

ATOMIC STRUCTURE

[MH5; Chapter 6]

- An atom consists of:
Nucleus : contains protons (+ve) and neutrons (no charge)
Outside nucleus : electrons (-ve)

- In a neutral atom:

$$\begin{array}{l} \# \text{protons} \\ \text{(Atomic Number)} \end{array} = \# \text{electrons}$$

- As we look at the arrangements of electrons in atoms, we are paying special attention to:

- 1) the relative energies of the electrons

"Energy Levels"

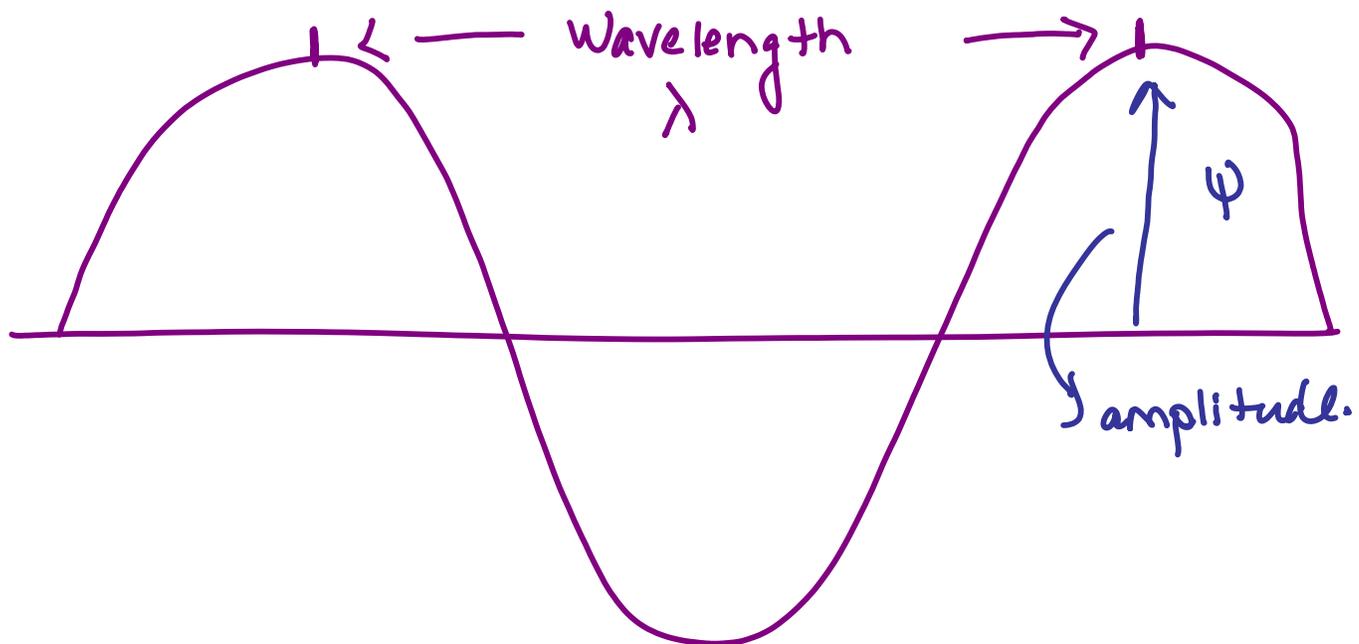
- 2) the spatial locations of the electrons

- places (regions) where we find the electrons "ORBITALS"

- The electron configuration (the actual arrangement of the electrons) of an element can be determined from its position on the Periodic Table.
- Recall that we have already used these positions can also be used to predict sizes of atoms and their tendencies to gain or lose electrons.

The Wave Nature of Light

- Light travels through space as a wave; the **wavelength**, λ , is the distance between successive crests or troughs. lambda
- The number of cycles that pass a given point in unit time is the **frequency**, ν , of the wave. "nu"
- A frequency of one Hertz, Hz, is one cycle per second.



- The speed of light, c , the speed at which a light wave moves through space is a constant, $2.998 \times 10^8 \text{ m s}^{-1}$. $c = \nu \lambda$ $\left(\nu = \frac{c}{\lambda} \right)$
- The eye sees only a small fraction of the electromagnetic spectrum, the Visible region, which has wavelengths ranging from 400-700 nm.
- Ultra violet (UV) and Infra red (IR) are two of several other regions.

UV - below 400 nm

IR - above 700 nm

The Particle Nature of Light

- Work by Max Planck and Albert Einstein during the years 1900-1910 showed that light is generated as a stream of particles, called photons, whose energy is given by the Einstein equation:

$$\begin{aligned} E &= h \nu \\ &= h \left(\frac{c}{\lambda} \right) \end{aligned}$$

- The quantity h is called **Planck's constant**, with a value of
 $h = 6.626 \times 10^{-34} \text{ J s}$

$$E \propto \frac{1}{\lambda} \quad (\text{keep } h \text{ and } c \text{ constant})$$

$$E \propto \nu$$

- Note that the energy of the photon is inversely proportional to wavelength, and directly proportional to frequency.

- shorter wavelengths of light have higher energy
- UV light from sun is more damaging to human tissue than visible light

Atomic Spectra

- White (or visible) light (from the sun) can be broken down into its colour components; this is called a **spectrum**.
- This spectrum is **continuous** and contains essentially all wavelengths between 400 and 700 nm.
- If an element is vaporized and then excited (given more energy); photons of light are emitted as the excited electrons return to their pre - excited energy level....this is called an **atomic spectra**.
- This is not a continuous spectra; the emitted light creates a **line spectra** in which each line corresponds to a specific wavelength of light.
- Atomic spectra are characteristic to the element in question; can be used for identification.
- As photons have only certain wavelengths, it follows that they can only have certain energies.
- As photons are produced when an electron moves from one energy level to another; it follows that the energy levels for an electron in an atom are limited to specific values.
- So we say that the energy of an atom is **quantized**.....it exists in certain fixed quantities.

The Hydrogen Atom

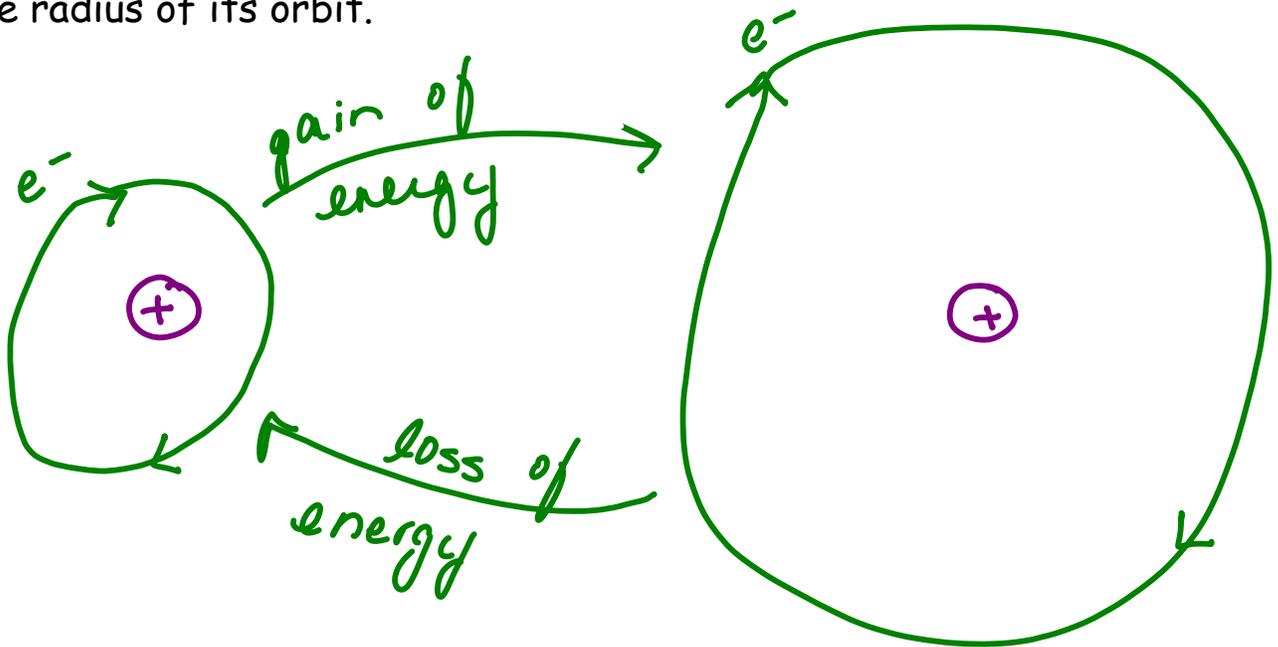
- Hydrogen atoms are produced when an electric discharge is struck through gaseous hydrogen $[H_2(g) \rightarrow 2 H^*(g, at)]$
- These gaseous hydrogen atoms emit radiation (light) at wavelengths which may be grouped into series.
- The first of these series to be discovered was the Balmer Series, which lies partly in the visible region.....
Red, 656.28; Green, 486.13; Blue violet, 434.05 and Violet, 410.18.

- different wavelengths from different energies.

- So we have seemingly contradictory results.....
 1) the continuous spectrum obtained from white light
 2) the line spectrum obtained from atoms
 - *all λ 's ; \therefore all energies*
 - *only a few λ 's ; \therefore only a few specific energies*

The Bohr Model of the Hydrogen Atom

- This model of the Hydrogen atom is a theoretical explanation of atomic spectra; based on classical mechanics.
- Bohr assumed a central proton, about which an electron moves in a circular orbit.
- The electrostatic attractive force between the positively charged proton and the negatively charged electron is balanced by the centrifugal force due to the circular motion.
- Energy would then be absorbed/radiated as the electron changed the radius of its orbit.



- Such a model predicts a continuous range of possible electron energies, which would give rise to a continuous rather than a line spectrum. *NOT what was observed*
- Bohr boldly **assumed** that only certain definite energies of the electron were allowed.
- He had no theoretical basis for this assumption, merely the need to explain the observed experimental result. He deduced:

$$E_n = -R_H / n^2$$

where R_H = Rydberg constant = $2.180 \times 10^{-18} \text{ J}$, and

n = integer = 1, 2, 3...

- This integer, n , becomes known as the **principal quantum number**, or **energy level** of the electron.

- Bohr's model established three general points..... *for the hydrogen atom*

- 1) Zero energy was designated as the point at which electron and proton are completely separated, i.e. with the electron at infinity. As the electron approaches the proton, it loses energy. All allowed electron energy states therefore have negative energies.

⇒ negative sign in Rydberg equation

- 2) The hydrogen atom is normally in the **ground state**, and the electron has principle quantum number (or energy level) $n = 1$.

It can absorb energy, and move to an **excited state**; $n > 1$.

The first excited state is $n = 2$; the second excited state is $n = 3$

Transitions are also possible between excited states, eg. from $n = 2$ to $n = 3$.

excited states always higher energy

- 3) When the electron gives off energy as a photon of light, it falls to a lower energy state. (eg. from $n = 2$ to $n = 1$ or $n = 3$ to $n = 2$...)
The energy of the photon evolved (and hence the wavelength/colour) is equal to the difference in energy between the two states:

$$\Delta E = E_{\text{high}} - E_{\text{low}} = h\nu$$

Since $E_n = -R_H / n^2$ the energy of the both states can be calculated, and thence the wavelength of the photon emitted.

Recall: $E = h\nu$ and $\nu = c/\lambda$

The model worked brilliantly for the hydrogen atom, accounted for the line spectrum observed, and Niels Bohr received the Nobel Prize for physics in 1922.

The Quantum Mechanical Model [MH5, p. 136]

- Bohr's model, although highly successful in explaining the line spectrum of the hydrogen atom, did not even work for He, much less more complicated atoms.
- It was soon realized that there was some fundamental problem with the Bohr model, and the fixed orbit of an electron idea was abandoned. *Bohr treated the electron as a particle*
- In 1924 Louis de Broglie suggested that perhaps electrons and light could behave in a similar manner.....

- light shows behavior of particles and waves

- maybe electrons can also behave like waves

- This new idea (the dual wave - particle nature of the electron) was experimentally confirmed and led to a whole new discipline commonly known as **quantum mechanics**.

- The Quantum Mechanical Model differs from the Bohr model in several ways; the two most important being:

1) The kinetic energy of an electron is inversely related to the volume of the region to which it is confined.

- smaller volume; e^- closer to nucleus
- electrostatic energy decreases
- e^- is moving in a smaller vol.; kinetic energy increases

$\therefore e^-$ doesn't "fall" into nucleus

2) It is impossible to specify the precise position of an electron in an atom at a given instant.

- can't tell actual path it takes
- estimate the probability of the position of the electron

- The region where we expect to find the electron is sometimes called the **electron cloud**.

- Electron density decreases as the distance from the nucleus increases.

- In 1926, Erwin Schrödinger, an Austrian physicist working in Zurich, wrote a differential equation to express the wave properties of an electron in an atom.
- From this equation, one could calculate the amplitude ψ (wave function) of an electron wave at various points in space.

The Schrödinger Equation

$$\frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m (E - V)}{h^2} \psi = 0$$

- for x (one dimension)
- could also solve for y and z !

- What is important is that, for a H atom, ψ^2 is directly proportional to the probability of finding the electron at a particular point.
- The 3 - dimensional Schrodinger equation (Ψ) can be solved exactly for the hydrogen atom, and approximately for atoms with 2 or more electrons.
- There are many solutions for Ψ , each associated with a set of numbers called **quantum numbers**. *4 Quantum Numbers*
- A wave function corresponding to a particular set of three quantum numbers (n, l, m_l ; to be defined shortly) is associated with an electron occupying an **atomic orbital**.
- From these numbers we can deduce the energy of that orbital, its shape and its orientation in space.
- A fourth quantum number, m_s , completes the description of a specific electron.

Quantum Numbers and Electron Configurations [MH5;6.3]

Principal Quantum Number, symbol n

- Derived from the Bohr atom quantum number n , this defines a principal energy level for the electron in the hydrogen atom.
- n may have **any** positive integral value > 0 , ie) $n = 1, 2, 3, 4...$
- As n increases, the energy of the electron and its distance from the nucleus increase.

Orbital Quantum Number, symbol l (Sublevels s, p, d, f)

- Each principal energy level includes one or more sublevels denoted by the orbital quantum number, l , which determines the general shape of the electron cloud.
- l may have integral values from 0 up to $(n - 1)$; so.....
If $n = 1$, only $l = 0$ is possible.
If $n = 2$, $l = 0$ or $l = 1$
- The number of sublevels in a given energy level (up to a point) is equal to the principal quantum number, n .
- We have 'names' for electrons with different values of l :
 $l = 0$, 's electrons' $l = 1$, 'p electrons'
 $l = 2$, 'd electrons' $l = 3$, 'f electrons'

Sublevel Designations for Principal Quantum Numbers 1 to 4											
n	1		2		3			4			
l	0		0	1	0	1	2	0	1	2	3
Sublevel	1s		2s	2p	3s	3p	3d	4s	4p	4d	4f

- Within a specific energy level (n), the sublevels increase in energy in the order: $ns < np < nd < nf$

Magnetic Quantum Number, symbol m_l

- Each sublevel contains one or more **orbitals**, which differ in the direction, or orientation in space taken by the electron cloud.
- The number m_l defines that direction and is related to l .
- m_l may have integral values from $-l$ through zero to $+l$.
- If $l = 0$ (s electron), $m_l = 0$; as there is just one s orbital, there can only be one possible orientation, or orbital.
- If $l = 1$ (p electron), $m_l = -1, 0$ or $+1$; there are **three** possible orientations in a p sublevel, or 3 p orbitals.
- Similarly for :
 - $l = 2$ a d electron
 $m_l = -2, -1, 0, +1, +2$
 - $l = 3$ an f electron
 $m_l = -3, -2, -1, 0, +1, +2, +3$
- All orbitals within a given sublevel have the same energy.

Spin Quantum Number, symbol m_s

- This quantum number is associated with spin, possessed by all electrons (and other fundamental particles).
- Regardless of the values of the other quantum numbers, m_s may be only $+\frac{1}{2}$ or $-\frac{1}{2}$.
- These values correspond to a clockwise or counterclockwise spin, but we don't have any idea which is which!
- Electrons with the same value of m_s (either both $+\frac{1}{2}$ or $-\frac{1}{2}$) are said to have **parallel** spins; if the values are different (one at $+\frac{1}{2}$ and one at $-\frac{1}{2}$), the electrons are said to have **opposite** spins.
- Spin is usually represented by arrows pointing up or down.....

~~$\uparrow\uparrow$ (parallel)~~

$\uparrow\downarrow$ (opposite)

- Recall that when the Schrödinger equation may also be solved for many-electron atoms, there are many solutions for Ψ , each associated with a set of **quantum numbers**.
- Each set of four quantum numbers describes a **different** electron in the atom.
- In 1925, Wolfgang **Pauli**, a colleague of Bohr, proposed the **Exclusion Principle**:

In one atom, no two electrons may have the same four quantum numbers.

- The result of this is that only **two** electrons (with opposite spins) can fit into any orbital.....

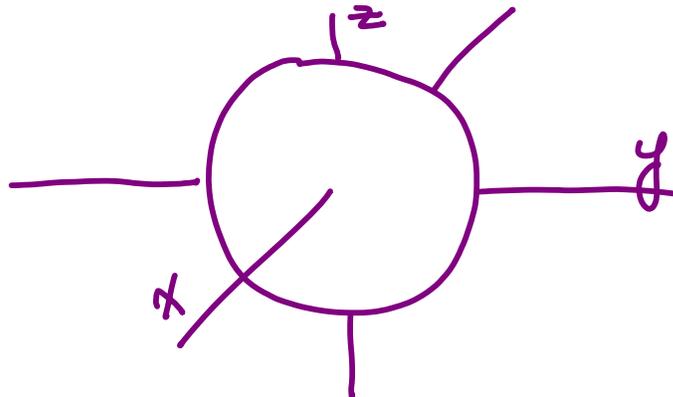
Values for Quantum Numbers through $n = 4$			
n	l	m_l	m_s
1	0 (1s)	0	$-\frac{1}{2}$ or $+\frac{1}{2}$
2	0 (2s)	0	$-\frac{1}{2}$ or $+\frac{1}{2}$
	1 (2p)	-1, 0, +1	
3	0 (3s)	0	$-\frac{1}{2}$ or $+\frac{1}{2}$
	1 (3p)	-1, 0, +1	
	2 (3d)	-2, -1, 0, +1, +2	
4	0 (4s)	0	$-\frac{1}{2}$ or $+\frac{1}{2}$
	1 (4p)	-1, 0, +1	
	2 (4d)	-2, -1, 0, +1, +2	
	3 (4f)	-3, -2, -1, 0, +1, +2, +3	

for each m_l

- We can use this chart to determine how many electrons we can fit in each energy level.....this works out to $2n^2$

Shape of s and p orbitals [MH5; 6.4, Figure 6.7]

- s orbitals are spherical; as n increases, the radius of the orbital becomes larger.
- These spheres are give a specific probability of finding the electron.
- So an electron in a 2s orbital is likely to be found further away from the nucleus than an electron in a 1s orbital.



- In p orbitals, the $\ell = 1$ sublevel, have electron probability density concentrated along the x, y and z axes:

Electron Configurations in Atoms [MH5; 6.5]

- Using the chart on page ~~264~~, we could assign quantum numbers to each electron in an atom. *112*
- Now we will assign electrons to specific energy levels, sublevels and orbitals.
- We do this using an **Electron Configuration**, which shows the number of electrons (indicated by a superscript) in each sublevel.
- The sum of the number of electrons in each sublevel must be equal to the total number of electrons in the atom....
- When determining an electron configuration, always begin with the electrons closest to the nucleus; those at $n = 1$.

EXAMPLE 1:

H: 1 electron; start at $n = \underline{1}$
 - only an s sublevel $\therefore \underline{1s^1}$

He: 2 electrons; start at $n = \underline{1}$
 $\therefore \underline{1s^2}$ $[2n^2 \Rightarrow 2(1)^2 = 2]$ - full

Be: 4 electrons; start at $n = \underline{1}$
 $\therefore \underline{1s^2}$ - go to $n = 2$; start at s
 $\therefore \underline{2s^2}$ (full) $\Rightarrow \underline{\underline{1s^2 2s^2}}$

EXAMPLE 2:

B: 5 electrons
 $\underline{1s^2} \underline{2s^2} \underline{2p^1}$

N: 7 electrons
 $\underline{1s^2} \underline{2s^2} \underline{2p^3}$

Cl: 17 electrons
 $\underline{1s^2} \underline{2s^2} \underline{2p^6} \underline{3s^2} \underline{3p^5}$
 $\underline{10e^-}$

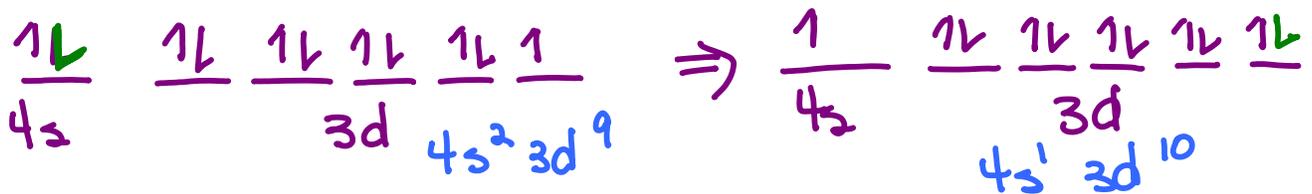
- So far, this doesn't seem too difficult.....In many cases, we simply slot electrons into the orbitals in increasing order of n value and, for the same n , in increasing order of orbital quantum number, l .
- This approach works for the first 18 elements, up to $_{18}\text{Ar}$, configuration $1s^2 2s^2 2p^6 3s^2 3p^6$.
- It is also consistent with MH5; figure 6.8.

- But after the 3p orbital has been filled, it looks like the 4s orbital is of lower energy.....so it fills next.
- In the next two atoms, K and Ca, the ground-state has electrons in the 4s orbital, giving $[\text{Ar}] 4s^1$ and $[\text{Ar}] 4s^2$ respectively.
- Note the **Noble Gas Configuration**.....one need only write the configuration past the preceding Noble Gas.
- In the next ten elements, Sc to Zn (the first transition series), the 3d orbital is filled. (After 4s, before 4p)

- There are two significant exceptions in electron configurations in the 3d subshell; Cr is one of them.
- The six electrons over the [Ar] core are arranged $4s^1 3d^5$ rather than $4s^2 3d^4$, both orbitals being partially filled.



- In this arrangement all six electrons are unpaired.
- Energies of all the orbitals are approximately equal, and this arrangement obeys Hund's rule and minimizes inter-electron repulsions.
- Towards the end of the transition series, with Cu, the energy of the 3d orbital has fallen below that of the 4s because of the increased nuclear charge, so the configuration is $3d^{10} 4s^1$.

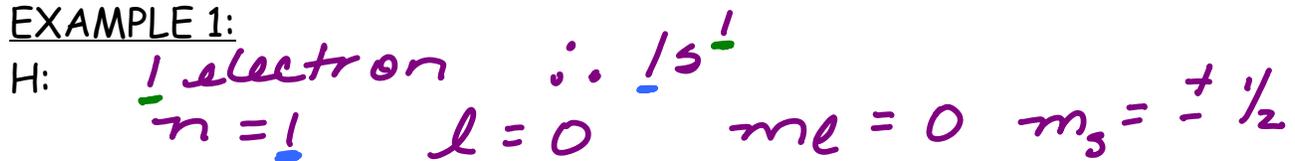


- Zn is, as expected, $3d^{10} 4s^2$. [Similar effects are seen in the second transition series.]

Relating Quantum Numbers and Electron Configurations

- Now we will actually write some sets of quantum numbers for electrons.....

EXAMPLE 1:



EXAMPLE 2: 7 electrons \therefore 1s² 2s² 2p³

N: 1st e⁻: n=1 l=0 m_l=0 m_s=+1/2
 2nd e⁻: n=1 l=0 m_l=0 m_s=-1/2
 3rd e⁻: n=2 l=0 m_l=0 m_s=+1/2
 4th e⁻: n=2 l=0 m_l=0 m_s=-1/2
 5th e⁻: n=2 l=1 m_l=-1 m_s=±1/2
 6th e⁻: n=2 l=1 m_l=0 m_s=±1/2
 7th e⁻: n=2 l=1 m_l=+1 m_s=±1/2
 all either (+) or (-)

- We can also determine whether or not a set of quantum numbers is correct for a particular electron in an atom....

EXAMPLE: Which of the following is a correct set of quantum numbers for a highest energy electron in As?

	n	l	m _l	m _s
x A)	3	1	0	+ 1/2
x B)	3	2	-1	+ 1/2
(C)	4	1	0	- 1/2
D)	4	2	+1	- 1/2
E)	4	0	0	+ 1/2

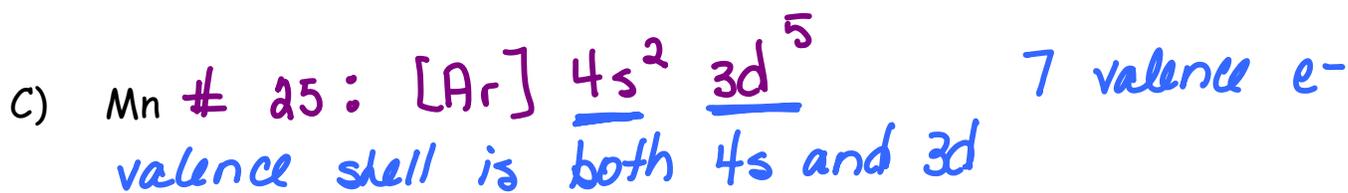
As: 33 electrons
^{18e⁻}
 [Ar] 4s² 3d¹⁰ (4p³) ^{highest energy}

n=4 l=1 m_l=-1, 0, +1
 m_s=±1/2

The Core plus Valence Shell Model

- The chemically important part of an atom is its **valence shell**, defined as **only** those subshells whose electrons influence chemical properties; valence and oxidation state in particular.
- It is only the valence shell electrons that participate in the formation of ions; gaining electrons to produce anions or losing electrons to produce cations.
- The main-group atoms from Group 13 to 17 can be confusing because the Periodic Table shows a filled d^{10} subshell from the core coming between the s and p subshells that constitute the **valence shell**.
- The transition atoms can also be confusing because here the ns subshell and the (n - 1) d subshell from the previous energy level are both part of the valence shell. * *d sublevel is NOT filled!*

EXAMPLES: Determine the valence shell for:



- There are eight main groups; for a main-group atom, the number of electrons in the valence shell is equal to either the group number [H and He are special cases] or the group number - 10.

Group 1 Li, Na, K, Rb, Cs, Fr	valence shell configuration ns^1 Alkali metals
Group 2 Be, Mg, Ca, Sr, Ba, Ra	valence shell configuration ns^2 Alkaline Earths
Group 13 B, Al, Ga, In, Tl	valence shell configuration $ns^2 np^1$
Group 14 C, Si, Ge, Sn, Pb	valence shell configuration $ns^2 np^2$
Group 15 N, P, As, Sb, Bi	valence shell configuration $ns^2 np^3$
Group 16 O, S, Se, Te, Po	valence shell configuration $ns^2 np^4$ Chalcogens
Group 17 F, Cl, Br, I, At	valence shell configuration $ns^2 np^5$ Halogens
Group 18 He ($1s^2$), Ne, Ar, Kr, Xe, Rn	valence shell configuration $ns^2 np^6$ Noble or Rare gases

- (He is in Group 18 because of its similarity to other atoms having a **filled** valence shell).
- Groups 1 and 2 are known as **s**-block atoms and Groups 13 to 18 are known as **p**-block atoms.
- Orbitals below the valence shell are referred to as '**core**' electrons.
- From the Periodic Table, you can determine the valence-shell electron configuration of any main-group atom from its position.
- Horizontal Rows of the Table may be denoted in two ways:
 - a) Period 1, 2, 3 corresponding to $n = 1, 2, 3 ..$ etc.
H-He, period 1. Li-Ne, period 2 etc.
 - b) Row is assigned differently with H and He ignored. Thus First-row elements are the series from Li to Ne, second-row elements from Na to Ar, etc.

Ionic Species [MH5; 6.7]

- Recall that ions are charged species which result from either the gain or loss of electrons.
- Electron configurations can also be written for ionic species.
- Anions are negatively charged species which are formed when an atom gains electrons.
- The electron configuration for an anion is the same as the atom which contains the identical number of electrons as does the anion...

EXAMPLE:

What is the electron configuration for the S^{2-} ion? The Br^{-} ion?

S^{2-} : S is #16 $\therefore 16e^{-} + 2e^{-} = 18e^{-}$

S^{2-} has same elect. config. as Ar

$[Ne] 3s^2 3p^6$

Br^{-} : Br is #35 $\therefore 35e^{-} + 1e^{-} = 36e^{-}$

Br^{-} has same elect. config as Kr; $[Ar] 4s^2 3d^{10} 4p^6$

Cationic Species

- Recall that cations are positively charged ions formed when an atom loses electrons.....
- When writing electron configurations for cations, one must first determine the orbital(s) from which the electrons were lost....
- The electrons lost when a cation forms are always lost from the valence shell.

EXAMPLES: Determine the electron configuration for:

A) Ca^{2+} $[Ca: [Ar] 4s^2] \Rightarrow Ca^{2+}: [Ar] 4s^0$

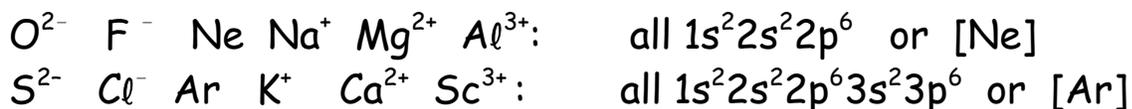
B) Bi^{3+} $[Bi: [Xe] 6s^2 4f^{14} 5d^{10} 6p^3]$ valence shell
-loses $3e^{-}$; lost from $6p \Rightarrow 6p^0$

C) Bi^{5+} -loses $5e^{-}$ (3 from $6p$, 2 more lost from $6s$)

$[Xe] 6s^0 4f^{14} 5d^{10} 6p^0$ - 121 -

- **Isoelectronic** species are atoms or ions with the same number of electrons arranged in the same way. *∴ same electron configuration*
- The following examples are ions having a noble-gas structure:

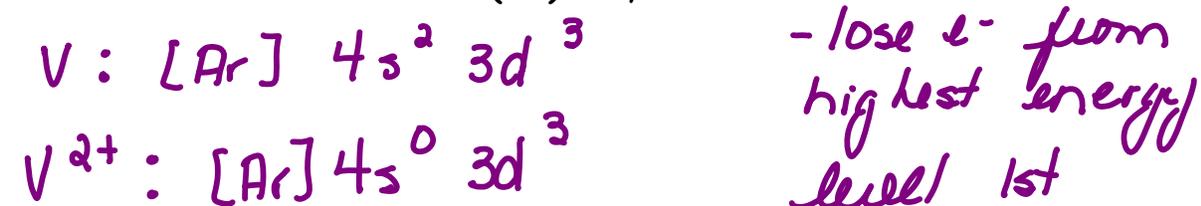
EXAMPLES:



- Since all these species have filled levels and sublevels, configurations characteristic of the unreactive or 'noble' gases, it is not too surprising that they are 'stable' species!
- When a transition metal forms a cation, the electrons are also lost from the valence shell, which includes the n s orbital and the $n - 1$ d orbital.....but remember that the electrons are lost from the s orbital first !!
- So....when electrons are lost from a transition-metal atom, giving a cation, any electrons remaining over the noble-gas core are always found in the d orbital(s).

EXAMPLES: Determine the electron configurations for:

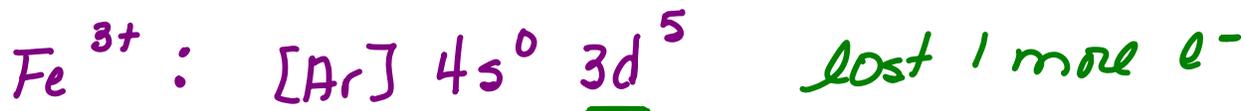
V atom → Vanadium(II) ion, V^{2+}



- Compare this result with the neutral Sc atom.
- Like neutral Sc, V^{2+} has three electrons over the [Ar] core, but the greater nuclear charge (more protons in nucleus) lowers the energy of the 3d below that of the 4s orbital....
- Iron behaves in a similar manner; the neutral Fe atom, $[\text{Ar}]3d^6 4s^2$,



loses electrons to form Fe^{2+} and Fe^{3+}



- Note that V^{2+} and Sc^0 , or Fe^{3+} and V^0 , are **NOT** isoelectronic pairs.
- They do have the same number of electrons over the [Ar] core (3 and 5 respectively), but the electrons are arranged differently in the orbitals.



- This difference is due to the increased nuclear charge (number of protons is greater than the number of electrons) in the cations.
- Electrons in a cation will take the lowest-energy arrangement possible.

ONE MORE EXAMPLE: Determine the electron configuration of:



* Valence shell
is both 4s and 3d



lost $2e^-$ from 4s

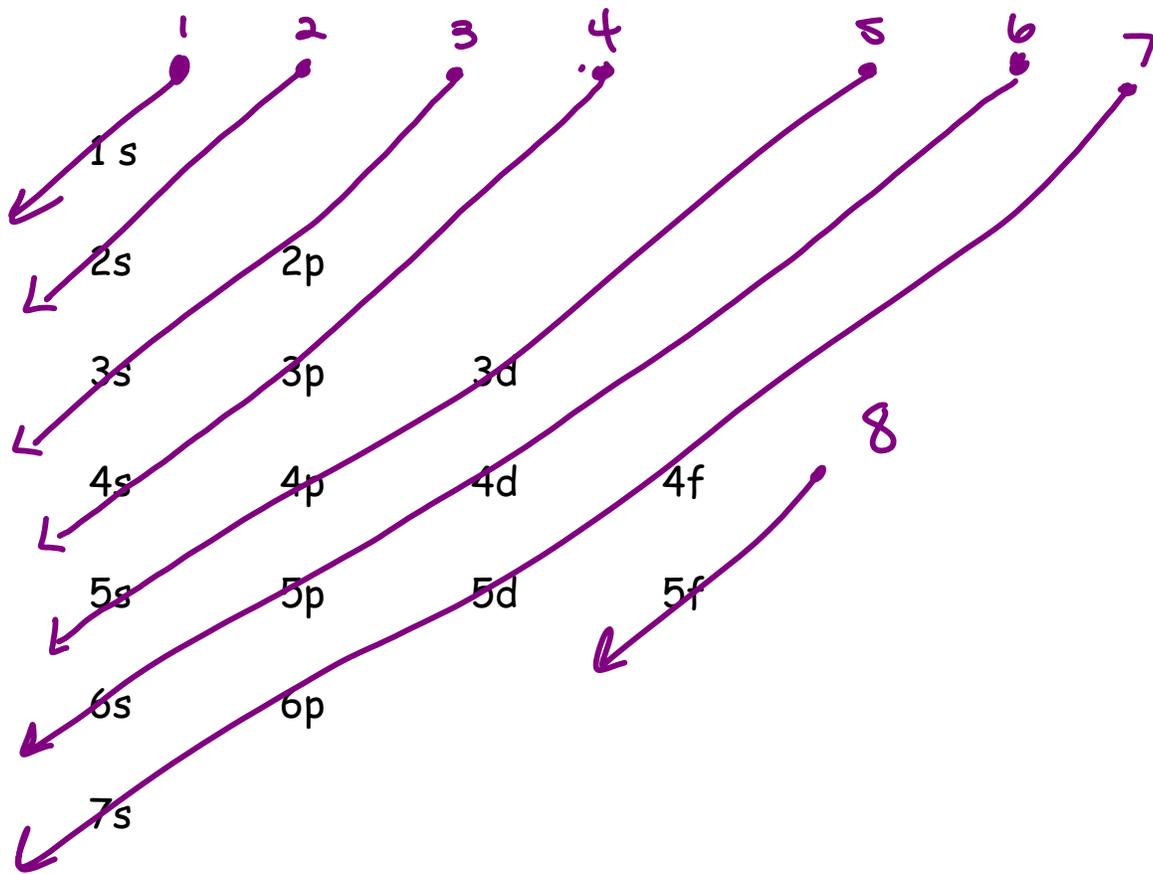


lost 5 more e^- from
3d

The Periodic Table and Electronic Configurations

- The Periodic Table is divided vertically into four blocks according to the subshell being filled: [see them color-coded in MH5; Figure 6.9] s-block in blue, p-block in green, d-block in pink, f-block in brown.
- Main Group atoms are those in which s or p subshells are being filled, other subshells being either full or empty.
- Transition elements, sometimes referred to as d-block atoms, are those in which d orbitals are being filled.
- Since each d orbital sublevel holds ten electrons, these fall into three series, filling respectively the 3d, 4d, and 5d orbitals.
- By convention, the last member of each series (Zn, Cd, and Hg) is thought of as a transition atom, even though the d orbital is full and is not disturbed in reactions. *can form Zn^{2+} , Cd^{2+} , Hg^{2+}*
- lose 2e⁻ from the s orbital
- The f-block elements, in which f orbitals are being filled. These orbitals hold a total of 14 electrons, so we have a series of 14 atoms known as the lanthanides, following (but not including) $_{57}La$, Lanthanum, in which the 4f orbital is filled.
- A second series following $_{89}Ac$, Actinium, contains 14 atoms known as the actinides, and the 5f orbital is irregularly filled.
- It consists entirely of radioactive atoms.
- Only $_{90}Th$, thorium, and $_{92}U$, uranium, occur in nature, the others have been synthesized in nuclear reactions.

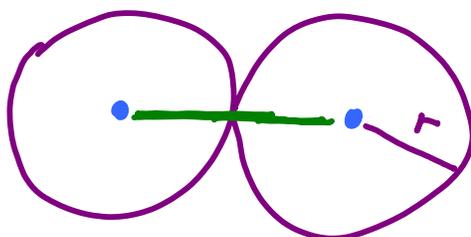
- A scheme to help you remember the order for filling the orbitals.....



Periodic Properties of Atoms [MH5; 6.8]

Atomic Size

- The size of the electron cloud is unlimited in extent, so the 'size' of a free atom cannot be exactly defined.
- A quantity called **atomic radius**, assumes a spherical atom and can be defined and measured.
- Atomic radius is taken to be one half the shortest distance of approach between atoms in an elemental substance; this gives us an effective size.....
- In a covalent bonding situation the size is easier to define; the covalent radius of an atom is the contribution that atom makes to the internuclear distance (or bond length).
- So the covalent radius of H is half the H—H bond length in H_2 .



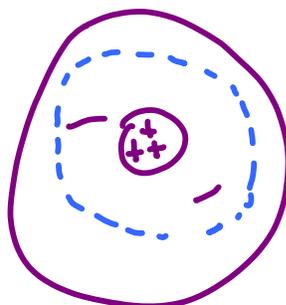
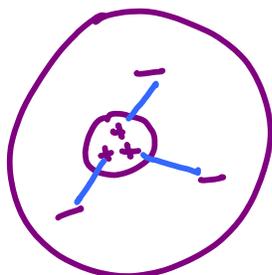
$$\text{Bond length} = 2r$$

- Ionic radius is used to describe ion sizes; the sum of the ionic radii equals the interionic distance.
- Loss of electrons (giving a cation) always leads to a reduction in size from the atomic radius:

Li atom
152 pm



Li⁺ cation + e⁻
90 pm radius.

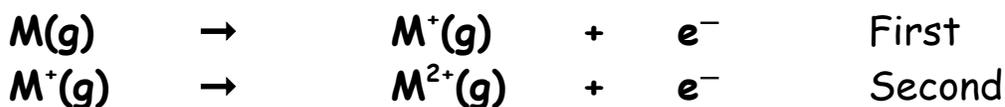


Ionization Energy [MH5; page 153]

- Ionization Energy, or I.E., is defined as the energy required to remove an electron completely (to infinite separation) from an isolated (gaseous) atom:



- An atom with several electrons will have successive I.E.'s



- Successive I.E. values always increase in magnitude because of the increasing ionic charge.
- Removal of an electron is always an energetically unfavorable (endothermic) process, but it varies in a periodic manner.....
- Generally speaking, I.E. increases from Group 1 through Groups 2, 13...18 as the number of electrons in the valence shell increases.
- Low I.E.'s are found when the valence shell contains only one electron shielded from nuclear attraction of the protons by the lower-energy core electrons. *eg) Li, Na, K*

EXAMPLE:



- H is an exception with I.E. 1312 kJ mol^{-1} because no core electrons are present.
 - Small anomalies are also found
- $$\begin{array}{l} \text{Be } (1s^2 2s^2) \quad \text{I.E. } 900 \text{ kJ mol}^{-1} \\ \text{B } (1s^2 2s^2 2p^1) \quad \text{I.E. } 801 \text{ kJ mol}^{-1} \end{array}$$
- This occurs because the electron lost in B, Boron, is the $2p^1$ electron, which is of higher energy than the $2s^2$.
 - A higher energy electron is more easily lost.

- As the next 5 electrons are added to the 2p orbitals, (B through Ne) the I.E. increases as the nuclear charge increases. But:



- The electron lost from the O atom is pushed out by the extra repulsion from the second electron in the same 2p_x orbital and thus O has a lower I.E. than N.

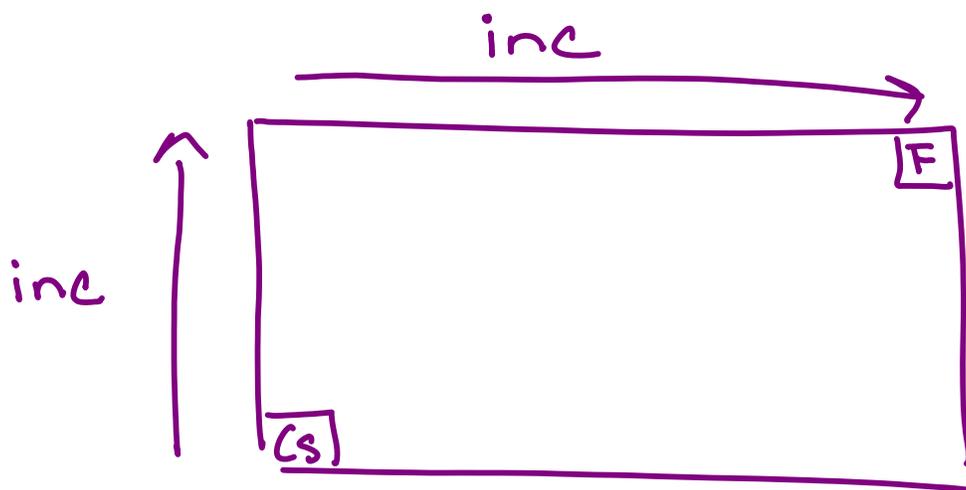
- For elements with similar valence shells, I.E. falls on going down the group:

Li	520	[He] 2s ¹
Na	496	[Ne] 3s ¹
K	419	[Ar] 4s ¹
Rb	403	[Kr] 5s ¹
Cs	377	[Xe] 6s ¹

group 1

- atoms become larger
 - valence e⁻ further away from nucleus
- ∴ easier to lose

General Ionization Energy trends in the Periodic Table:



Electronegativity [MH5; page 154]

- The tendency of an atom covalently bonded in a molecule to attract to itself the electron pair forming the covalent bond.
- The greatest electronegativity values are found with small non-metals.....

Some Electronegativity Values

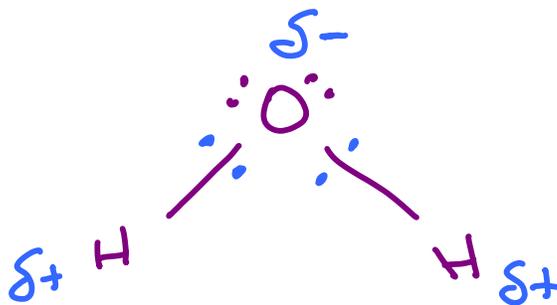
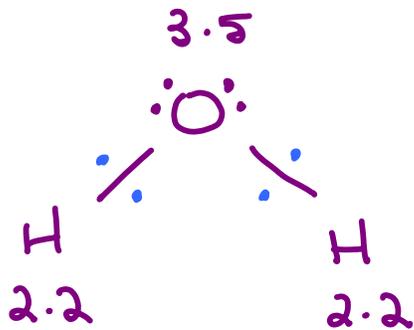
F	O	Cl	Br,N	I	S	C	H	Na
4.0	3.5	3.2	3.0	2.7	3.6	2.5	2.2	0.9

- Electronegativity is important in covalent bonding, because a bond between two atoms of different electronegativity will be **polarized** as a result.

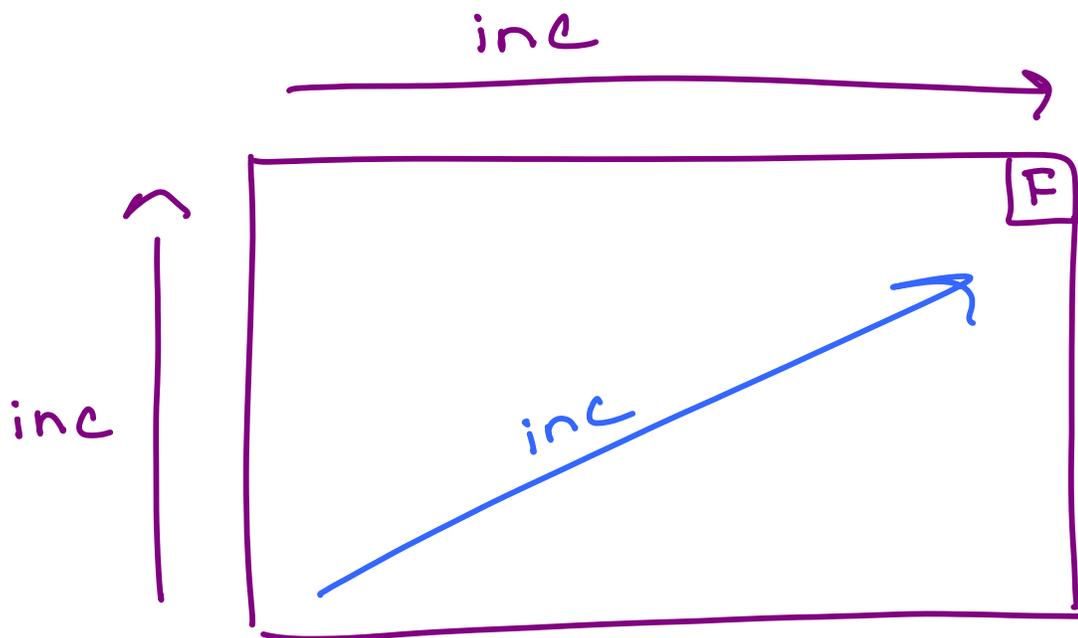
EXAMPLES:



H₂O:



General Trend for Electronegativity in the Periodic Table

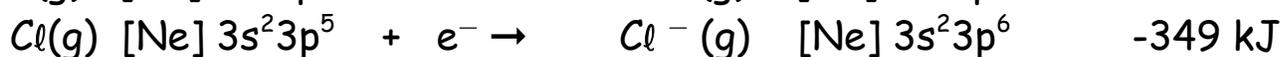
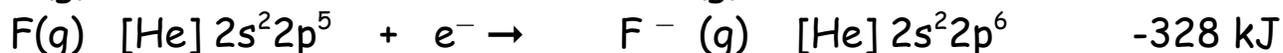
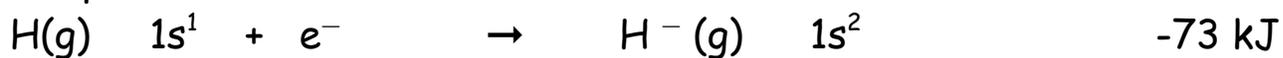


Electron Affinity

- This is opposite of I.E; a gaseous atom gains an electron



- This process may be favourable (exothermic) or unfavourable (endothermic).
- Favourable values of E.A. are found when a valence shell is being completed:



- These anions are formed when the element meets a reactive metal, e.g. $Li^{+} H^{-}$.

- Addition of a second electron is always unfavourable because of like-charge repulsion:



- Nevertheless the O^{2-} ion is very common, as it is stabilized by attraction to cations....

EXAMPLES:

In MgO: Mg^{2+} and O^{2-}

In BaO: Ba^{2+} and O^{2-}

In H_2O : $2 H^{+}$ and O^{2-}

