) The wave functions graphed against distance from the nucleus r . (c) The squares of the wave functions.

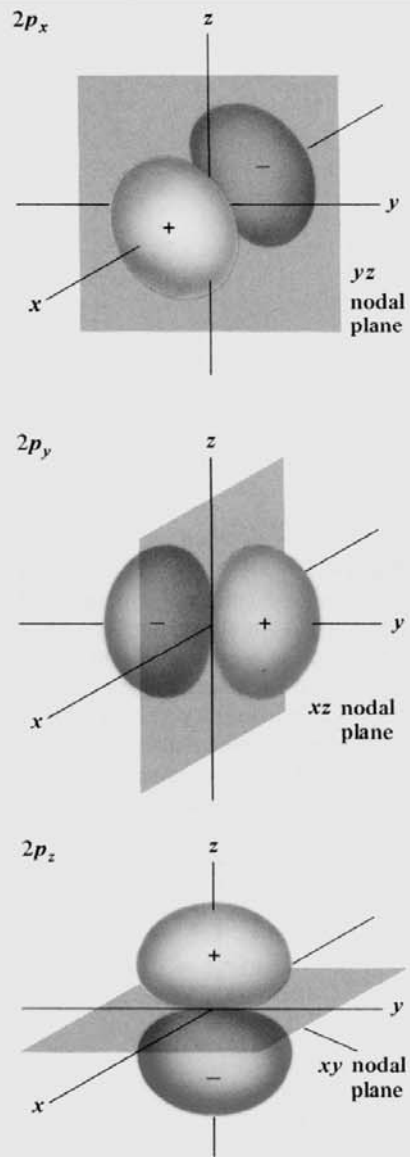
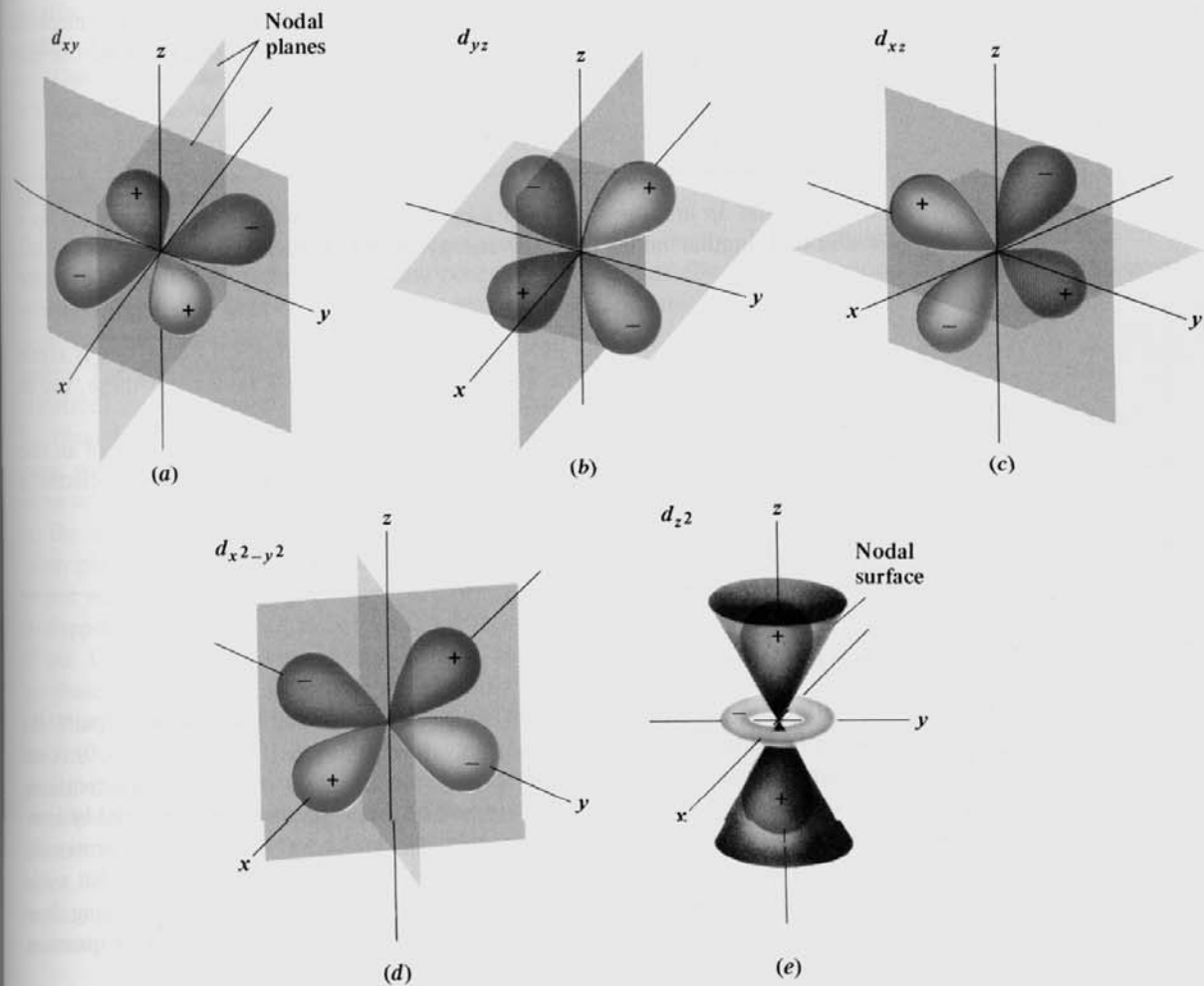


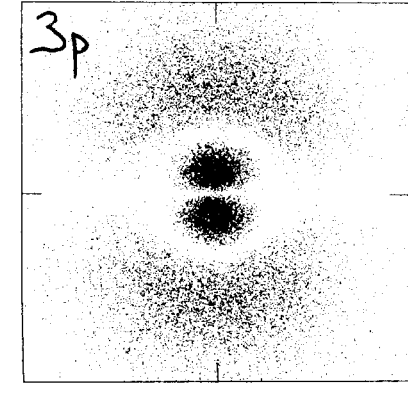
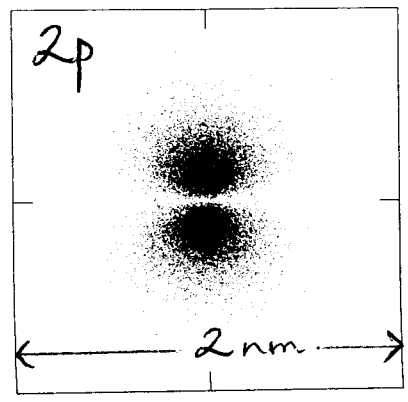
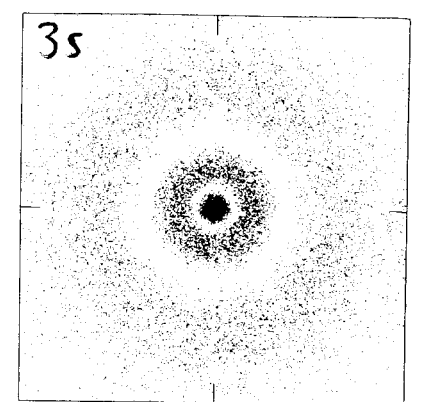
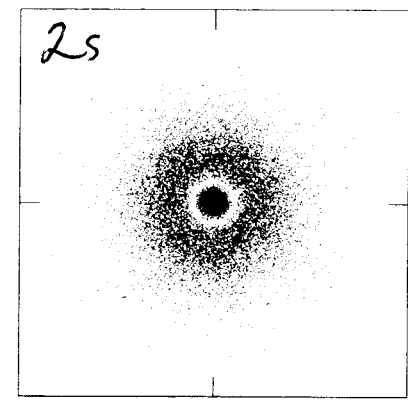
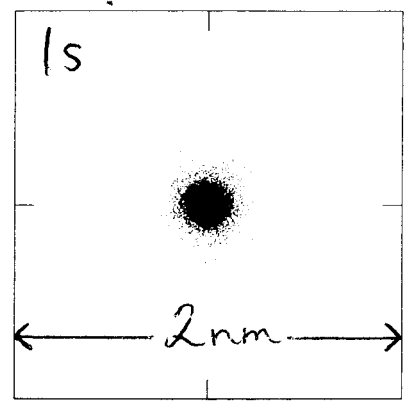
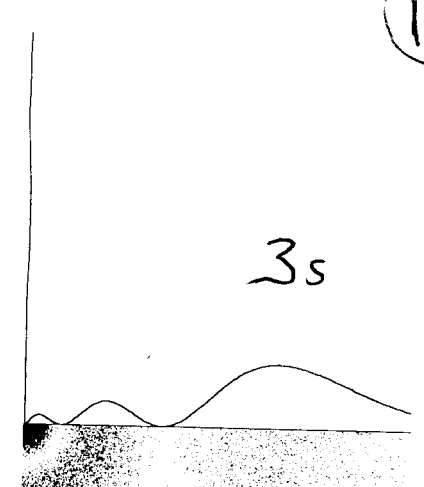
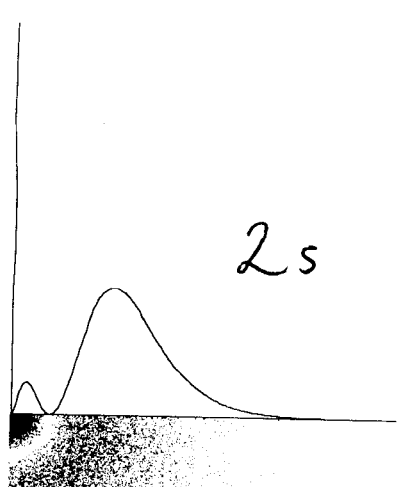
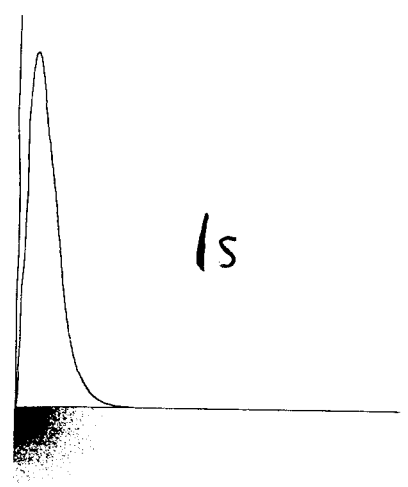
Figure 13-20

The distribution of electron density in the three $2p$ orbitals, with phases and nodal planes indicated.

Figure 13-22

The shapes of the five $3d$ orbitals, with phases and nodal surfaces indicated.





Screening

The outer electrons do not feel the full positive charge of the nucleus because the core electrons screen this charge. (core electrons are between the nucleus and the outer electrons.)

The outer electrons experience a charge of roughly $Z - C$ where Z = nuclear charge, C = core electron charge

Size of atoms → see Fig 8.30

- going down a group, atoms get larger.

Why? The effective (screened) charge is constant but the outer electrons get farther from the nucleus (n increases)

- going across a row, atoms get smaller.

Why? The outer electrons feel an increased effective charge because C does not change, Z is increasing.

Hence the outer electrons get pulled in tighter to the nucleus as we go across a row.

Anions → larger than the atom it comes from
gain electrons : gets larger

Cations → smaller than the atom it comes from
lose electrons : shrinks

Ionization Energy

Energy required to remove an electron from an isolated atom or ion.



units: usually expressed in kJ/mol

a mole (symbol mol) is defined as 6.022×10^{23} objects

so a mole of electrons is 6.022×10^{23} electrons

It turns out that one mole of ^{12}C atoms has a mass of 12.00g
so it brings us up to the macroscopic scale.

Ionization energies are low for the alkali metals

Why? because they like to donate an electron to form binary salts
NaCl

Ionization energies are high for the halogens

Why? because they like to accept an electron rather than lose one.

2^{nd} ionization energy always higher than 1^{st} one
for a given element.

In general, larger atoms have lower ionization energies.

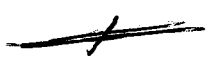
However, there are irregularities related to

$1/2$ full or full subshells (see page 343)

Electron Affinity

Opposite: measures $X(g) + e^- \rightarrow X^-(g)$

Trend as you would expect: Cl likes gaining an electron more than Na. see Fig. 8.33



Chapter 9: Chemical Bonding

We will look at ionic bonding (salts)
and covalent bonding (molecules)

Ionic compounds: form by a transfer of electrons
the resulting electrostatic attraction between
anions and cations is called an ionic bond.

The fundamental reason some elements combine to
form ionic compounds is that this arrangement lowers
their potential energy the most.

(the process is exothermic \rightarrow gives off heat)