
Atomic Structure

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I. What is Light?

Debate in 1600's: Since waves or particles can transfer energy, what is light?

Newton – light energy is transferred by particles

Huygens – light energy is transferred by waves

Types of Waves: Transverse and longitudinal

Properties of Waves

Rectilinear propagation

Reflection

Refraction

Diffraction

Interference

Since diffraction and interference can only be explained using wave ideas, the electromagnetic wave theory of light was generally accepted by the middle 1800's.

Parts of a wave

wavelength (λ) meters, centimeters, Angstroms

frequency (n) cycles per second or Hertz

velocity (v) meters per second, centimeters per second

amplitude

$$v = \lambda n$$

Light waves are also called electromagnetic waves because they have both an electric and magnetic wave component.

There are many types of electromagnetic radiation – all of which travel at the same speed in a vacuum (3×10^8 m/s) but have different average speeds in different materials. The symbol “c” is often used for the speed of light in equations.

Types (in increasing order of frequency)

Radio waves, microwaves, infrared, visible, ultraviolet, x rays and gamma rays.

High frequency radiation is more dangerous than low frequency. The next slide shows us why.

Problems with the wave formulation of light

1. According to classical wave theory the energy of a light wave should depend on its amplitude, but this does not match the results from light emitted by a hot object.

Solution: Max Planck proposed that the electromagnetic energy radiated by a hot object is bundled in packets called quanta. These packets are now called photons.

$$E=hn$$

h (Planck's constant) = 6.63×10^{-34} J/Hz

Thus high frequency light has more energy per packet and more destructive power.

2. Photoelectric Effect - emission of electrons from a surface when electromagnetic radiation of appropriate frequency is shone on the surface.
(This is how "Solar Cells" work.)

If the intensity of light was increased, there was no increase in the KE of emitted electrons, but as the frequency of light increased, the KE of electrons did increase.

Solution: Albert Einstein proposed that light energy hitting the surface was bundled in Planck's packets (photons) with $E=hf$ per packet.

$$E = f + KE$$

f = energy needed to get electron off surface

KE = energy of emitted electron

E = energy of incoming photon = hf

As a result our modern idea of light incorporates a dual nature. Light can have wave and particle characteristics.

And if light can have a dual nature, what about electrons and other “particles”?

The Atomic Model

Thomson (1900)

Discovery of electron and proton properties

Proposed "jelly-filled doughnut" model of the atom

Rutherford (1910)

Gold foil leaf experiment proved small, dense positively charged nucleus with lots of empty space

Diameters

Atom	10^{-10} m
Nucleus	10^{-14} m
Proton	10^{-15} m
Neutron	
Electron	10^{-18} m

Bohr (1910-1920)

1. Electrons are particles that travel in circular orbits about the nucleus.
2. Orbits are quantized - only certain ones are allowed- the lowest one is called the ground state.
3. Energy is absorbed going from lower to higher orbits (lower ones are closer to the nucleus, higher ones are farther away). Energy is emitted going from higher to lower.
4. Energy levels get closer together as we go farther from the nucleus.

Chadwick

Discovered neutron about 1930. Why so late?

The Bohr model works well for hydrogen but not for any other element. We need a better model!

A new approach - Quantum Mechanics

deBroglie - wave particle duality

$$\lambda = \frac{h}{mv}$$

Heisenberg uncertainty principle

$$\Delta p \Delta x \geq \frac{h}{4\pi}$$

Schrodinger wave equation

Incorporates ideas of Bohr, deBroglie and Heisenberg to give a wave equation (Ψ) which describes the motion of the electron around the nucleus as a type of wave motion. The electron's path is quantized because it must form an integral number of wavelengths.

The Big Idea

Quantum mechanics makes use of the Schrodinger equation to study the behavior of small particles going at high speeds. Classical mechanics studies large particles going at relatively slow speeds.

Since electrons are small particles going at high speeds the electron (and thus chemistry) can only be understood through the use of quantum mechanics.

Quantum numbers

Four numbers (conditions) must be met to solve the Schrodinger equation. These are called quantum numbers. They can be thought of as an electron's address.

<u>letter</u>	<u>Name</u>	<u>Property</u>	<u>Values</u>
n	principal quantum number	energy level	1,2,3....
l	angular momentum quantum number	energy sublevel	0 to (n-1)
m_l	magnetic quantum number (momentum in z direction)	# of orbitals in sublevel	-l to +l
m_s	spin quantum number	# of electrons in an orbital	$\pm 1/2$

How are the quantum numbers used ?

1) Each individual number can be used to calculate the numerical value of a property of the electron.

n	energy
l	angular momentum
m _l	angular momentum in the z (magnetic) direction
m _s	spin

Good to remember - max # of electrons in any energy level = $2n^2$

2) Together they can be used to get the wave function Ψ .

How can Ψ then be used?

1. First choose a set of n, l, m_l, and m_s and solve for Ψ

2. Dirac found that Y^2 is a probability function (tells us how likely it is to find the electron at a location) so square the function Y .
3. Into Y^2 substitute values for x , y , and z coordinates to get the probability of the electron being at that point
4. Repeat for all space
5. This generates a "shape" for that electron location - this shape is called the electron cloud

Shapes

1. Each sublevel is spherical
2. Sublevels are divided into orbitals

The quantum numbers generate the electron cloud shapes so that we know the size, shape, and orientation of the electron probability cloud in space for each electron as follows :

n	size of cloud
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l	shape of cloud
m_l	orientation of cloud in space

There are special letter names that we give to the l quantum number sublevels

- The $l=0$ sublevel is the “s” sublevel. “s” orbitals are spherical.
- The $l=1$ sublevel is the “p” sublevel. The 3 “p” orbitals are dumbbell shaped and combine to make a spherical cloud.
- The $l=2$ sublevel is the “d” sublevel. The 5 “d” orbitals combine to make a spherical cloud.
- The $l=3$ sublevel is the “f” sublevel. The 7 “f” orbitals combine to make a spherical cloud.

Spectroscopic notation

When writing electron addresses chemists often use a shorthand notation called spectroscopic notation for electron configurations. To write in this notation remember that:

$l = 0$	s sublevel	1 orbital	2 electrons
$l = 1$	p sublevel	3 orbitals	6 electrons
$l = 2$	d sublevel	5 orbitals	10 electrons
$l = 3$	f sublevel	7 orbitals	14 electrons

This allows for a condensed form of notation. For example the 6 electrons in energy level 2 and the p sublevel would be referred to as $2p^6$

Now let's write electron configurations for the elements on the periodic table. This will enable us to understand better and somewhat predict oxidation numbers, bonding, shapes of molecules, properties of compounds and more! You can see that this is a very important skill.

Thankfully the placement of the elements in the periodic table is on the basis of electron configuration.

Electron Configurations

The filling of electron orbitals

To predict how many electrons will be in each energy level and sublevel we need to know the energies of electron orbitals. We will use as a general rule the idea that electrons will fill the lowest energy orbitals available. This is called the *Aufbau principle*.

Due to the increasing closeness of the energy levels and the sublevel splitting of the energy level the energy sublevels from one level start to overlap the sublevels of the next energy level at $n = 3$.

As a result of the overlap described above the electrons fill the orbitals of energy level 1 and 2 completely but do not fill energy level 3 completely until part of energy level 4 is filled.

Electron configurations

The filling of the energy levels, sublevels, and orbitals is often summarized with the following 3 laws.

1. *Aufbau principle* - electrons fill the lowest energy levels first (notice that all p orbitals are equal in energy to each other, they are degenerate; the same holds for d and f orbitals) Use the Periodic Table as your guide.
2. *Hund's Rule* - "electrons don't pair unless they have to" the minimum energy (most stable) configuration is to have the maximum number of electrons in a sublevel unpaired and to have all with the same value for m_s .
3. No two electrons can have the same set of quantum numbers. This is the *Pauli Exclusion principle* – this is shown in the solving of the Schrodinger equation.

The Periodic Table is an invaluable aid in determining the order of sublevel filling.

Remember:

- . blocks of two will correspond to the filling of the s sublevel (alkali and alkaline earth metals)
- . blocks of 6 the p sublevel (this includes the halogens and noble gases)
- . blocks of 10 the d sublevel (the transition metals)
- . blocks of 14 the f sublevel. (the lanthanide and actinide series)

Exceptions:

1. Major (know)

- Cr and Mo are $s^1 d^5$ and not $s^2 d^4$. This can be explained by the extra stability of a half-filled d sublevel
- Cu, Ag and Au are $s^1 s^{10}$ not $s^2 d^9$. This can be explained by the extra stability of a full sublevel.

2. Minor (be aware)

- Nb, Ru, Rh, Pd, Pt
- Many of the Lanthanide and Actinide series

Unpaired Spins

The condensed notation we have used above does not show the individual orbitals. According to Hund's rule there should be unpaired electrons in some of the elements. These unpaired electrons result in diamagnetism and paramagnetism.

Paramagnetic substances are those that contain unpaired spins and are attracted by a magnet.

Diamagnetic substances do not contain unpaired spins.

We can predict and show these unpaired spins by writing the outermost electron configuration showing the individual orbitals such as p_x , p_y , p_z . For example a configuration of $2p^4$ for oxygen could be shown as $2p_x^2, 2p_y^1, 2p_z^1$.

Another useful way to visually show this is by using an "orbital diagram" using box notation where boxes represent orbitals.