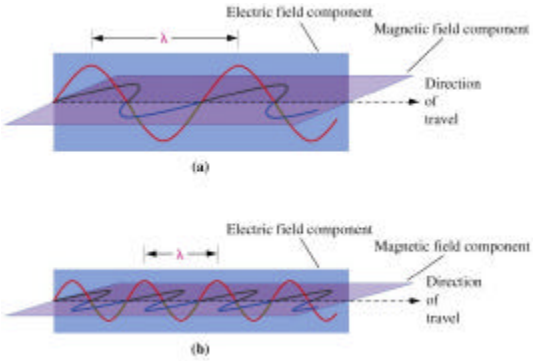
Chapter 5: Electrons in Atoms
Light (Electromagnetic Radiation)

- Light has the properties of both waves and particles.
- Light waves carry energy through space.

wavelength (λ) meters
frequency (ν) Hz (s^{-1})
amplitude (a) intensity

All light travels at the same speed,
c = 2.99792 x 10^8 m/sec (vacuum)



The ***frequency*** (ν is pronounced "nu") is the number of wavelengths that pass a point in a given period of time. (cycles per second) or s^{-1} where 1Hz = $1s^{-1}$

The ***wavelength*** (λ is pronounced "lambda") is the distance between wave crests in meters
(m, cm, nm, pm, Å (angstrom, 10^{-10} m))

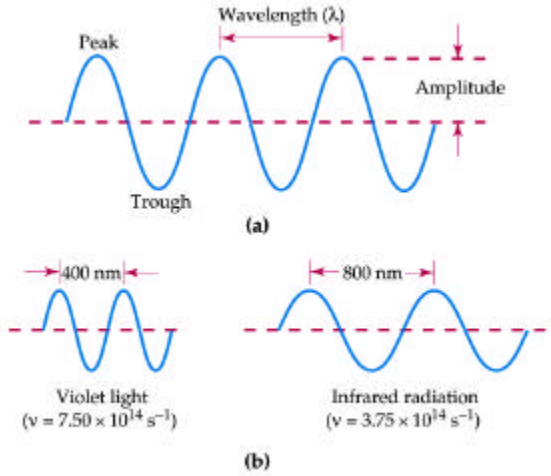
The product of frequency and wavelength for all forms of electromagnetic radiation (light) is a constant, the speed of light "c".

$$ë \times õ = c$$

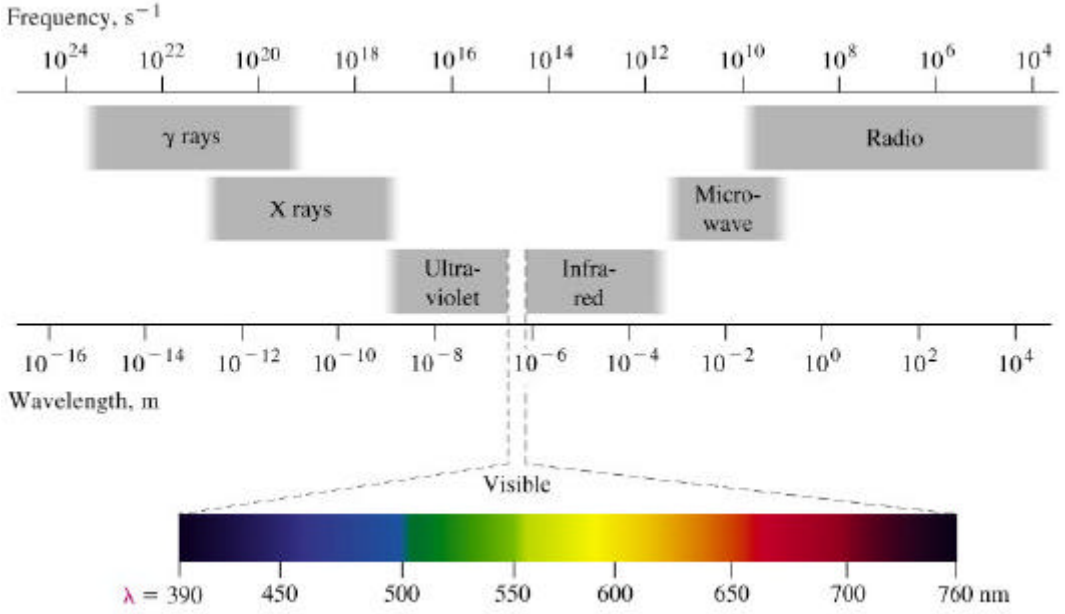
$$õ = \frac{c}{ë} \quad \text{and} \quad ë = \frac{c}{õ}$$

frequency and ***wavelength*** are inversely related:

high frequency corresponds to short wavelength
long wavelength corresponds to low frequency



The Electromagnetic Spectrum



Example:

What wavelengths correspond to FM radio (MHz) signals?

$$\lambda \times \nu = c$$

$$\lambda = \frac{c}{\nu}$$

$$\lambda = \frac{3.00\times10^{8}\ \mathrm{m/s}}{93.5\ \mathrm{MHz}\times\frac{10^{6}\ \mathrm{Hz}}{1\ \mathrm{MHz}}\times\frac{1\ \mathrm{s^{-1}}}{\mathrm{Hz}}} = \qquad 3.21\ \mathrm{m}$$

What frequencies correspond to microwaves?

$$\lambda \times \nu = c$$

$$\nu = \frac{c}{\lambda}$$

$$\nu = \frac{3.00\times10^{8}\ \mathrm{m/s}}{1\ \mu\mathrm{m}\times\frac{1\times10^{-6}\ \mathrm{m}}{1\ \mu\mathrm{m}}} = \qquad 3.00\times10^{14}\ \mathrm{Hz} = 3.00\times10^{8}\ \mathrm{Mz}$$

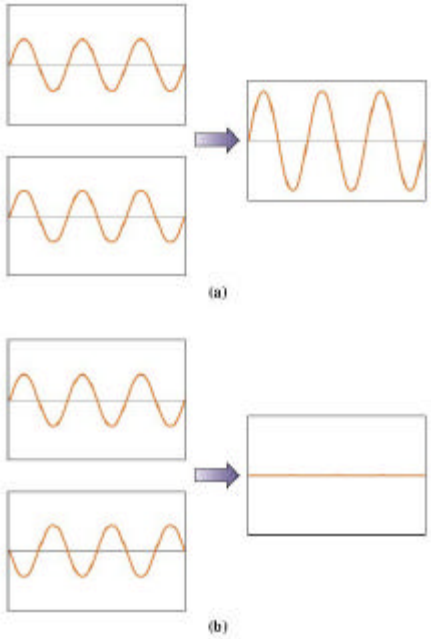
Properties of waves:

(a) ***Constructive inference:***

When waves that are in phase interact, they do so such that the amplitudes add in a positive manner.

(b) ***Destructive Interference:***

When waves that are out of phase interact, they do so such that the amplitudes cancel one another.



Light and Energy: Planck's Law

Planck's Law: *Energy is discontinuous; the transmission of energy can only occur in finite amounts or "**Quanta**"*

$E_{photon} = h \cdot \nu$ h = Planck's constant = 6.626×10^{-34} J·s

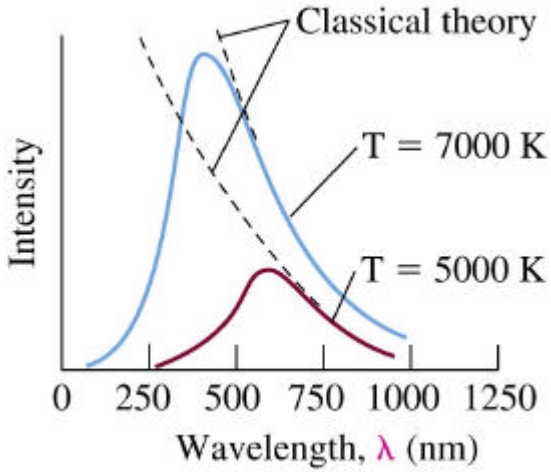
Planck's Law is based on the phenomenon known as the

"***Ultraviolet Catastrophe"***

Classically, the intensity of light should increase with decreasing wavelength.

If this were so, the intensity of UV light would go to infinity with decreasing wavelength.

I order to explain the observations of ***black-body*** radiation, Planck surmised that light is released in defined packets or ***quanta***.



As the frequency of light increases, the energy ***increases***.

As the wavelength of light increases, the energy ***decreases***.

$$E_{photon} = h \cdot n = \frac{hc}{l}$$

Red Light (650 nm)

$$E_{photon} = \frac{hc}{ë} = \frac{6.626\times10^{-34}\ \text{Js}\times3.00\times10^{8}\ \text{m/s}}{650\ \text{nm}\times\frac{1\ \text{m}}{10^{9}\ \text{nm}}} = 3.06\times10^{-19}\ \frac{\text{J}}{\text{photon}}$$

Blue Light (400 nm)

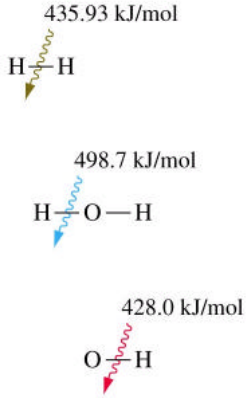
$$E_{photon} = \frac{hc}{ë} = \frac{6.626\times10^{-34}\ \text{Js}\times3.00\times10^{8}\ \text{m/s}}{400\ \text{nm}\times\frac{1\ \text{m}}{10^{9}\ \text{nm}}} = 4.97\times10^{-19}\ \frac{\text{J}}{\text{photon}}$$

Calculate the energy of a mole of photons of 400 nm light.

$$E_{photon} = \frac{hc}{ë} = \frac{6.626\times10^{-34}\ \text{J}\cdot\text{s}\times3.00\times10^{8}\ \text{m/s}}{400\ \text{nm}\times\frac{1\ \text{m}}{10^{9}\ \text{nm}}}\times\frac{6.022\times10^{23}\ \text{photons}}{\text{mole photons}} =$$

$$2.99\times10^{5}\ \frac{\text{J}}{\text{mole photons}}$$

Bond energies also correspond to the energies of individual photons. The process of light breaking chemical bonds is known as ***photodissociation***.



$$435.93\frac{\text{kJ}}{\text{mol}}\times\frac{1\ \text{mol}\ H_2}{6.022\text{x}10^{23}\ H_2}\times$$

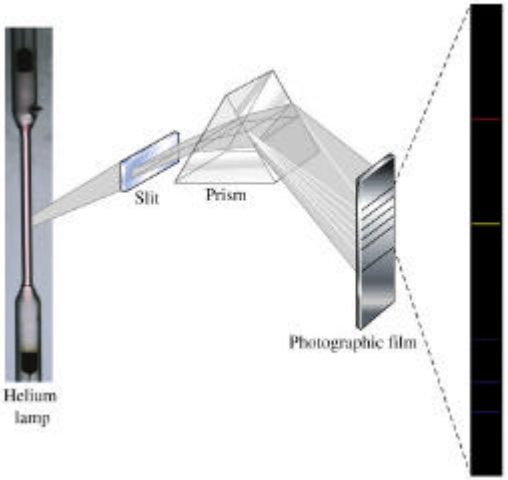
$$\frac{H_2}{\text{photon}}\times\frac{10^{3}\ \text{J}}{\text{kJ}} = 7.24\ \text{x}\ 10^{-19}\ \frac{\text{J}}{\text{photon}}$$

$$E_{photon} = \frac{hc}{ë} \qquad ë = \frac{hc}{E_{photon}}$$

$$ë = \frac{6.626\times10^{-43}\ \text{J}\cdot\text{s}\times3.00\times10^{8}\ \text{ms}^{-1}}{7.24\ \text{x}\ 10^{-19}\ \frac{\text{J}}{\text{photon}}}$$

$$= 2.75\times10^{-7}\ \text{m} \quad \text{or}\ 275\ \text{nm}$$

Quantum Theory: Atomic Spectra:



Atomic Spectrum

When a discharge is passed through a tube filled with He, the light emitted spreads into a series of lines rather than a normal spectrum of light.

This indicates that something in the atom is not governed by a continuum…

Something is ***Quantized***!

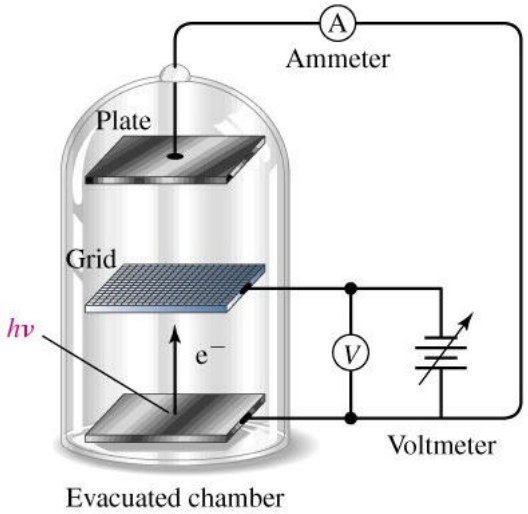
Recall that Quantization was used to explain the "***Ultraviolet Catastrophe***" (Planck)

Einstein's work on the "***Photoelectric Effect***" also contributed to the concept of ***quantization***.

When light strikes the surface of certain metals, electrons may be ejected.

The light must be of a certain frequency (color) in order for this to occur.

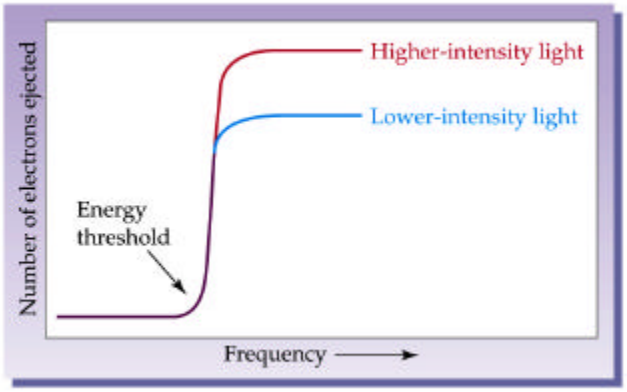
The behavior exhibits a threshold effect such that below a minimum energy, no electrons are ejected.



The threshold behavior for the "***Photo-electric Effect"***

Since E = hν

Only photons of frequency greater than the minimum frequency (ν_o) can eject electrons
Any excess energy from the photon goes into the kinetic energy of the electron.



E (electron) = E (photon) - Φ = ½$m_e v^2$

E (photon) = hν
m_e = 9.11 x 10^{-31} kg
v = velocity of the ejected electrons
Φ = ejecton threshold "*Work function*"

ν_o = Φ/h "Threshold frequency"

If…

ν (photon) < ν_o no electrons are ejected

ν (photon) = ν_o electrons are removed with no KE

ν (photon) > ν_o electrons are ejected

Example:

A certain metal has a threshold frequency (ν_o) of 3.66 x 10^{-14} s^{-1}.

Will 532 nm light cause electrons to be ejected?

E (electron) = E (photon) - Φ

if ν (photon) > ν_o then electrons are ejected

$$\nu \cdot \lambda = c$$

$$\acute{\imath} = \frac{c}{\ddot{e}} = \frac{3.00 \times 10^8 \frac{m}{s}}{532 \text{ nm x } \frac{m}{10^9 \text{ nm}}} = 5.64 \times 14 \text{ s}^{-1}$$

ν (photon) > ν_o Electron are ejected

What is the velocity of the ejected electrons?

E (electron) = E (photon) - Φ = ½$m_e v^2$

$$\frac{1}{2} m_e v^2 = \frac{hc}{\lambda} - h\nu_o$$

$$\frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\ J \cdot s \times 3.00 \times 10^{8}\ \frac{m}{s}}{532\ nm \times \frac{1m}{10^{9}\ nm}} = 3.74 \times 10^{-19}\ J$$

$$h\nu_o = 6.626 \times 10^{-34}\ J \cdot s \times 3.66 \times 10^{14}\ s^{-1} = 2.43 \times 10^{-19}\ J$$

$$\frac{1}{2} m_e v^2 = 1.31 \times 10^{-19}\ J$$

$$v = \sqrt{2 \times \frac{1.31 \times 10^{-19}\ J}{9.11 \times 10^{-31}\ kg}} = 5.36 \times 10^{5}\ \frac{m}{s}$$

The Bohr Atom:

The concept of the atom derived form the Rutherford gold film experiment failed to explain hoe the electrons ordered them selves about the nucleus.

In 1913, Niels Bohr proposed a model for electron distributions that was a combination of classical and the new emerging quantum theories.

1. Electrons move in circular ***orbits*** about the nucleus.
2. These "orbits" are fixed or discrete in terms of allowed energies governed by states of ***angular momentum***.
3. Electrons can only pass between these allowed levels and nowhere in between.

Conclusion: The energy levels of the electrons are ***quantized***! This explains the observance of line spectra in atom emission.

To explain the spectral line puzzle, Bohr came up with a radical model of the atom, which had electrons orbiting around a nucleus.

Because of these "***signature colors***" or emission lines, Bohr stated that electrons had to exist in discrete orbits or "***quantized***" levels and that the spectral lines occurred when the electron jumped between the allowed levels.

Each level is designated by a "***Quantum Number***", n

n = 1,2,3,4…. infinity

the radius of each orbit is given by:

$r_n = n^2 a_o$ The Bohr radius $a_o = 0.53$ Å or 53 pm

The energy of each level is given by:

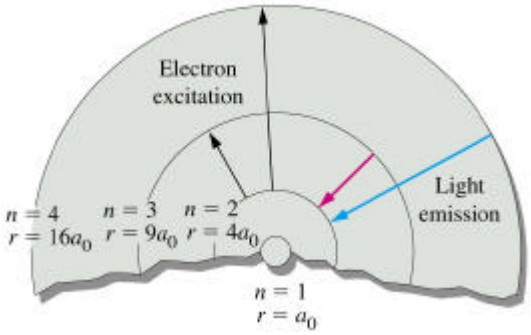
$$E_n = \frac{-Z^2 R_H}{n^2}$$

Where $R_H = 2.179 \times 10^{-18}$ J

The Bohr Model:

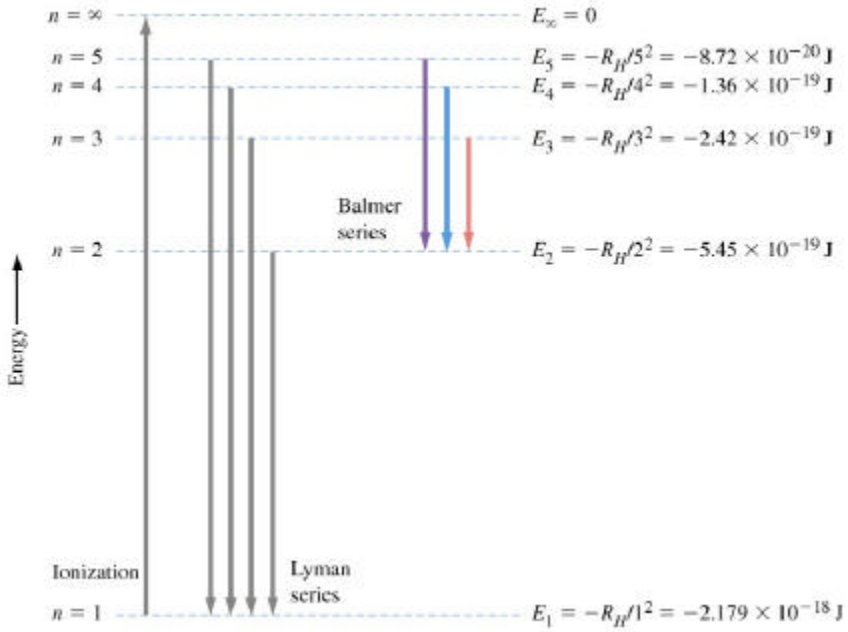
$$r_n = n^2 a_o$$

n = 1, 2, 3, 4…



The Energy Levels:

$$E_n = \frac{-Z^2 R_H}{n^2}$$



The Lowest energy level corresponds to n = 1

Where, n = 1 "Ground State"
n = 2 "1st excited state"
n = 3 "2nd excited state"
n = n-1 "nth excited state"

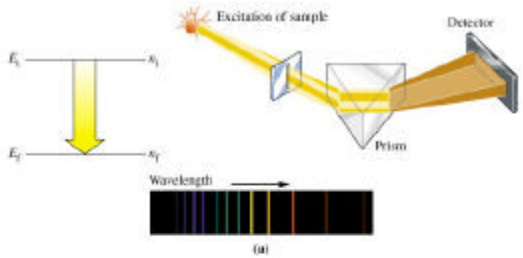
Absorption and Emission

When an electron jumps form a lower state to a higher state, Energy (light) is absorbed.

When an electron jumps form a higher state to a lower state, Energy is (light) emitted

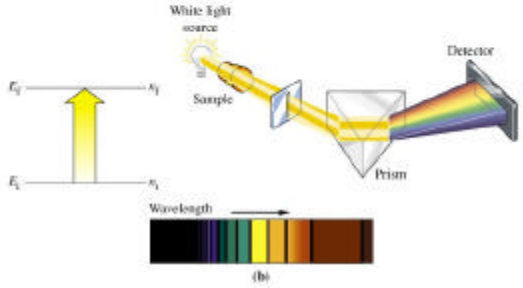
Emission of Light:

Electrons move from a higher level (state) to a lower level (state)



Absorption of Light:

Electrons move from a lower level (state) to a higher level (state)



$$E_n = \frac{-Z^2 R_H}{n^2} \quad \text{for} \quad Z = 1$$

$$\Delta E = E_{fin} - E_{in} = \frac{-R_H}{n_{fin}^2} - \frac{-R_H}{n_{in}^2} = E_{photon}$$

$$\Delta E = R_H \times \left(\frac{1}{n_{in}^2} - \frac{1}{n_{fin}^2} \right) = h \cdot n = \frac{h \cdot c}{l}$$

$$\frac{1}{l} = \frac{R_H}{h \cdot c} \times \left(\frac{1}{n_{in}^2} - \frac{1}{n_{fin}^2} \right)$$

A negative signs indicates ***emission***, positive ***absorption***.

The Wave-like Nature of a Particle

The Wave Particle Duality:

Louis de Broglie in response to Planck & Einstein's assertion that light was "particle-like" (photon) stated that small particles moving fast could exhibit a characteristic wavelength.

$$E = mc^2$$

$$h\nu = mc^2$$

$$\frac{h\nu}{c} = mc = p \quad \text{(momentum)}$$

$$\text{since} \qquad \frac{\nu}{c} = \frac{1}{\lambda}$$

$$\frac{h}{\lambda} = p \quad \text{or} \quad \lambda = \frac{h}{p} = \frac{h}{m \cdot u} \qquad u = \text{velocity}$$

What is the wavelength associated with an 80g tennis ball (d = 8 cm) moving at 115 miles per hour?
Compare that to an electron moving at 1/100 the speed of light.

$\lambda = \frac{h}{p}$ λ (tennis ball) = 2 x 10^{-34} m $\qquad \frac{\lambda}{d} \times 100 =$ 2 x 10^{-31} %

λ (electron) = 2 x 10^{-10} m $\qquad \frac{\lambda}{d} \times 100 =$ 70000 %The electron looks like a wave!

Heisenberg Uncertainty Principle:

The more precisely the position is determined, the less precisely the momentum is known in this instant, and vice versa.

$$\Delta p \, \Delta x \geq h / 4\pi$$

Δp = uncertainty in momentum (velocity)
Δx = uncertainty in position

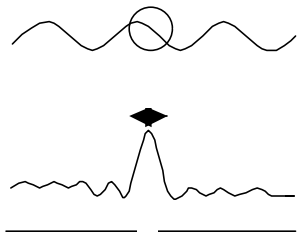
Classically, i.e., in our *macroscopic world*, I can measure these two quantities to infinite precision (more or less). There is really no question where something is and what its momentum is.

In the ***Quantum Mechanical world***, the idea that we can measure things exactly breaks down, i.e. there is a limit to the precision.

This ***uncertainty*** leads to many strange things.

> For example, in a ***Quantum Mechanical world***, I cannot predict where a particle will be with 100 % certainty. I can only speak in terms of probabilities.

A consequence of the ***Quantum Mechanical*** nature of the world is that particles can appear in places where they have no right to be (from an ordinary, common sense [classical] point of view)!

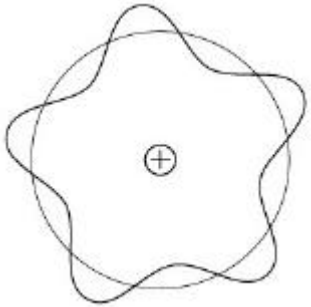


The results state that there is a "probability" of finding the particle in space at position "x" with an uncertainty of Δx.

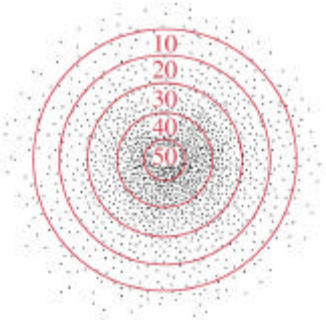
The location of a particle is given by a localized increase in the amplitude of the wave at position x.

Probability Distributions:

The ***mental picture*** of an electron corresponds to a wave superimposed upon the radial trajectory of a particle orbiting the nucleus.

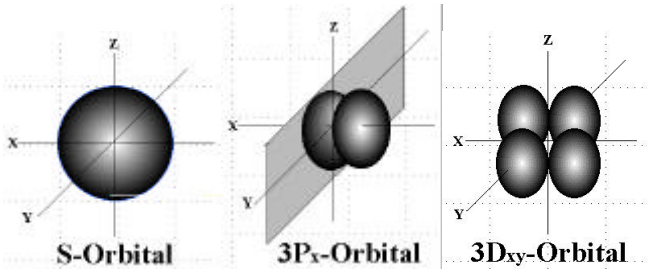


The position of an electron is best described by the image of a dart board: As the ***Schrödinger Wave Equation*** is solved time and time again, the position of an electron is found such that each "hit" builds up a pattern.



The build up of "hits" yields the probability in 3-dimensons for the likelihood of finding and electron about the nucleus.

- It is these ***probability functions*** that give rise to the familiar hydrogen-like orbitals that electrons occupy.



Quantum numbers and Electron Orbitals

Quantum Numbers are terms that were developed to aid in describing electron behavior according to the Schrödinger equation.

Principal Quantum Number "n"

n = 1, 2, 3, 4…up to infinity

Azimuthal or Angular Quantum Number "*l*"

l = 0, 1, 2, 3…up to a maximum of "n – 1"

Magnetic Quantum Number "m_l"

m_l may take on the value an integer from
$-l$ to $+l$

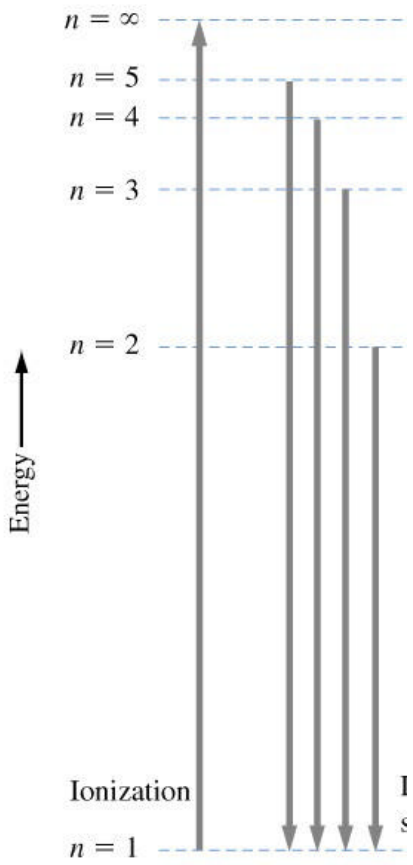
Spin Quantum Number "m_s"
$m_s \pm 1/2$

The ***Quantum numbers*** give information about the location of an electron, like an address.
The ***principal*** quantum number indicates the "state" where the electron is located, the ***angular momentum*** quantum number indicates the town, the ***magnetic*** QN is the street address and the ***spin*** quantum number corresponds to the right or left side of a duplex.

Each n-level defines a ***principle energy level*** or ***shell***.
n = 1, 2, 3… and

$$E_n = -\frac{Z^2 R_H}{n^2}$$

Z = atomic number of the nucleus and R_H = Rydberg constant.



Each "*l*" within an "n-level" represents a ***subshell***.
l = 0 "s" subshell
l = 1 "p" subshell
l = 2 "d" subshell
l = 3 "f" subshell

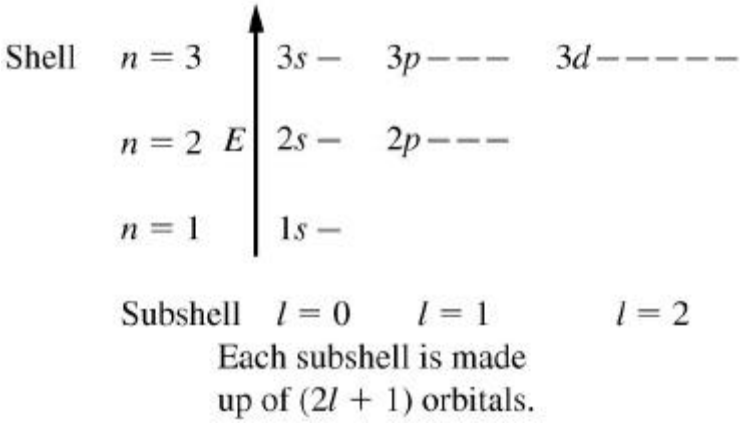
Each "*l*" subshell is divided into m_l orbitals, where m_l designates the spatial orientation of each orbital. (Cartesian coordinates, x, y & z)

for *l* = 0 m_l = 0 (no orientation)

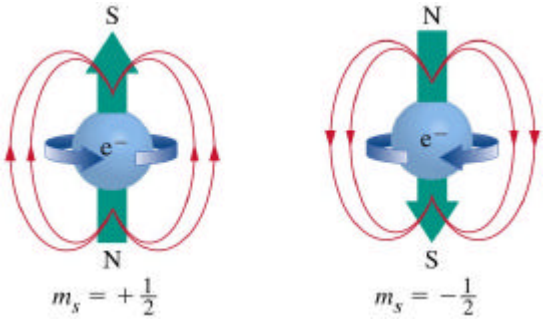
for *l* = 1 m_l = -1 0 +1
p_x p_y p_z

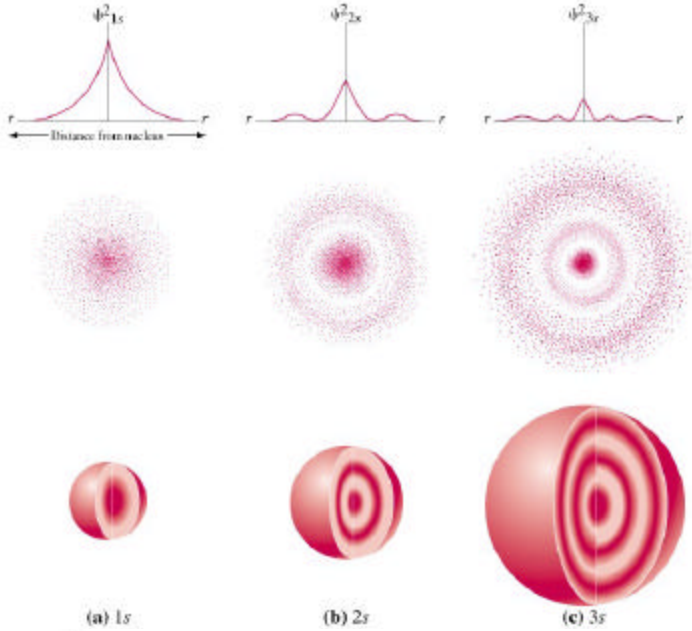
for *l* = 2

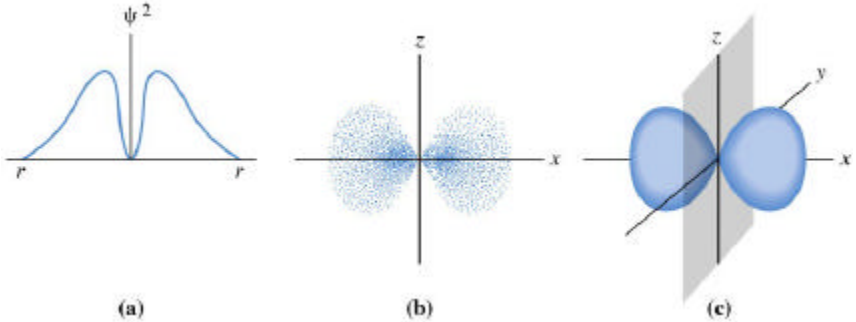
m_l = -2 -1 0 +1 +2

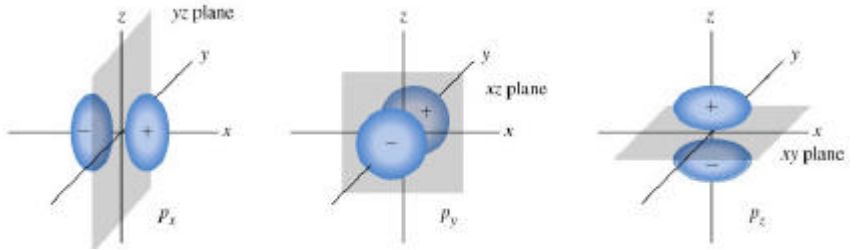


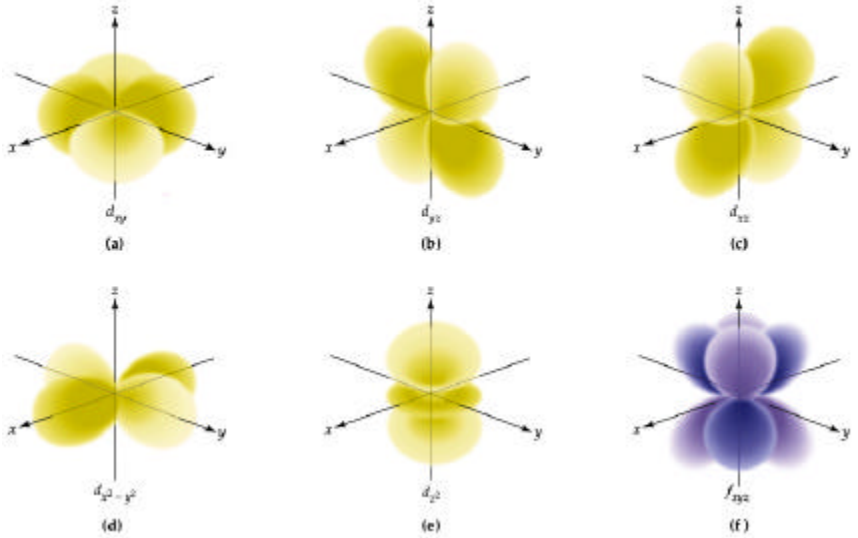
Each orbital can hold ***2 electrons***, one designated by $m_s = +½$ and one by $m_s = -½$




Distance from nucleus
(a) 1s
(b) 2s
(c) 3s


(a)
(b)
(c)


yz plane
xz plane
xy plane

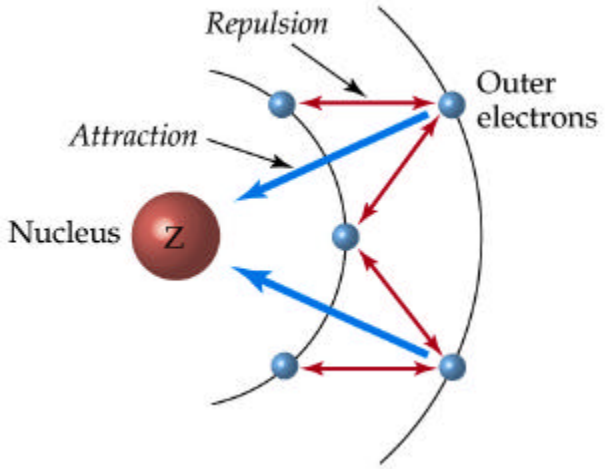

(a)
(b)
(c)
(d)
(e)
(f)

Electron Configurations: ***Multi-electron atoms***

The ideas presented thus far have focused on the H-atom, a one-electron system.

What happens when there are two or more electrons in an atom?

The diagram to the right explains:



- The innermost electrons screen or "***shield***" the nucleus from the view of the outer electrons.
- The outermost electrons in effect see a charge that is less that the actual charge on the nucleus, Z.

Shielding of Electrons:

The further out an electron exists from the nucleus, the greater the effect of shielding. (There are more electrons to screen the nucleus charge)

Since the s-orbitals have no ***nodal*** properties at the nucleus, they can ***penetrate*** more effectively.

This increase in the ability to penetrate magnifies the ability to screen.

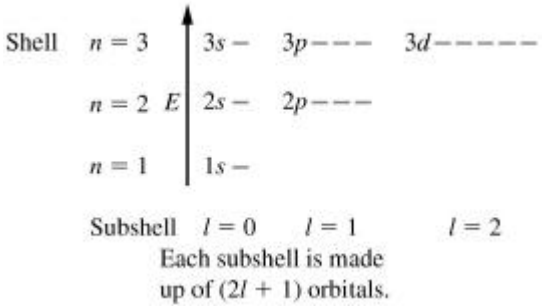
s-orbitals > p or d-orbitals

Increasing Screening

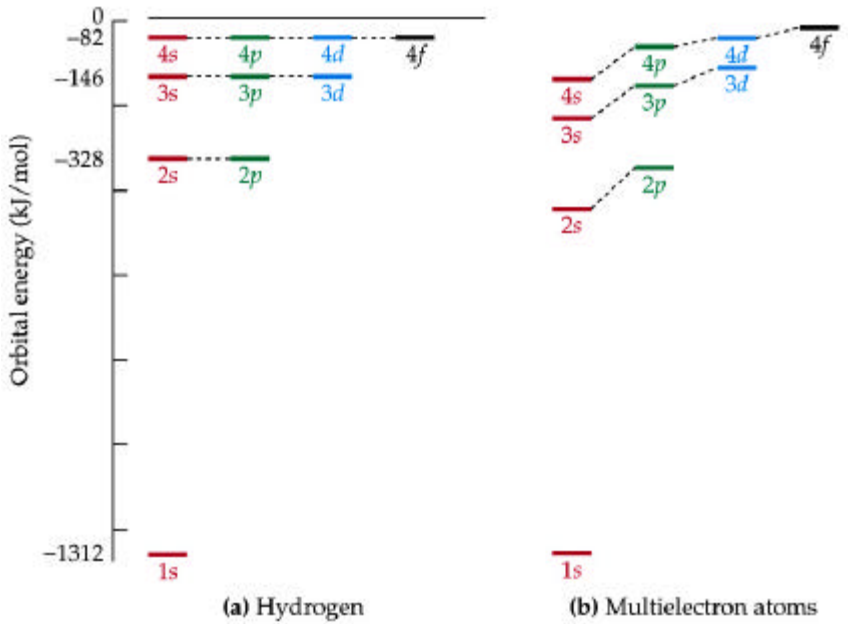
The effect of Shielding:

In a hydrogen atom, the orbitals are arranged as a function of "n" only.

For each value of n, the *l*-sub shells are degenerate (of the same energy).



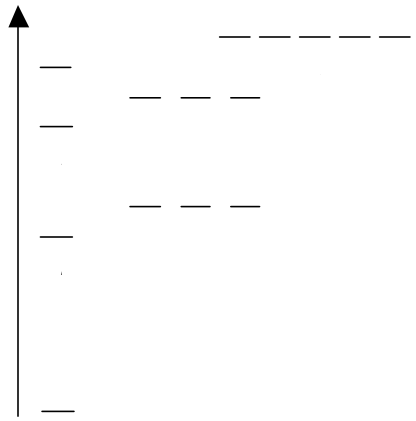
Shielding brought upon by the presence of more than one electron causes the orbital energies to split.



The result of shielding causes the orbitals to arrange in terms of increasing n + *l*

This results in the 4s-orbital having a lower energy that that of the 3d-orbital.

n = *l* = 4 + 0 vs. 3 + 2



Electron Configuration of Many Electron Elements

The electrons of a many-electron atom occupy the orbitals in accordance with a series of rules.

The Pauli Exclusion Principle:

Only two electrons with opposite spin can occupy an atomic orbital.

Stated another way, **no two electrons have the same 4 quantum numbers *n, l, m_l, m_s*.**

In applying this rule, you should realize that an atomic orbital is an **energy state**.

Hund's rule:

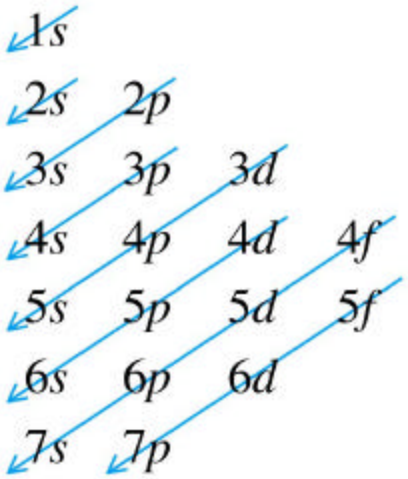
Electrons prefer parallel spins in separate orbitals of sub shells.

Electrons will fill across a set of degenerate orbitals until forced to pair with opposite spins.

The Aufbau (Building up) Principle:

Electrons fill from the lowest energy states (orbitals) up.

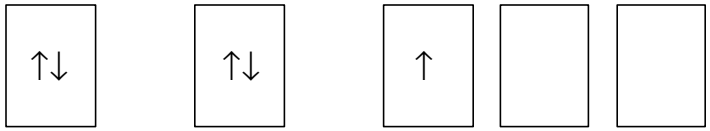
The Aufbau procedure (filling order of atomic orbitals) is used to work out the electron configurations of all atoms.



Electron Configurations of the 1st and 2nd Period:

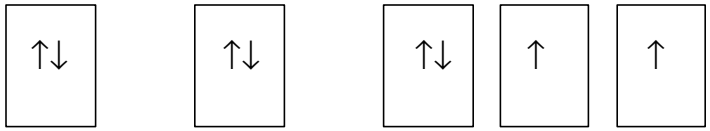
H = $1s^1$	C = $1s^2\ 2s^2\ 2p^2$
He = $1s^2$	N = $1s^2\ 2s^2\ 2p^3$
Li = $1s^2\ 2s^1$	O = $1s^2\ 2s^2\ 2p^4$
Be = $1s^2\ 2s^2$	F = $1s^2\ 2s^2\ 2p^5$
B = $1s^2\ 2s^2\ 2p^1$	Ne = $1s^2\ 2s^2\ 2p^6$

B Z = 5 5 electrons



$1s^2 2s^2 2p^1$

O Z = 8 8 electrons



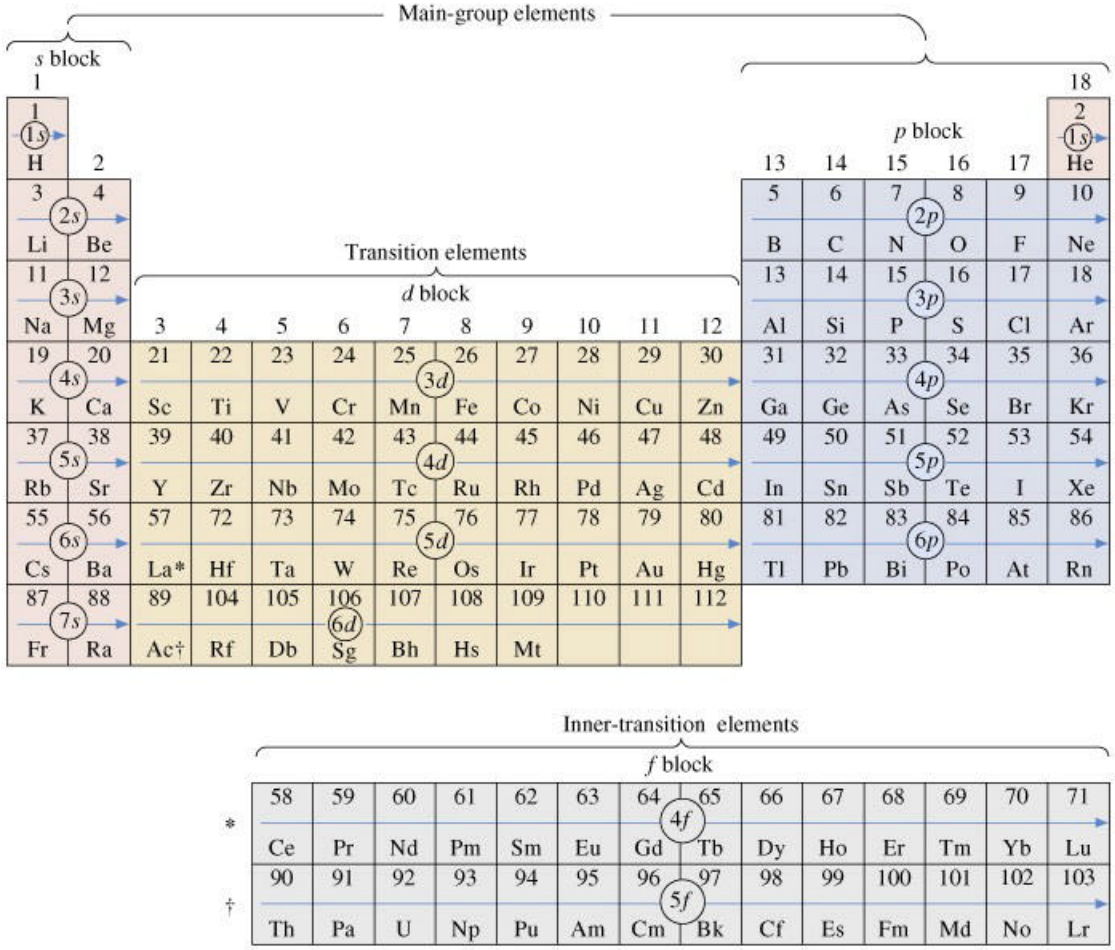
$1s^2 2s^2 2p^4$

Valence Electon Blocks:

Electron Configurations continued:

Electrons in the outermost shell are called ***valence electrons*.**

- It is the ***valence electrons*** determine an atom's chemical properties.
- Electrons in the inner shells are inner electrons or ***core electrons***.
- Regions in periodic table are designated as the ***s-block*, *p-block***, ***d-block*** and the ***f-block***.



Core Notation:

[Nobel Gas]
nd(n+1)s

Some anomolies in filling are seen in the d-elements

For d^4 and d^9 elements, an s-electron can jump over to create a ½ filled (d^5)or completely filled (d^{10}) d-orbital.

This lowers the overall energy of the atom.

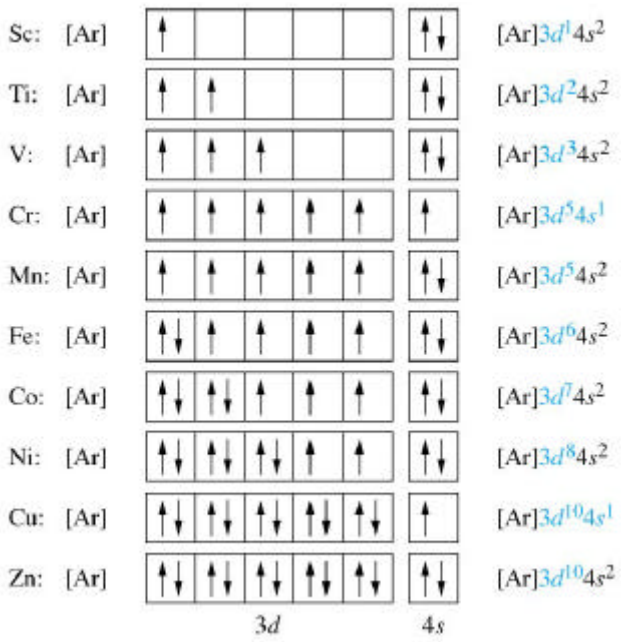
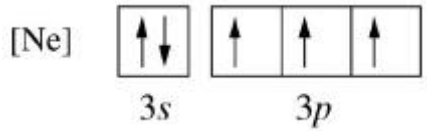


TABLE 9.2 Electron Configurations of Some Groups of Elements

Group	Element	Configuration
1	H	$1s^1$
	Li	$[He]2s^1$
	Na	$[Ne]3s^1$
	K	$[Ar]4s^1$
	Rb	$[Kr]5s^1$
	Cs	$[Xe]6s^1$
	Fr	$[Rn]7s^1$
17	F	$[He]2s^22p^5$
	Cl	$[Ne]3s^23p^5$
	Br	$[Ar]3d^{10}4s^24p^5$
	I	$[Kr]4d^{10}5s^25p^5$
	At	$[Xe]4f^{14}5d^{10}6s^26p^5$
18	He	$1s^2$
	Ne	$[He]2s^22p^6$
	Ar	$[Ne]3s^23p^6$
	Kr	$[Ar]3d^{10}4s^24p^6$
	Xe	$[Kr]4d^{10}5s^25p^6$
	Rn	$[Xe]4f^{14}5d^{10}6s^26p^6$

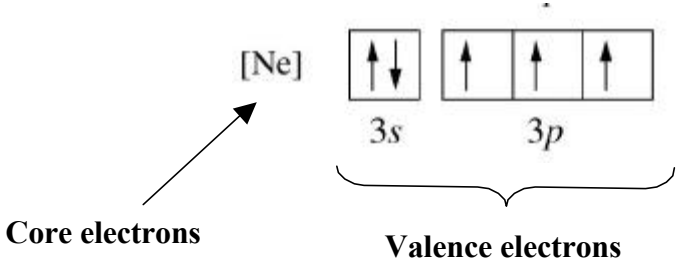
What is the ***electron configuration*** of the element as shown on the right?



Which electrons are the ***valence electrons*** and which are the ***core electrons***?

Answers:

$1s^22s^22p^63s^23p^6$ P (***phosphorous***)



Electron Configurations of ions:

When an atom gains or loses electrons it becomes an ion.

Loss of electrons: **Cation** Gain of electrons: **Anion**

(+)

(-)

Atoms of group 1, 2 and the non-metals will lose or gain electrons to attain the electron configuration of a ***Nobel gas (ns^2np^6).***

Example: Sodium forming sodium ion:

Na **Na^+**

[Ne] [Ne]

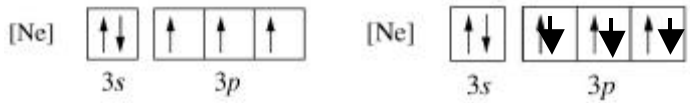
3s

$1s^2 2s^2 sp^6 3s^1$ $1s^2 2s^2 sp^6$

All group 1 cations (+1) will have the electron configuration of the previous Noble gas.

The formation of the phosphide ion:

P $(1s^2 2s^2 2p^6 3s^3 3p^3)$ P^{3-} $(1s^2 2s^2 2p^6 3s^3 3p^6) = [Ar]$



All group 5 (15) anions (-3) will have the electron configuration of the next Nobles gas.

Electron configurations of Transition Metal Ions:
The charge states on most transition metals cannot be equated to the electron configurations of the Noble gases. You will see why in chem. 2C (ch. 24 and 25)

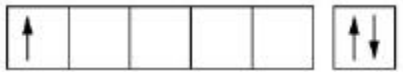
The electron configurations of transitions metal cations must be determined from the charge state.

Fe^{3+}… 3 electrons lost Ni^{2+}… 2 electrons lost and so on.

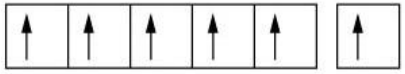
- When ***transition metals*** ionize, they lose the s-electrons first.
- This may seem odd as it is opposite to the filling order.
- From a stability argument, the removal of the s-electrons first results in lower energy configuration when we take into account ionization energies of s vs. p and d electrons.

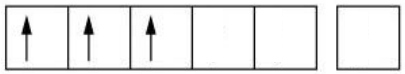
$3d^1$ $4s^2$

Examples:

Sc: [Ar]  [Ar]$3d^1 4s^2$

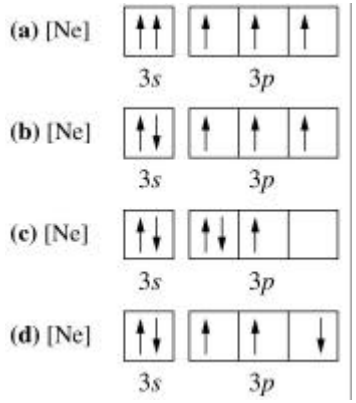
Sc^{3+}: [Ar] [Ar]

Cr: [Ar]  [Ar]$3d^5 4s^1$

Cr^{3+}: [Ar]  [Ar] $3d^3$

Electron Configurations:
Excited States

Which of the electron configurations to the right corresponds to phosphorous?



Answer: c
The rest are excited states of phosphorous.