Chapter 7: Historical Review

Discovery of the electron

1807 Davy suggested electrical forces held compounds together

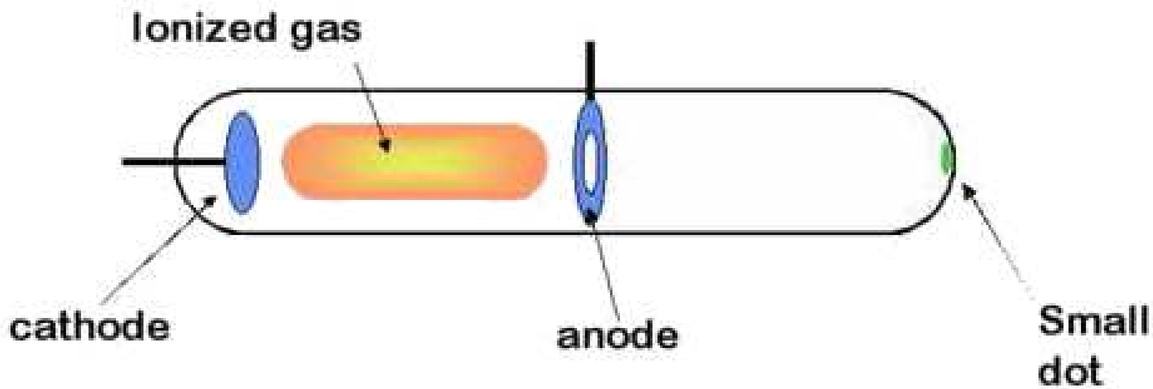
1833 Faraday's electrolysis experiments shown electricity needed to free elements from compounds

1891 Stoney: electricity exists as e^-

1897 Thomson measured e^- properties

Historical Review

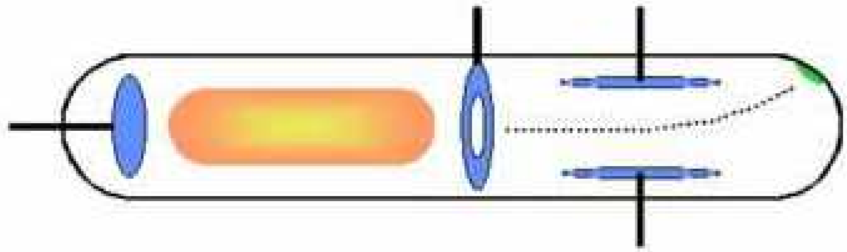
Discovery of the electron



Thomson **Discovered cathode rays were composed of electrons**

Historical Review

Discovery of the electron



Thomson electric/magnetic fields moved dot

Historical Review

Discovery of the electron

Thomson couldn't measure mass or charge of electron

Could measure mass : charge ratio

= 6×10^{-12} kg/C

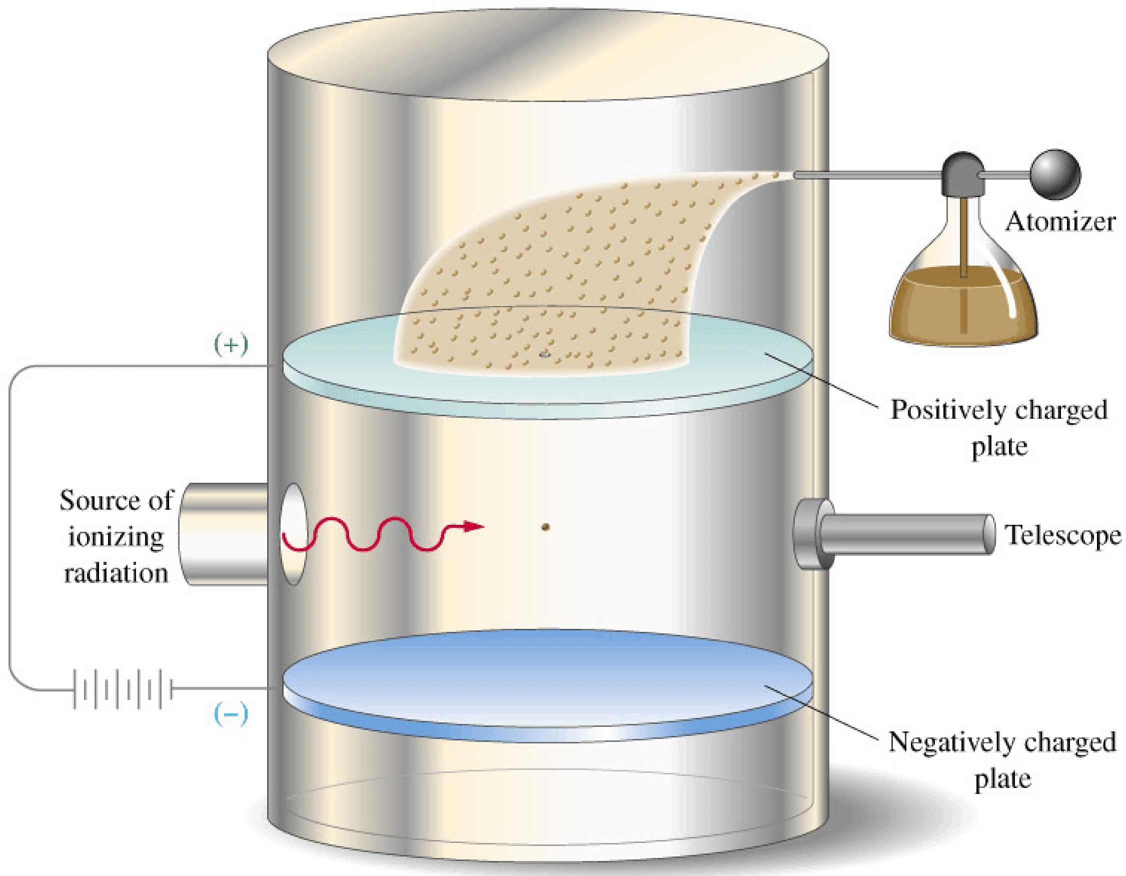
Columb (C) = SI unit of charge

Historical Review

Discovery of the electron

Millikan measured electron charge

Applied electric fields to charged oil drops



Historical Review

Discovery of the electron

Millikan measured electron charge

Electron charge: -1.602×10^{-19} C

Once charge AND mass/charge ratio were known, the mass of the electron could be determined

Historical Review

Discovery of the electron

m_e = (mass/charge ratio) x charge

modern value = 9.109×10^{-31} kg

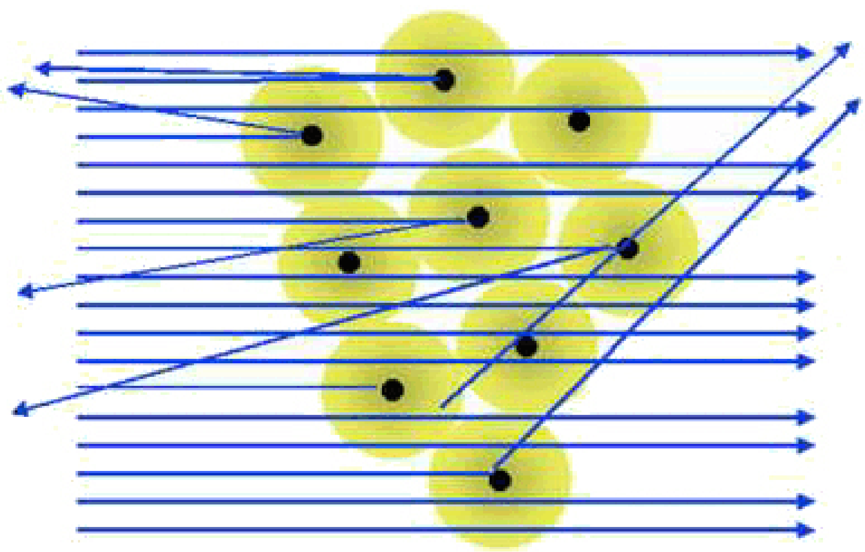
Historical Review

Discovery of the nucleus

1909 Rutherford fired alpha particles at metal foils

1 in 8000 alpha particles was deflected

Deflection indicated the existence of a small, dense, positively charged nucleus



Historical Review

Discovery of the nucleus

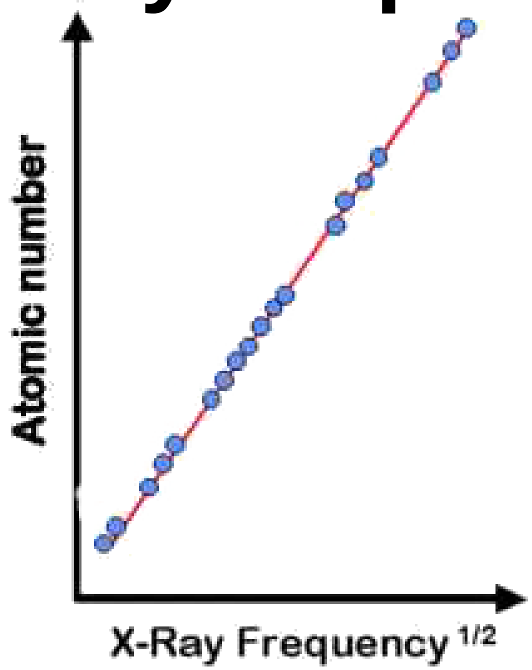
Moseley determined nuclear charge

Detected X-rays in cathode ray tubes

Historical Review

Discovery of the nucleus

Found direct relationship between atomic number and square root of the X-ray frequency



Concluded that the charge of the nucleus was an interger

- same as number of electrons

Historical Review

Discovery of protons

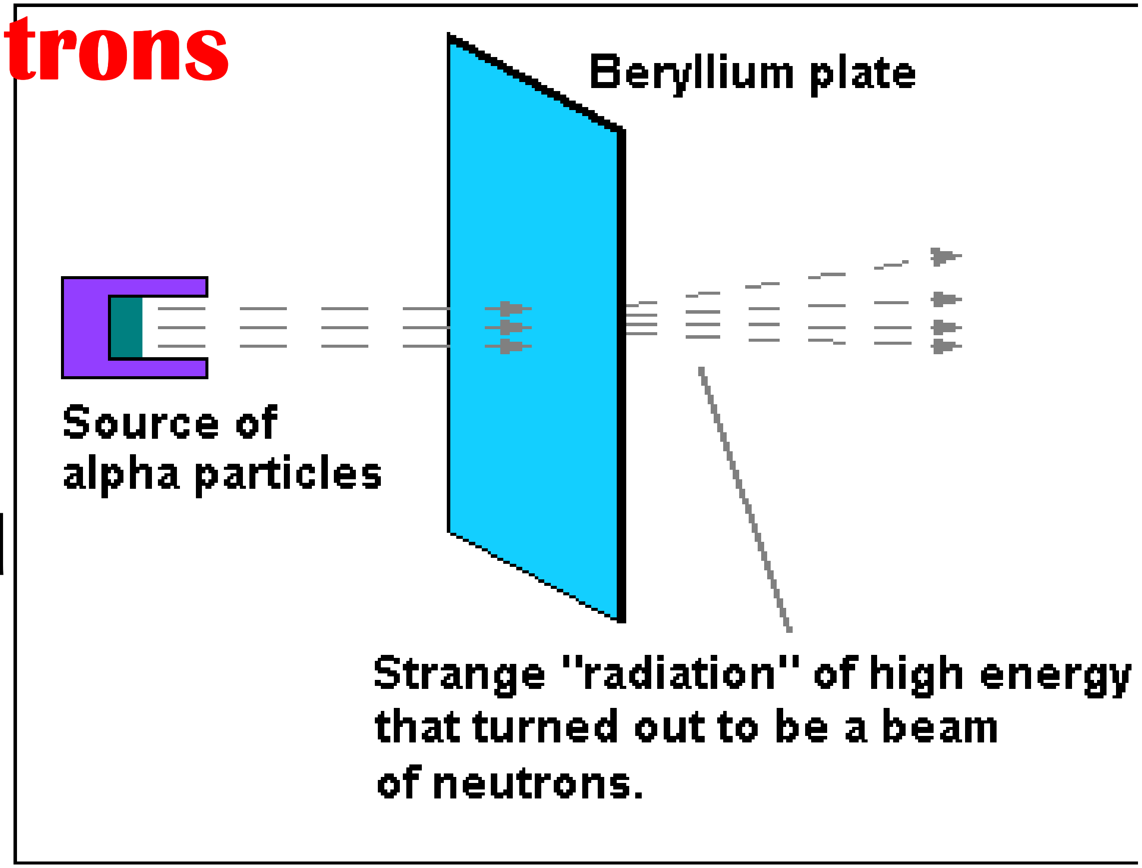
Measurements of charge:mass ratio of nucleus showed ratio dependent of element studied

Hydrogen had particles with lowest mass, & common to all atoms
= protons

Historical Review

Discovery of neutrons

1932: Chadwick studied beryllium-9. When hit with "- rays, produced particles with same mass as protons but with no charge



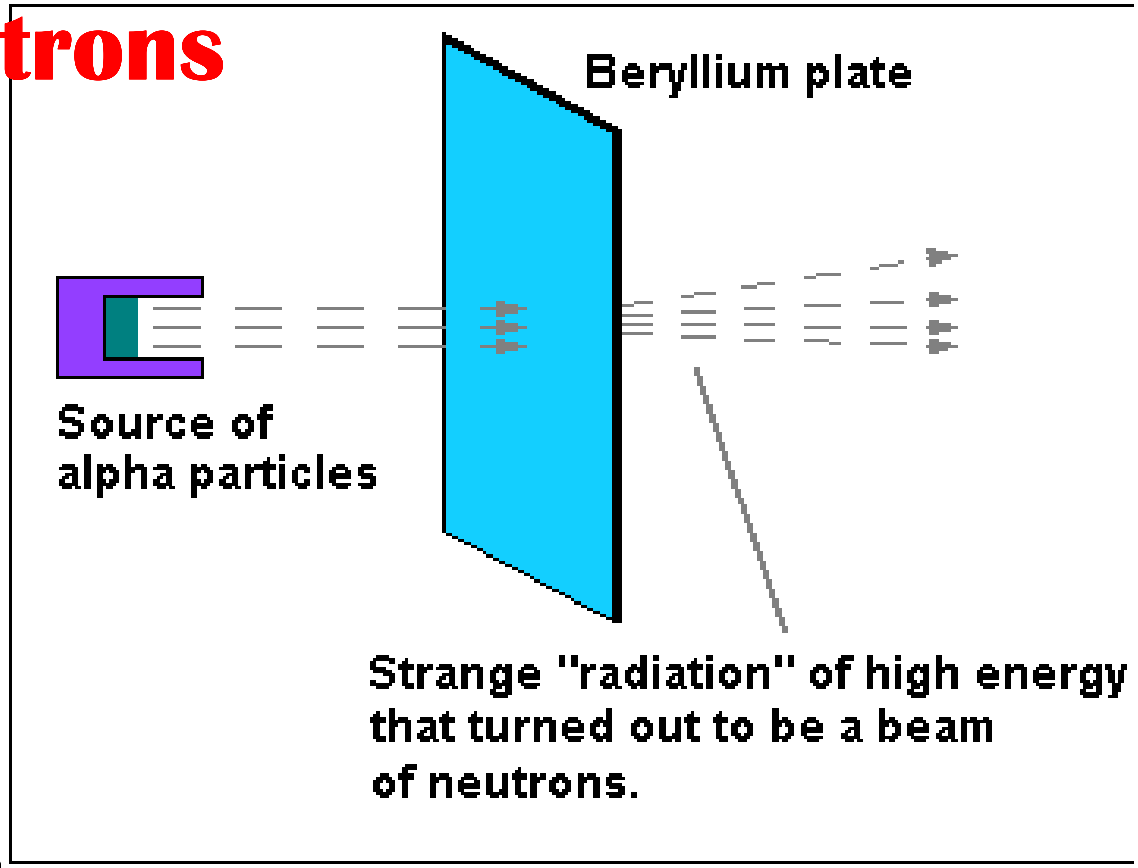
Detection of neutrons

Historical Review

Discovery of neutrons

Called neutrons; in all atoms except H

Contribute to binding force that holds nucleus together & reduce protons repulsive force

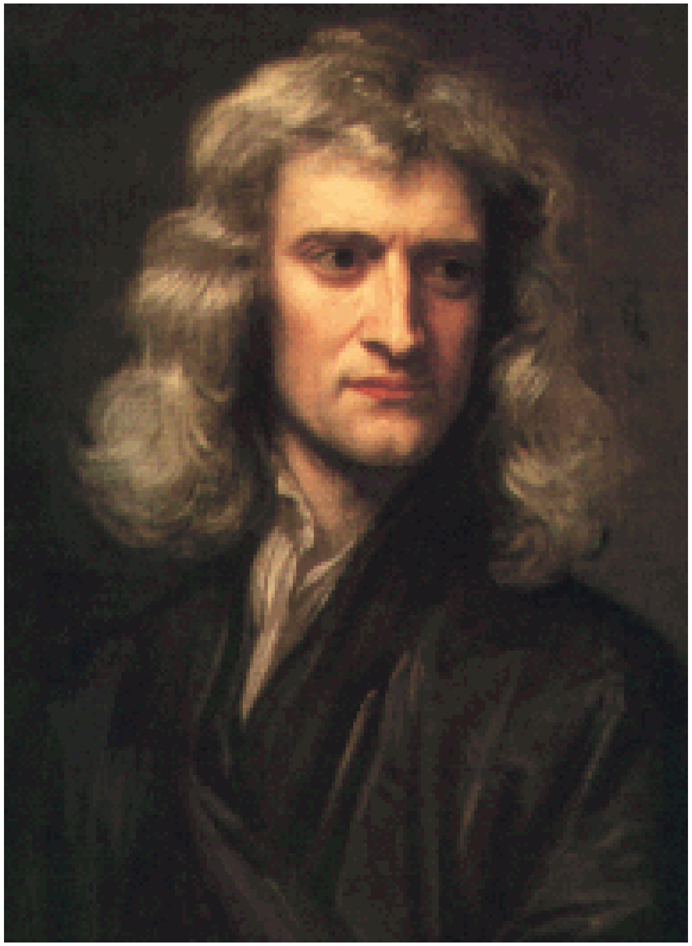


Detection of neutrons

Electromagnetic Radiation

Light was used to study the structure of atoms. Visible light most common

Electromagnetic Radiation



NEWTON

Electromagnetic Radiation

Light is a form of energy

A color has specific amount of energy

Heated matter can give off light

Electromagnetic Radiation

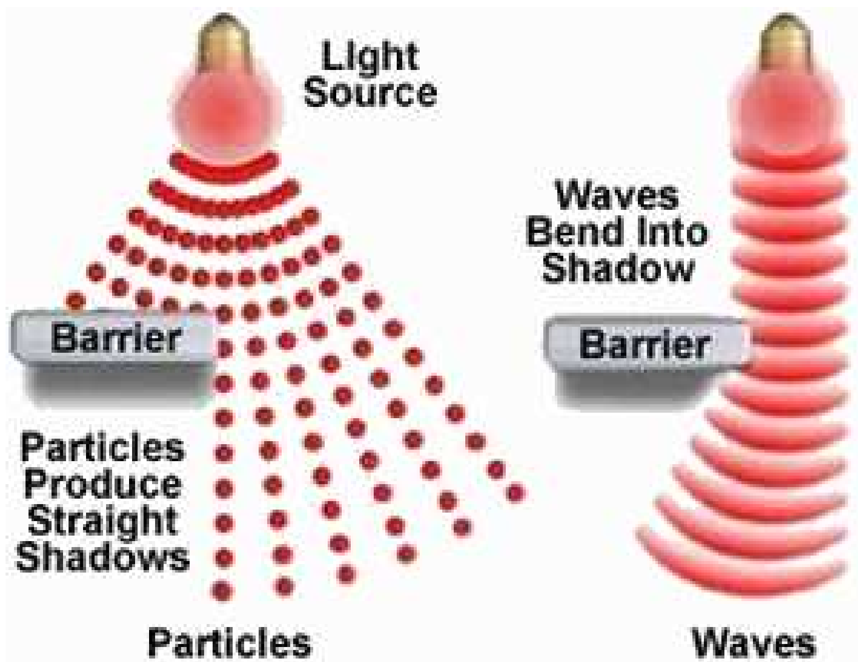
Two types

1. **Particulate radiation**

2. **Electromagnetic radiation (EMR)**

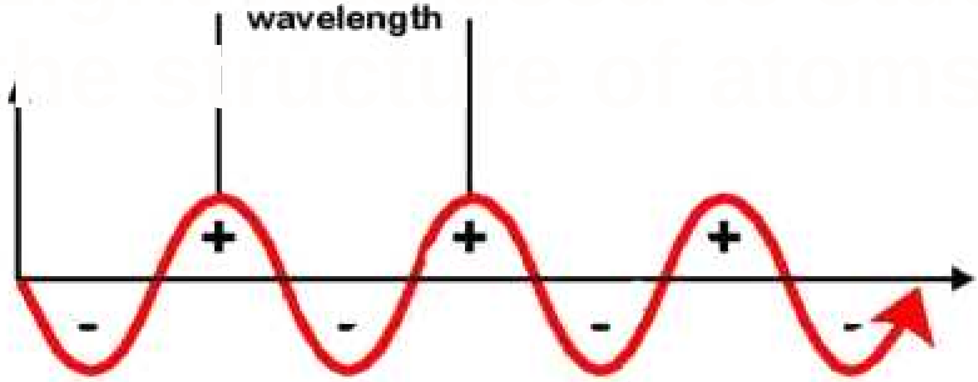
a form of energy consisting of perpendicular electrical and magnetic fields

Dual nature of light



Electromagnetic Radiation

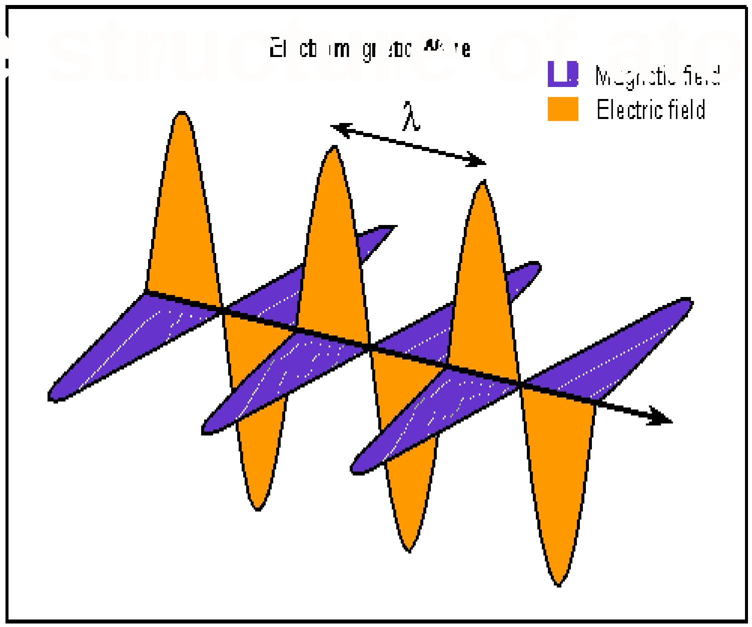
Light was used to study the structure of atoms



Light travels in waves

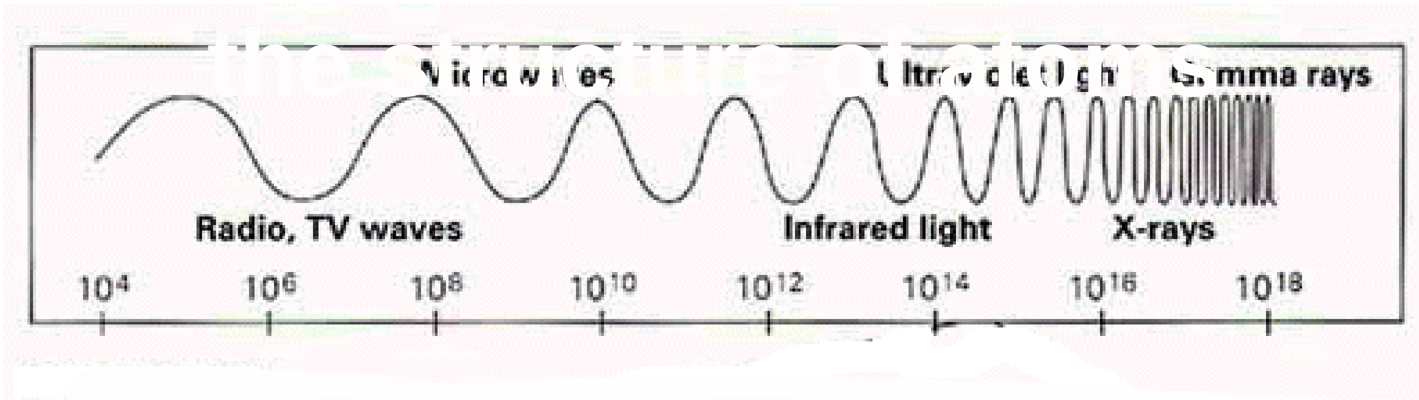
Visible light is one form of
electromagnetic radiation (EMR)

Light was used to study
the structure of atoms

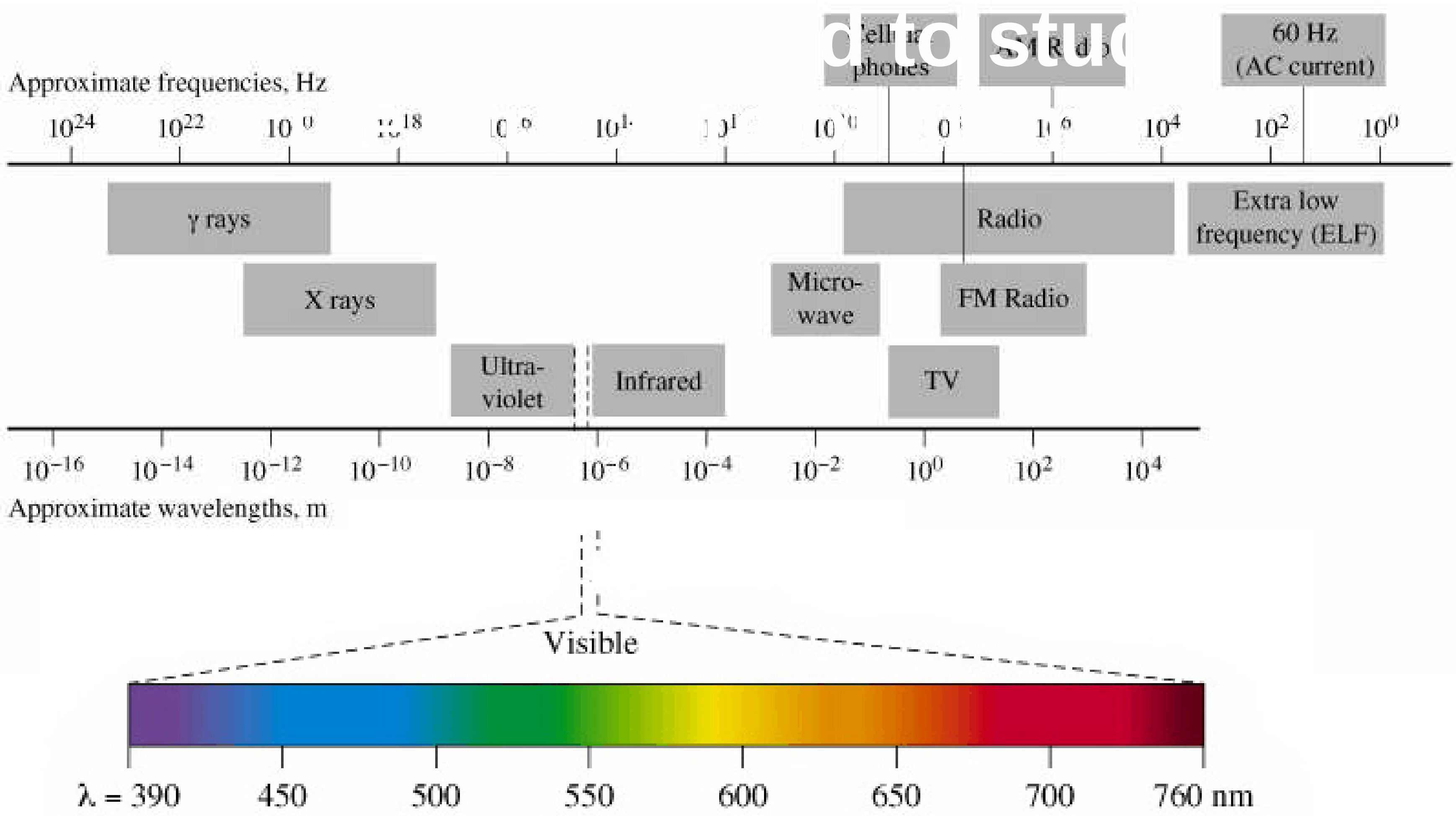


Electromagnetic Radiation

Light was used to study the structure of atoms



Electromagnetic Radiation

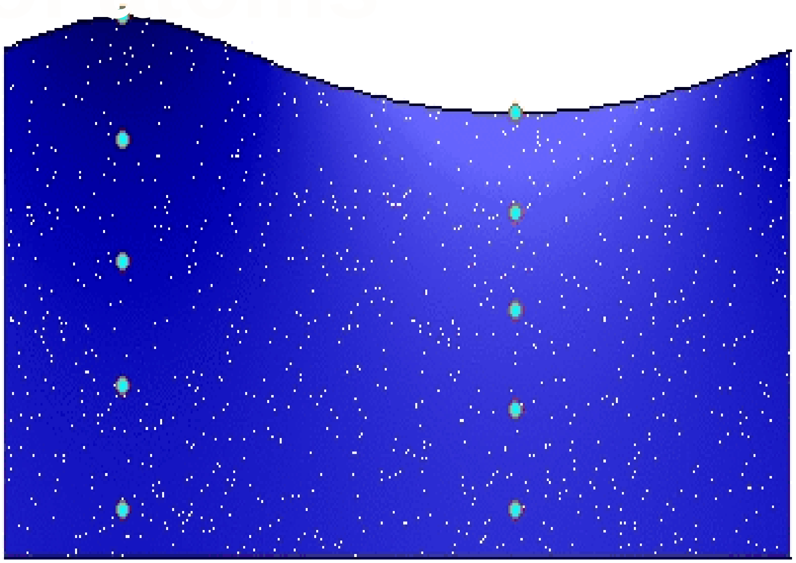


EMR and Waves

Waves can travel through solids, liquids, gases

EMR and Waves

Think of water waves



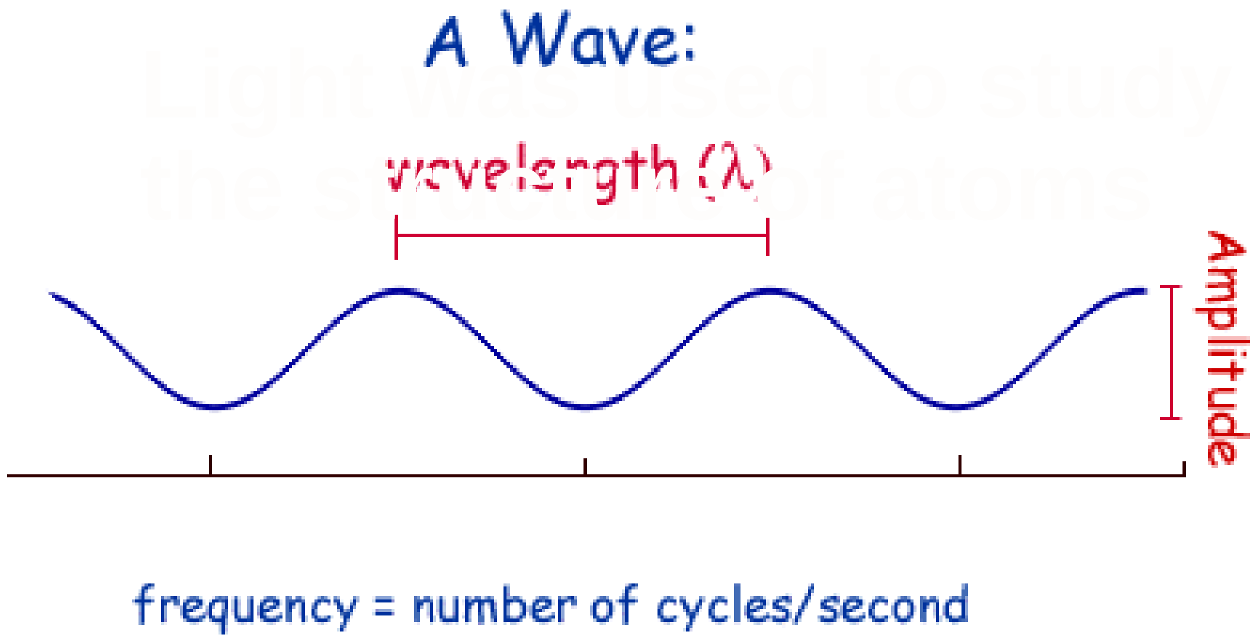
EMR and Waves

Water waves: 2 m/sec

Sound travels at
750 miles/hr = 340 m/sec

EMR travels at
186,000 miles/sec = 300,000 km/sec

EMR and Waves



Light was used to study the structure of atoms

EMR and Waves

SI unit of frequency (<): Hertz, Hz

$$1 \text{ Hz} = 1 \text{ sec}^{-1}$$

Wavelength (8, lambda)
units: nm or D

nm = nanometer

D = Dngstom = 10^{-10} m

EMR and Waves

Wavelength and frequency are related

8< = c

c is speed of light
c = 2.998 x 10^8 m/s

EMR and Matter

What happens when EMR & matter interact?

1. **Transmission: EMR passes through; no interaction**
2. **Absorption: EMR absorbed by atom or molecule 6 higher energy state**
3. **Emission: EMR absorbed by atom/molecule releases light energy; 6 lower energy state no interaction**

Light and Waves

Gamma rays: high frequency

Radio waves: low frequency

Gamma rays: focus on tumors

UV Light

Damages cell DNA

causing two pyrimidine bases to link as a dimer

Human skin cells have enzyme to repair damage

excise dimer and closes gap

Three regions of UV light:

- **UV A - least energy**
- **UV B**
- **UV C - most energy**

Skin sensitivity also a factor

SPF

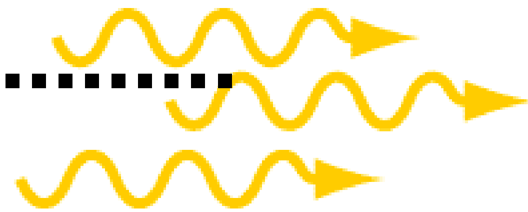
Sunscreen Protection Factor

SPF 10: stay in sun 10 times longer than if sunscree not used

SPF >15
no major advantage

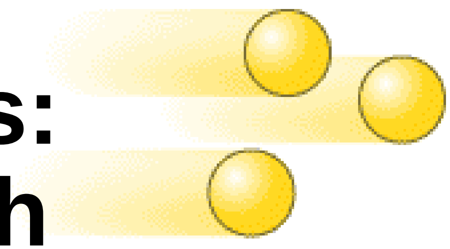
Dual nature of EMR

Does light travel as ....



Waves

Light has properties of waves



or particles?

Light has wavelike properties: speed, frequency, wavelength

It's only when the mass of a particle gets small enough that its wavelike properties show up.

Photoelectric Effect

Photoelectric effect offers proof light also travels as particles

First observed by Hertz

Later explained by Einstein

When exposed to light some metals eject electrons

Electron will have a specific energy

Energy of electrons depends on light frequency = photoelectric effect

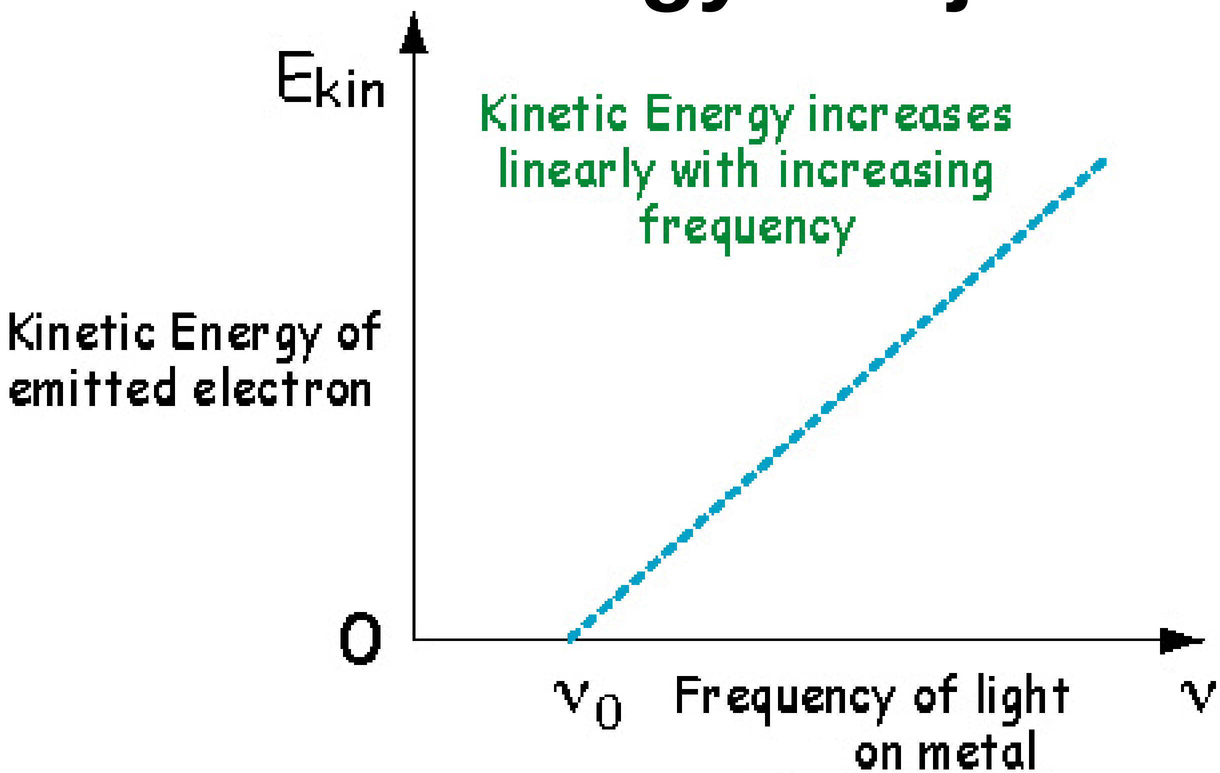
Think of water waves:
energy depends on size of wave

Energy of ejected electrons does NOT increase when intensity of light increased

Brighter light ejects more electrons, but energy remains unchanged

Does energy of electrons depend on any other factor?

Varying the frequency of the light DOES increase energy of ejected electrons



Each metal has a critical frequency - below which no electrons ejected

E = h<

h called *Planck's constant*

Inconsistent with light as a wave. Suggested light existed as small “packets” of radiation: photons

$E = h<$ $\quad h = 6.626 \times 10^{-34}$ **J.s**

since $8< = c$ $\quad$ Y $\quad E = \dfrac{hc}{8}$

In summary-

light is a particle,
but has some wave-like behavior

Albert Einstein first explained the photoelectric effect
Nobel Prize in Physics

Calculating photon energy

Find energy of a photon with 8 of 486 nm

$$E = \frac{hc}{8}$$

$$= \frac{(6.626 \times 10^{-34}\ \text{J.s})\ (2.998 \times 10^{8}\ \text{m/s})}{4.86 \times 10^{-7}\ \text{m}}$$

$$= 4.09 \times 10^{-19}\ \text{J (per photon)}$$

What about for 1 mole of photons?

multiply by Avogadro's Number

$$= (4.09 \times 10^{-19}\ \text{J}) \times (6.02 \times 10^{23})$$

$$= 2.46 \times 10^{5}\ \text{J} \quad \text{or} \quad 246\ \text{kJ/mol}$$

Light and Waves

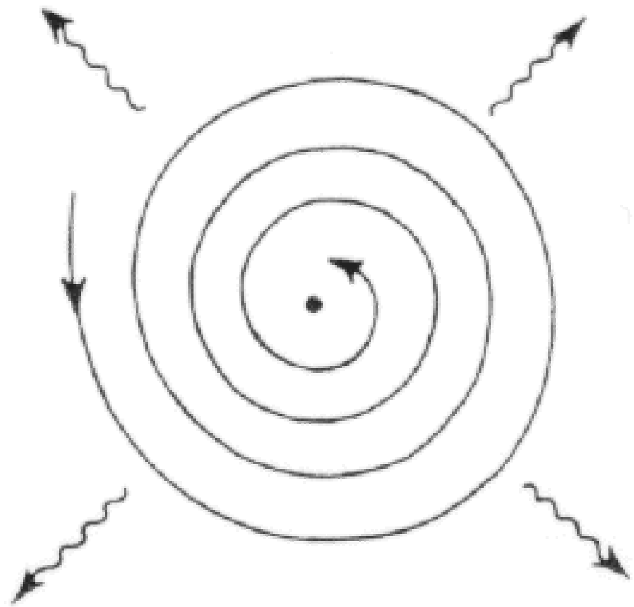
Much of what has been learned about atomic structure has come from observing how visible light interacts with matter

Bohr Model of the Atom

Niels Bohr (1885-1962)

Problem with Rutherford atom model:

– **electrons would lose energy and spiral into the nucleus**

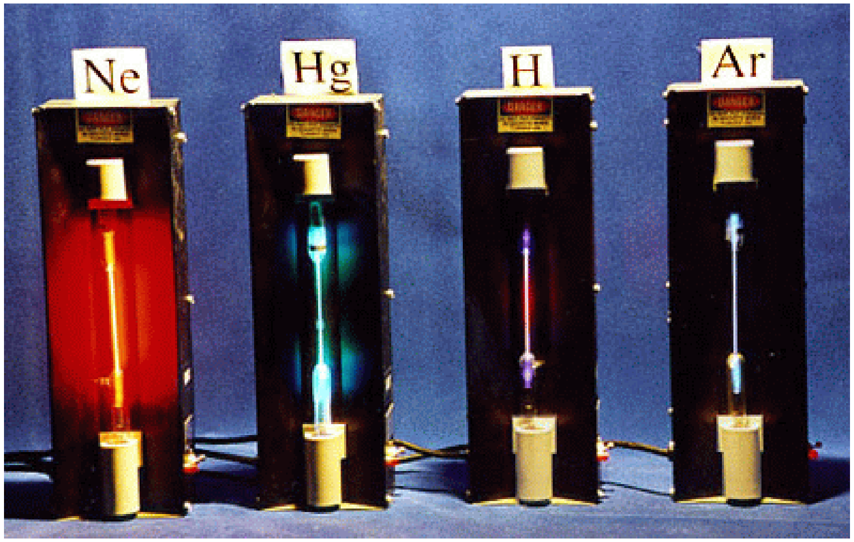


Problem with Rutherford atom model:

- **atom lifetime would be < 1 second**

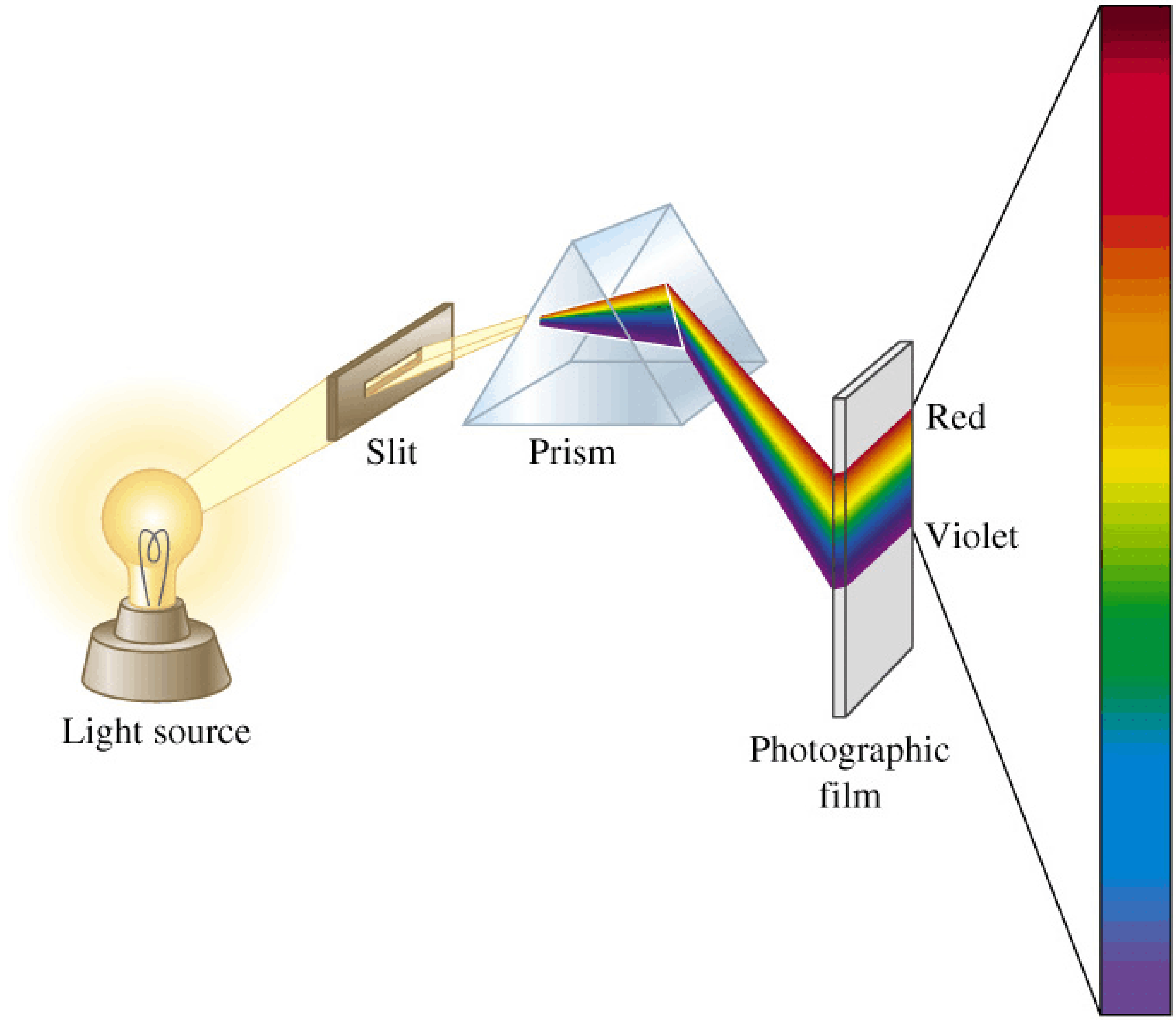
Preposed EMR consists of a stream of minute bundles called quanta

Bohr studied the line spectra produced when atoms were excited in a gas discharge tube

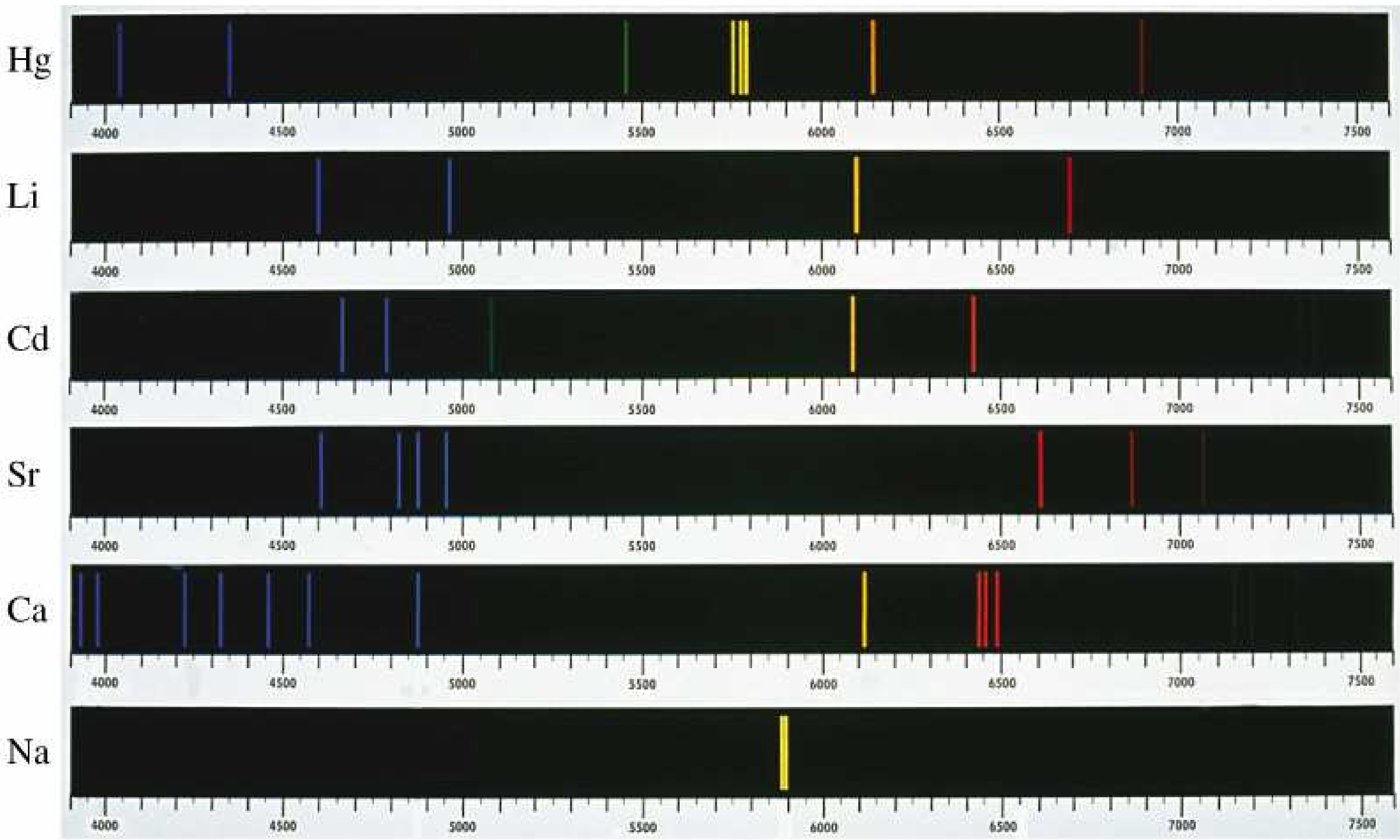


Observed each element produced its own set of characteristic lines

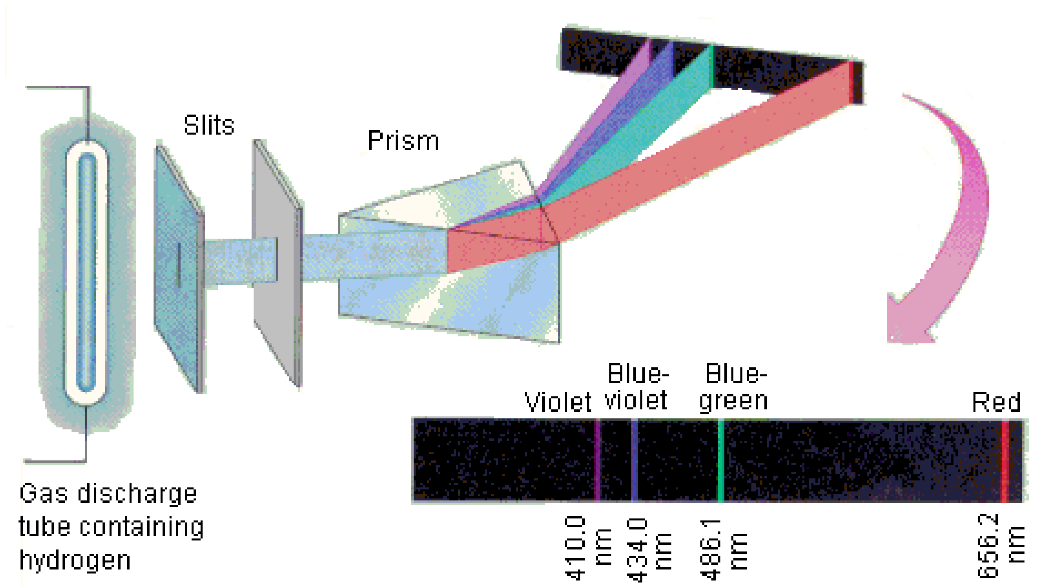
What is a line spectrum?



line spectrum of white light



line spectra of some elements


Slits
Prism
Gas discharge
tube containing
hydrogen
Violet
Blue-
violet
Blue-
green
Red
410.0
nm
434.0
nm
486.1
nm
656.2
nm

(a)

Bohr explained why electrons did not fall into the nucleus

Also wanted to account for the spectral lines he observed

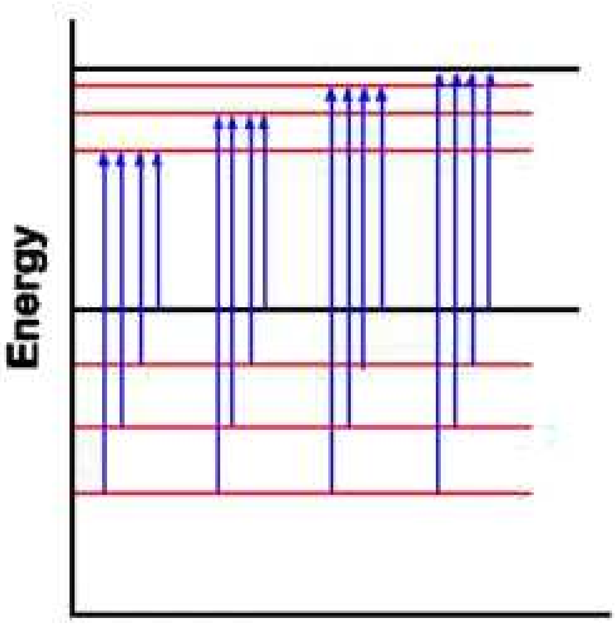
He proposed a new model of the atom

Balmer later found a mathematical relationship for hydrogen spectral lines

$$\frac{1}{\lambda} = \mathbf{1.097 \times 10^{-7}\ m^{-1} \times \left(\frac{1}{2^2} - \frac{1}{n^2} \right)}$$

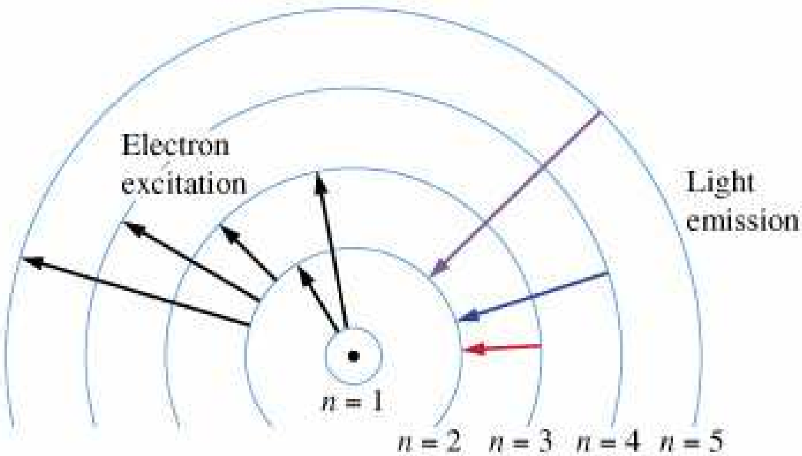
n = 2,3,4.....

Similar relationships found for other atoms



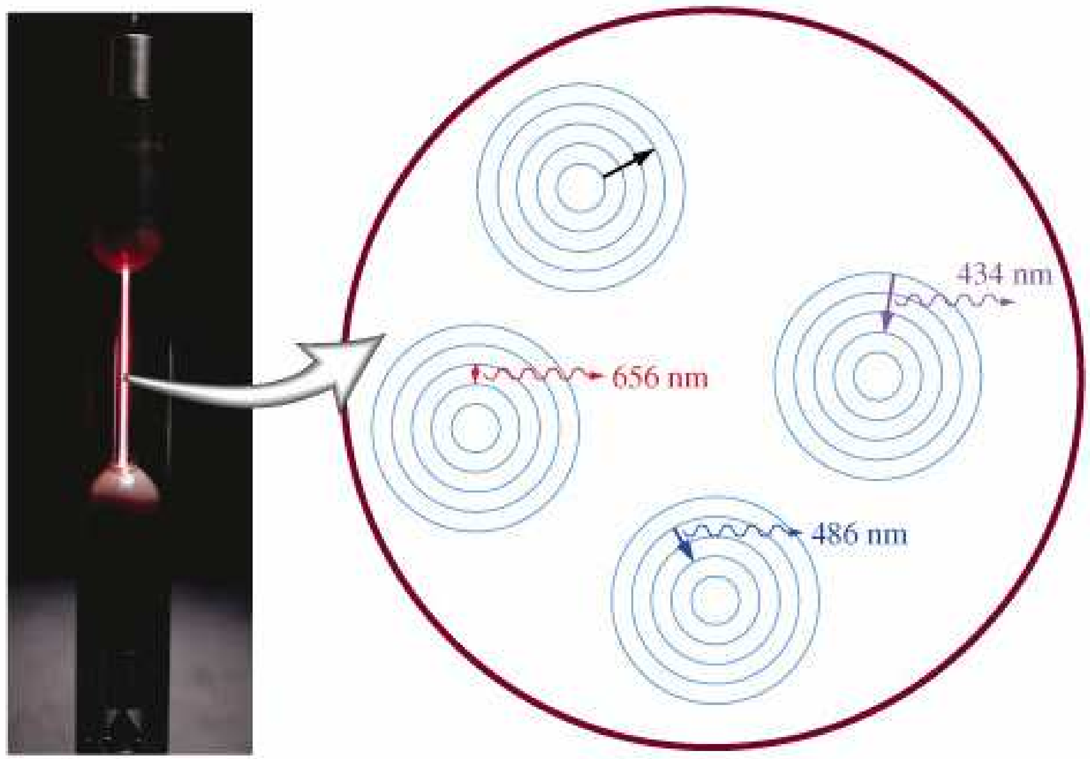
Electrons only exist at specific energy levels or orbits

Each orbit assigned a principal quantum number, n



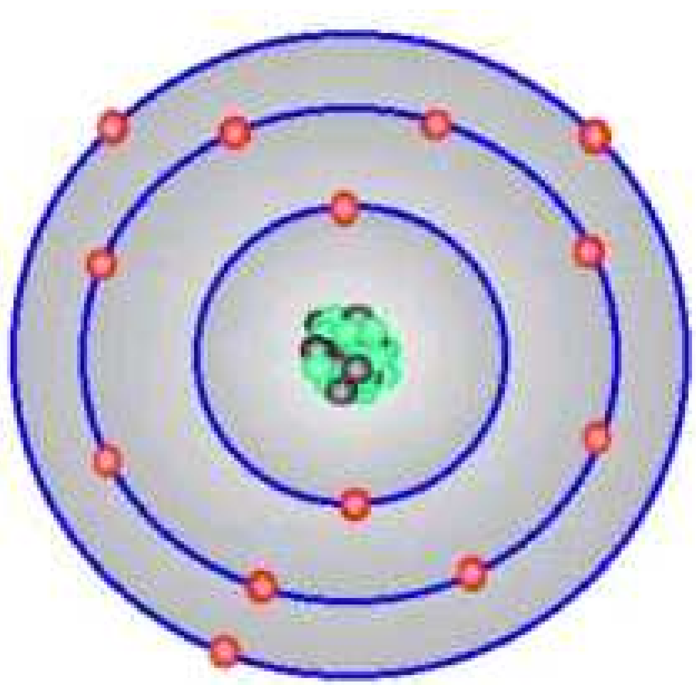
Electron
excitation
Light
emission
n = 1
n = 2
n = 3
n = 4
n = 5

(a)



434 nm
656 nm
486 nm

(b)



Bohr model is a "planetary" type

Each principal quantum number represents a new orbit or layer

Nucleus is at the center of the model

Bohr's ideas ....

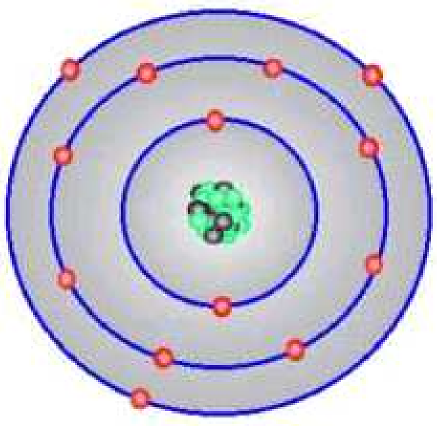
- Proposed (1913) quantized shell model of the atom
- Explained how electrons can have stable orbits around nucleus
- Electrons move in orbits of fixed size and energy
- Electron energy depends on the size of the orbit
- Electrons jump from one orbit to another

When electron is in lowest orbit

þ **ground state**

When electron absorbs energy

þ **excited state**



Model did account for spectral lines

Enabled radius of H atom to be calculated

Model did not work for other atoms

Concept of moving electrons in fixed orbits later abandoned

Wave Theory of Electrons

1924: De Broglie suggested electrons have wave properties to explain why their energies are quantized

Electrons are fixed in space around nucleus

De Broglie proposed all particles have a wavelength:

$$8 = \frac{h}{m<}$$

8 **= wavelength (m)**
h = Planck's constant
m = mass (kg)
< **= frequency (m/s)**

Wavelength of electron:

$$8 = \frac{h}{m<}$$

(Bohr had calculated < for an electron)

$$8 = \frac{6.6 \times 10^{-34}\ \mathrm{kgm^2s^{-1}}}{(9.1 \times 10^{-31}\ \mathrm{kg})(2.2 \times 10^{5}\ \mathrm{m/s})}$$

$$8 = 3.3 \times 10^{-10}\ \mathrm{m}$$

Heisenberg uncertainty principle

To observe electrons,
hit them with photons
of very short wavelength
(high E)

Such photons would
change the motion
and speed of electrons

Heisenberg: can’t know both position and
speed of objects (e^-) precisely

Heisenberg: can’t know both position and speed of objects (e^-) precisely

He developed equations for the position and speed of electrons

Can only know the probability of electron path or position

Electrons in ORBITALS
Region of 3D space where high probability of finding electrons

Quantum Numbers

Schrödinger: equation to describe behavior & energies of electrons in atoms

Each electron described in terms of its quantum numbers

1. **n: principle QN or shell number**
   n = 1,2,3…… (also K,L,M,N,O..)
   Indicates distance from nucleus

2. **l: subsidiary QN**
   l = 0 spherical, s l = 1 2 lobes, p l = 2 4 lobes, d l = 3 8 lobes, f Indicates shape of orbital

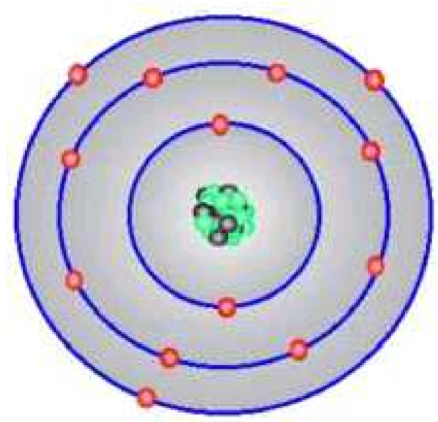
Combine n and l Y subshells
1s 2s 2p 3s 3p 4s

3. m_l: magnetic QN
Direction on x,y,z axis

4. m_s: spin QN = $\pm \frac{1}{2}$

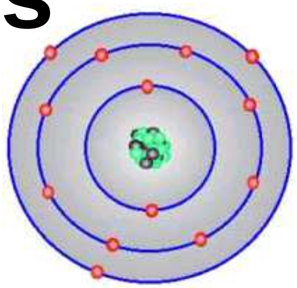
Knowing all quantum numbers helps build a picture of the atom

- **We can think of an atom as a series of layers**



Quantum Model of the Atom

- Each layer called a **shell**
  Holds a certain number of electrons
- Moving away from the nucleus, layers get larger and hold more electrons



- Shells assigned letters (K,L,M...) or numbers 1,2,3...

– **Each shell can hold a maximum number of electrons, no more:**
No. electrons = $2n^2$
where n is the shell number

when	**$n = 1$**	**-**	**$2\ e^-$**
	$n = 2$	**-**	**$8\ e^-$**
	$n = 3$	**-**	**$18\ e^-$**
	$n = 4$	**-**	**$32\ e^-$**

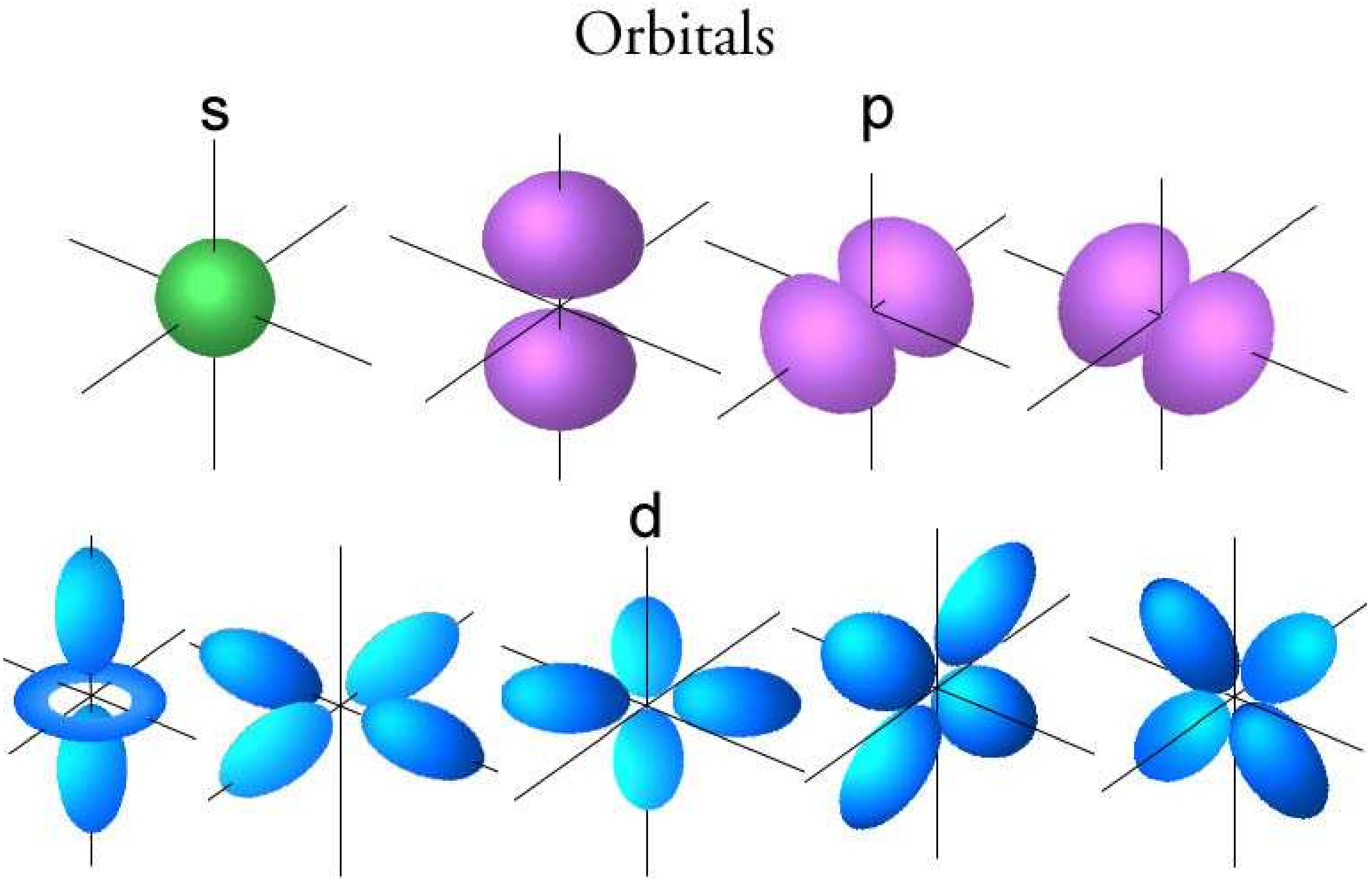
- Each shell divided into subshells
- The number of subshells in a shell is the same as the shell number

In the 3rd shell there are 3 subshells

In the 5rd shell there are _5_ subshells

– Subshell can hold only so many e^-

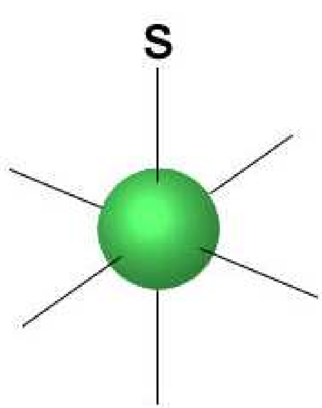
Subshells called	s	p	d	f
Maximum No. electrons	2	6	10	14

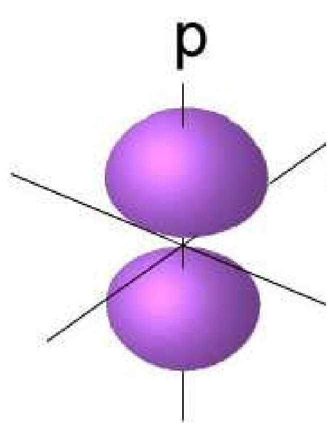


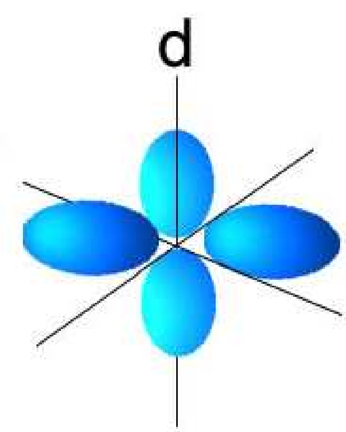
Figs 7.16, 7.17

Orbitals

One s orbital
Three p orbitals: p_x p_y p_z
Five d orbitals: d_{xy} d_{xz} d_{yz} d_{z^2} $d_{x^2-y^2}$







Electron configurations

Show which shells/subshells the electrons are found in

Indicated by: 1s 2p 3d

Electron configurations

number of electrons in subshell

shell or principal quantum number (1,2,3,4 ......)

$$nl^x$$

subshell letter (s,p,d,f)

Electron configurations

Rules

orbitals hold 0,1 or 2 electrons

electrons go into orbitals of lowest energy first: Aufbau process

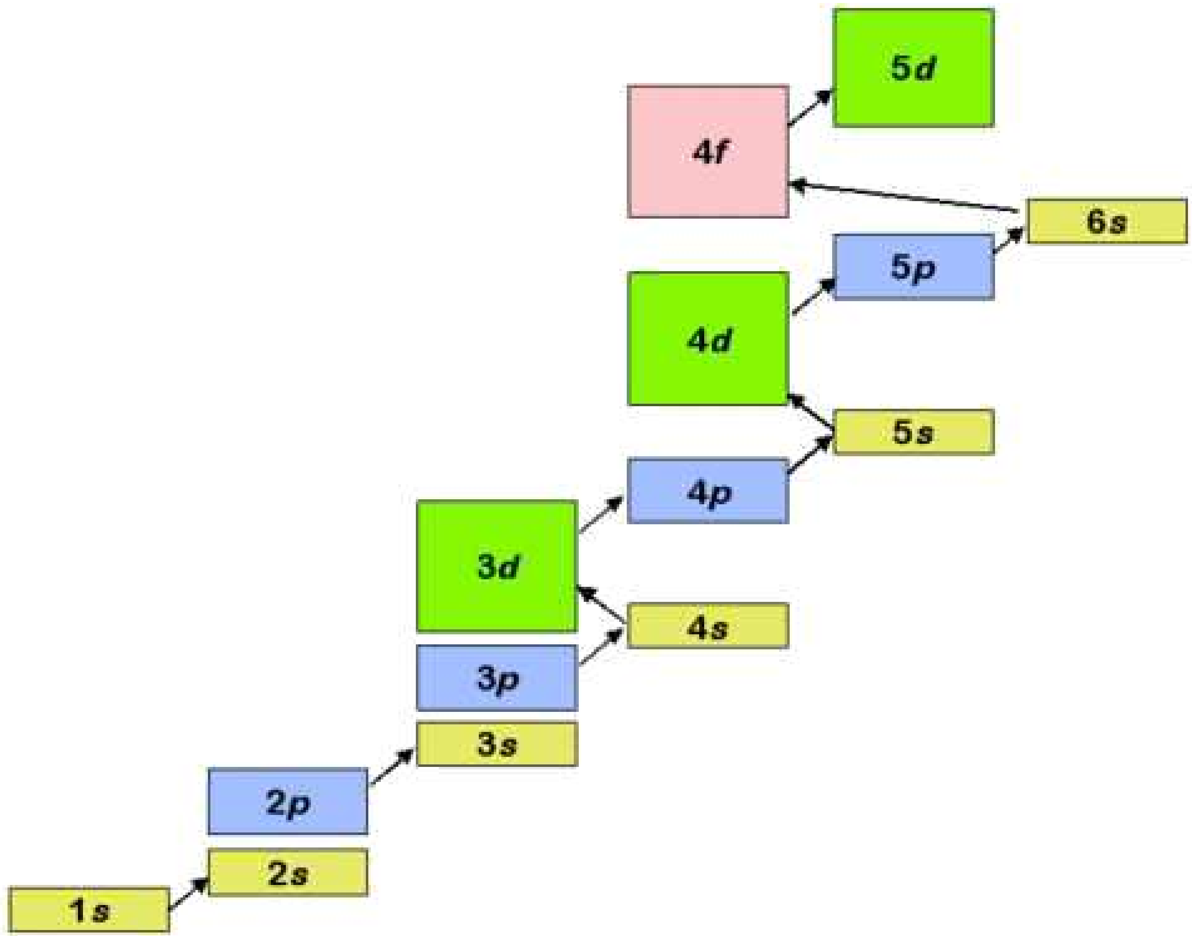
orbitals in same subshells are degenerate

electrons go into empty orbital before pairing up in same subshell

electrons can have same/opposite spins

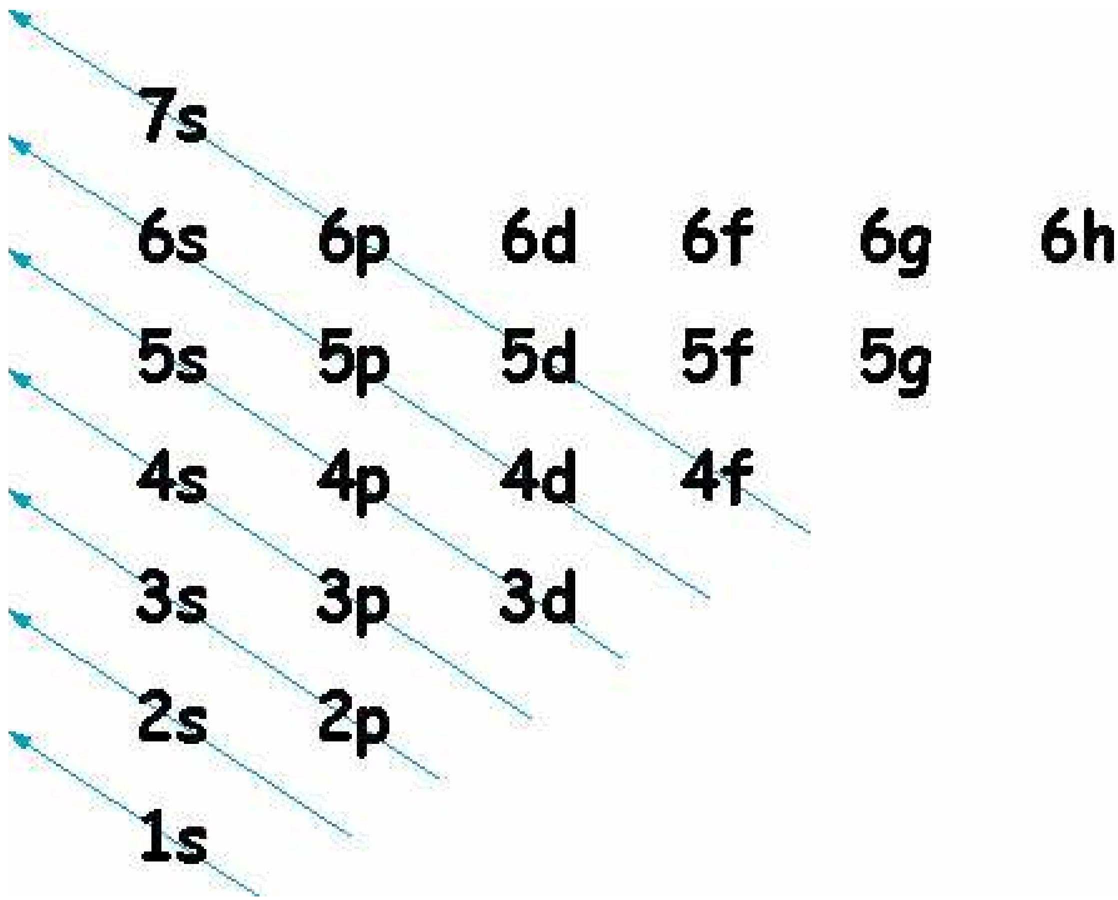
Electron configurations

Aufbau process



Electron configurations

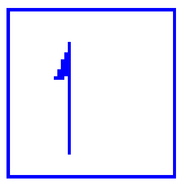
Aufbau process



see Fig 7.20

Electron configurations

Show which shells/subshells the electrons are found in
Indicated by: 1s 2p 3d

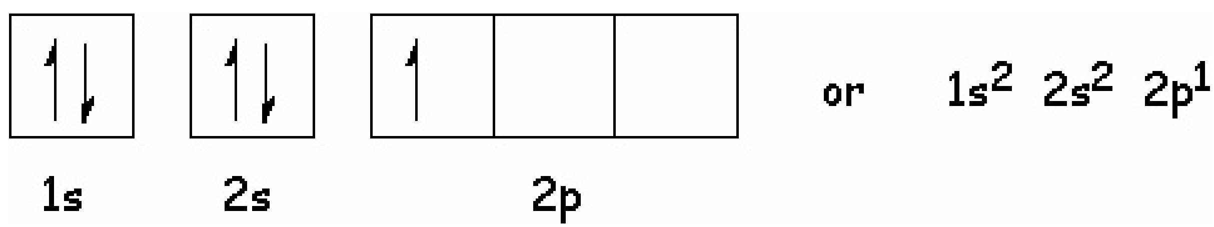


for $1s^1$ H-atom

$1s^1$

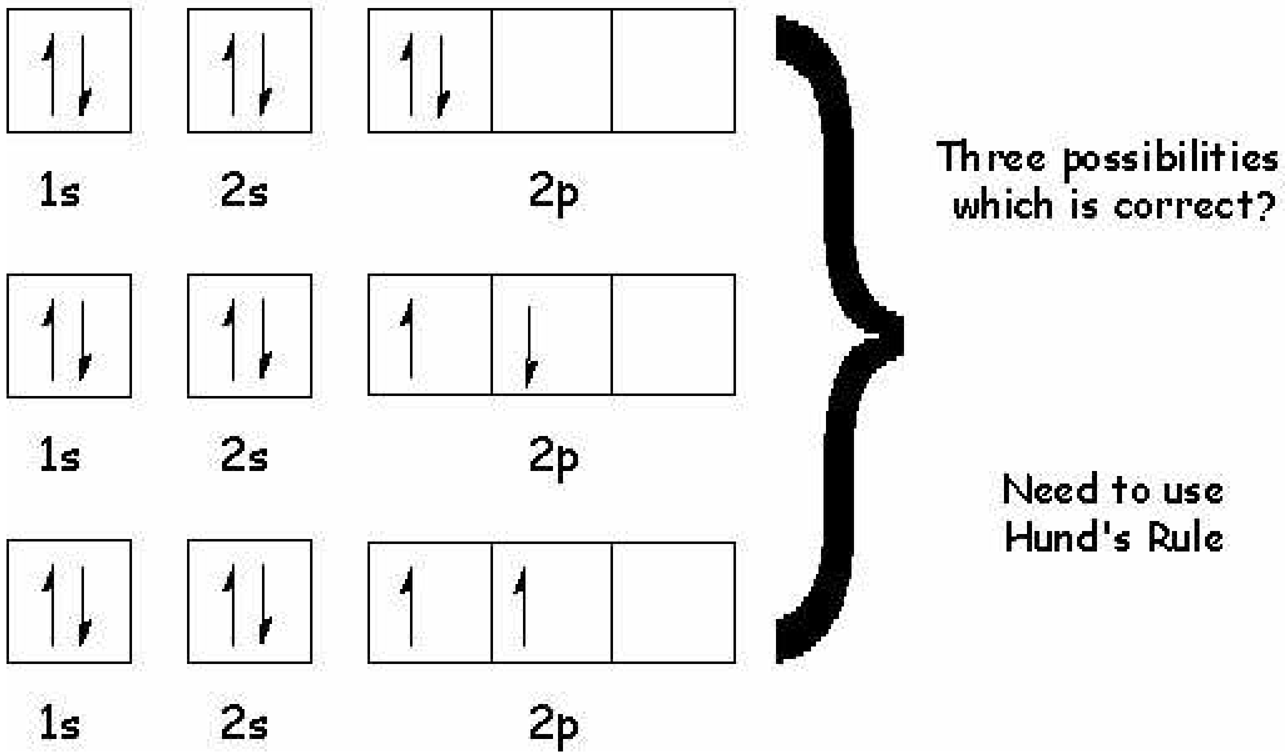
Electron configurations

Boron



Electron configurations

Carbon



Electron configurations

Subshells fill in order of increasing energy as follows:

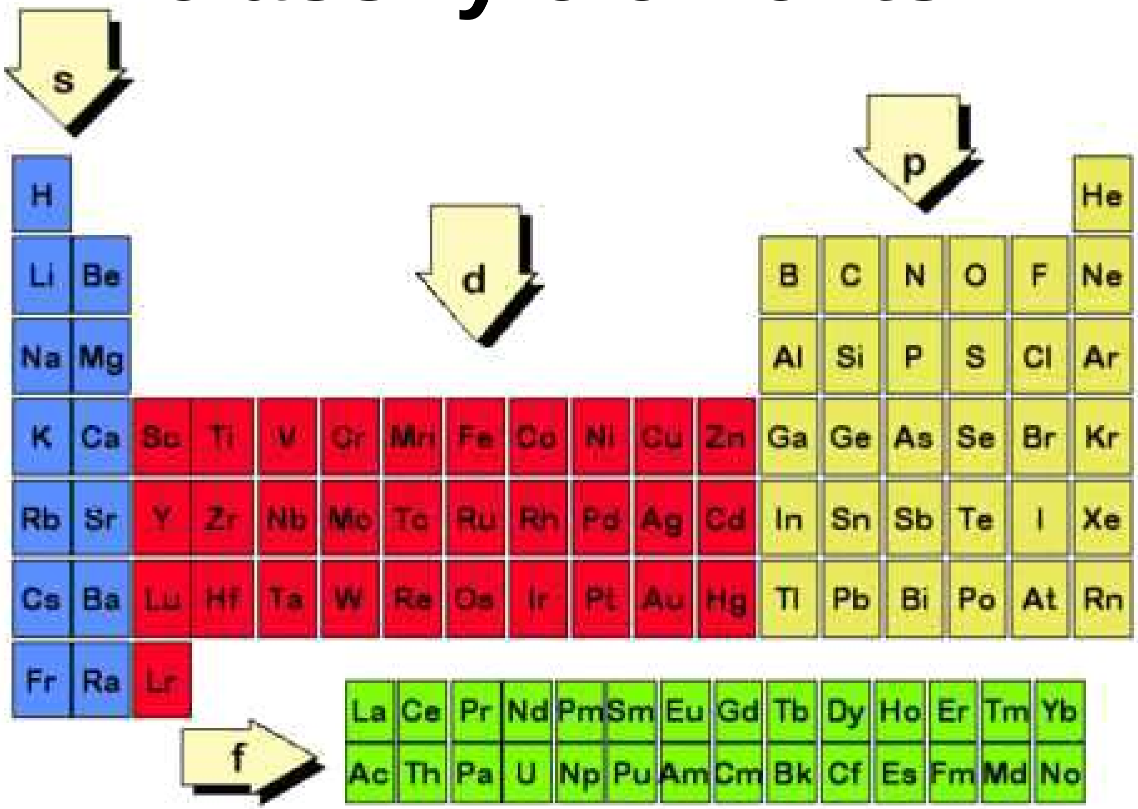
1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f ...

$$S = 1s^2\,2s^2\,2p^6\,3s^2\,3p^4$$

$$Ni = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^8$$

Electron configurations

classify elements



Electron configurations

Why are e^- configurations important?

The valance electrons giveinformation about an atom’s reactivity

Periodic table shows relationship between electron configuration and chemical properties of elements