Historical Perspective – Atomic Structure

		1976	Custer’s Last Stand
Cathode rays, William Crookes	1879		
“Electron”, G. Johnstone Stoney	1881		
Hydrogen spectrum, Johann Balmer	1885		
Cathode rays, Eugen Goldstein	1886		
Electron e/m, J.J Thomson	1897	1897	Klondike gold rush
		1898	Spanish-American War
$E = hf$, Max Planck	1900		
		1903	Wright brothers flight at Kitty Hawk
Quantized radiation, Albert Einstein	1905		
Charge on electron, Robert A. Millikan	1909		
Nuclear atom, Ernest Rutherford	1911		
Hydrogen atom model, Niels Bohr Meaning of atomic number, Henry Moseley	1913		
		1914	World War 1 begins
		1917	Russian Bolshevik Revolution
		1919	Treaty of Versailles ends World War I
$\lambda = h/mf$, Louis de Broglie	1923		
Wave/mechanical atomic model, Schrodinger Uncertainty principle, Werner Heisenberg	1926		
Electron diffraction, Davisson and Germer	1927	1927	Transatlantic flight by C. Lindbergh
		1929	U.S. stock market crash, beginning of Depression
Neutron, James Chadwick	1932		
		1933	Adolf Hitler becomes Chancellor of Germany

Hahn & Strassmann discovered atomic fission 1939

1945. Hiroshima & Nagasaki Destroyed by fission bombs

Nuclear fusion bomb (H_2 bomb) at Bikini Atoll1952

1956. First nuclear fission power-Station, Calder Hall, Cumbria

Attempts to harness nuclear fusion, the Hunting of the quark.	1960s
Development of theories of matter Particles based on quarks and leptons.	1970’s
Discovery of bosoms, search for ‘Grand Universal discovery’.	1980s

Trends Across the Periods and Down the Groups of the Periodic Table

Atomic Radius

- increases going down a group
- decreases moving across a period

Why?

The same pattern generally follows for the IONS of the elements.
NOTE: The **POSITIVE IONS** are much **SMALLER** that their parents atoms while the **NEGATIVE IONS** are much **LARGER** that their parents atoms. Why should this be?

Ionization Energy (Ionization Potential)

This is the energy required to remove an electron from a neutral atom of an element or an ion in the gaseous state. It is usually given in kJ/mol.
i.e. The energy needed to remove 6.02×10^{23} electrons from a mole of atoms.

$$M_{(g)} + IE \rightarrow M^{+}_{(g)} + 1\acute{e}$$

NOTE: The ionization energy is the **first ionization energy**, the energy needed to remove the first electron. In your Data Book you will find a periodic table with the first ionization energies in kJ/mol.

A LOW ionization energy indicates that an electron is easily lost. The lowest numbers are found for the Alkali Metals (group I). A HIGH ionization energy indicates that an electron isn't easily removed. The highest values are found for the Inert Gases (group VIII).

Factors affecting ionization energy...

1: Nuclear Charge:
2: Radius:
3: Sublevel:
4. Half filled shells (For some reason half filled shells are more stable than other fractions)
(See anomalous electron configuration for Cu and Cr) ***(I.B. Favourite)***

Ionization energies generally INCREASE from LEFT to RIGHT across a given period.
Ionization energies generally DECREASE from TOP to BOTTOM as one goes down a group, due to the SHIELDING EFFECT of the inner shells.

Thus, the IEs range from Cs at 377 kJ/mol to He at 2370 kJ/mol.

The figure below shows both trends. The low numbers are for the Alkali Metals, while the "peaks" correspond to the Noble Gases.

Electron Affinity $X_{(g)} + e^{-1} \longrightarrow X_{(g)}^{-1} + \text{Energy}$

Electron Affinity is the energy released when an electron is added to a neutral atom. The elements that "need" electrons the most (Group IV and VII) have the highest electron affinities, while the elements that don't need extra electrons (Group I and II) will have low electron affinities.

Like ionization energies, there is an INCREASE from LEFT to RIGHT and a DECREASE from TOP to BOTTOM.
Why?
∴ Metals:

∴ Non-Metals:

Electronegativity

In 1960 Linus Pauling derived a set of values based on ionization energies and electron affinities which give and indication of attraction of an atom for electrons.

ELECTRONEGATIVITY is a measure of the attraction of an atom for the **electrons in the bond** between itself and another atom.
They range from a low 0.7 for Cs to a high of 4.0 for F.
i.e. Fluorine is the most electronegative element.
(NOTE: There are no Electronegativity values given for the Noble Gases, since they don't form bonds with other atoms normally.)

Electronegativity generally INCREASES from LEFT to RIGHT and DECREASES from TOP to BOTTOM.
Thus the most electronegative elements are found at the TOP RIGHT CORNER and the most electropositive elements are found at the BOTTOM LEFT CORNER.

∴ Metals:

∴ Non-metals:

Melting Point and Boiling Point

MP and BP generally DECREASE from LEFT to RIGHT across a period. With the exception of Groups I and II, MP and BP generally INCREASE as one goes down a group.
e.g. Fluorine and Chlorine are gases, Bromine is a liquid and Iodine and Astatine are solids.

ELECTRONEGATIVITY AND CHEMICAL BONDING

The difference in electronegativity between the atoms is an indication of the TYPE of bonding that the compound will have. The table below is a ROUGH indicator of how one can use the difference (by subtraction) in the electronegativity values to find the nature of the bond between most elements. This isn't an absolute scale and must be used as a rough guide to bond type.

Effect of Electronegativity on the Nature of Bonds

Electronegativity difference	Per	Percent of Ionic Character	Typ	Nature of Bond
0.2	1		Non-	Polar covalent…polarity if present isn't significant
0.4	4			
0.6	9			
0.8	15			
1.0	22		Polar	Covalent
1.1	26			
1.2	30			
1.3	34			
1.4	39			
1.5	43			
1.6	47			
1.7	50		50% 50%	Ionic Covalent
1.8	55		Ionic	
1.9	59			
2.0	63			
2.2	70			
2.4	76			
2.6	82			
2.8	86			
3.0	89			
3.2	92			

Other factors such as bond angles and hybridization come into play and contradict the values shown here.
e.g. The electronegativity difference between Na (0.9) and Cl (3.0) is 2.1. The table indicates an ionic bond and Sodium Chloride is an ionic compound.

When two atoms bonded together covalently are of the same element the sharing of those electrons is equal and the bond is said to be a **pure covalent bond.**

Compounds made of different elements, with different electronegativities will form a polar bond. The electrons will be attracted to the atom with the higher electronegativity, more of the time.

See: Electronegativity Notes

Atomic Theory – What atoms are made of

ATOM

–the smallest unit of an element, made of many particles, the most important are protons, neutrons and electrons — protons and neutrons in the central nucleus, electrons in the outer regions, have no net charge (i.e. the number of protons = the number of electrons)

ATOMIC NUMBER

-the number of protons in the nucleus of an atom (because atoms are uncharged, the atomic number will also tell you how many electrons are present in the atom)

-is characteristic of an element (i.e. each element can be identified by its won atomic number)

ELECTRON

–very small particle located in the outer region of an atom, each electron has a charge of –1

-each electron has a mass about 2000 times smaller than that of a proton or a neutron

-it is the loss or gain of electrons which makes uncharged atoms into charged ions

ION

-atom which has either lost or gained electrons and therefore has either a net negative or a net positive charge (i.e. loss of electrons produces positively charged ions and gain of electrons produces negatively charged ions.)

ISOTOPE

See Notes: MASS SPECTROSCOPY

-although different atoms of the same element will always have the same number of protons (i.e. the same atomic number), they may have slightly different numbers of neutrons (making their mass numbers different). Such atoms are known as isotopes. Isotopes are usually represented in the following manner: $^{A}_{Z}X$ where X represents the chemical symbol for the element. A is the mass number and Z is the atomic number.

-Isotopes are often simply listed with identifying mass numbers (their atomic numbers are all the same). Example: Three common isotopes of lead are lead-206, lead-207 and lead-208.

MASS NUMBER

-the total number of protons (i.e. the atomic number) and neutrons in the nucleus

-can vary with different isotopes of the same element

NEUTRON

-uncharged particles located in the nucleus of the atom, has about the same mass as a proton

-atoms of the same element may have different numbers of neutrons (such atoms are said to be isotopes)

NUCLEUS

-central, massive, positively charged core of the atom: contains the neutrons and protons of the atom

PROTON

-each proton has a charge of +1 and a mass about equal to a neutron, located in the nucleus of the atom

PRACTICE PROBLEMS

1. A neutral atom of a particular element has an atomic number of 32 and a mass number of 173. Identify this element and state how many electrons, protons and neutrons it contains.
2. The nucleus of an atom of bromine contains 35 protons and 45 neutrons. What is the atomic number and the mass number of the atom?
3. Two common isotopes of copper are copper-63 and copper-65. How many protons, neutrons and electrons does each one of these isotopes possess?
4. a) Determine the atomic number, the mass number and the number of protons, electrons and neutrons in a Br^{1-} ion made from the atom described in question 2 above.
   b) Determine the atomic number, the mass number and the numbers of protons, electrons and neutrons in a Cu^{2+} ion made from the atom of copper-63.
5. Define the terms: electronegativity, electron affinity, and ionization energy and explain their trends on the periodic table of elements.
6. Draw the Bohr model for the following: a) $^{42}_{19}K$ b) $^{65}_{30}Zn^{2+}$

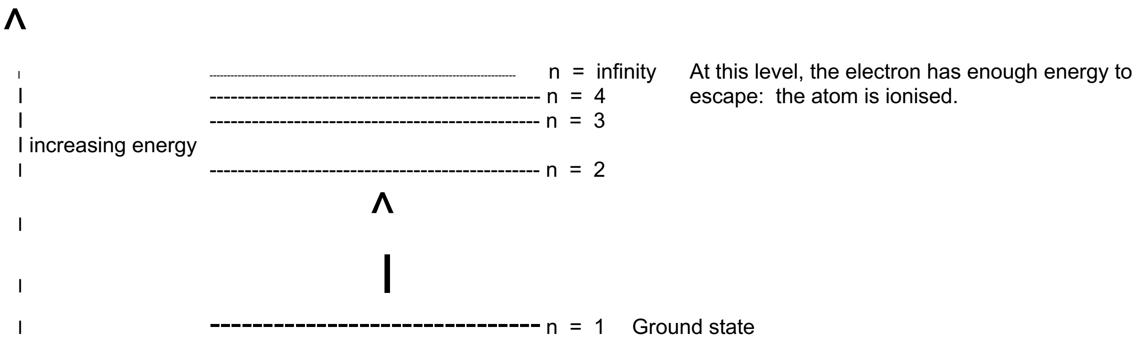
Where are the electrons exactly?

Although the mass of an atom is concentrated in the nucleus, it is the electrons which are largely responsible for chemical behaviour. Once the existence of the nucleus was established, models of the atom began to concentrate on the electron configuration of an atom (i.e. the arrangements of electrons around the nucleus) to try to provide clues to the chemical behaviour of atoms.

The Bohr Model of the Atom

Bohr proposed that electrons could possess only specific quantities of energy called quanta (singular is quantum). Each specific quantity corresponded to a specific energy level located a particular distance from the nucleus. Bohr identified each energy level using an integer, n, called the **principal quantum number**. This number could have any whole-number value from once to infinity. The larger the value of n, the further from the nucleus is the energy level and the greater the energy associated with the electron.

In the diagram below, the single electron of hydrogen is represented by an arrow. The electron normally remains in the lowest energy level (n=1). When in its lowest energy level, the electron is said to be in its **ground state**. If energy is added to the atom, the electron many absorb enough energy to move to a higher energy level. The electron is then said to be in an **excited state**. When the electron falls back to lower energy levels it emits energy in the form of light. (This is why each element has a **characteristic line spectrum**.)



The principal energy levels of the hydrogen atom come closer together as the value of the principal quantum number, *n*, increases from 1 to infinity.

The principle energy levels of the hydrogen atom come closer together as the value of the principal quantum number, n, increases from 1 to infinity.
Bohr proposed that the electron configurations of atoms with more that one electron follow the same pattern as is shown above for hydrogen. He also outlined two rules that apply as electrons are added to different energy levels:

1. Additional electrons always occupy the lowest available energy level.
2. The maximum number of electrons that can be placed in any particular energy level is given by the formula: maximum no. of electrons = $2n^2$ where n = the value of the principle quantum number.

SOMMERFELD'S ADDITIONS TO THE BOHR MODEL

Arnold Sommerfeld showed that each of the principal energy levels (except the first one) split into two or more sublevels having slightly different energies. These sublevels can be identified using the **secondary quantum number**, *l*. Numerically, for any given n, *l* may range from *l* = 0 to *l* = n-1. The number of sub-levels in an energy level is equal to the value of n. It is common to describe the sublevels by the letters **s, p, d, f** … in order of increasing energy instead of by the corresponding numerical values. The tables below summarize the relationship between n and l. Fill in the blanks.

Value of l	0	1	2	3	4	5…
Letter description	s	p	d	f	g	h…

Value of n	**Values of l (range from l = 0 to l = n-1)**	**Letter designation**
1	0	s
2		
3		
4		
5		

From such diagrams and other aspects and other aspects of Sommerfeld's work the following became apparent:

1. The number of sublevels in a given energy level correspond to the value of n.
   e.g. when n = 2 there are two sublevels: 2s and 2p

2. n s sublevel can hold 2 electrons, a p electron can hold 6, a d sublevel can hold a maximum of 10 and an f sublevel can hold up to 14 electrons (each successive level holds 4 more electrons than its predecessor).

3. Because the energy levels are closer together as the value of n increases, the energy of sublevel 4s is less than that of 3d, so 4s fills before 3d. This can get a bit confusing at higher levels of n. A pattern for orbital filling is shown below.

These observations led to the revelation that similarities among elements within Periodic Table groups and the very structure of the Periodic Table could be explained using electron configurations…

ELECTRON CONFIGURATIONS AND THE PERIODIC TABLE

In making up the periodic table, elements are arranged in order by increasing atomic number, and elements with similar properties are placed in the same vertical column.

For example, Li, Na and K are all listed in group 1A. They are very similar. Some of the properties they have in common are:

Using similarities in properties to decide which columns elements go into results in the following shape for the periodic table.

s^1 s^2 **p^1 p^2 p^3 p^4 p^5 p^6**
d^1 d^2 d^3 d^4 d^5 d^6 d^7 d^8 d^9 d^{10}

f^1 f^2 f^3 f^4 f^5 f^6 f^7 f^8 f^9 f^{10} f^{11} f^{12} f^{13} f^{14}

The numbers of columns in each section of the periodic table are:

___ ___ ___ ___

N.B. These numbers are the same as the number of electron occupying the s, p, d, f subshells as described in Observation #2 above!!

The periodic table gives us an easy way for figuring out **electron configurations**. The subshells being filled are given below:

	1s	
2s		2p
3s		3p
4s	3d	4p
5s	4d	5p
6s	5d	6p
7s		
	4f	
	5f	

THE WAVE MECHANICAL MODEL OF THE ATOM

Although the Bohr model of the atom is very useful for determining basic electron configurations, it isn't adequate to account for all experimental evidence. A probability or quantum mechanical model must be used that treats electron as a wave rather than as a particle. The work of max Planck and Albert Einstein in the early 1900's had indicated that electromagnetic waves could behave like little discrete bundles, or photons, of *hf* energy — that they could have particle characteristics. Bohr had proposed that the energy of electrons in atoms was quantized.

Then in 1924, **Louis de Broglie** discovered electrons could be bent or diffracted by passing a beam of them through a crystal in much the same way as light is diffracted by a prism. This led to the conclusion that, like light, electrons had a wave type character. De Broglie put his ideas on a mathematical basis:

Electron as a wave : photon $E = hf$
Electron as a particle: mass $E = mc^2$
de Broglie Equation $\lambda = h / m v$

De Broglie's equation correctly predicts the wavelength of a particle of mass and velocity. This equation states that a particle of mass *m* travelling at a velocity, v, will have associated with it a wavelength, λ. Thus, this equation expresses the wave-particle duality of nature.

Note that as mass, m becomes larger, λ becomes smaller. For a particle of large mass, λ is very small, such that the relationship has little meaning. However, for a tiny particle such as the electron, with a mass of $\sim 10^{-28}$ g, the associated wavelength becomes large enough to be significant. The wavelength of a typical electron in an atom is $\sim 3 \text{ x}10^{-8}$ cm.

Following the notion that the electron could be treated as a wave, Werner Heisenberg, (1925), realized that the dual particle and wave nature of the electron made it impossible to determine both its energy and its position at the same time (**Heisenberg's uncertainty principle**) the way Bohr's strict orbit-type model did.

In order to describe an object in terms of its position and energy, visible light of low energy must be used, so that upon contact, the velocity of the object does not change. Thus, to see an electron, the probe would have to be light of a very small wavelength, because the electron is so small. When the wavelength is small, the frequency is high, ($\lambda \propto 1/f$), and the energy is large. Thus the "bullet"of *hf* energy needed to locate the position of the electron would surely disturb it upon collision, changing its velocity and hence its momentum (mass times velocity). Hence, it can be seen that the probe which one needs to look at something is bound to change the object's momentum, then one cannot locate precisely the electron.

The uncertainty principle states that for tiny particles such as electrons, the position and momentum cannot be determined simultaneously, i.e to say that one cannot speak of definite pathways in which the electron is moving. All we can do is deal with the probability, or chance of locating it. Heisenberg's argument is irrefutable, and Bohr's model for electrons in definite pathways did not obey this important principle.

Instead, the mathematical equations of Erwin Schrodinger, (1926), had to be used to describe the behaviour of the electron as a wave. A solution to Schrodinger's wave equation for an electron indicates:

a) where the probability of finding the electron is high and where it is low for a given energy level.

b) Information about which orbital within an energy sublevel the electron occupies.

Orbitals are volumes of space where the probability of finding the electron is high. Each orbital may contain a maximum of two electrons.
We know that each s sublevel can contain only 2 electrons (see your work on electron configurations and the Periodic Table) so it consists of just one 2 orbital. Each p sublevel may contain up to 6 electrons and so consists of three p orbitals. Each d sublevel may contain a maximum of 10 electrons and so consists of 5 d orbitals, etc. All the electrons contained in a particular sublevel of a neutral atom will have the same energy, no matter which of its available orbitals it occupies.

THE THIRD QUANTUM NUMBER - MAGNETIC QUANTUM NUMBER (m_l)

Distinguishing one orbital from another one in the same sublevel requires a third quantum number, the magnetic quantum number (m_l).
This quantum number describes how an orbital is oriented in space relative to other orbitals.
Possible values of m_l range from $-l$ to $+l$.
This means that when $l = 0$ (as for an s subshell), m_l can only have the value of 0 so an s subshell has only one orbital.
A p subshell has $l = 1$ which means that m_l can have the values of –1, 0, +1. Thus, a p subshell has three orbitals….etc.

A d orbital can have ______ possible orientations, and the f orbitals can have _______.
Note that as the orbital quantum number goes from s to p to d to f, the number of orientations increases as odd numbers from 1 to 3 to 5 to 7.

Shapes of the orbitals

Determined using the Schrodinger Equation
s-orbital, $l = 0$, present in every energy level, spherical
p-orbitals, $l = 1$, m_l = ? ? ?
present in every energy level except the first ($n = 1$), three orbitals of equal energy ... degenerate orbitals.
d-orbitals, $l = 2$ m_l = ? ? ?
Present in every energy level except the first and the second, five orbitals of equal energy.

THE FOURTH QUANTUM NUMBER- SPIN QUANTUM NUMBER (m_s)

The **Pauli Exclusion Principle** states that no two electrons in the same atom may have identical values for all four quantum numbers.
If two electrons occupied the 1s orbital of an atom, each electron would have n = 1, l = 0 and m_l = 0. Because electrons act as tiny magnets though, each member of a pair of electrons will spin in a different direction (i.e. either clockwise or counter-clockwise). This means that one of the electrons in the 1s sub-shell described will have $m_s = +1/2$ and the other will have $m_s = -1/2$.

Because each orbital can contain a maximum of 2 electrons, the spin quantum number ensures the Pauli Exclusion Principle holds true.

Review

Definition: An orbital is a 3-dimensional space where an electron is likely to be found.

The *principal quantum number-n- identifies the energy possessed by the electrons.*

$= 1 \longrightarrow \infty$

$= 2n^2$ *number of electrons in an energy level*

= *n types of orbitals*

$= n^2$ *actual orbitals*

There are an infinite number of energy levels, but as you move further away from the nucleus (higher in energy level) the levels are closer and soon become indistinguishable (recall: spectra).

There are four types of orbitals whose shapes have been worked out, using wave mechanics. They are referred to by letters: **s, p, d,** and **f.** These are the initial letters of the words ‘sharp’, ‘principal’, ‘diffuse’, and ‘fundamental’, originating from work carried out on the hydrogen spectrum which led to our present-day view of energy levels and sublevels.

n=1	1 type of orbital	1 actual orbital	“s” orbital, spherically shaped
n=2	2 types of orbitals	2^2 actual orbitals(4)	an “s” orbital, same shape as above, only bigger, there are also three “p” orbitals...
n=3	3 types of orbitals	3^2 actual orbitals	one “s”, 2 “p”, ___ “d” orbitals
n=4			

Questions

1. Explain why p-orbitals are labelled ‘ p_x ’, ‘ p_y ’, and ‘ p_z ’.
2. How many electrons can be held in (i) an s-orbital, (ii) a set of three p-orbitals
3. Use one word in each case to describe the shape of (i) an s-orbital, (ii) a p-orbital.
4. Fill in the following Table...

Energy Level	# and type of orbitals	Max. # of electrons in each set of orbitals	Max. # of electrons in energy level
n=1	one s		
n=2	one s three p		
n=3	one s three p five d		
n=4	one s three p five d seven f		

Order of Filling

Now, we will consider the order in which orbitals are filled. First we need to know something about their energy levels...

n = 4	
	__ __ __ __ __ 3 d
	__ 4 s
	__ __ __ 3 p
n = 3	__ 3 s
	__ __ __ 2p
n = 2	__ 2 s
n = 1	__ 1 s
Bohr Energy Levels	**Modern Atom Orbitals**

Note: Now that with more orbitals available, many more electronic transitions are possible, thus explaining all the extra lines in the spectra observed earlier. The letters correspond to the first letter in each series of lines observed.

The electrons fill according to the following set of rules...

The Aufbau Principle

Each electron to an electron configuration will occupy the lowest available energy level.

The Pauli Exclusion Principle

No two electrons within an atom can have the same set of quantum numbers.

Hund's Rule

Electrons must be distributed among orbitals of equal energy in such a way that as many electrons remain unpaired as possible.

Review of Quantum Numbers:

Think of Quantum numbers as a type of postal code for electron...

n	The principal quantum number	Tells you the shell the electron is in
l	The secondary quantum number	Tells you what type of orbital the electron is in (s, p, d, f, etc)
m_l	The magnetic quantum number	Tell you the orientation of the electron
m_s	The spin quantum number	Tells you the spin on the electron

PRACTICE PROBLEMS

1. Fill in the following chart.

Value of n	Values of *l* (ranges from 0 to n-1)	Values of m_l (ranges from $-l$ to $+l$)	Sub-shell identity	Number of orbitals
1	0			
2	0 1			
3			3s 3p 3d	

2.a) For n = 5, what are the possible values of l?
b) For l = 2, what are the possible values of m_l?
c) Which quantum numbers must be the same in order that orbitals be degenerate (a) in a hydrogen atom, and (b) in a many- electron atom?
3. Within a given shell, how do th energies of th es, p, d and f subshells compare for a many electron atom? How do the energies of the orbitals of a given subshell compare?
4. Explain why the effective nuclear charge experienced by a 3s electron in magnesium is larger than that experienced by a 3s electron in sodium.

5. What is the maximum number of electrons in an atom that can have the following quantum numbers:
a) $n = 3$, (b) $n = 3, l = 2$, (c) $n = 4, l = 3, m_l = 2$, (d) $n = 2, l = 1, m_l = 0, m_s = -½$

6. List the possible values of the four quantum numbers for a 2p electron in beryllium.
7. Write the electron configurations for the following atoms using the appropriate noble-gas inner core for abbreviation: (a) Ca (b) Ge (c) Br (d) Co (e) Hf (f) Cr (g) Cu (h) Sb

8. Identify the group of elements that corresponds to the following electron configuration:
a) $1s^2 2s^2 2p^4$ (b) [Ne] $3s^2 3p^5$ (c) [Ar] $4s^1$ (d) [Ar] $4s^1 3d^5$ (e) [Kr] $5s^2 4d^{10} 5p^1$

9. Identify the group of elements that corresponds to the following electron configurations:
a) [noble gas] $ns^2\ np^3$ (b) [noble gas] $ns^2 (n-1)d^{10} np^2$ (c) [noble gas] $ns^2 (n-1)d^6$

10. What is the subshell designation for each of the following cases:
a) $n = 2, l = 0$ (b) $n = 4, l = 2$ (c) $n = 5, l = 1$ (d) $n = 4, l = 3$?

11. Why can the 2p subshell of an atom hold more electrons than the 2s subshell?

12.Write the electronic configurations of the following species:
a) Na^{+1} (b) Mg^{+2} (c) O^{-2} (d) H^{-1} (e) Fe^{+2} (f) Cr^{+3} (g) Cu^{+1} (h) Br^{-1}

13. In chart form, generate a complete set of quantum numbers for the last four electrons in an atom having the electronic configuration: [Kr] $5s^2\ 4d_1^1 4d_2^2$

ATOMIC SPECTROSCOPY

The spectra produced by certain gaseous substances, consists of only a limited number of coloured lines with dark spaces between them. These discontinuous spectra are called **atomic or line spectra**. Each element has its own distinctive line spectrum – a kind of atomic fingerprint, this regularity in the line spectra was the key to understanding electronic structure.

The most extensively studied atomic spectra is that of hydrogen. Hydrogen is the simplest of the atoms, consisting of a single proton and a single electron. The emission spectrum of hydrogen is of interest because this spectrum was the first to be completely explained by a theory of atomic structure, by the scientist Niels Bohr.

Atoms absorb and emit radiation as light of fixed, characteristic wavelengths when excited. This absorption and emission of light is now known to correspond to electrons within the atom moving away from the nucleus (energy absorbed) or closer to the nucleus (energy emitted).

Atoms emit and absorb energy of only certain wavelengths (bright or dark lines in the spectrum) because electrons don’t move randomly away from and toward the nucleus, but may only move between certain fixed, allowed “orbitals”, each of which is at a definite distance from the nucleus.

When an electron moves from one of the fixed orbitals to another orbit, the attractive force of the nucleus changes by a definite amount that corresponds to a specific change in energy. The quantity of energy absorbed or emitted by an electron in moving from one allowed orbit to another is called a quantum (photon), and the energy of a particular quantum is indicated by the wavelength (or frequency) of the light emitted or absorbed by the atom. The energy of a photon is given by the Planck equation:

$$E = hf \qquad E = hc / \lambda \qquad c = \lambda f$$

where 'f' is the frequency of light emitted or absorbed and λ is the wavelength (m), corresponding to that frequency (has units of cycles per seconds, since cycles is a dimension-less quantity, the unit is written s^{-1}, reciprocal seconds.

In the SI system one cycle per second is a hertz, Hz, $1\ Hz = 1\ s^{-1}$), and h is the Planck's constant, it has the units of energy x time, and has a value of 6.626×10^{-34} Js.

The speed of light in a vacuum, $2.9979 \times 10^{8}\ ms^{-1}$, is one of the fundamental constants of nature and doesn't vary with the wavelengths or any other properties of light.

A quantum is like a package or bundle of something that is available only in specific and separate amounts. A quantum is somewhat like the scoops of ice cream, you can order one scoop, or two scoops, but not 1.5 or 2.35 scoops. The amount of ice cream that you can get is "n" times the size of the scoop.
Something that is **quantized** is restricted to amounts that are whole-number multiples of the basic unit, or quantum, for the particular system; energy exists only in discrete amounts called quanta (the energy of a photon). A quantum of radiant energy is called a **photon**, and each photon has energy equal to hf. (Quanta is the plural of quantum.)

A whole-number multiplier that specifies an amount of energy (or anything else that is quantized) is called a **quantum number**.
Quantum theory is a general term for the idea that energy is quantized and the consequences of that idea.

Bohr postulated that the energy of an electron when it is in a particular orbit was given by the formula:

$$E_n = -\frac{\text{constant}}{n^2}$$

where n is the number of the orbit as counted out from the nucleus (n = 1 means the first orbit, n = 2 means the second orbit, etc.) and is called the principle quantum number.

The proportionality constant in Bohr's theory is called the **Rydberg constant** (given the symbol $\mathbf{R_H}$) and has the value 2.179×10^{-18} J.

The electron energy value becomes negative, with its value lowered, energy has been released.

According to Bohr's theory, if an electron were to move from an outer orbit (designated as n_{outer}) to an inner orbit (designated by n_{inner}), a photon of light should be emitted, having energy given by:

$$\Delta E = E_{inner} - E_{outer} = -R_n \left(\frac{1}{n^2_{inner}} - \frac{1}{n^2_{outer}} \right)$$

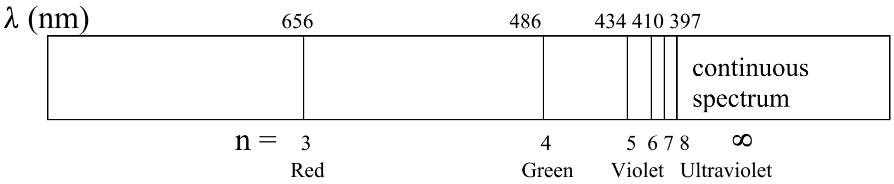
The wavelength, λ of this photon would be given by the Planck's formula as:

$$\lambda = \frac{hc}{\Delta E}$$

The spectral lines observed in the visible spectrum of hydrogen arise from transitions from upper states back to the n = 2 principal quantum level. Calculate the predicted wavelengths for the spectral transitions of the hydrogen atom from the

$n = 6 \longrightarrow n = 2$
$n = 5 \longrightarrow n = 2$
$n = 4 \longrightarrow n = 2$
$n = 3 \longrightarrow n = 2$,

levels in atomic hydrogen. These transitions to the n = 2 level are referred to as the Balmer Series of lines in the spectrum, as shown in the diagram below:



Because the differences between energy levels are limited in number, so are the energies of the emitted photons. Therefore only certain wavelengths (or frequencies) are observed for the spectral lines. The intervals between the frequencies of the lines become smaller and smaller towards the high frequency end of the spectrum until the lines run together or converge to form a continuum of light.

Bohr performed calculations of wavelengths for various values of the principal quantum number, n, and found that the predicted wavelengths from theory agreed exactly with experimental wavelengths measured with a spectroscope. Bohr even went so far as to predict emissions by hydrogen atoms in other regions of the electromagnet spectrum (ultraviolet, infrared) that had not yet been observed experimentally but that were confirmed almost immediately.

In addition to the visible lines in the hydrogen emission spectrum, atomic hydrogen also emits short-wavelength ultraviolet radiation (for example, sunburns are a result of such radiation from the sun). Ultraviolet emissions arise from transitions back to the ground state (n = 1) level – this is referred to as the Lyman Series.

Beginning with the n = 6 level, calculate the wavelengths for the ultraviolet emissions of atomic hydrogen.

Bohr's simple atomic theory of an electron moving between fixed orbits helped greatly to explain observed spectra and formed the basis for the detailed modern atomic theory for more complex atoms with more than one electron. The spectra of larger atoms are considerably more complicated than that of hydrogen, but generally a characteristic spectrum is seen.

The hydrogen spectrum consists of five series of lines, named for the men who discovered them. The first interpretation of the hydrogen spectrum was an empirical one based on the observed spectrum, **Lyman (n = 1), Balmer (n = 2), Paschen (n = 3), Brackett (n = 4), Pfund (n = 5).**

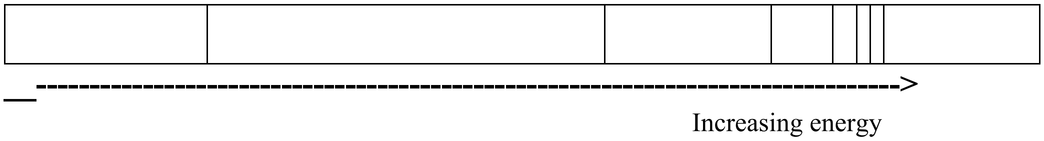
Complete Assignment: Quantum Mechanics Calculation

A number of common metallic elements emit light strongly in the visible region when ions of the metals are excited. A number of metallic elements from Groups I and II have especially bright emission lines in the visible light region. The emissions are so strong and characteristically coloured that these elements can often be recognized by the colour they impart when aspired into a burner flame. For example, Li^{+1} impart a red colour, Na^{+1}, a yellow/orange colour, K^{+1} a violet colour, Ca^{2+} a brick red colour, Sr^{2+}, a brighter red colour, Ba^{2+} a green colour.

Upon examination with the spectroscope, it is noted that the spectra of these ions contain several additional lines, but generally the brightest line in the spectrum corresponds to the colour imparted to a flame.
The red lights of many advertising signs are produced by discharge lamps containing the gas neon, and orange street lamps are discharge tubes containing sodium vapour.
One of the lines in the spectrum of caesium is used to define the unit of the second. The light from this line has 9.192×10^9 vibrations per second.

Assignment

1.The following diagram represents the atomic emission spectrum of hydrogen.



a) Explain why it is composed of lines, and say what each line indicates.
b) Why do the lines become closer together as you read from left to right?
c) state in which direction frequency increases.
d) What do the transitions in these series all have in common?

Bonding

Chemical bonding between atoms involves the interaction of the electrons in the valence shells of the atoms. There are **three fundamental types of chemical bond**:
1) ionic, 2) covalent and 3) metallic,
although there are examples of bonds intermediate between these.
The bond type depends on the attraction for electrons of the atoms involved, i.e. their electronegativity. If the elements have very different electronegativities then ionic bonding results. If both of the elements have quite high electronegativities then the bonding will be covalent, whereas if they both have low electronegativities they form a metallic bond. Each type of bonding gives rise to distinctive physical properties for the substances formed.

Ionic Bonds

How do these work?

$$\begin{array}{lll} \text{metal} \; + & \text{non-metal} \xrightarrow{\text{transfer of electrons}} & \text{metal}^{+} + \text{non-metal}^{-} \\ \text{low IE} & \text{High IE} & \text{(isoelectronic with noble gas)} \\ \text{low EA} & \text{High EA} & \end{array}$$

An ion is a charged sphere surrounded by a uniform electric field and therefore attracts oppositely charged spheres in all directions – no particular orientation is favoured, thus ionic bonding is considered non-directional, i.e. the forces of attraction are non-directional ions, ∴ tend to cling together in large clusters known as ionic crystal lattices (ionic giant structures, ionic crystals). Ionic lattices are made up of a regular array of positively and negatively charged ions, held together by electrostatic attraction. The lattice extends in three dimensions. The particular arrangement of ions depends on the relative charges and sizes of the ions.

The formation of an ionic compound can be considered as the sum of a number of individual processes…
-converting the elements into gaseous atoms
-losing and gaining electrons to form the cations and anions
-finally the coming together of these ions to form a solid compound

Lattice Energy: is the standard enthalpy change when one mole of an ionic substance is formed from its gaseous ions.

The magnitude of the lattice energy depends upon the nature of the ions involved:

1) the charge on the ions: the greater the charge, the greater the electrostatic attraction and hence the lattice energy
2) the size of the ions: the larger the ions, then the greater the separation of the charges and the lower the lattice energy.

Example:
a) LiCl, NaCl
b) NaF, NaI
c) MgO, BaO

Covalent Bonding

How do these work?
Covalent bonding occurs between atoms that have quite high electronegativities, i.e. between two non-metals. In covalent bonding the two atoms involved share some of their valence electrons. The attraction of the two nuclei for these shared electrons results in the atoms being bonded together.

Example:

The Octet Rule

When forming covalent bonds, the atoms involved, other than hydrogen, tend to form bonds until they are surrounded by eight valence electrons. Therefore: # bonds = 8 - # valence electrons

Examples:
Carbon:
Oxygen:
Nitrogen:

Two covalent bonds between atoms constitutes a double bond, e.g. O_2

Three covalent bonds between atoms constitutes a triple bond, e.g. N_2

Polar Covalent Bonds

When two atoms bonded together covalently are the same element, the sharing of those electrons is equal and the bond is said to be a pure covalent bond. Compounds made of different elements, with different electronegativities will form a polar bond. The electrons will be attracted to the atom with the higher electronegativity, more of the time.

Example: H F

Coordinate Covalent Bond (Dative Bonds)

Up until now we have always assumed that each element found in a covalent bond was responsible for providing one electron each to the bond. In a coordinate covalent bond, both electrons are contributed by one atom, e.g.

NH_4^{+1} H_3O^{+1} CO N_2O NHO_3

A coordinate bond differs from a covalent bond in only one respect. What is this?

Resonance Structures

Single bonds are longer than double bonds. Double longer than triple. (Look up the bond lengths in your Data Book)

Consider the Lewis structure for SO_3…

All of the above structures are equivalent, each has a double bond and two single bonds. So you would expect that if the bond lengths were measured there would be some differences, right! Well, that isn't the case. The bond lengths are all the same. It is theorized that one pair of electrons is spread over all three bonds. These are called **delocalized electrons**.

Covalent compounds with fewer than eight outer shell electrons per atom

When the elements with fewer than four outer-shell electrons per atom form compounds they usually lose those electrons to form ions. However, for small atoms, the relevant ionization energies may be so high that covalent bonding occurs instead. Since there are fewer than four electrons available for sharing, there will be fewer than eight outer – shell electrons per atom in the resulting compound.

Look at the ionic radii of elements with fewer than four electrons in their outer shells and select the three most likely to form covalent compounds. Explain your choice.

Draw Lewis structures for the following:

$BeCl_2$

BF_3

$AlCl_3$

How many outer-shell electrons are there around the central atom?

The above molecules exist in certain conditions, but in each case there is a tendency for the ‘stable octet’ to be reached by means of coordinate bonding.

Example:
The molecule formed by the combination between NH_4 and BF_3…

Covalent compounds with more than eight outer-shell electrons per atom

If the noble gas rule or the octet rule always applied, no atom could have more than eight electrons in its outer shell. As a result, no atom could have more than four single covalent bonds (or the equivalent) associated with it. The octet rule always applies for elements in the first two periods of the Periodic Table (H to Ne) but many other elements show a covalency greater than four in some of their compounds.

Examples:
PF_5 BrF_5 SF_6 SiF_6^{-3} PCl_6^{-1} IF_7 XeF_3

Outermost shells of twelve electrons are quite common.
Only elements in the third and subsequent rows can do this because they make use of the unused d-orbitals.
The heavier noble gases do form a few compounds. Why?
Neil Bartlett at the University of BC prepared the first Noble gas compounds.

Lewis Structures

Lewis Structures are used to show which atoms are bonded together in a molecule. A single bond between atoms occurs when one pair of electrons (i.e. two electrons) are shared between 2 atoms. A double bond results when two electron pairs are shared and the sharing of three electron pais is a triple bond.

STEPS FOR LEWIS STRUCTURE CONSTRUCTION

STEP 1- Decide which atoms are bonded together and arrange the atoms on your page to reflect your decision, (see the “skeletal structures, p.225). It helps to first determine a “central atom”, an atom to which many of the other atoms are bonded. Usually, the central atom is the atom which requires the most bonds to complete its valence octet. Another way to determine the central atom is usually the least electronegative (i.e. Si in SiF_4 or S in $SOCl_2$) Caution - this does not always work, especially where hydrogen is involved. Hydrogen in never the central atom.

STEP 2- Count all the valence electrons.

Example: BF3	B → 1 atom x 3 valence electrons = 3 e
	F → 3 atoms x 7 valence electrons = 21 e
	TOTAL valence electrons = 24 e

NOTE: The charge on an ion indicates whether it contains extra electrons (negative ions) or has lost electrons (positive ions). Be sure to take these gains and losses into account where necessary.

Example: SO_4^{2-}	-add two electrons to the total number of valence electrons contributed by one atom of S and four atoms of O
NH_4^{1+}	-subtract one electron from the total number of valence electrons contributed by one atom oh N and 4 atoms of H

STEP 3- Place 2 electrons (i.e. one pair of electrons) in each bond.

STEP 4- Complete the octets of the atoms attached to the central atom by adding electrons in pairs.

STEP 5- Place any remaining electrons on the central atom.

STEP 6- If the central atom does not have an octet, form double bonds. If necessary, form triple bonds.

NOTE- There are EXCEPTIONS to the Octet Rule

1. The valence shell for H is completed by 2 electrons (1 electron pair).
2. The valence shell for Li and all members of its family is completed by 2 electrons (1 electron pair).

3. The valence shell for Be is completed by 4 electrons (2 bonding pairs).
NOTE: Although Be is an alkaline earth metal and therefore expected to form ionic compounds with non-metals, its ionization energy is too high for this to occur. Instead, it forms covalent bonds with a high degree of ionic character.

4.The valence shell for B is completed by 6 electrons (3 bonding pairs).
NOTE: Although the other members of its family will form ionic compounds with most non-metals, B doesn’t for the same reason sited above for Be. It, too, will form covalent bonds with a high degree of ionic character.

5. Valence electrons of elements of the third and subsequent rows of the Periodic Table may absorb enough energy during bonding so that some or all are excited into their own unfilled d

orbital (one electron per orbital). This means that many more bonds then expected may form. (e.g. P with 5 valence electrons may form up to 5 bonds and S with 6 valence electrons may form up to 6 bonds.

6. Some atoms, ions and molecules have orbitals containing a single unpaired electron. These are called **paramagnetic** because the unpaired electron(s) is/are affected by a magnetic field. Paramagnetic substances have an ODD number of valence electrons so no matter how hard you try, your Lewis structure will always show an unpaired electron. e.g. NO and NO_2

Assignment

1. Draw the Lewis electron dot structure for:
(a) CH_4 (b) CH_2Cl_2 (c) PCl_3 (d) PO_4^{-3} (e) BrO_3^{-1} (f) NO^{+1} (g) HCN (h) CH_2O

2. Draw the Lewis electron dot structure for:
(a) SO_3 (b) O_3 (c) NO_3^{-1} (d) NO_2^{-1} (e) CO_3^{-2} (f) $HCOO^{-1}$