

# Chapter 1

①

4 men associated with key experiments behind concept of a nuclear/electrostatic atom

Michael Faraday, JJ Thomson, Robert Millikan  
& ER Rutherford

From 1813 - 1911

atom held together by electrical forces so understanding structure of atom implies understanding electrical particles & forces

1813 Napoleon in Russia - wearing marshals at  
start of 1812 war in  
Beethoven's 7th Symphony

bombs were  
prohibited in  
Boston

Michael Faraday

1813 Faraday went to the British Royal Institution to work as a laborer/assistant to Humphry Davy, investigated chemical effects of electricity. In 1807, Davy invented voltaic piles or batteries & used them to produce metallic Na and F from their hydroxides. This was the 1st isolations of these elements since no chemical reaction is capable of producing them.

Faraday extended Davy's work

- quantitative relationship between chemical change & transport of electricity

- electrolysis studies

- showed transport of given amount of electric charge always deposits same weight of an element on an electrode

- (2)
- concept of electrochemical equivalent ratios of weights deposited for different elements
  - term "faraday" refers to quantity of electrical charge (96,487 coulombs) that will deposit 1 equivalent weight (in grams) of an element
  - suggested that the attraction between unlike charges was the source of energy binding molecules together
  - v. broad range of compounds studied suggested an electrical nature was common to all elements
  - idea of electrochemical equivalents  $\Rightarrow$  some definite quantity of electrical charge that is added or taken from a neutral atom to make an ion
  - calculate by dividing 1 faraday by Avogadro's number:

$$\begin{aligned}
 & \frac{\text{charge in charge}}{\text{atom}} = \frac{\text{charge per equivalent}}{\text{atoms per mole}} \\
 & = \frac{96487 \text{ C/equivalent}}{6.022 \times 10^{23} \text{ atoms/mole}} \\
 & = 1.6021 \times 10^{-19} \text{ C/atom}
 \end{aligned}$$

if 1 electrochemical equiv. equals 1 mole of the element, (sometimes 2 or 3 or 4) but never less than this  
 $\Rightarrow$  basic unit of electricity

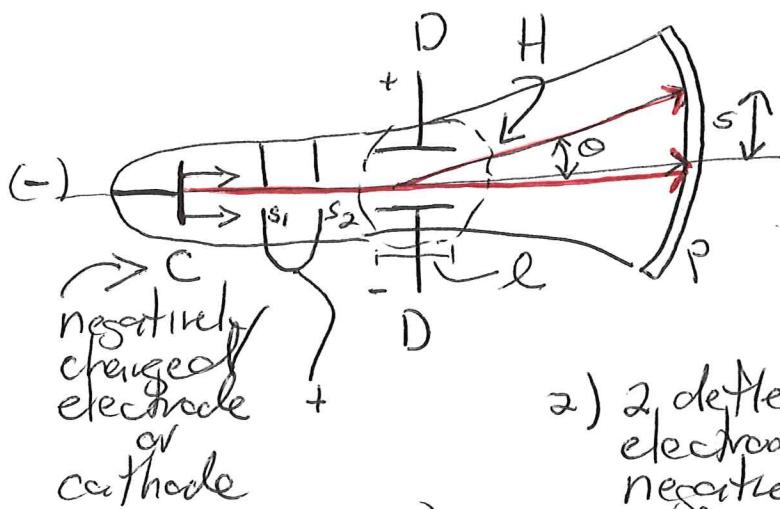
1874 British physicist G.J. Stoney proposed charged particle, called an "electron"

Stoney's proposal not immediately accepted (3)

- controversial
- agreed for aqueous solution
- electricity also conducts through gases at very low pressures & this conduction did not represent action of particles

2 electrodes placed in evacuated tube & one gives negative charge at v. high voltage relative to the other, the negative electrode or cathode emitted radiation called cathode rays, & experiments suggested cathode rays were some sort of electromagnetic radiation like visible light but of a different frequency.

JJ Thomson: established 1) cathode rays were particles (electrons)



1) cathode rays produced at C pass through 2 slits S<sub>1</sub> & S<sub>2</sub>, produce narrow beam that passes down tube & strikes phosphor P at far end of tube

2) 2 deflection plates D are separate electrodes that can be positively or negatively charged

3) Thomson found that the cathode rays were deflected towards the positively charged plate, expected for a negatively charged particle

4) A magnetic field established in some region of D made by passing current through coils, in a direction  $\perp$  to both that of the electric field & that of cathode rays. H produces deflection of rays that can be made to oppose the deflection by the electric field.

By varying strengths of H & E, Thomson could cause the cathode ray to pass undeviated through the tube (equal but opposing forces). (4)

$$\text{Force} = F_E = Ee \quad E = \text{electric field}$$

$$\text{Force} = F_H = Hev \quad H = \text{magnetic field}$$

$e$  = electric charge on the supposed particles  
 $v$  = their velocity

$$Ee = Hev \Rightarrow v = \frac{E}{H}$$

When H turned off, only E acted on beam, giving it a displacement:

$$s = \frac{1}{2}at^2$$

away from central axis. Particles acquired the acceleration "a" toward the positive plate in the time "t", it took for them to traverse the length of the condenser "l"

Since  $v = \frac{l}{t}$ ,  $t + a$  can be calculated

Newton's Second Law:  $F = ma$

$$F_E = m_e a = Ee$$

Thus:  $\frac{e}{m_e} = \frac{a}{E} = \frac{2S}{t^2 E} = \frac{2Sv^2}{l^2 E} = \frac{2SE}{l^2 H^2}$  only measurable quantities

$$s = \frac{1}{2}at^2$$

$$v = \frac{l}{t}$$

$$v = \frac{E}{H}$$

$$S, E, l$$

$$\frac{2S}{t^2} = a$$

$$t = \frac{l}{v}$$

$$t^2 = \frac{l^2}{v^2}$$

$$v^2 = \frac{E^2}{H^2}$$

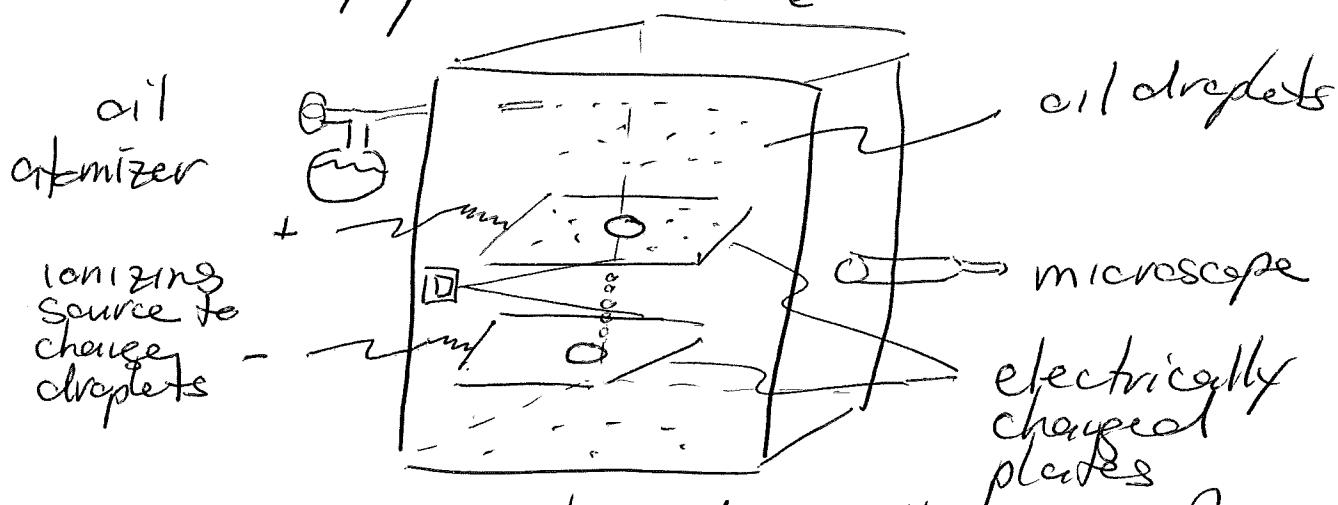
$$+ H$$

$$\frac{e}{m_e} \text{ determined as } 1.7588196 \times 10^{-10} \frac{\text{C}}{\text{Fr}_S}$$

(5)

(Phil. Mag. 44, 293, 1897)

Robert Millikan (student H A Fletcher) performed an experiment to determine the value of the electric charge & not simply the ratio  $\frac{e}{m_e}$ .



tiny drops of oil become charged by collisions with electrons or ionized gas molecules in surrounding air

a charged oil drop (with charge  $Q$ , mass  $M$ ) situated in an electric field between 2 plates is subjected to 2 forces, gravity  $-Mg$  causing it to fall electric field  $QE$  causing it to rise

by adjusting the electric field to balance 2 forces & independently determining drop's masses  $M$  from their falling speeds in absence of  $E$ , Millikan showed charge  $Q$  always an integral multiple of the same basic charge  $1.59 \times 10^{-18} \text{ C}$ .

$\Rightarrow$  different oil drops carried integral numbers of a fundamental charge, assumed to be the charge of a single electron.

(6)

$$\text{modern values: } 1.6021773 \times 10^{-19} \text{ C}$$

$$\frac{e}{m_e} \text{ Thomson: } m_e = 9.109390 \times 10^{-31} \text{ kg}$$

(Phys. Mag. XIX, 6 (1910) pg 209)

## Nucleus

Thomson's studies: positively charged particles formed when electrons were pulled off atoms by an electric field

called "canal rays" observed in cathode ray tubes, but traveled in opposite direction than  $e^-$  & were thousands of times more massive than  $e^-$ .

Thomson: atomic model:  $e^-$  imbedded in a jelly-like fluid of positive charge

"plum pudding" model  
each atom had an integral # of electrons & whose charge was exactly balanced by the jelly-like positive charge, making the atom electrically neutral.

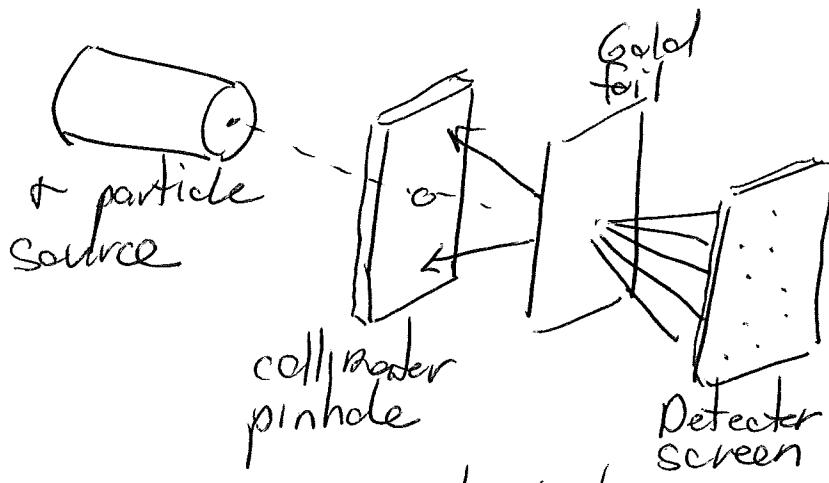
$\Rightarrow e^-$  new particle, but + charge was not?

1911: Ernest Rutherford (students Hans Geiger & Ernest Marsden) performed a set of experiments very expected to fail, but hadn't yet been done!

$\Rightarrow$  investigated properties of  $\alpha$ -particles emitted from Radium, an element recently isolated by Marie & Pierre Curie

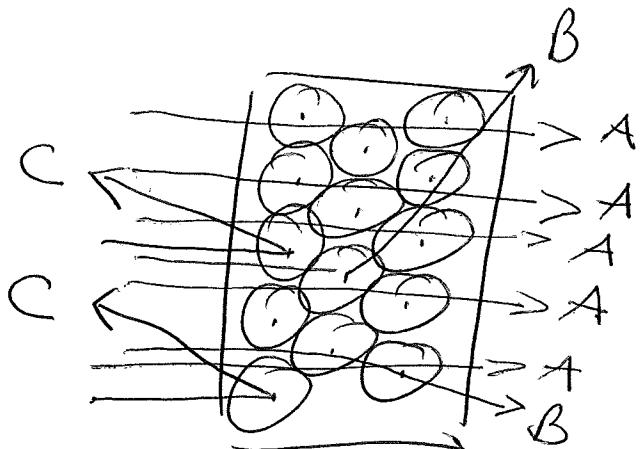
(7)

Rutherford's experiment: bombarding thin gold foil ( $6 \times 10^{-5}$  cm thick) with these particles & observing their deflections via the scintillations they produced on a ZnS fluorescent screen.



20 per minute high angles  
132,000 per minute low angles

$\alpha$  particles  
helium nuclei  
atomic weight 4  
 $\approx 10,000x$  mass Fe  
also have high velocities  
 $\rightarrow e^-$  would not be able  
to deflect them  
significantly



- most  $\alpha$  particles pass through the space between nuclei & experience only small deflections
- A few pass close to a nucleus & are more sharply deflected
- some are scattered backward

If Thomson's model of atom was correct, even if relatively massive atoms & the nuclei would not deflect the  $\alpha$ -particles significantly as the + charge was thought to be spread out over a large volume.  
full repulsion of + charges of atom &  $\alpha$ -particle same of atom on either side of the atom

(8)

"It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper & it came back & hit you."

Calculations showed:

- 1) statistically impossible for a series of small deflections to add up to these large deflections
- 2) worked only if + charge in atom were concentrated on a single v. small, v. massive nucleus could a particle experience the full repulsion of the + charge & be occasionally deflected so sharply.
- 3) center called "nucleus"  $\rightsquigarrow$  G. N. Lewis Kernel + outer shell nucleus e
- 4) analysis of trajectories of scattered particles estimated radius of gold nucleus to be less than  $10^{-12}$  cm & the + charge on each nucleus to be  $\sim 1/100e$  (actual value is  $+79e$ )

$10^{-14} \text{ m}$   
 $\text{~}1.6 \times 10^{-15} \text{ m}$

Rutherford model:

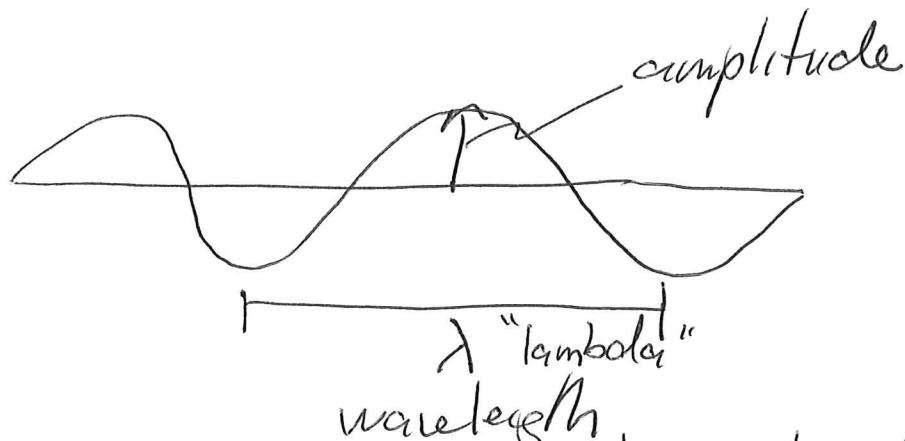
atom: nucleus possesses a net charge of  $+Ze$   
 $Z$  electrons surrounding the nucleus  
 out to a distance of  $10^{-8} \text{ cm}$ .

nearly all volume of an atom is occupied by its electrons, nearly all of its mass concentrated in the nucleus

model has is accepted today

# Preliminaries Wave Motion & Light

(9)



$$\text{speed} = \frac{\text{distance}}{\text{time}}$$

frequency: counts # peaks or troughs observed at a fixed point in space per second

"nu" units of cycles per second or  $s^{-1}$  (Hz)

if 12 water wave peaks are observed at a certain point in 30 seconds,

$$\nu = \text{frequency} = \frac{12}{30 \text{ s}} = 0.40 \text{ s}^{-1}$$

wavelength & frequency for wave are related through its speed - the rate at which a particular wave crest moves through the medium.

In a time interval  $\Delta t = \nu^{-1} (\frac{1}{\nu})$  the wave moves through 1 wavelength, & so the speed (distance traveled divided by time elapsed) is

$$\text{speed} = \frac{\text{distance traveled}}{\text{time elapsed}} = \frac{\lambda}{\nu^{-1}} = \lambda \nu$$

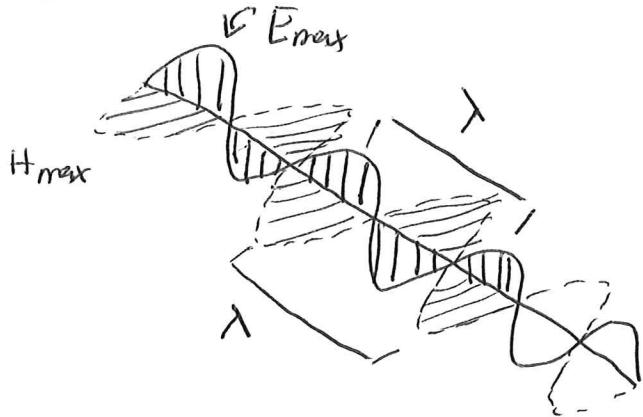
speed of a wave is the product of its wavelength & its frequency

# Electromagnetic Radiation

(10)

1865 JC Maxwell: light is electromagnetic radiation

Civil War consists of oscillating electric & magnetic fields  
Periodic Table  $\perp$  to direction of propagation.



E & H: oscillating electric (E) & magnetic (H) fields  $\perp$  to each other & to the direction of propagation of light

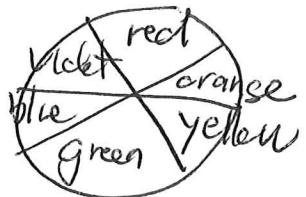
speed of light c in a vacuum is equal to the product  $\lambda\nu$

$$c = \lambda\nu = 2.9979 \times 10^8 \text{ m s}^{-1}$$

c universal constant, same for all types of light throughout the electromagnetic spectrum

regions of spectrum: characterized by different values of wavelength & frequency

wavelength	color	complementary color
< 400	ultraviolet	
400-450	violet	yellow
450-490	blue	orange
490-550	green	red
550-580	yellow	violet
580-650	orange	blue
650-700	red	green
> 700	infrared	



11

SI unit for frequency  $s^{-1}$  is hertz (Hz)  
 SI unit for wavelength m meter

$$\text{cm} \quad 1 \text{ cm} = 1 \times 10^{-2} \text{ m}$$

$$\mu\text{m} \quad 1 \mu\text{m} = 1 \times 10^{-6} \text{ m}$$

$$\text{nm} \quad 1 \text{ nm} = 1 \times 10^{-9} \text{ m} = 1 \times 10^{-7} \text{ cm} = 10 \text{ \AA}$$

$$\text{pm} \quad 1 \text{ pm} = 1 \times 10^{-12} \text{ m} = 1 \times 10^{-10} \text{ cm} = 10^{-2} \text{ \AA}$$

$$\text{\AA} \quad 1 \text{ \AA} = 1 \times 10^{-10} \text{ m} = 1 \times 10^{-8} \text{ cm} = 100 \text{ pm}$$

Anders Ångström (1814-1874)  
 Swedish physicist

outside visible region:

warmth from stone pulled from fire:  
 IR (Infrared) radiation

$$\lambda_{IR} > \lambda_{visible}$$

radio > microwave > IR > visible > UV >  $\gamma$ -ray  
 >  $\gamma$ -ray > cosmic rays

Almost all commercially available microwave ovens employ radiation with a frequency of  $2.45 \times 10^9 \text{ s}^{-1}$ . Calculate the wavelength of this radiation.

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{2.45 \times 10^9 \text{ Hz}} = 0.122 \text{ m}$$

so the wavelength is 12.2 cm

# Blackbody Radiation

(12)

Problems with electromagnetic radiation & classical physics.

$\uparrow$  temp  $\Rightarrow$  objects glow (incandescence)  
as object heated to  $\uparrow T$ , glows more brightly &  
color of light it gives off changes from  
red  $\rightarrow$  orange  $\rightarrow$  yellow  $\rightarrow$  white

qualitative observations

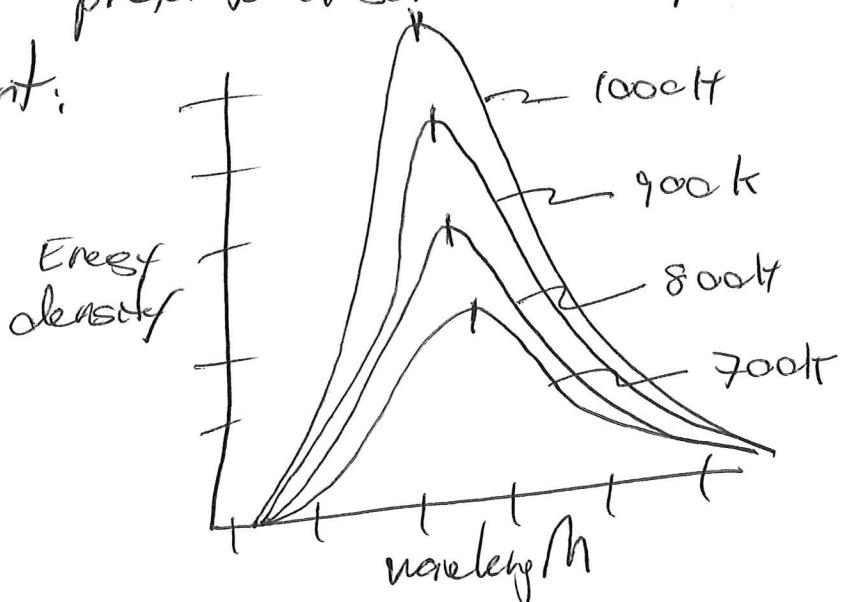
science: theory  $\Rightarrow$  quantitative

measure intensity of radiation at each  $\lambda$   
& repeat at different values of  $T$

$\Rightarrow$  caused one of the greatest revolutions that have  
ever occurred in science

hot object: black body (means object does not  
favor one  $\lambda$  over another  $\lambda$ , i.e., does not  
prefer to absorb or emit one  $\lambda$  over another)

Experiment:



emitted  
radiation at  
different  $\lambda$  by  
a heated  
black body  
for a series  
of  $T$  values

(13)

Note: as  $T \uparrow$ , maximum intensity of radiation emitted occurs at shorter  $\lambda$ 's

1879 Josef Stefan: brightness as  $T \uparrow$

total intensity of radiation emitted over all  $\lambda$  values  $\uparrow$  as  $4^{\text{th}}$  power of  $T$

Stefan-Boltzmann law Total intensity = constant  $\times T^4$

$T$  absolute temperature Kelvin scale

$$\text{constant} = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} \quad \text{W = watt}$$

1893: Wilhelm Wien: shift in color ( $\lambda_{\text{max}}$ ) of black body radiation as  $T \uparrow$

I found  $\lambda_{\text{max}} T = \text{constant}$  Wien's Law

$$\lambda_{\text{max}} \propto \frac{1}{T} \quad \text{as } T \uparrow, \lambda \downarrow$$

$$C = 2.9 \text{ K mm}$$

Scientists could not account for these laws by classical physics.

UV catastrophe: classical physics predicted that any hot body should emit intense UV radiation, even X-rays &  $\gamma$ -rays!

used simple harmonic oscillators oscillating them

Theory predicted a hot object would produce far too much high frequency radiation

$\Rightarrow$  even human body at  $37^\circ\text{C}$  would glow in the dark, i.e., there would be no darkness,

Classical: a blackbody consists of a large collection of oscillators

(135)

classical physics/statistics tell us that each frequency should carry the same amount of energy (equipartition principle)

# of possible frequencies of oscillators inside a box or blackbody increases as the square of the frequency, so that the blue or UV end of the spectrum should have more intense radiation than the red or IR end due to its higher frequency rather than less.

Solution: 1900 German physicist Max Planck (14) proposed heat exchange of energy between matter & radiation occurs only in quanta or packets of energy, focused on hot, rapidly oscillating electrons & atoms in the black body.

$\Rightarrow$  charged particles oscillating at  $\nu$  can exchange energy with surroundings by generating absorbing electromagnetic radiation only in discrete packets of energy

$$E = h\nu$$

constant  $h$  Planck's constant ( $6.626 \times 10^{-34} \text{ Js}$ )

If oscillating atom releases  $E$  into surroundings then radiation of  $\nu = \frac{E}{h}$  will be detected.

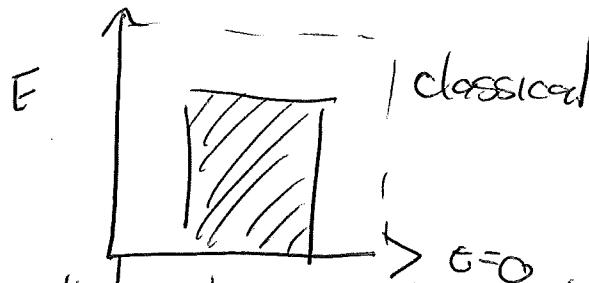
Planck: ① each frequency did not carry the same amount of energy but rather that the energy from oscillator has to do  $\nu$ .

② energy of these oscillators was quantized so that an oscillator could acquire or lose energy only in units of  $h\nu$ .

This causes low intensity of high frequency radiation since the oscillator could acquire the energy to radiate  $h\nu$  only from a thermal energy of the black body  $kT$ . If  $kT \ll h\nu$  there is only a very small chance that the oscillator will have sufficient thermal energy to emit high frequency radiation.

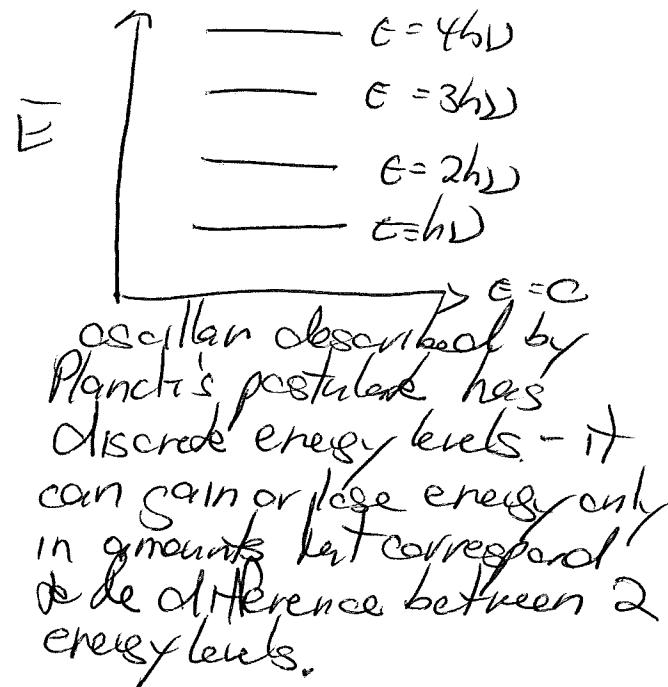
Proposal:  $E = nh\nu$   $n=1, 2, 3, 4, \dots$

Contrast between Planck's postulate & classical picture



oscillator obeying classical mechanics has continuous values of energy & can gain or lose energy in arbitrary amounts

could not explain distribution



oscillan described by Planck's postulate has discrete energy levels - it can gain or lose energy only in amounts that correspond to the difference between 2 energy levels.

$$\exp[-h\nu/k_B T] \quad k_B \text{ Boltzmann's constant}$$

(similar to Maxwell-Boltzmann speed distribution for molecules later in term.)

Planck discarded classical physics (no restriction on how small an amount of energy may be transferred from one object to another) proposed energy transferred in discrete packets

latter claim needed more evidence

... Einstein's explanation of the photoelectric effect

# Photoelectric Effect

(16)

1888, Heinrich Hertz discovered that when light strikes the surface of certain metals, electrons are ejected.

- ① - electron emission only occurs when the frequency of the incident light exceeds a particular threshold value ( $\nu_0$ ). When this condition is met, it is further observed that
- ② - # electrons emitted depends on the intensity of the incident light, but
- ③ - the # of electrons emitted depends on the frequency of the light

According to classical theory, E associated with electromagnetic radiation depends only on the intensity & not the frequency. Why then could a very weak beam of blue light eject electrons from sodium when an intense red beam had no effect?

Einstein showed (1905) that this is what would be expected with a particle interpretation of radiation. He proposed that electromagnetic radiation has particle-like qualities and that "particles" of light subsequently called photons by G.N. Lewis, have a characteristic energy given by Planck's equation  $E = h\nu$ .

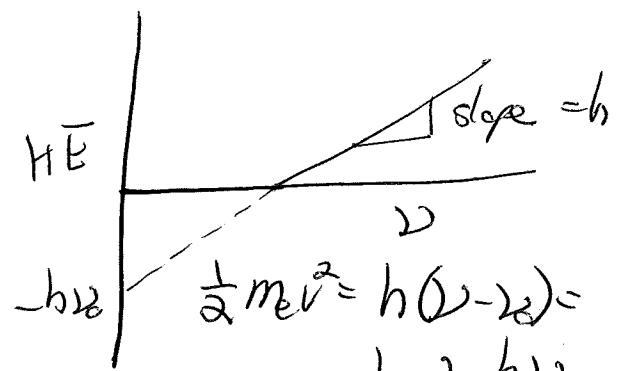
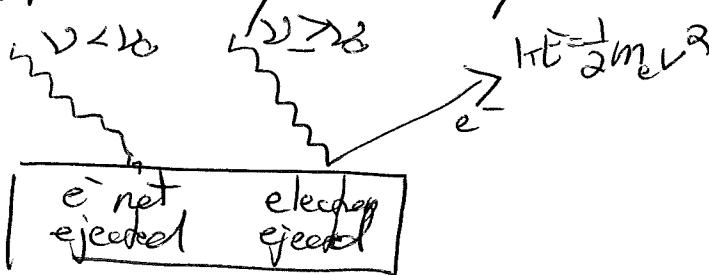
photons  $\propto$  packets of energy  $\Rightarrow E = h\nu$   
recall: intensity of radiation  $\Rightarrow$  # of photons present  
 $E = h\nu$ , measure energy of each photon

In particle model, a photon of energy  $h\nu$  strikes a bound electron which absorbs the photon energy. If photon energy  $h\nu >$  energy binding the electron to the surface (work function  $\Phi$ ) (phi), a photoelectron is liberated. Thus, the lowest frequency light producing the photoelectric effect is the threshold frequency & any energy in excess of the work function appears as  $hE$  in the emitted photoelectrons.

$$E_{max} = h\nu - \Phi = \frac{1}{2} m_e v^2$$

$\Phi = h\nu_0$  is a constant characteristic of the metal.

Einstein's theory predicts that the maximum kinetic energy is a linear function of the frequency, can be used to test validity of theory.



Examine several frequencies

$E_{max}$  vs  $\nu$  linear

Slope of line  $\Rightarrow$  numerical value of  $h$  ( $v$ )  
same as blackbody radiation

(18)

Light with  $\lambda = 400 \text{ nm}$  strikes surface of Cs

In a photocell, the maximum KE of  $e^-$  ejected is  $1.54 \times 10^{-19} \text{ J}$ . Calculate the work function of Cs & the largest  $\lambda$  of light that is capable of ejecting  $e^-$ 's from Cs metal.

The frequency of light is

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{4.00 \times 10^{-7} \text{ m}} = 7.50 \times 10^{14} \text{ s}^{-1}$$

binding energy  $h\nu_0$  can be calculated from Einstein's formula:

$$\left(\frac{1}{2} m_e v^2\right)_{\text{max}} = h\nu - h\nu_0$$

$$1.54 \times 10^{-19} \text{ J} = (6.626 \times 10^{-34} \text{ Js})(7.50 \times 10^{14} \text{ s}^{-1}) - h\nu_0 \\ = 4.97 \times 10^{-19} \text{ J} - h\nu_0$$

$$\underline{\nu_0} = h\nu_0 = (4.97 - 1.54) \times 10^{-19} \text{ J} = 3.43 \times 10^{-19} \text{ J}$$

The minimum frequency  $\nu_0$  for the light to eject  $e^-$ :

From  $E=hn\nu$

$$\nu_0 = \frac{3.43 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ Js}} = 5.18 \times 10^{14} \text{ s}^{-1}$$

& from this, the maximum  $\lambda_0$  is:

$$\lambda_0 = \frac{c}{\nu_0} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{5.18 \times 10^{14} \text{ s}^{-1}} = 5.79 \times 10^{-7} \text{ m} \\ 579 \text{ nm}$$

# Atomic Spectra

(18)

Visible spectrum: continuous since diffracted light consists of numerous wavelength components

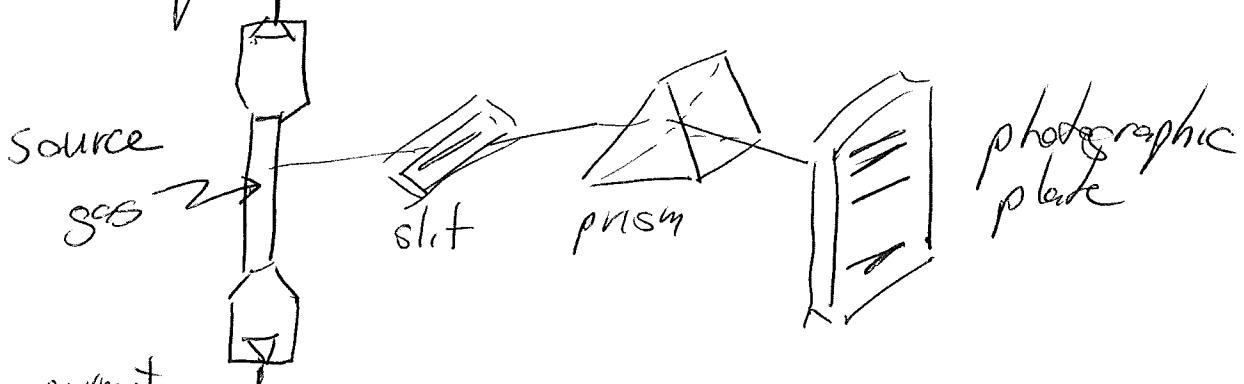
light through prism

If source for spectrum produces a small number of wavelength components, discontinuous spectrum

⇒ gas flame, add ionic compound to flame  
Flame acquires distinctive color indicative of metal ion present  
 $\text{Li}^+$  red  $\text{Na}^+$  yellow  $\text{H}$  violet  $\text{Cs}^+$  blue  
 $\text{Rb}^+$  deep red

⇒ limited # discrete wavelength components observed as colored lines with dark spaces between them

⇒ discontinuous spectra are called atomic or line spectra



each element has its own distinctive line spectrum  
atomic fingerprint.

Robert Bunsen (1811-1899) Gustav Kirchhoff (1824-1887)  
developed 1<sup>st</sup> spectroscope & used it to identify elements

1860: new element discovered cesium

(Latin, caesius, sky blue)

distinctive blue lines in its spectrum

1861: rubidium (Latin, rubidius, deepest red)

1868: helium (Greek, helios, sun) observed in spectrum of the sun observed during solar eclipse of 1868

He not isolated on Earth for another 27 years

1885: Johann Balmer (trial & error) examined He spectrum  
of hydrogen:

656.3 nm red

486.1 nm greenish blue

434.0 nm violet

410.1 nm violet

$$\nu = 3.2881 \times 10^{15} \text{ s}^{-1} \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \quad n = 3, 4, 5, \dots$$

Rydberg constant  
(109,677,581 cm<sup>-1</sup>)

red ↑ greenish blue  
 ↑ ↑  
 violet ↓ violet ↓ violet

n = integer > 2

Atomic spectra consisted only of limited # well-defined wavelengths.

suggests only a limited # energy values available  
& excited gaseous atoms

⇒ classical (19<sup>th</sup> century) physics could not provide an explanation of atomic spectra  
(not continuous but discrete)

# Bohr Atom

(21)

Rutherford's description atom: nucleus with  $e^-$  orbiting  
but major problems  $\Rightarrow$  no longer accepted

$e^-$  orbiting + nucleus: attraction of opposite charges  
and rapid motion sideways  
but perpetually moves  $le^-$  out  
 $\uparrow$  the way of the nucleus

constant  $\checkmark$  around a point: acceleration  
severe problem: classical electromagnetic  
theory insists that an accelerating  
electric charge must emit radiation  
which uses up some of its energy

Rutherford atom: orbital motion of  $e^-$  would  
continuously emit radiation losing up  
energy so that it would drop further &  
fall into the potential-energy well  
 $\uparrow$  the nucleus & would spiral in,  
eventually the nucleus destroying because

But, H-atom (1 proton, 1  $e^-$ ) does not emit  
radiation continuously & is quite  
stable (does not collapse).

Bohr: Rutherford's model based on Cornell experimental  
fact, but no account had been taken of the  
quantization of  $e^-$ 's energy as he wrote &  
Planck & Einstein demanded

Bohr: if  $e^-$  were not to fall into nucleus, radius of orbit must be constant (22)

if radius does not change, forces on  $e^-$  in radial directions must exactly cancel each other

attractive force between 2 unlike charges: Coulomb's law  
 attraction  $\propto$  product of charges  $\propto$  inversely proportional to square of distance between charges

$$\text{attractive force} = \frac{q_1 q_2}{r^2}$$

In this case,  $q_1 = Ze$  necessary for attractive force (neg attraction is repulsion)

$Z = \#$  positive charges,  $\#$  nucleus  
 $e = \text{magnitude of each charge unit}$

$q_2 = -e$  charge of electron

$$\text{attractive force} = \frac{Ze^2}{r^2}$$

must be balanced by a force trying to pull  $e^-$  & nucleus apart, centrifugal force on the circle  $e^-$  in Newtonian physics: centrifugal force =  $\frac{mv^2}{r}$

Now  $\frac{Ze^2}{r^2} = \frac{mv^2}{r}$        $m$   $e^-$  mass  
 $v$  velocity  
 $r$  distance from nucleus

but,  $e^-$  would spiral down

Bohr: introduced idea of quantization of energy proposed angular momentum  $\Delta e^-$  was quantized in multiples of  $\frac{h}{2\pi}$  ( $\hbar$ )

$$(L = r \times p)$$

$$r \times mv$$

cross product

conserved quantity

or

angular momentum

$mvr = \frac{n\hbar}{2\pi}$

$n = \text{number of quanta}$   
 $\Delta \text{angular momentum}$

(23)

$$mv^2 = \frac{nh}{2\pi} \Rightarrow v = \frac{nh}{2\pi mr}$$

$$\frac{Ze^2}{r^2} = \frac{mv^2}{r} \Rightarrow \frac{Ze^2}{r^2} = \frac{m}{r} \left( \frac{nh}{2\pi mr} \right)^2$$

$$\frac{Ze^2}{r^2} = \frac{n^2 h^2}{4\pi^2 m r^3}$$

cancelling  $r^2$ :

$$Ze^2 = \frac{n^2 h^2}{4\pi^2 m r} \quad \text{or}$$

$$r = \frac{n^2 h^2}{4\pi^2 m Ze^2} = \frac{n^2}{Z} a_0$$

$$\text{where } a_0 = \frac{h^2}{4\pi^2 m e^2}$$

right side all constants,  $\Rightarrow$  only certain radii are possible for  $e^-$ , namely when  $n=1, 2, 3\dots$

smallest Bohr radius for H atom  $n=1 = a_0$   
some constants:  $0.529 \text{\AA}$

Is energy quantized?

Total energy of  $e^-$  is sum of KE + PE  
 $PE = 0$  at infinite separation of charges

$$E = \frac{1}{2} mv^2 - \frac{Ze^2}{r}$$

kinetic  
energy

Coulomb  
attractive/  
potential  
energy

Notice: Coulomb attractive energy is different from the Coulomb attractive force

(24)

PE is the integral of force over distance from the potential energy 0 at  $\infty$  separation to Bohr radius  $r$ :

$$\int_{\infty}^r \frac{Ze^2}{r^2} dr = -\frac{Ze^2}{r} \Big|_{\infty}^r = -\frac{Ze^2}{r} + \frac{Ze^2}{\infty} = -\frac{Ze^2}{r}$$

force

Total energy e:  $E = \frac{1}{2}mv^2 - \frac{Ze^2}{r}$

but  $\frac{mv^2}{r} = \frac{Ze^2}{r^2} \Rightarrow mv^2 = \frac{Ze^2}{r}$

so

$$E = \frac{1}{2} \frac{Ze^2}{r} - \frac{Ze^2}{r} = -\frac{1}{2} \frac{Ze^2}{r}$$

Now, substitute quantized expression for  $r$

$$E = -\frac{1}{2} \frac{Ze^2}{(n^2 h^2 / 4\pi^2 m Ze^2)} \quad \text{or}$$

$$E = -\frac{2\pi^2 m Z^2 e^4}{n^2 h^2}$$

Total energy of  $e^-$  is quantized with the quantum number, an integer, appearing squared in the denominator.

Reasonable?  $E$  is negative logical (recall  $0$  at  $\infty$  separation) means must put  $E$  into order to get  $e^-$  out to an infinite distance

If  $E$  must be added to set up to zero, initial energy must have been negative.  
(ionization energy) (25)

- Bohr atom:-  $e^-$  moves in circular orbit about nucleus with motion described by classical physics
- $e^-$  has only fixed set of allowed orbits  $E$  constant & no  $E$  emitted in such state quantized angular momentum  $\frac{n\hbar}{2\pi}$
  - $e^-$  can pass from 1 allowed orbit to another & fixed quantities  $\Delta E$  &  $\Delta E$  are involved, either absorbed or emitted

H-spectra:

$$\Delta E = h\nu \Rightarrow$$

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h} = \frac{1}{h} \left( -\frac{2\pi^2 m_e Z^2 e^4}{n_2^2 h^2} + \frac{2\pi^2 m_e Z^2 e^4}{n_1^2 h^2} \right)$$

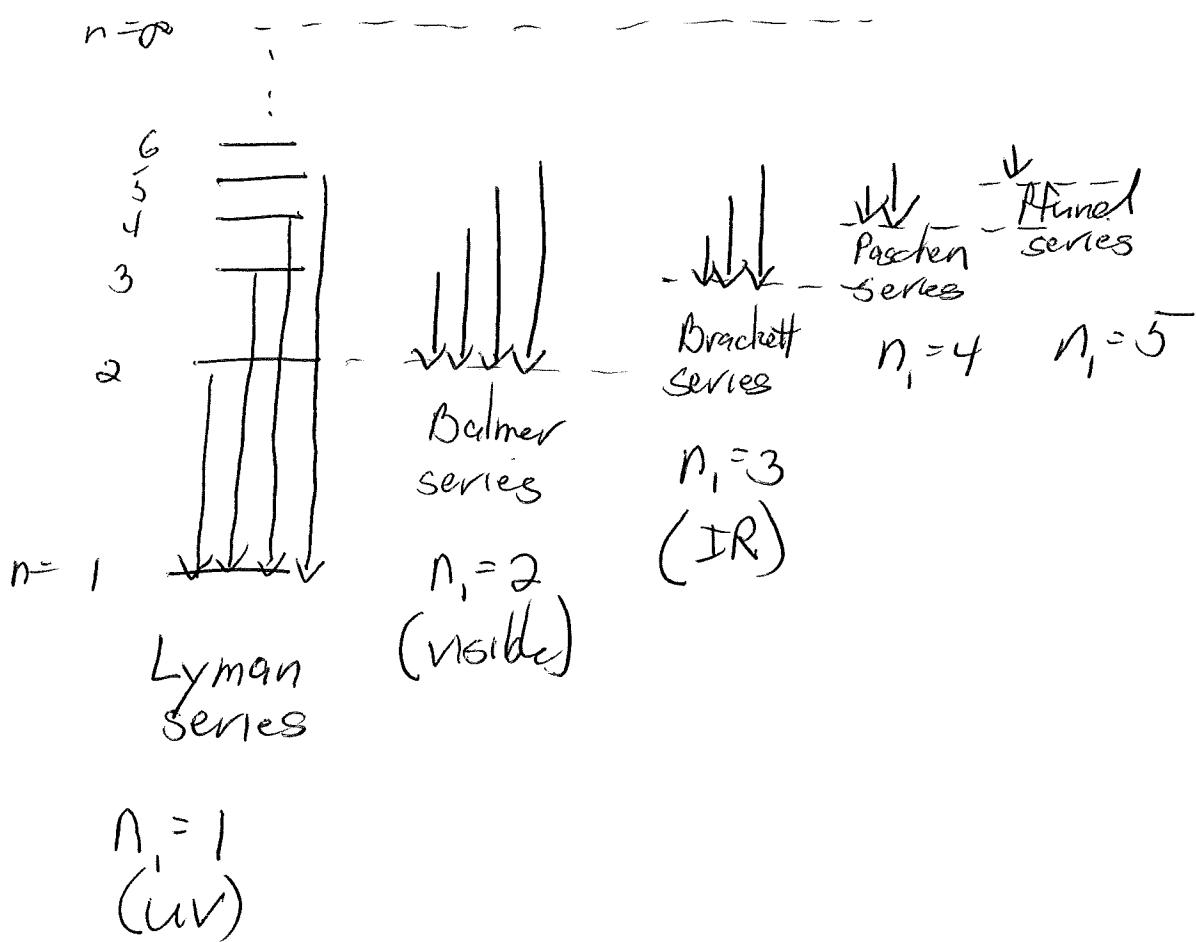
$$\nu = \frac{2\pi^2 m_e Z^2 e^4}{h^3} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Since  $Z=1$  for H,

$$R = \frac{2\pi^2 m_e e^4}{h^3} \text{ or } \frac{2\pi^2 m_e e^4}{ch^3} \text{ (in cm}^{-1}\text{)}$$

Bohr model: predicts Rydberg formula & gives fundamental constant equal Rydberg constant ( $109678 \text{ cm}^{-1}$ )

H atom:



$$\nu = (3.29 \times 10^{15} \text{ s}^{-1}) Z^2 \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$n_f > n_i = 1, 2, 3, \dots$  absorption

Problems: only works for emission spectra. Sodius & Ions with 1  $e^-$  + 1 nucleus, not conceivable to move 1  $e^-$ .

Inevitably mix classical & non-classical physics

Bohr: no fundamental basis for postulate of quantized angular momentum forcing an  $e^-$  into circular orbit. (made so theory would agree with expt)

Need new fundamental theory: Quantum

# (22)

## Two ideas leading to New Quantum Mechanics

To explain photoelectric effect, Einstein suggested that light has particle-like properties, which are embodied in photons.

Other phenomena dispersion of light into a spectrum by a prism, best defined by wave theory.

Light  $\Rightarrow$  dual nature

1924 Louis de Broglie considering nature of light and matter proposed:

"Small particles of matter may at times display wave-like properties."

How?  $E=mc^2$  Einstein

combined with Planck's relationship of energy of a photon,  $E=h\nu$

$m$  relativistic mass of photon  
 $c$  speed of light  
 Latin: celeritas  
 "swiftness"

$$h\nu = E = mc^2$$

$$\frac{h\nu}{c} = mc = p \quad p = \frac{\text{momentum}}{\text{photon}}$$

$$\text{using } \nu\lambda = c \quad p = \frac{h\nu}{c} \Rightarrow p = \frac{h\nu}{\lambda\nu} = \frac{h}{\lambda}$$

For material particle (electron) de Broglie substituted for de momentum  $p$  its equivalent mass of particle  $m$  & its velocity  $v$ .

# de Broglie's relationship

(28)

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

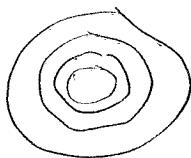
de Broglie called waves associated with material particles "matter waves"

if true, beams of particles ( $e^-$ ) should exhibit characteristic properties of waves,  $\Rightarrow$  diffraction

 if distance between objects that scatters waves is  $\approx$  same as wavelength of radiation, diffraction occurs & an interference pattern is observed

X-rays:  $\lambda \approx 1\text{\AA}$  (100pm)

X-rays scattered by atoms in Al metal (2.2\text{\AA}, 200pm) apart, get diffraction pattern



1927 C.J. Davisson, L.H. Germer (US) beam of slow  $e^-$  is diffracted by crystal of Ni.

G.P. Thomson (Scotland) beam of  $e^-$  at metal foil observed same diffraction pattern as with X-rays of same wavelength.

Thomson & Davisson shared 1937 Nobel Prize in Physics: G.P. Thomson son of J.J. Thomson 1906 Nobel Prize for discovery of  $e^-$

 electron is a wave

 electron is a particle

Fowler / Son showed wave-particle duality of electrons

(29)

What is the wavelength associated with electrons traveling at 0.1 c?

$$m_{e^-} = 9.109 \times 10^{-31} \text{ kg}$$

$$v = 0.100c = 0.100 \times 3.00 \times 10^8 \frac{\text{m}}{\text{s}} = 3.00 \times 10^7 \frac{\text{m}}{\text{s}}$$

$$h = 6.626 \times 10^{-34} \text{ Js} = 6.626 \times 10^{-34} \frac{\text{kg m}^2}{\text{sec}^2} \text{ s}$$

$$= 6.626 \times 10^{-34} \frac{\text{kg m}^3}{\text{s}}$$

$$\lambda = \frac{h}{mv} = 6.626 \times 10^{-34} \frac{\text{kg m}^2}{\text{s}}$$

$$(9.109 \times 10^{-31} \text{ kg})(3.00 \times 10^7 \frac{\text{m}}{\text{s}})$$

$$= 2.42 \times 10^{-11} \text{ m} = 24.2 \text{ pm}$$

value  $\approx$  radius of the first Bohr orbit of a H atom

$\Rightarrow$  only when  $\lambda$ 's are comparable to atomic or nuclear dimensions should you concern yourself with the wave particle duality concept

$\Rightarrow$  little meaning when applied to macroscopic objects (baseballs) because  $\lambda$ 's too small to measure; laws of classical physics are quite adequate

# Uncertainty Principle

classical physics: physical behavior can be predicted with certainty

1920's Niels Bohr Werner Heisenberg

studied behavior of subatomic particles

2 variables: position  $x$  momentum  $p = m v$

found  $\Delta x \Delta p \geq \frac{h}{4\pi}$  Heisenberg uncertainty principle

- if you locate position of a particle with great precision, you know where it is found, but you cannot also know precisely where it came from or where it is going.
- if you know precisely how a particle is moving, you cannot also know precisely where it is

$\Rightarrow$  study an electron in a hydrogen atom using a microscope

smallest particle you can see with a microscope has about the same dimensions as wavelength of light (radiation) needed to (electron microscope) illuminate it

1<sup>st</sup> Bohr orbit of H atom  $\sim 53$  pm diameter of atom about  $100$  pm ( $10^{-10}$  m,  $1\text{\AA}$ )

$e^-$   $\ll$  atoms in which they are found assume  $\sim 10^{-14}$  m for diameter of electron

$\nu = \frac{c}{\lambda}$  lets you calculate frequency & light & this wavelength, so

$$\nu \approx 3 \times 10^{28} \text{ s}^{-1} \Rightarrow E = h\nu = 2 \times 10^{-19} \text{ J}$$

but:  $2.179 \times 10^{-18} \text{ J}$  required to ionize the electron in an H atom

a photon of this energy would not help us to see the electron in the atom, it would knock the  $e^-$  out of the atom.

trying to kick out  $e^-$  in atom would drastically change the situation from an electron bound in a H atom to an ionized  $e^-$  free of the atom

$$\text{visible light: } \sim 5 \times 10^{14} \text{ s}^{-1} \Rightarrow E = 3 \times 10^{-19} \text{ J}$$

has no effect on a macroscopic object  $\Rightarrow$  uncertainties are insignificant

$\Gamma$  calc. uncertainty of position of  $e^-$

$DeV e^-$  has speed of  $2.05 \times 10^6 \text{ m/s}$

assume uncertainty (precision) of this value is  $\sim 1.5\%$

What precision can we simultaneously measure besides  $e^-$ ?

$$m_e = 9.109 \times 10^{-31} \text{ kg}$$

$$\rho = mu = (9.11 \times 10^{-31} \text{ kg})(2.05 \times 10^6 \text{ m}) \\ = 1.87 \times 10^{-24} \frac{\text{kg m}}{\text{sec}}$$

$$\Delta p = (0.015) \times 1.87 \times 10^{-24} \frac{\text{kg m}}{\text{sec}} = 2.80 \times 10^{-26} \frac{\text{kg m}}{\text{sec}}$$

$$\Delta x = \frac{h}{4\pi\Delta p} = \frac{6.63 \times 10^{-34} \frac{\text{kg m}^2}{\text{sec}}}{4 \times 3.14 \times 2.80 \times 10^{-26} \frac{\text{kg m}}{\text{sec}}} \\ = 1.89 \times 10^{-9} \text{ m} = 1890 \text{ pm}$$

(31)

1870pm  $\approx$  15-20 atomic diameters (10 fm) (32)  
heavier elements)

With this measurement of  $e^-$ 's momentum, cannot determine  
its position with any great precision ]

Consequence of wave-particle duality is Heisenberg's uncertainty principle, fundamental error of Bohr model was to  
constrain  $e^-$  to a one-dimensional orbit (1D in fact  $e^-$   
cannot move off the orbit) (circle 1D: all pts 1 node from center)

## Wave Mechanics

DeBroglie's relationship  $e^-$  are matter waves,  
consequence of wave-particle duality is Heisenberg's  
uncertainty principle

### Standing Waves

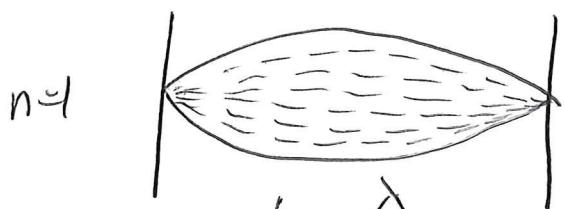
traveling waves: ocean, travel distance



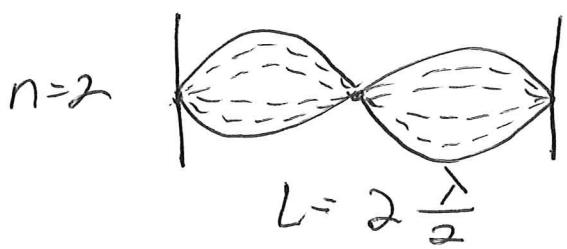
- every portion of rope goes through an identical up-down motion
- wave transports energy along entire length of rope

Standing wave: plucked guitar string

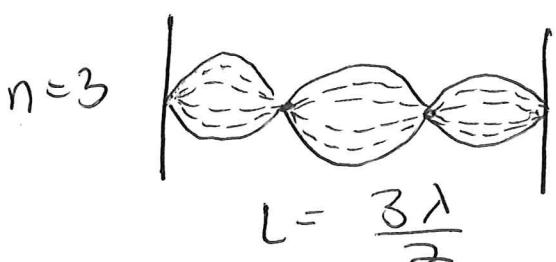
Segments of string experience up & down motion (displacements) with time & they oscillate or vibrate between limits set by maximum displacement



$\Rightarrow$  NB crests & troughs of wave occur at fixed points (positions) and the amplitude of the wave at the fixed ends is zero.



$\Rightarrow$  magnitudes of oscillations differ from point to point along wave & include certain points called nodes, but undergo no displacement at all.



characteristics of standing wave

\* note: higher the number of the harmonic  $n$ , the more numerous the nodes, the shorter the wavelength, the higher the frequency, & the higher the energy of the standing wave

permitted wavelengths of standing waves are quantized equal to twice the length ( $L$ ) divided by a whole number  $n$ , ie

$$\lambda = \frac{2L}{n} \quad n=1, 2, 3$$

(or  $n \frac{\lambda}{2} = L$ )

total # nodes =  $n+1$

plucked guitar string: 1D standing wave  
same as Bohr orbit (34)

Bohr theory requires integer # wavelengths  
problem: 1D, e<sup>-</sup> in H must be 3D

1 standing wave requirement

$$n\lambda = 2\pi r \quad n=1, 2, 3 \quad \lambda = \frac{h}{mv}$$

Bohr's assumption angular momentum

$$2\pi r = \frac{nh}{mev} \rightarrow mevr = n \frac{h}{2\pi} \Rightarrow 2\pi r = n \left[ \frac{h}{mev} \right]$$

but  $n\lambda = n \frac{h}{mev} \Rightarrow \lambda = \frac{h}{P}$  deBroglie's equation

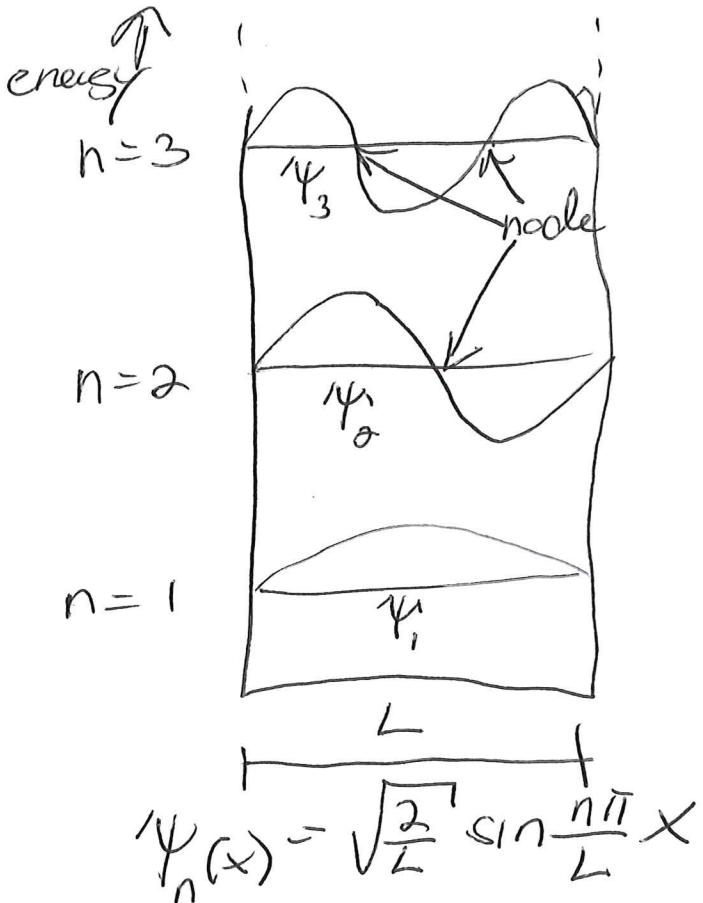
1927 Erwin Schrödinger  
expert in theory vibrations + standing waves  
suggests that e<sup>-</sup> (or any other particle) exhibiting  
wave-like properties should be describable by a  
mathematical equation called a wave function  $\psi$

Wave function should correspond to standing wave  
within boundary of system

simplest: 1-dimensional system: particle confined  
to area in a circle  
direction in a box

similar to guitar string  
but now represent periodic  
waves for particle

$\Rightarrow$  Since particle constrained to be in box, waves must also  
be inside the box



length of box  $L$   
particle wavelength & direction  
equation is:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad n=1, 2, 3, \dots$$

$n$  = quantum number  
labels wave function

sine function undergoes  
some additional method  
characteristics of waves

consider  $n=2$

when

$$x=0 \quad \sin \frac{2\pi x}{L} = \sin 0 = 0$$

$$\psi_n(0) = 0$$

$$x=\frac{L}{4} \quad \sin \frac{2\pi \left(\frac{L}{4}\right)}{L} = \sin \frac{\pi}{2} = 1$$

$$\psi_n\left(\frac{L}{4}\right) = \left(\frac{2}{L}\right)^{1/2}$$

$$x=\frac{L}{2} \quad \sin \frac{2\pi \left(\frac{L}{2}\right)}{L} = \sin \pi = 0$$

$$\psi_n\left(\frac{L}{2}\right) = 0$$

$$x=\frac{3L}{4} \quad \sin \frac{2\pi \left(\frac{3L}{4}\right)}{L} = \sin \frac{3\pi}{2} = -1$$

$$\psi_n\left(\frac{3L}{4}\right) = -\left(\frac{2}{L}\right)^{1/2}$$

$$x=L \quad \sin \frac{2\pi L}{L} = \sin 2\pi = 0$$

$$\psi_n(L) = 0$$

- at one end of box ( $x=0$ ) both sine function & wave function are zero
- at  $\frac{1}{4}$  length of box ( $x=\frac{L}{4}$ ), sine function & wave function both reach maximum values

- at midpoint of box, both are again zero  
the wave function has a node

- at  $\frac{3}{4}$  of the box length, both functions reach their minimum values (negative quantities)

- at far end of box, both functions are zero again

→ consider quantum #  $n$ : particle under investigation is freely moving (not acted upon by any outside forces) with TE:

$$E_k = \frac{1}{2}mv^2 = \frac{m u^2}{2m} = \frac{p^2}{2m}$$

Now can associate this TE with a wave, use de Broglie's relationship ( $\lambda = h/p$ ) & set

$$E_k = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} \leftarrow \left( p = \frac{h}{\lambda} \right)$$

wavelengths of matter wave must fit the same standing wave conditions discussed earlier for standing waves for guitar string ( $\lambda = \frac{2L}{n}$   $n=1, 2, 3, \dots$ )

Thus,

$$E_k = \frac{h^2}{2m\lambda^2} = \frac{h^2}{2m(2L/n)^2} = \frac{n^2 h^2}{8m L^2}$$

⇒ standing wave condition naturally gives rise to quantization of the wave's energy  
allowable values of  $E_k$  determined by the value of the quantum number  $n$

Note: as you decrease size of box  
HE of particle increases

(according to uncertainty principle, our knowledge  
of momentum must decrease)

Note: energy of particle cannot be zero  
lowest possible energy ( $n=1$ ) is called the  
zero-point energy

zero point energy is not zero, particle  
cannot be at rest

- consistent with uncertainty principle since  
position & momentum both must be uncertain,  
& there is nothing uncertain about a  
particle at rest.

Interpretation of  $\Psi$ : what does + or -  $\Psi$  values  
mean?

unlike trajectory of a classical particle,  $\Psi$  &  
a particle has no physical significance

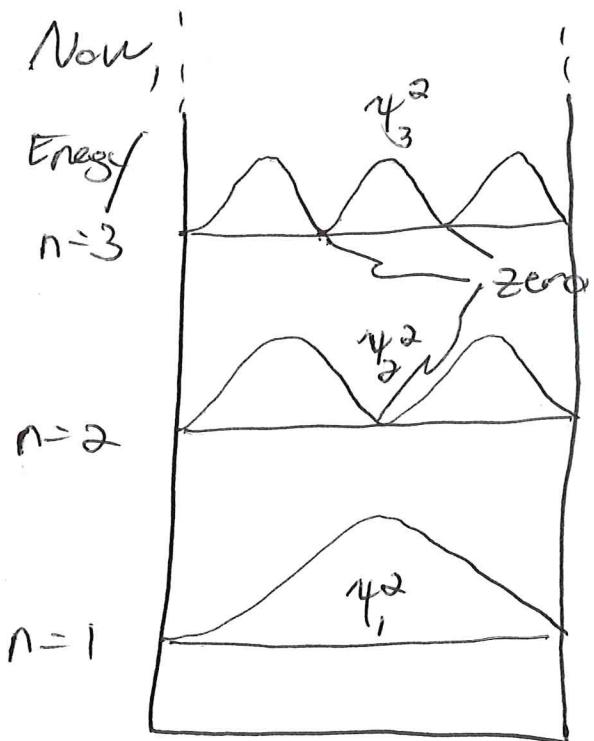
Motl Born (1926): electron as particle standpoint,  
want to know probability that electron is  
at some particular point; from electron as wave  
standpoint, interest is in electron charge  
density

Classical wave: (visible light) amplitude of wave corresponds to & Intensity of the wave to  $\gamma^2$ . (38)

Intensity relates to: photon density  
# photons present in a region

For an electron wave,  $\gamma^2$  relates to electron charge density  
electron probability & electron charge density  
both these quantities are associated with  $\gamma^2$

\* Born's interpretation of wave function: the value of  $\gamma^2$  is the probability density of finding an  $e^-$  in a small volume of space  
 $\Rightarrow$  total probability of finding  $e^-$  in that small volume is  $\gamma^2$  times the volume of interest



$$\gamma_n^2(x) = \frac{2}{L} \sin^2\left(\frac{n\pi}{L}x\right)$$

the probabilities

$\Rightarrow$  even where  $\gamma_n(x)$  is negative, probability density is positive (as it should be)

$\Rightarrow$  probability density for  $n=1$  highest value of  $\gamma^2$  is at center of box, i.e., particle is most likely to be found there

$\Rightarrow$  probability density for  $n=2$  particle most likely to be found between the center of the box & the walls

$\Rightarrow$  no chance of finding particle at points where  $\gamma^2 = 0$  (nodes)

wave particle duality prevents the question  
 of how an  $e^-$  gets from one side of the  
 node to the other (appropriate for classical particles) (39)

$\rightarrow$  all we know is that in  $n=2$  state, the  $e^-$   
 is somewhere in the box, when make measurement  
 particle on one side of the node or the other

extension to 3D box: particle can move in all  
 three directions ( $x, y, z$ ) & the quantization  
 energy is described by

$$E_{n_x n_y n_z} = \frac{\hbar^2}{8m} \left[ \left( \frac{n_x^2}{L_x} \right) + \left( \frac{n_y^2}{L_y} \right) + \left( \frac{n_z^2}{L_z} \right) \right]$$

Note: 1 quantum  $\hbar$  for each dimension  
 3D system requires 3 quantum numbers

## Wave Functions of H-Atom

1927 Erwin Schrödinger showed that wave functions  
 for quantum mechanical system can be obtained  
 by solving a new equation (now called Schrödinger  
 equation).

Classical physics of waves: solution for  
 standing wave in 1 dimension for a simple system  
 for a particle in a box

$$\frac{d^2\psi}{dx^2} = -\left(\frac{2\pi}{\lambda}\right)^2 \psi \quad \text{differential equation}$$

$\Rightarrow$  solution of this equation is the wave function for the system

(40)

Form of equation: by differentiating the wave function twice, we obtain the wave function times a constant

$$\text{Now, } \lambda = \frac{h}{p} \text{ or } \frac{1}{\lambda} = \frac{p}{h} \text{ so}$$

$$\frac{d^2\psi}{dx^2} = -\left(\frac{2\pi p}{h}\right)^2 \psi$$

$$\frac{-h^2}{4\pi^2 p^2} \frac{d^2\psi}{dx^2} = \psi + E_T = \frac{p^2}{2m}$$

$$\frac{-h^2}{4\pi^2 p^2} \frac{p^2}{2m} \frac{d^2\psi}{dx^2} = E_T \psi$$

$$\frac{-h^2}{8\pi^2 m} \frac{d^2\psi}{dx^2} = E_T \psi$$

Schrödinger equation  
of a free particle  
moving in 1 dimension

If particle is also subjected to a force  $V(x)$ , then we have

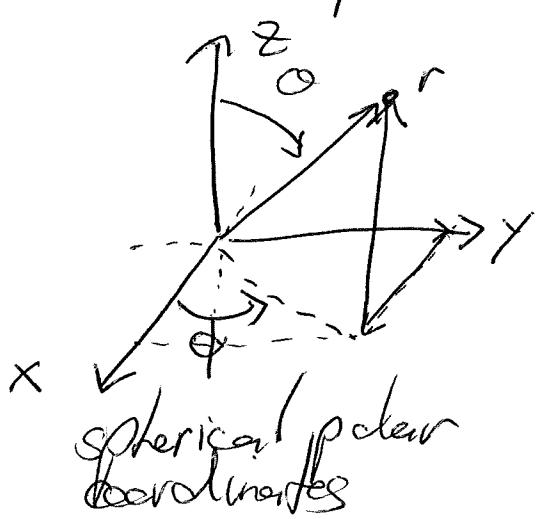
$$\frac{-h^2}{8\pi^2 m} \frac{d^2\psi}{dx^2} + V(x) \psi = E_{\text{total}} \psi$$

extending this treatment to 3D, we obtain Schrödinger equations for H-atom where the force  $V(r)$  is equal to  $-\frac{Ze^2}{r}$ , attractive force between  $e^-$  & nucleus

$$\frac{-h^2}{8\pi^2 m_e} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) - \frac{Ze^2}{r} \psi = E \psi$$

Solutions of Schrödinger equation for H-atoms (41)  
 size wave functions for the electrons in the H-atoms

These wave functions are called orbitals to distinguish them from the orbits of the Bohr atom theory  
 more complex form than for particle in a box, but can be interpreted



$$x^2 + y^2 + z^2 = r^2$$

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

wavefunctions are expressed in terms of the 3 variables required to define a point wrt the nucleus.

Cartesian coordinate system: + x + y + z dimensions

Eugene Wigner suggested Schrödinger use spherical polar coordinates to solve it rather than Cartesian coordinates

spherical polar coordinates: r distance of point from nucleus

angles  $\theta$  (theta) &  $\phi$  (phi)  
 describe orientation of distance line r wrt x, y, z

either system could be used to solve equations  
 in Cartesian system, orbitals would involve all three variables x, y, z

in spherical polar coordinates, orbitals expressed

(42)

in terms of one function  $R$  that depends only on  $r$ , and a second function  $\psi$  that depends on  $\theta$  and  $\phi$ .

$$\Psi(r, \theta, \phi) = R(r) Y(\theta, \phi)$$

↑                              ↑  
 radial                        angular  
 wave                        wave  
 function                    function

each orbital has 3 quantum numbers, & a given set of particular set of quantum numbers corresponds to a particular function (term) of  $R(r)$  and  $Y(\theta, \phi)$

## Quantum Numbers & Electron Orbitals

3 quantum numbers in a wave function for each orbital

different combinations of quantum numbers produce different orbitals

### Assigning Quantum Numbers

1<sup>st</sup> principal quantum number  $n$

only has positive, non zero integral values  
 $n=1, 2, 3, 4, \dots$

2<sup>nd</sup> orbital angular momentum quantum number  $l$

zero or a positive integer  
not larger than  $n-1$

$$l=0, 1, 2, 3, \dots, n-1$$

3<sup>rd</sup> magnetic quantum number  $m_l$  (43)  
 negative or positive integer, including zero  
 ranging from  $-l$  to  $+l$

$$m_l = -l, -l+1, -l+2 \dots 0, 1, 2, 3 \dots l-1, l$$

all orbitals with same value of  $n$  are in the same principal electronic shell or principal level  
 all orbitals with the same  $n$  and  $l$  values are in the same subshell or sublevel

$\Rightarrow$  principal electronic shells are numbered according to the value of  $n$

1 <sup>st</sup> principal shell:	$n=1$	value $n$ relates to energy & most probable distance from $e^-$ from nucleus
2 <sup>nd</sup>	$n=2$	
3 <sup>rd</sup>	$n=3$	
	:	

higher value of  $n$ , greater electron energy, farther on average,  $e^-$  is from nucleus

$\Rightarrow$  # subshells in a principle electronic shell is the same as the # of allowed values of the orbital angular momentum quantum #  $l$

$n=1$   $l=0$  ( $n-1=0$ ) single subshell

$n=2$   $l=0, 1$  two subshells

$n=3$   $l=0, 1, 2$  three subshells

\* because there are  $n$  possible values of the  $l$  quantum number ( $0, 1, 2 \dots (n-1)$ ) the # subshells in a principle shell is equal to  $n$ , the principle quantum #.

(48)

- one subshell for  $n=1$
- two subshells for  $n=2$
- three subshells for  $n=3$
- four subshells for  $n=4$
- ⋮

name of subshells

$l=0$	$l=1$	$l=2$	$l=3$
S	P	d	f
(sharp	principal	diffuse	fundamental
$m_l=0$	$m_l=0, \pm 1$	$m_l=0, \pm 1, \pm 2$	$m_l=0, \pm 1, \pm 2, \pm 3$
1 orbital	3 orbitals	5 orbitals	7 orbitals

$$\# \text{ orbitals in a subshell} = \# \text{ allowed values for } m_l \text{ per particular value of } l \\ = 2l + 1$$

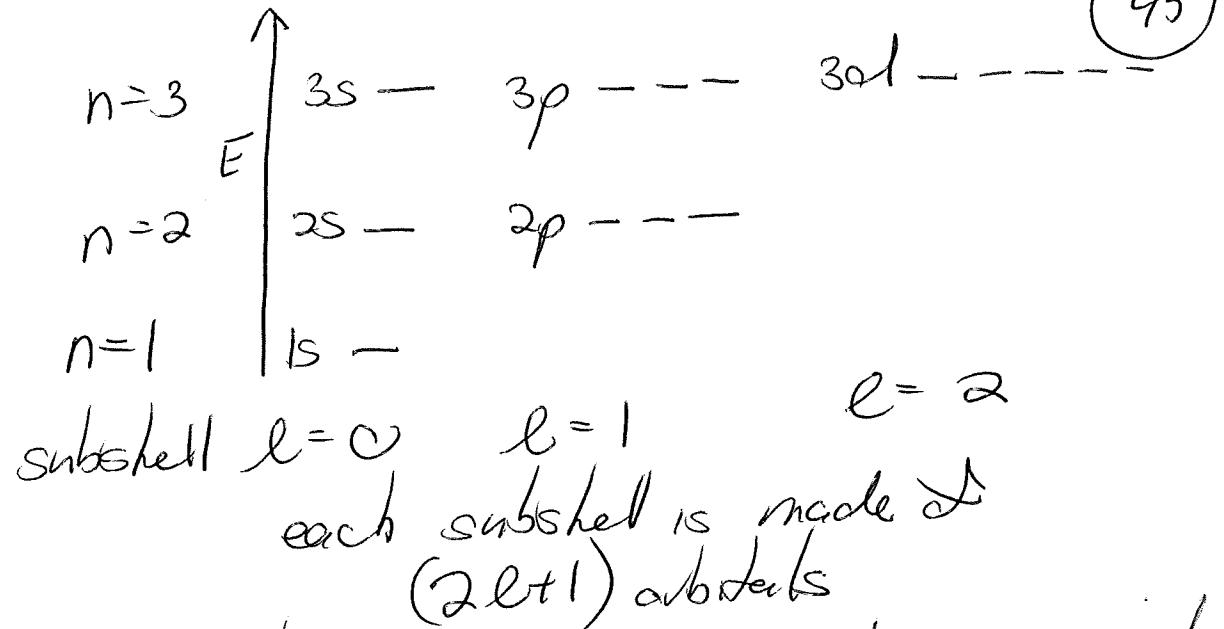
to designate the particular principal shell in which a given subshell or orbital is found, use of combinations of number & a letter

- 1s first principal shell
- 2p second principal shell & any of the 3 p orbitals in that shell

Energy of the orbitals for an H-atom, in joules, given by

$$E_n = -2.178 \times 10^{-18} \frac{1}{n^2} \text{ J} \quad \text{just like Bohr}$$

orbitals for H atom depend only on principal quantum number  $n$ : all subshells within a principal shell have the same energy & all the orbitals within a subshell



orbitals at the same energy level are said  
to be degenerate

### Interpreting & Representing the Orbitals

describe the 3D probability density distributions  
for various orbitals in the H atom

Born approximation/interpretation: probability densities  
examine distinctive shapes

$\Psi$  has no physical significance

$\Psi^2$  probability

Table / chart in text: radial function  $R(r)$   
angular wave function  $\Psi(\theta, \phi)$

S orbitals:  $\Psi_{n,l,m}$  ( $l=0, m=0$ )

(46)

$\Psi(0, \phi)$  constant, does not depend on  $\phi$  or  $\theta$

$\Rightarrow$  all S orbitals are spherically symmetrical about nucleus

Probability of finding  $e^-$  depends only on its distance  $r$  from nucleus & not on its direction in space

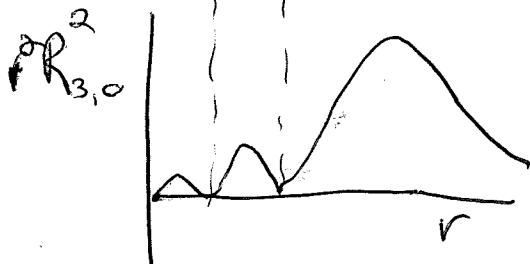
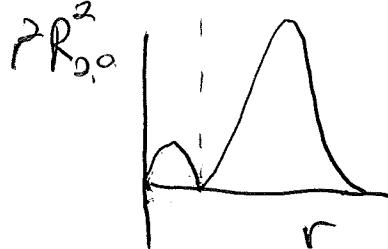
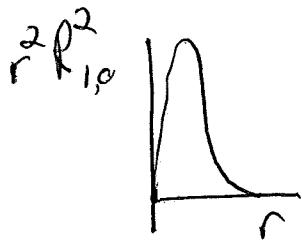
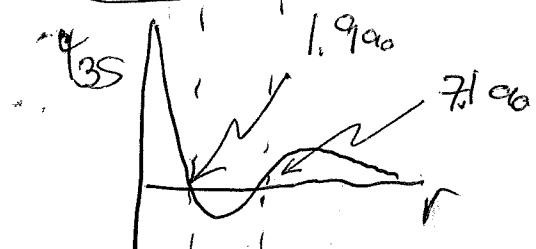
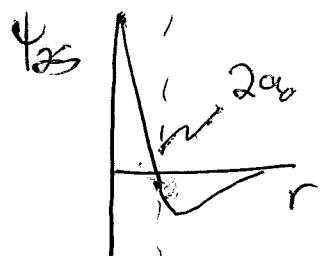
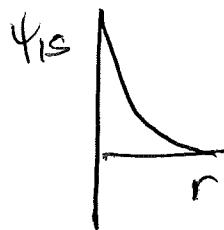
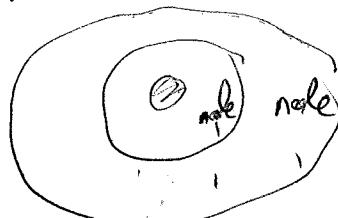
representations:  $\Psi$  and  $r^2 R_{n,l}^2(r)$

$\hookrightarrow$  probability of finding  $e^-$  at any point in space

$\Leftarrow$  at distance  $r$  from nucleus &  $\theta$  &  $\phi$

$r^2 R_{n,l}^2(r) dr$   
probability of finding  $e^-$  anywhere within thin spherical shell of thickness  $dr$  located distance  $r$  from nucleus

90% of electron probability typically known



(47)

Note: 1)  $e^-$  most likely found farther from nucleus in ns orbitals for larger  $n$

2)  $\exists$  a small but finite probability for finding  $e^-$  near the nucleus in both 2s and 3s ( $\neq$  ns).

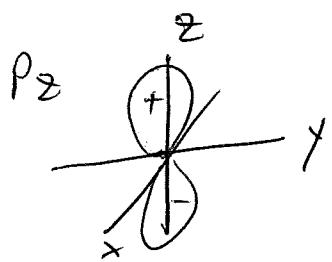
3) ns orbital has  $n-1$  radial nodes  
(a radial node is a sphere about the nucleus on which  $\psi^2 = 0$ )

more numerous the nodes  $\Rightarrow$  higher the energy of corresponding state

P orbitals: not spherical

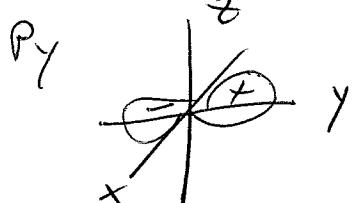
$$l=1 \quad m_l = -1, 0, 1$$

typically take linear combinations that give 3 orbitals with same shapes but different orientations

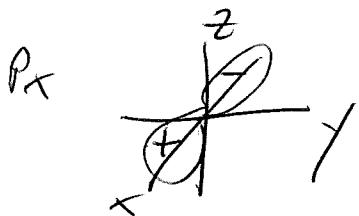


$$n=2 \quad l=1, 0, -1$$

p<sub>z</sub> orbital: proportional to  $\cos\theta$   $\Rightarrow$  maximum amplitude along z axis ( $\theta = 0$  or  $\pi$ ) & node in xy plane ( $\theta = \frac{\pi}{2}$  so  $\cos\theta = 0$ )



points along z axis, positive phase on side of xy plane with + axis, negative phase on side where z axis is negative

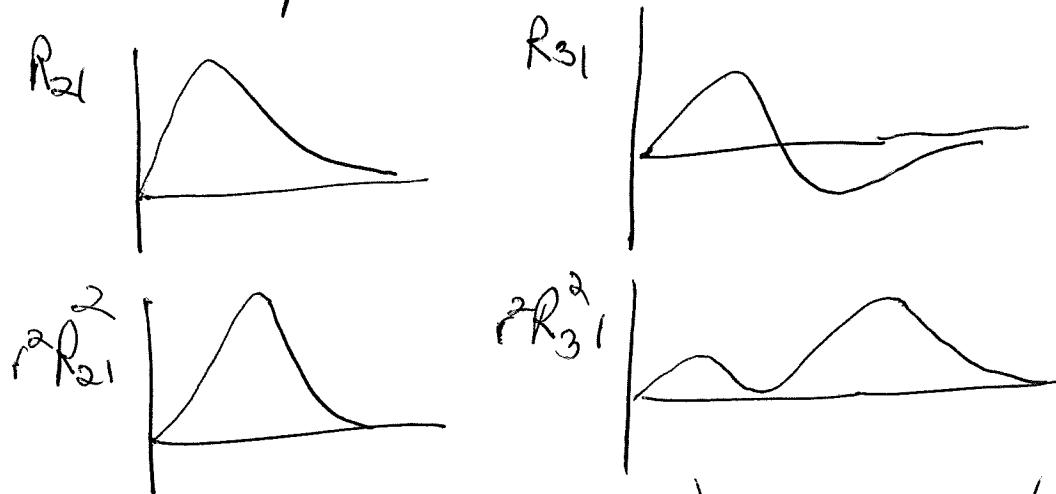


$e^-$  in  $p_z$  orbital: highest probability of being found along  $z$  axis & has zero probability of being found in  $xy$  plane.

nodal plane  $\Rightarrow$  angular node  
 $\psi$  changes sign across plane

$p_x$  same shape but points along  $x$  axis  
 $p_y$  " "  $y$  axis

radial parts of  $p$  wave functions ( $R_{n,l}$ )



$p$  orbitals (like  $s$  orbitals) may also have radial nodes ( $e^-$  density vanishes at certain distances from nucleus irrespective of direction).

$R_{2p}$  no nodes     $R_{3p}$  1 node     $4_{4p}$  2 nodes

$R_{n,l}$  radial wave functions have  $n-2$  nodes  
 but because angular part of  $p$  always have  
 1 nodal plane

total # nodes is  $n-1$   
 $(n-2$  radial, 1 angular)

Note: The probability of finding the  $e^-$  outside the nucleus for all wave functions with  $l > 0$  is zero, unlike s orbitals. (49)

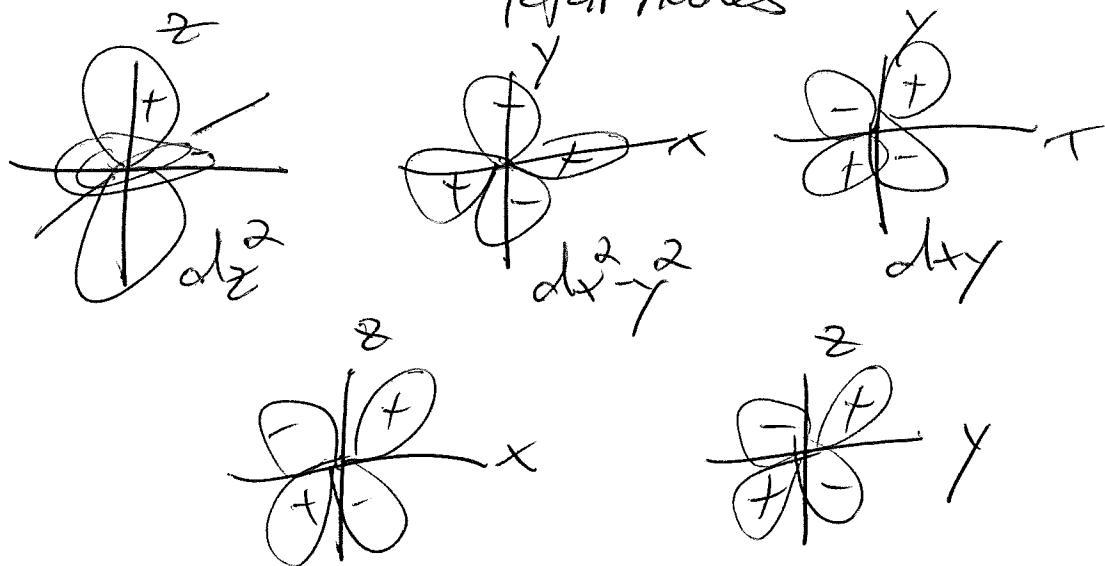
D Orbitals 5 d orbitals:  $l = 2, 1, 0, -1, -2$   
 $d_{x^2-y^2}, d_{z^2}, d_{xy}, d_{xz}, d_{yz}$

$d_{xy}$ : 4 lobes, 2 with positive phase  
 2 with negative phase  
 maximum amplitude is at  $45^\circ$   
 to the  $x+y$  axes

$d_{x^2-y^2}$ : maximum amplitude along  $+x+y$  axes

$d_{z^2}$ : max along z axis + "doughnut" in xy plane

each d orbital has 2 angular nodes  
 radial functions  $R_{nl}(r)$  have  $n-3$  radial nodes  
 again, giving  $n-1$  total nodes



## Magnetic Properties

related to e configuration & atoms & ions behavior in magnetic field

diamagnetic atom or ion: all  $e^-$  are paired individual magnetic effects cancel out

- weakly repelled by H<sub>o</sub>

paramagnetic atom or ion: has unpaired  $e^-$ , individual magnetic effects do not cancel out

- attracted into an external magnetic field

He Ne Ar Kr Xe Rn diamagnetic

## Summary

(50)

- 1) For a given value of  $l$ , an increase in  $n$  leads to an increase in the average distance of the  $e^-$  from the nucleus & hence in the size of the orbital.
- 2) An orbital with quantum #  $n+l$  has  $l$  angular nodes &  $n-l-1$  radial nodes giving a total of  $n-1$  nodes.
  - for a  $K$  atom or ion, energy depends only on # nodes, i.e.  $n$  but not  $l$  or  $m$ .
- 3) As  $r$  approaches 0,  $\psi(r, \theta, \phi)$  vanishes for all orbitals except  $s$  orbitals.
  - only  $s$  orbitals can "penetrate to the nucleus" i.e. have a finite probability of being found right at the nucleus.

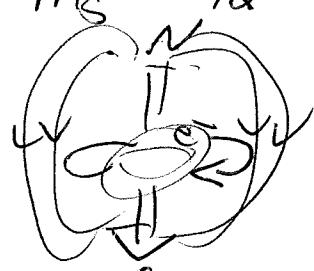
## Electron Spin 4<sup>th</sup> Quantum #

1925 George Uhlenbeck Samuel Goudsmit  
 $e^-$  behavior consistent with it having 2 spins

$$m_s = +\frac{1}{2} \uparrow \quad m_s = -\frac{1}{2} \downarrow$$



$$m_s = +\frac{1}{2}$$

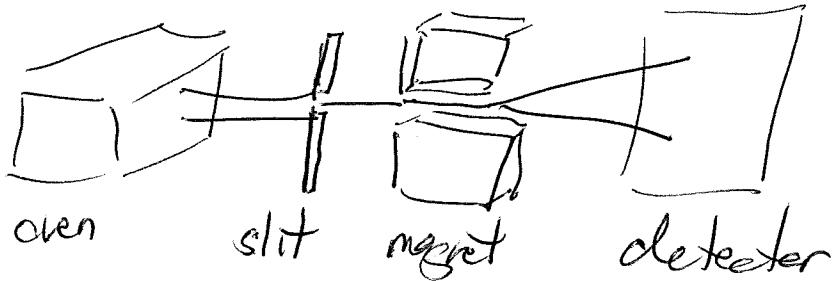


$$m_s = -\frac{1}{2}$$

$m_s$  does not depend on any of the other 3 quantum numbers

(57)

1920 Otto Stern, Walter Gerlach



- 1)  $e^-$ , owing to "spin", generates magnetic field
- 2) pair  $e^-$  with opposing spins has no net magnetic field
- 3)  $_{47}^{Ag}$  atom: 23  $e^-$  spin  $\neq$  1 type, 24 other type  
direction of net magnetic field produced depends only on the spin of the unpaired  $e^-$
- 4) beam  $\Delta$  large  $\neq$   $Ag$  atoms, equal chance that unpaired  $e^-$  will have a spin of  $+\frac{1}{2}$  or  $-\frac{1}{2}$   
- magnetic field induced by  $Ag$  atoms interacts with non-uniform field  $\rightarrow$  beam of  $Ag$  atoms splits into 2 beams

## Multielectron Atoms

Schrödinger developed wave equations for H-atom - an atom containing just one electron.

multi-electron atoms: must consider mutual repulsion between electrons

In Schrödinger equation for hydrogen, the energies of the orbitals will be same  
principal quantum number  $n$  are degenerate -  
they have the same energy ( $2s, 2p$  are same)  
 $3s, 3p, 3d$  are same)

(52)

In multielectron atoms, attractive force of the nucleus for a given  $e^-$  ↑ as nuclear charge increases  
⇒ orbital energies become lower (more negative) with ↑ atomic number  
⇒ orbitals with different value of  $l$  within a principal shell are not degenerate

### penetration + shielding

$e^-$  in orbitals closer to nucleus screen or shield nucleus from electrons farther away

⇒ screening  $e^-$  reduce the effectiveness of the nucleus in attracting particular more distant electron.

⇒ effectively reduce the nuclear charge

magnitude of reduction of nuclear charge depends on types of orbitals the inner  $e^-$  are in & the type of orbital that the screened  $e^-$  is in

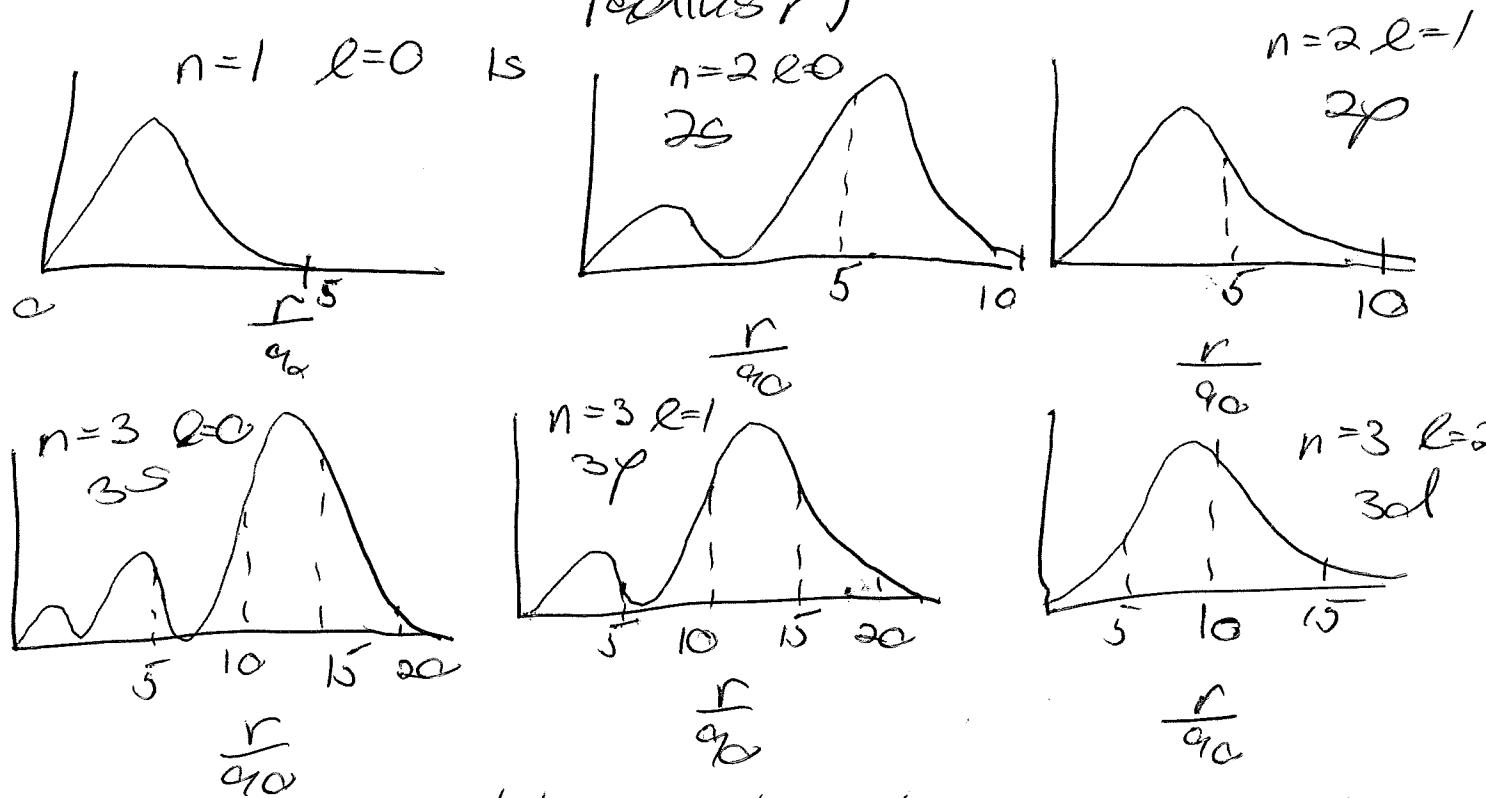
s orbitals: high probability density at the nucleus, p & d have 0 probability

(53)

$e^-$  in s orbitals more effective at screening nucleus from outer  $e^-$  because electrons in p and d orbitals

$\Rightarrow$  ability  $e^-$  in s orbitals to get close to nucleus is electron penetration

Example  $4\pi r^2 R^2(r)$  radial probability density  $R^2(r)$   
by  $4\pi r^2$  (area of sphere of radius  $r$ )



1s  $e^-$  greater probability of being close to nucleus than 2s  $e^-$ , greater than 3s  $e^-$ .

2s  $e^-$  greater penetration than 2p  $e^-$   
 $e^-$  have  $\frac{1}{r}$  penetration effectively blocked by new same in an outer orbital ("looking" for the nucleus)

nuclear charge:  $Z$  ~~electrons would see  
with any interference~~

(54)

nuclear charge actually experienced due to  
reduction by intervening  $e^-$   
 $Z_{eff}$

S  $e^-$  experiences  $\uparrow Z_{eff}$ , is held more tightly  
and at lower energy than a p electron  
p  $e^-$  lower energy, than s  $e^-$  of electrons in the  
same principal shell

all orbitals within subshell ( $p, d$ ) have the same  
radial characteristics & experience the same  
effective nuclear charge  $Z_{eff}$ , so they have the  
same energy.

### Electron configurations:

1)  $e^-$  occupy orbitals in a way that minimizes the  
energy of the atom

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

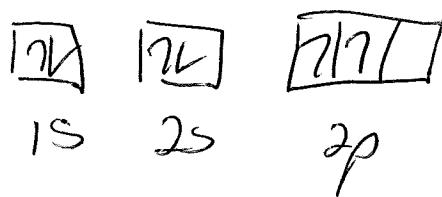
1s, 2s, 2p, 3s, 3p, 4s, 3d  
4p, 5s, 4d, 5p, 6s, 4f, 5d,  
6p, 7s, 5f, 6d, 7p

2) No 2 e<sup>-</sup> in an atom have all 4 quantum #s alike - Pauli exclusion principle  
 1926 Wolfgang Pauli  
 (only 2 e<sup>-</sup> may occupy the same orbital & these e<sup>-</sup> must have opposing spins)

3) When orbitals of identical energy (degenerate orbitals) are available, electrons initially occupy those orbitals singly  
 (Hund's rule : atoms tend to have as many unpaired electrons as possible)  
 get as far apart as possible

### Aufbau Process (building up)

$Z=1$	H	1s <sup>1</sup>
$Z=2$	He	1s <sup>2</sup>
$Z=3$	Li	1s <sup>2</sup> 2s <sup>1</sup> [He] 2s <sup>1</sup>
$Z=4$	Be	1s <sup>2</sup> 2s <sup>2</sup> [He] 2s <sup>2</sup>
$Z=5$	B	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>1</sup> [He] 2s <sup>2</sup> 2p <sup>1</sup>
$Z=6$	C	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup> [He] 2s <sup>2</sup> 2p <sup>2</sup>



$Z = 7-10$

(56)

N	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/>
O	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/>
F	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/>
Ne	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/>

1s    2s    2p

$Z = 11-18$

similar to Li  $\rightarrow$  Ne except e<sup>-</sup> go into 3s & 3p subshells

electrons that are added to the electronic shell of the highest principal quantum number (outermost or valence shell) are called valence electrons.



## Periodic Table

elements in the same group of the table have similar electron configurations

Group 1 : alkali metals have single outer shell valence e<sup>-</sup> in ns orbital ns<sup>1</sup>

Group 17 atoms (Chalcogens) 7 outer shell (53)  
(valence) electrons in configuration  $ns^2 np^5$

Group 18 atoms (Noble gases) with exception of He  
( $2e^-$ ) have outermost shells with  $8 e^-$   
 $ns^2 np^6$

valence  $e^-$ :  $e^-$  that occupy outermost shell

core  $e^-$ :  $e^-$  in inner shells, closer to nucleus + lower in energy

### Trends:

for elements in same column, radius  $\uparrow$  as  $Z \uparrow$

$\Rightarrow$  mainly because, b/c Pauli exclusion principle excludes additional  $e^-$  from region occupied by core electrons so, forces an increase in size as more distant  $e^-$  shells are occupied

but, Coulomb (electrostatic) forces cause radii of atoms to  $\downarrow$  with  $Z \uparrow$  (across a period)

$\Rightarrow$  as  $Z$  increases,  $e^-$  in valence shells "are ineffective" in shielding each other from the  $+ve$  charges. "Incomplete shielding" of added protons by nucleus by added  $e^-$  when going from  $Z \rightarrow Z+1$  leads to an increase in  $Z_{eff}$  across a period

## Ionization Energies

- atoms do not eject  $e^-$  spontaneously
- $e^-$  attracted to positive charge on the nucleus of the atom & energy is needed to overcome the attraction
- more easily  $e^-$  lost, more "metallic" we consider an atom to be

Ionization energy  $I_1$  is the quantity of energy a gaseous atom must absorb so that an  $e^-$  is stripped from it.

The  $e^-$  lost is the one most loosely held

$I_1$ , 1<sup>st</sup> ionization energy from neutral atom

$I_2$ , 2<sup>nd</sup> ionization energy

In general, ionization energies decrease as atomic radius increases

across a period  $\Rightarrow Z_{eff} \uparrow$ ,  $n$  remains constant  
ionization energy  $\uparrow$

down a group  $\Rightarrow$  as  $n \uparrow$ ,  $Z_{eff}$  slightly increases  
ionization energy  $\downarrow$

Some exceptions:  $I_1$  of Al smaller than that of Mg

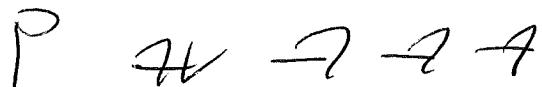
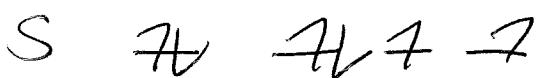
expect  $I_1$  of Al  $>$  Mg but Mg loses 3s  $e^-$   
Al loses 3p  $e^-$

takes more energy to remove an  $e^-$  from lower energy 3s than 3p

$I_1$  for  $S < P$

(59)

$I_1$  for  $S < P$  is slightly lower than for  $P$ , since although both remove  $e^-$  from  $3p$  orbitals,



easier to remove  $e^-$  due to repulsion from remaining from  $\frac{1}{2}$ -filled shell

## Electron Affinity (EA)

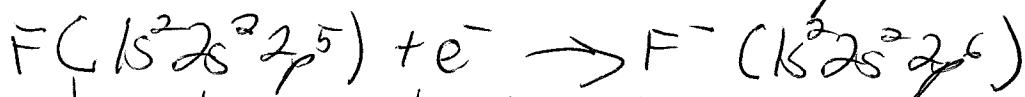
is a measure of the energy change that occurs when a gaseous atom gains an  $e^-$



when F atom gains an  $e^-$ , energy is given off exothermic, EA is a negative quantity

$e^-$  approaches F atom from "infinite" distance  
 $e^-$  sees center positive charge & is attracted  
attraction overcomes effect by repulsive effect  
of other  $e^-$  in atom

as long as attractive force exceeds repulsive  
force,  $e^-$  is gained & energy is given off



Some atoms have no tendency to gain an  $e^-$

Noble gases; added  $e^-$  would have to enter  
empty S orbital & net +ve ionic  
(shell)

Groups 2 & 12; where  $e^-$  would enter p subshell