THE WAVE MECHANICAL MODEL OF THE ATOM

The Birth of the Quantum Theory

At the beginning of the 20th century it was thought that the theories and ideas of physics and chemistry could explain just about every known phenomenon. However, classical theory could not explain several observations:

a. the spectral distribution of radiation emitted by a heated body, known as blackbody radiation,
b. the photoelectric effect, (ejection of electrons by radiation),
c. the fact that the spectra of certain atoms showed discrete lines
d. the various postulated models for electrons in atoms.

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. These "wavefunctions", denoted by the Greek letter Ψ (psi) can be described mathematically by sine functions. This is a reflection of the fact that waves can sometimes have particle-like behaviour, and particles can behave as waves.

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 energy $E = hf$ — that they could have particle characteristics. Planck explained blackbody radiation, and Einstein explained the photoelectric effect. 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 $\lambda = \frac{h}{m v}$

De Broglie's equation correctly predicts very small particles, e.g. electrons would show wavelike character. Thus, the electron would be expressed as having wavelength, λ, of a particle of mass, m and velocity, v.

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 $\sim 3 \times 10^{-8}$ 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.

[To explain the Heisenberg's Uncertainty principle, consider the following situation:
Waves in the ocean, next to a beach. In order for a wave to be disturbed, it must hit something of roughly the same size or of bigger size than the wavelength. What will happen when the wave runs into a pebble? A boulder instead?
Hence, to see exactly where an electron is, what would be a characteristic of the light that we would bounce off of it?
If light with a very small wavelength (high frequency, high energy) struck the electron, what would happen? ?We would lose information about the electron's velocity.
If we hit it with a long wavelength (low energy and frequency), we would not gather information about its position (see boulder-pebble analogy above).
Thus, we will never be able to know an electron's velocity and position at the same time.
The best we can do is calculate the **probability** of where an electron might be.**]**

The Heisenberg's uncertainty principle states that for tiny particles such as electrons, the position and momentum, (mass x velocity) 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.

An orbital is sometimes referred to as a charge cloud, charge density is greatest nearest the nucleus, where the probability of finding the electron is great.

Sommerfeld’s addition 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: $l = 0$ up 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.

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

The tables below summarize the relationship between *n* and *l*.
Fill in the blanks.

Energy level, n	**Values of *l* (range from *l* = 0 to *l* = n - 1)**	**Letter designation**
1	0	1s
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. An *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:

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 electrons occupying the s, p, d, f sublevels as described in Observation #2 above!!

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

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

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 sublevel), m_l can only have the value of 0, so an s sublevel has only one orbital:
n = 1 $l = 0$ $m_l = 0$ (i.e. only one orbital possible)

A *p* sublevel has $l = 1$ which means that m_l can have the values of $-1, 0, +1$. Thus three orbitals possible:
Thus, a *p* sublevel has three orbitals: p_x p_y p_z

A *d* sublevel, $l = 2$ can have m_l = _ _ _ _ _ possible orientations, thus _____ orbitals;

the *f* sublevel can have $l = 3$ can have m_l = _ _ _ _ _ _ _ possible orientations, thus _____ orbitals.

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, dumb-bell shaped or hour-glass shape.

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, $m_s = \pm \frac{1}{2}$

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:

$n = 1$ $l = 0$ $m_l = 0$

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 $m_s = + \frac{1}{2}$ and the other will have $m_s = - \frac{1}{2}$

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

Review of Quantum Numbers:

Think of Quantum numbers as a type of postal code for an electron:

n	The principal quantum number	Tells you the main energy level the electron is in
l	The secondary quantum number	Tells you what type of orbital the electron is in, the shape, (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

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.

Interpretation of orbitals in terms of quantum numbers:

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 + three "p" orbitals
n = 3	3 types of orbitals	3^2 actual orbitals	one "s"+ 3 "p" type + 5 "d" type
n = 4			

Review Practice 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	Total # of orbitals in an energy level	Max. # of electrons in the 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			

Electron Configuration: Order of filling electrons in atoms

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

n = 1	1s				
n = 2	2s	2p			
n = 3	3s	3p	3d		
n = 4	4s	4p	4d	4f	
n = 5	5s	5p	5d	5f	5g

From the above we obtain the following orbital diagram in a many-electron atom:

Periodic Table row number	**Order of filling**	
	__ __ __ __ __ 3 d	/\ **Increasing Energy**
n = 4	**__ 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.

Filling Electron Energy Levels

Hydrogen	$_1H$	1e	1s	
Helium	$_2He$	2e	$1s^2$	
Lithium	$_3Li$	3e	$1s^2\ 2s^1$	
Beryllium	$_4Be$	4e	$1s^2\ 2s^2$	
Boron	$_5B$	5e	$1s^2\ 2s^2\ 2p_x^{\ 1}$	
Carbon	$_6C$	6e	$1s^2\ 2s^2\ 2p_x^{\ 1}\ 2p_y^{\ 1}$	**Note: Hund's Rule**

Now complete electron configuration up to $_{20}$ Calcium.

What happens when scandium, $_{21}Sc$, is filled?

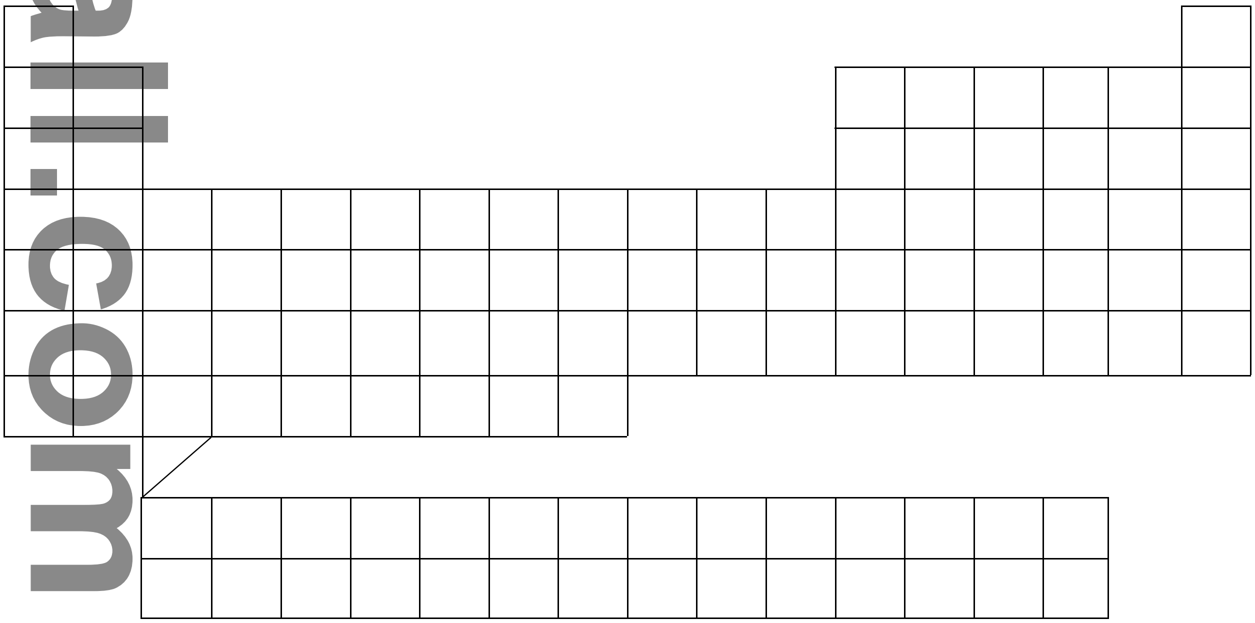
Note the exception for chromium and copper:

Fill electron configuration up to $_{54}Xe$:

Abbreviated Electronic Structure:
Example: Potassium can be written as: [Ar] $4s^1$

Electron Configuration of Ions:
Write the electron configuration for :
Na^{+1}
Fe^{+3}
Br^{-1}

Periodic Table and Electronic Configuration:



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	1 3 5

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 sublevel compare for a many electron atom? How do the energies of the orbitals of a given sublevel 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] $ns^2 (n\text{-}1)d^{10} np^2$ (c) [noble gas] $ns^2\ (n\text{-}1)d^6$

10. What is the sublevel 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 sublevel of an atom hold more electrons than the 2s sublevel?

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] $5s^2\ 4d_1{}^1 4d_2{}^2$