NAZARBAYEV
UNIVERSITY

General Chemistry I

Atomic Structure and Properties

Dr. Ould Ely
School of Science and Technology

Chapter 3

- **Picture of the Atom**
- **Electromagnetic radiation and Atomic Spectra**
- **The Nature of Electron and Atomic Orbitals**
- **Many-electron atoms**
- **Atomic properties and Periodicity**
- **Nuclear chemistry**

Part I

3.1.1 Atomic concept,
3.1.2 Subatomic particles,
3.1.3 Atomic structure: first ideas

The classical picture of the atom

Dalton Atomic Theory

1. Elements are made of tiny particles called atoms

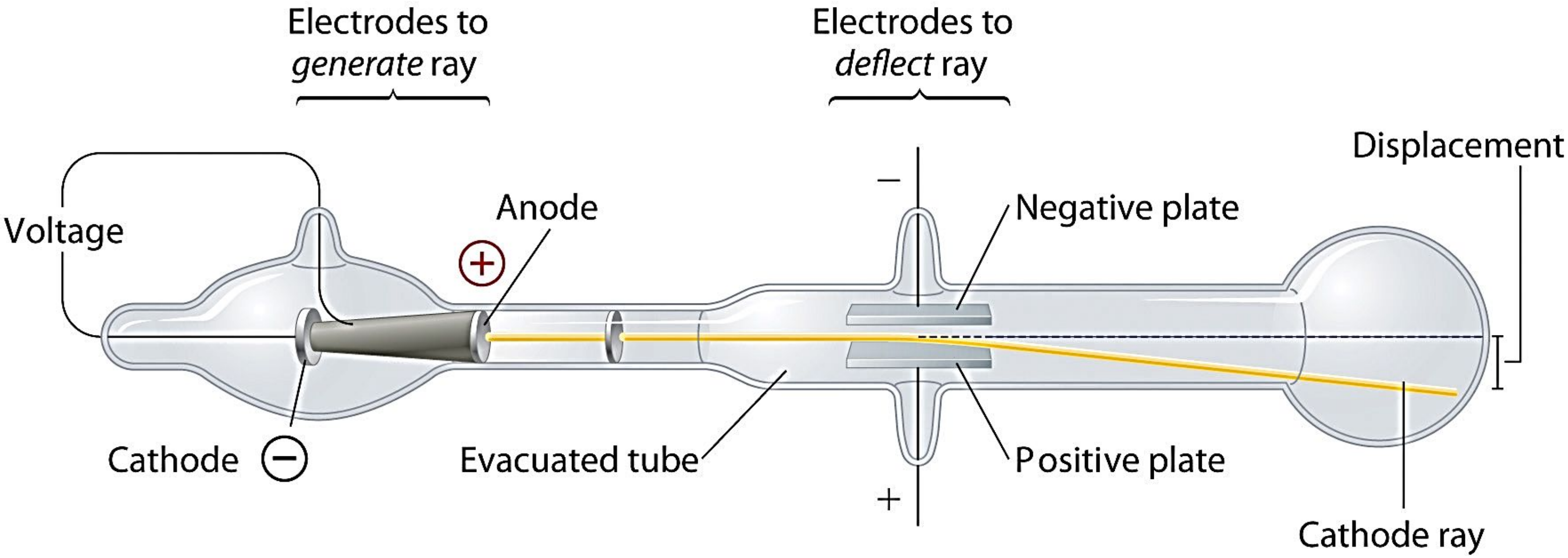
2. The atoms of a given elements are identical

3. Chemical compounds are formed when atoms combine with one another. A given compound has the same relative numbers and types of atoms

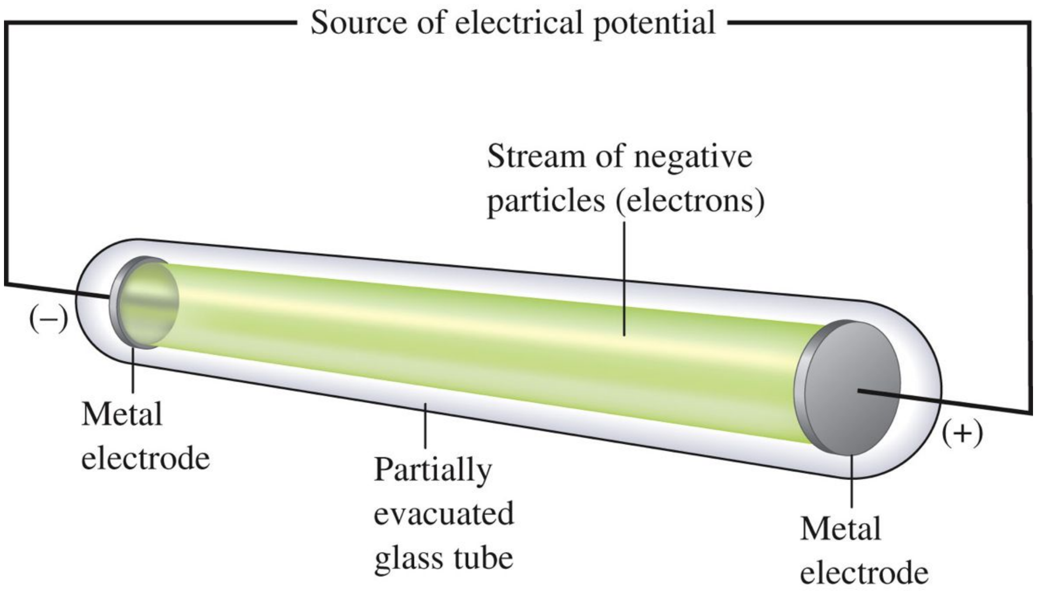
4. Chemical reaction involve reorganization of the atoms. The atom themselves are not changed.

J.J. Thomson’s Cathode Tube

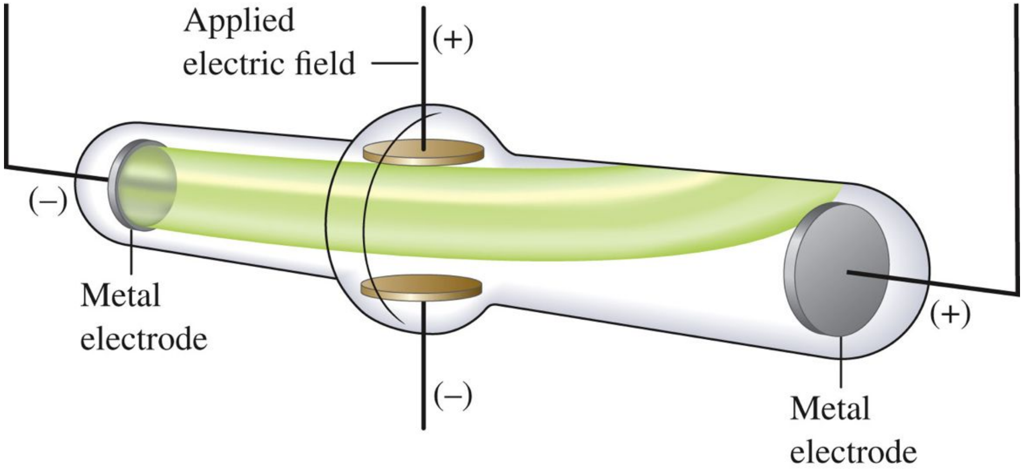
- Charge-to-mass ratio



The Atom : J. J. Thomson (1856-1940)



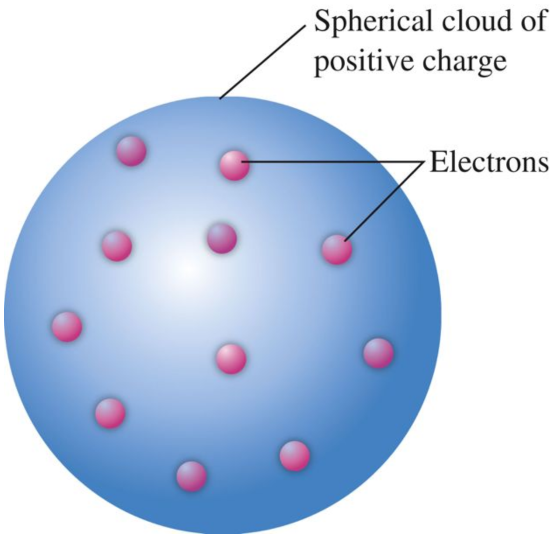
$e/m = -1.76 \times 10^8$ C/g



Experiment date
1898-1903

The Atom based on Thomson's experiment

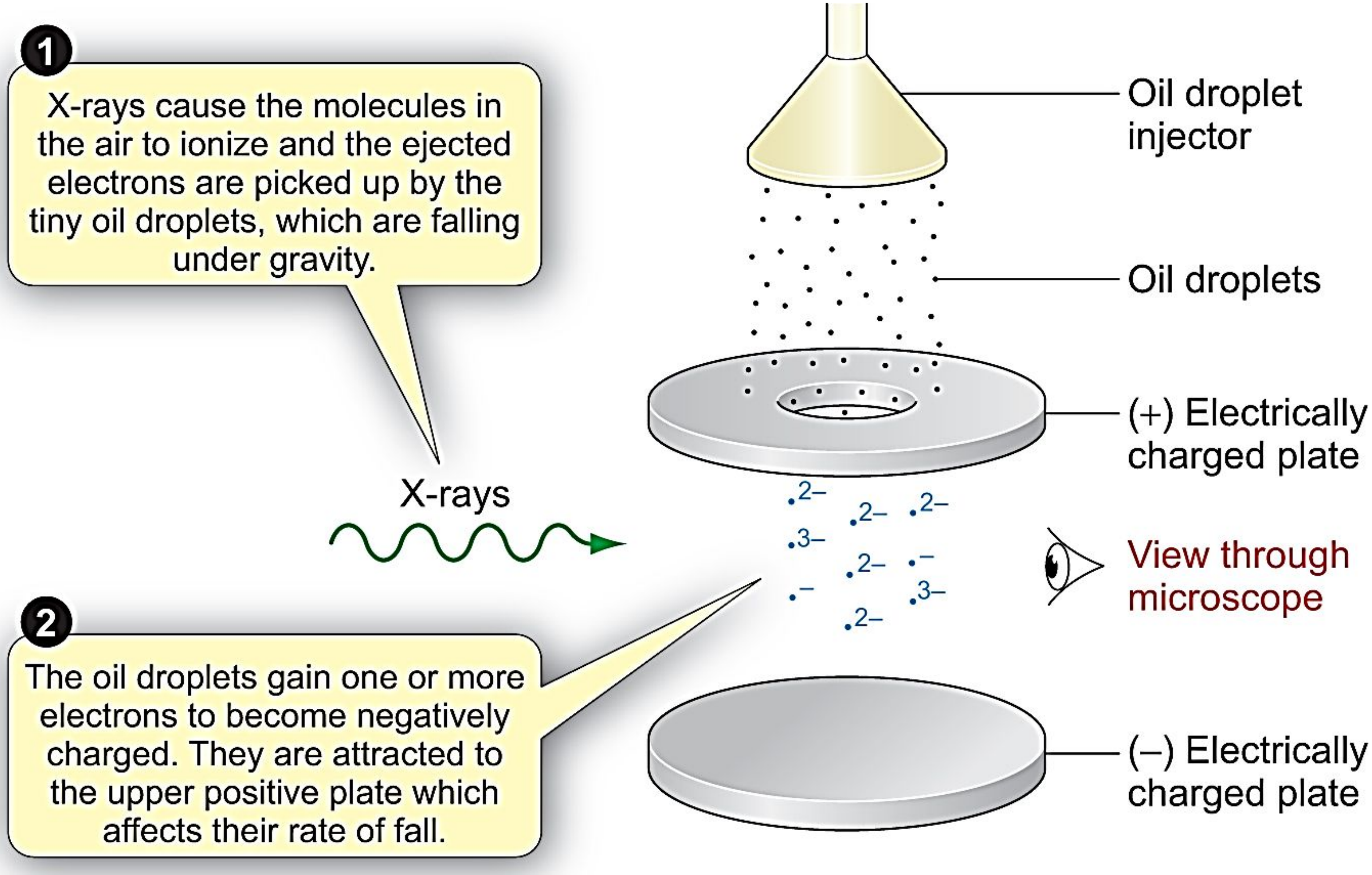
- A ray of particles is produced between two metallic electrodes.
- These particles are negatively charged
- Since electrons could be produced from electrodes made of various types of metals, all atoms must contain electrons
- e/m = -1.76×10^8 C/g
- Atoms = neutral! Positive charges are located somewhere.



Mass of electron

Mass of a single electron

$e = -1.6 \times 10^{-19}$ C **$m = 9.11 \times 10^{-31}$ kg (Millikan)**



1 X-rays cause the molecules in the air to ionize and the ejected electrons are picked up by the tiny oil droplets, which are falling under gravity.

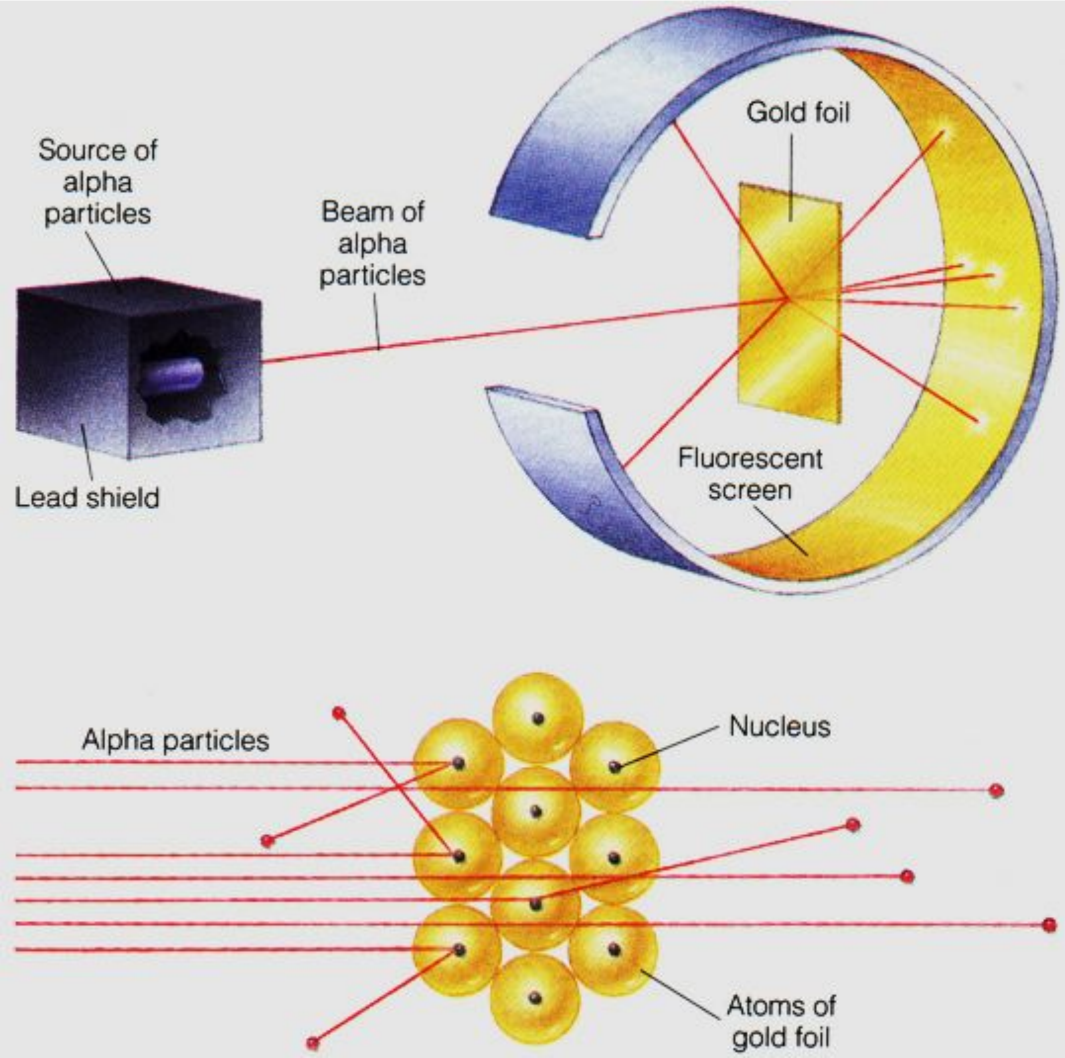
2 The oil droplets gain one or more electrons to become negatively charged. They are attracted to the upper positive plate which affects their rate of fall.

http://www.youtube.com/watch?v=XMfYHag7Liw

Rutherford Experiment

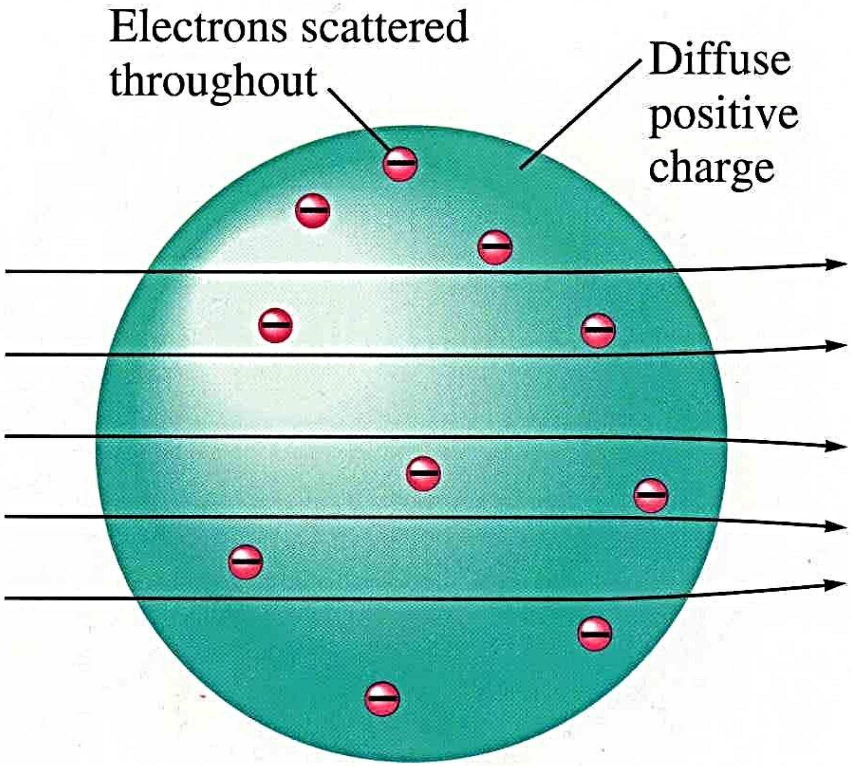
Ernest Rutherford – 1911

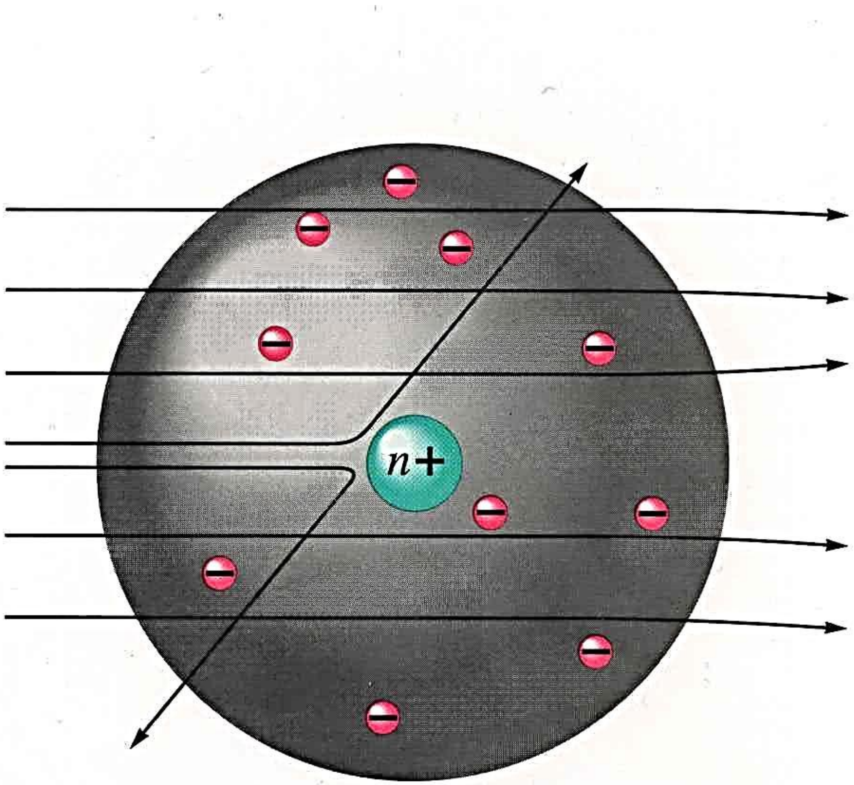
- With Thomson Model : a particles should travel through the atom without deflection.



http://sun.menloschool.org/~dspence/chemistry/atomic/ruth_expt.html

Rutherford Experiment

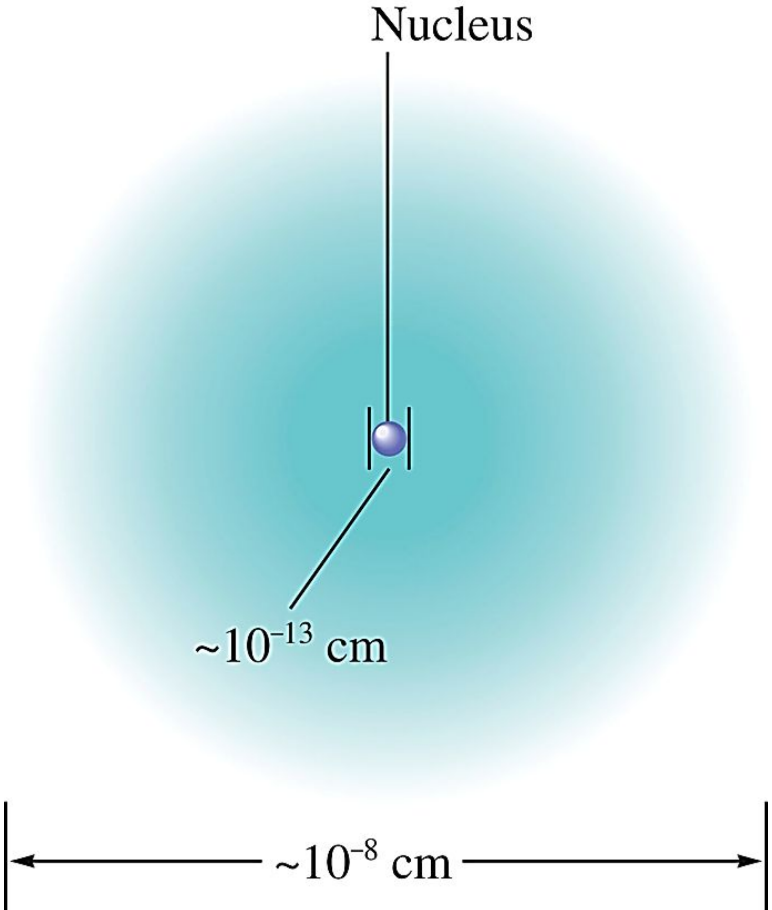




The Nucleus

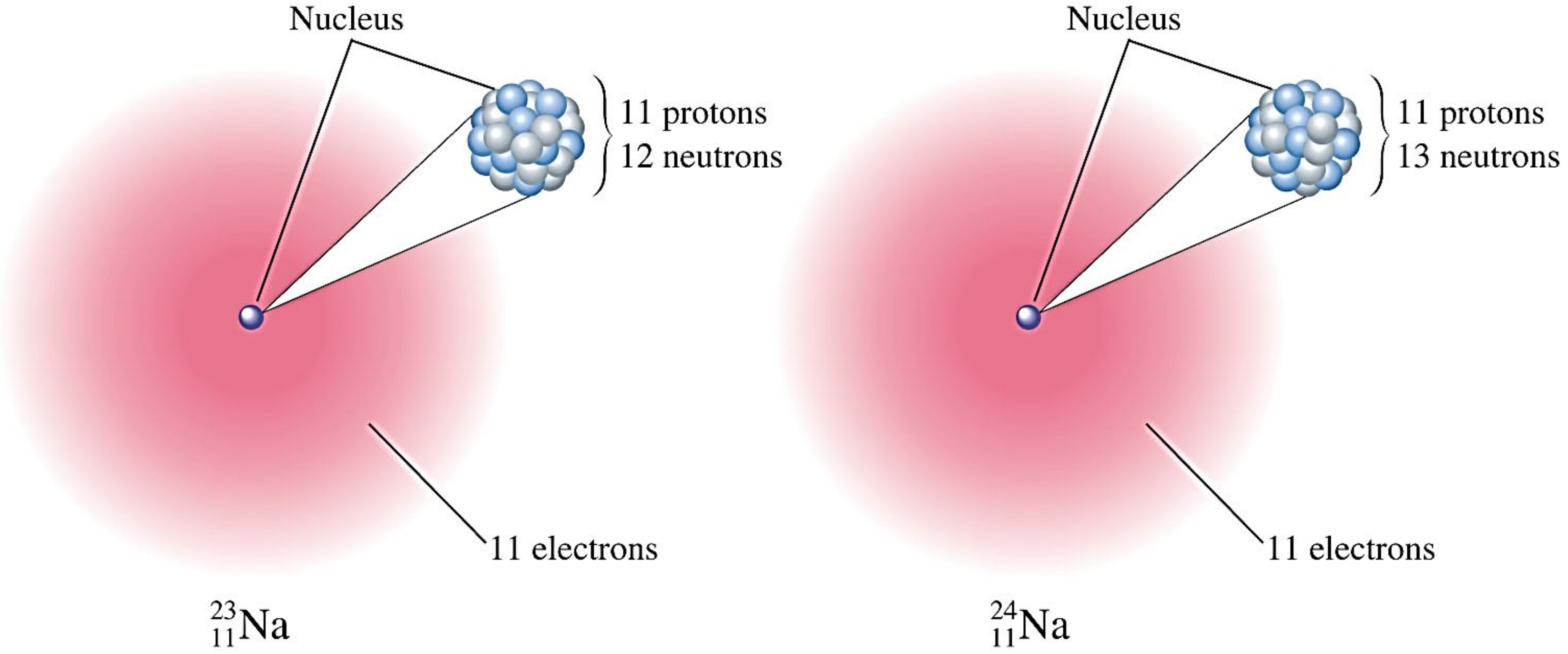
Ernest Rutherford – 1911

Conclusion : Dense positive center with electrons far from the nucleus

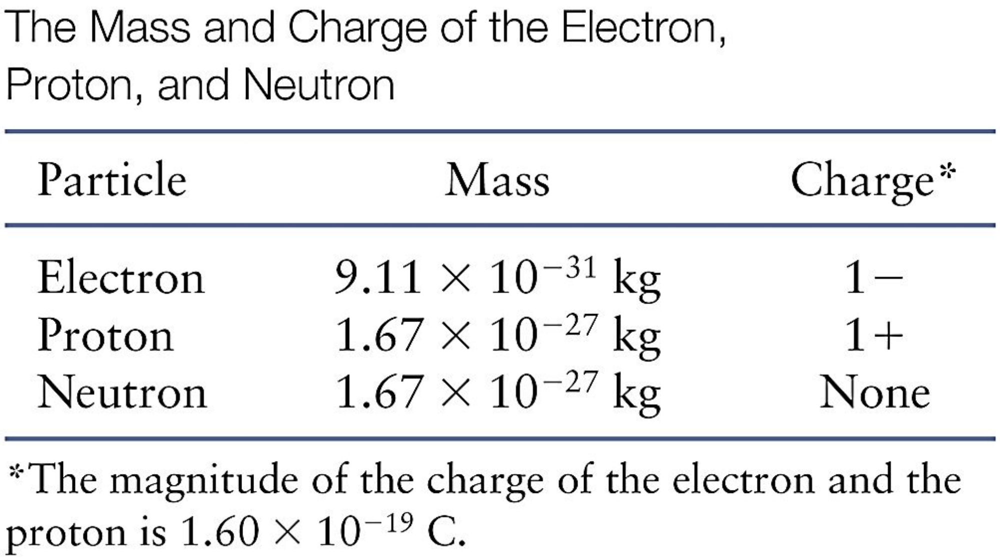


Its great density is dramatically demonstrated by the fact that a piece of nuclear material about the size of a pea would have a mass of 250 million tons

Modern View



$^{23}_{11}\text{Na}$ $^{24}_{11}\text{Na}$



The Mass and Charge of the Electron, Proton, and Neutron

Particle	Mass	Charge*
Electron	9.11×10^{-31} kg	1−
Proton	1.67×10^{-27} kg	1+
Neutron	1.67×10^{-27} kg	None

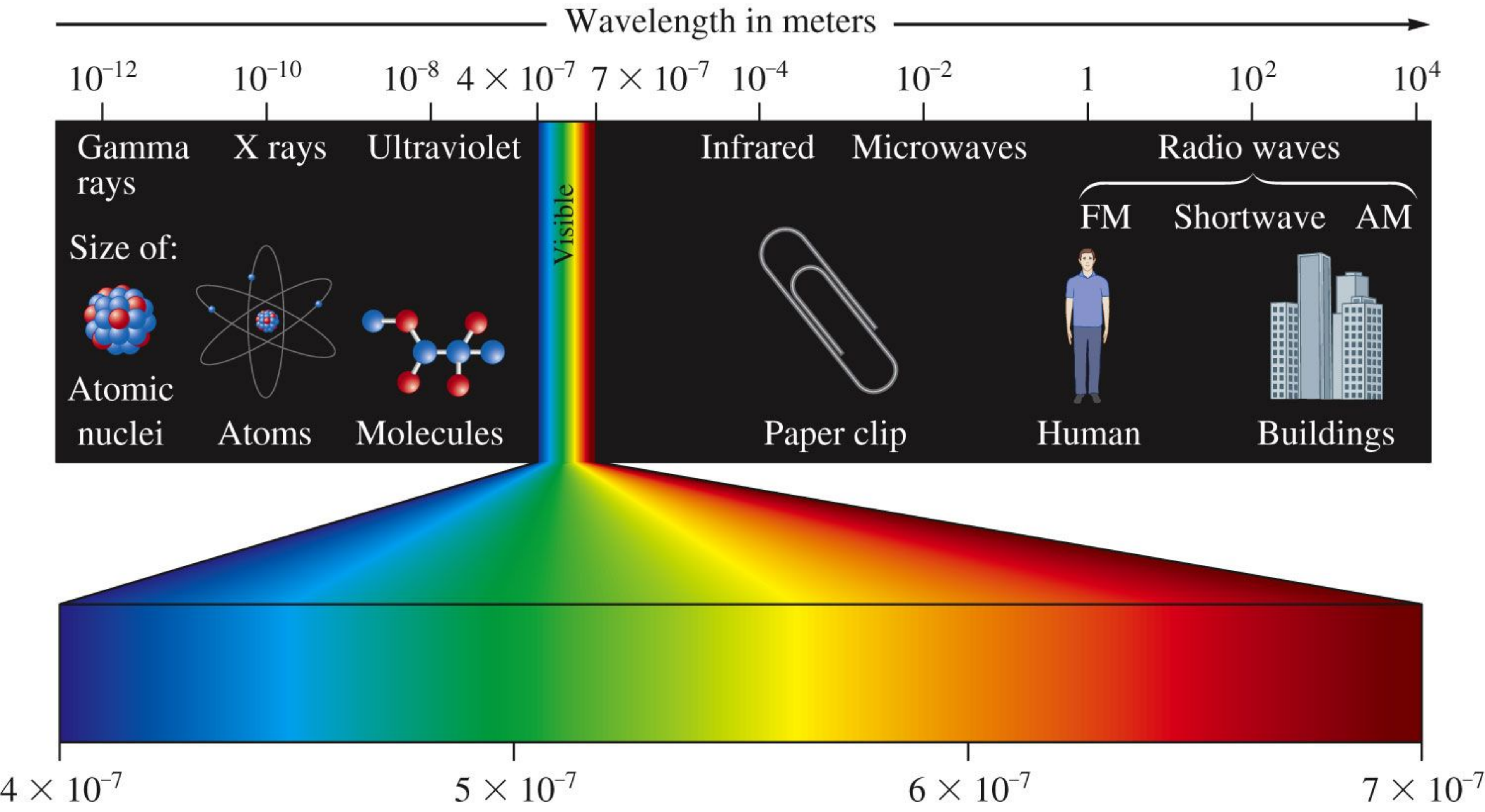
*The magnitude of the charge of the electron and the proton is 1.60×10^{-19} C.

$$^{A}_{Z}X$$

3.2. Electromagnetic Radiation and Quantization

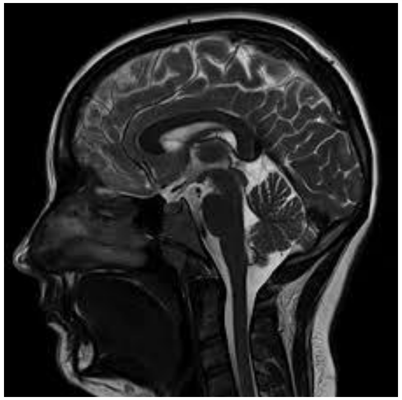
- 3.2.1: Electromagnetic Radiation
- 3.2.2: Quantization
- 3.2.3: The Atomic Spectrum of Hydrogen

Spectrum


Wavelength in meters
10^{-12}
10^{-10}
10^{-8}
4×10^{-7}
7×10^{-7}
10^{-4}
10^{-2}
1
10^{2}
10^{4}
Gamma rays
X rays
Ultraviolet
Visible
Infrared
Microwaves
Radio waves
FM
Shortwave
AM
Size of:
Atomic nuclei
Atoms
Molecules
Paper clip
Human
Buildings
4×10^{-7}
5×10^{-7}
6×10^{-7}
7×10^{-7}

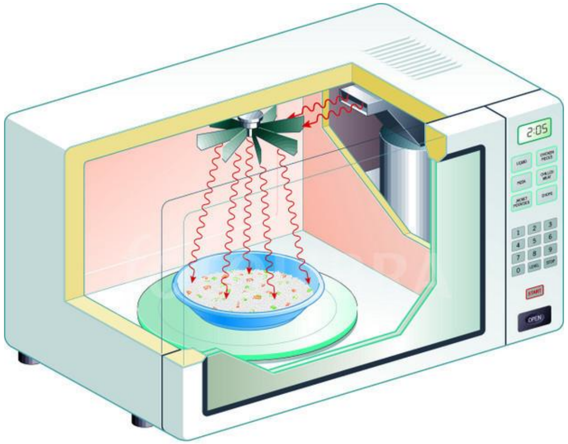
Electromagnetic radiation

X-ray



MRI

Light

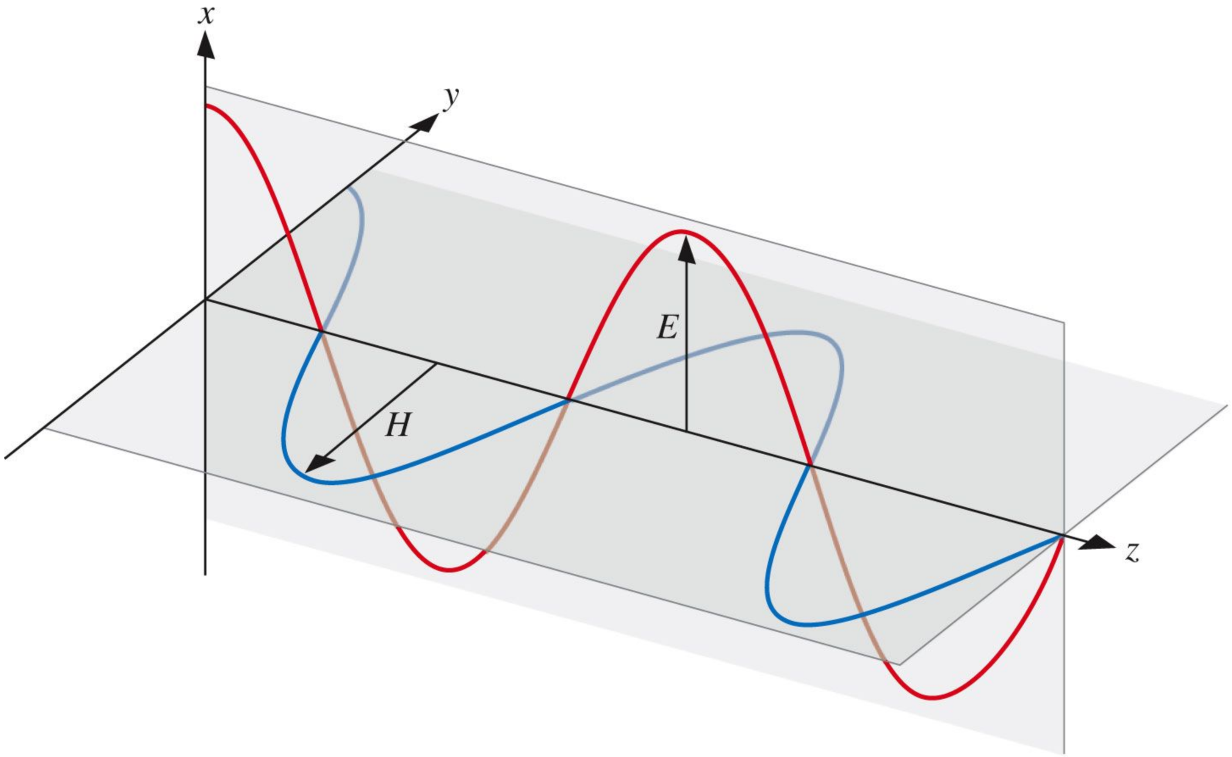


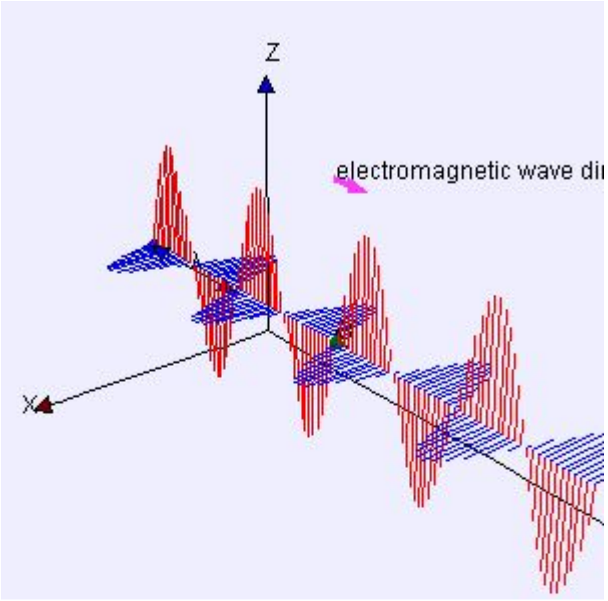
Microwave

Travel like a wave
Travel with the speed of light

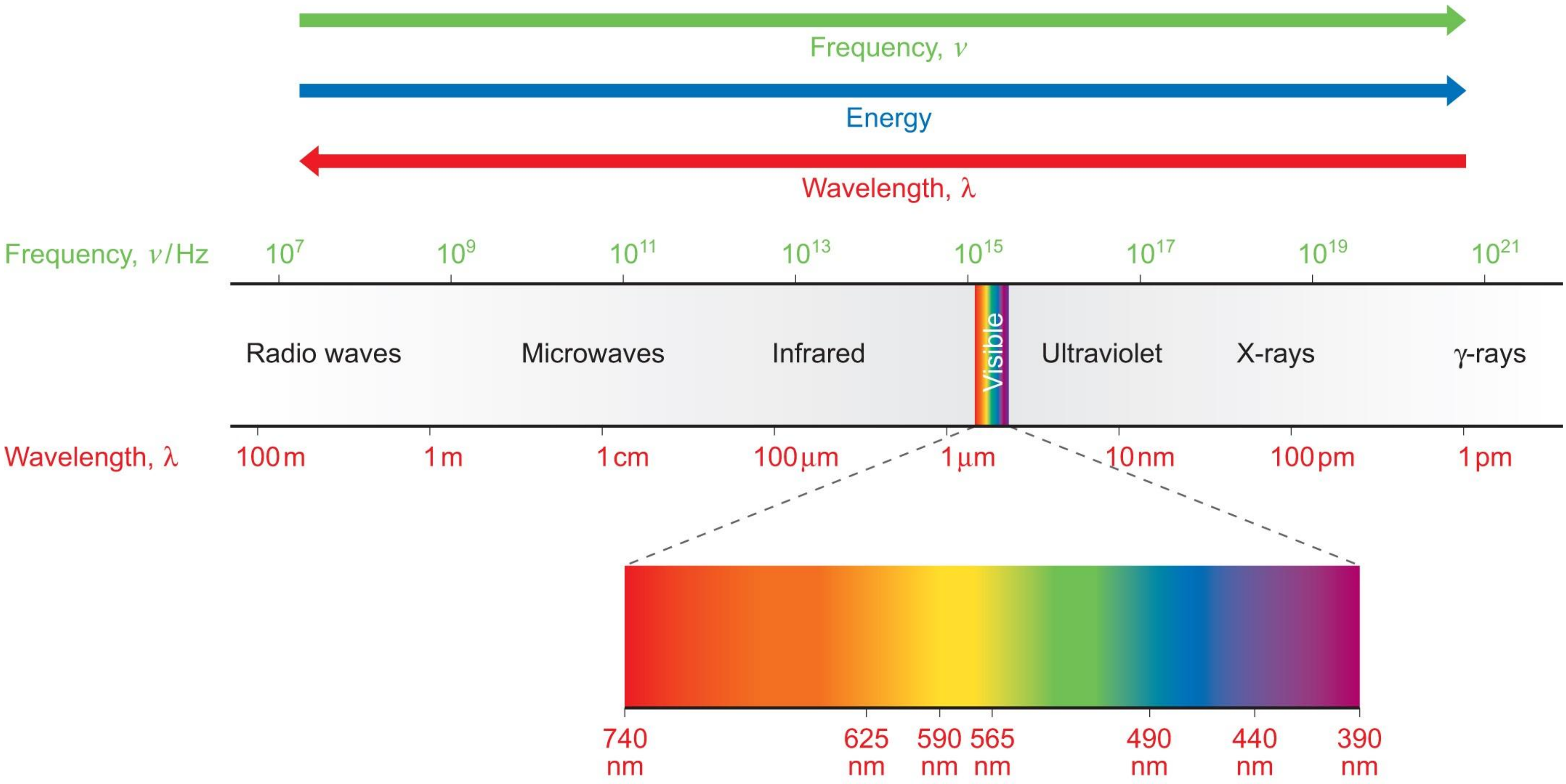
Electromagnetic Radiation

Electromagnetic Radiation = a way for energy to travel.
2 oscillating fields (H and E)

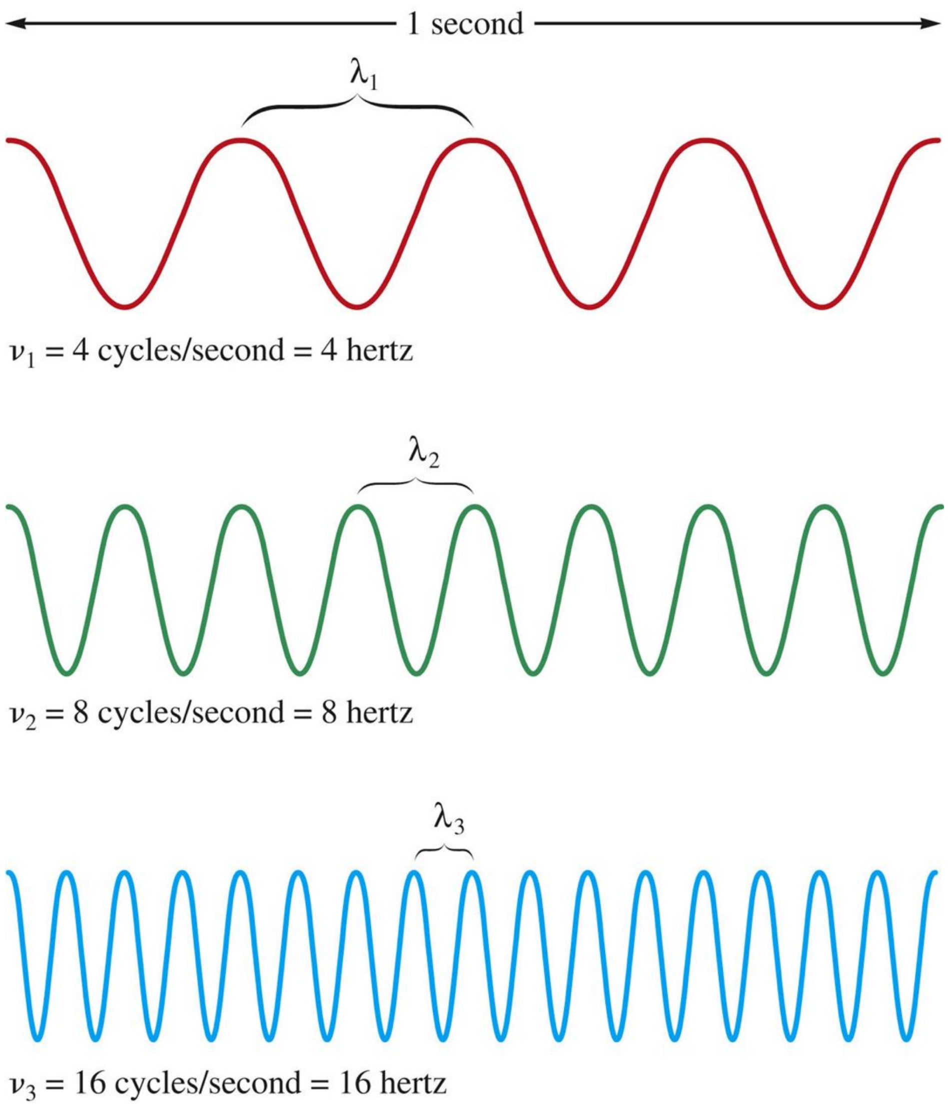




ELECTROMAGNETIC RADIATION



Electromagnetic Radiation - Characteristics



λ = wavelength = distance between two peaks or two troughs in a wave. (m)

ν = frequency = number of waves / s at a specific point of space. (s^{-1} or Hz)

$\lambda \infty 1/v$

$$\lambda \nu = c$$

Because speed = c = 3×10^8 m/s

The radiation with the shortest wavelength has the highest frequency

Radio in the 909kHz. What wavelength does it correspond to?

$\lambda = c/v = 330 \text{ m}$

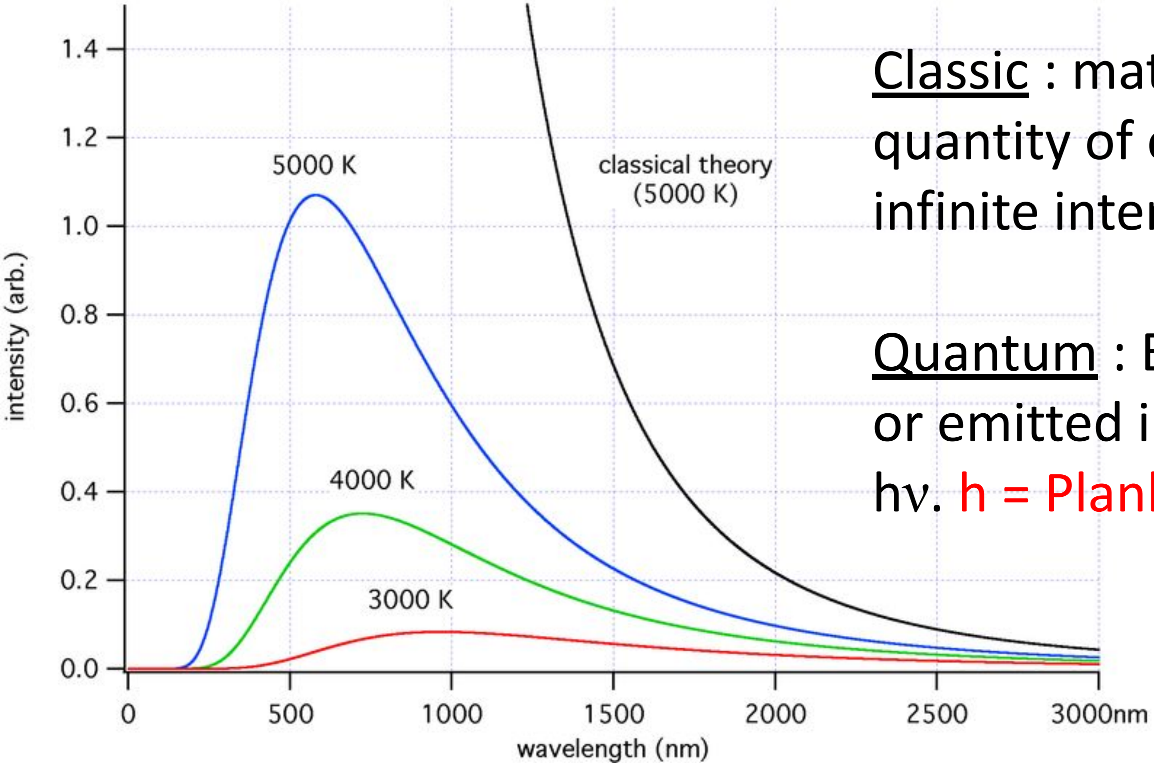
$C = 2.998\ 10^{8}\ ms^{-1}$

$v = 909.\ 10^{3}\ s^{-1}$

Nature of Matter

At the end of the 19th century :
Matter ≠ Energy
Matter = particles and Energy = electromagnetic radiations

Max Planck and the black body radiation :



Classic : matter can absorb or emit any quantity of energy □ no maximum □ infinite intensity at very low wavelength.

Quantum : Energy could only be gained or emitted in whole number multiples of hν. h = Plank's constant = 6.626×10^{-34}Js

$$\Delta E = nh\nu$$

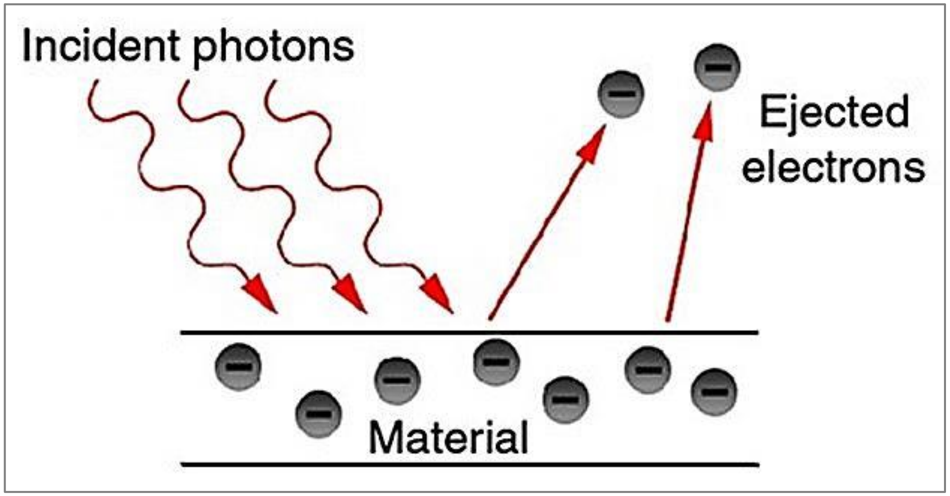
Albert Einstein Theory :

Energy itself is quantified and radiation could be seen as a stream of particles (photons)!

$$E_{photon} = h\nu = \frac{hc}{\lambda}$$

Photoelectric effect

When UV radiation hits a metal surface, electrons are ejected – **photoelectric effect.** (in 1905 explained by Albert Einstein using a quantum approach)



$$h\nu = \Phi + E_{KE}$$

Φ - **work function** – minimum energy required to remove the electron

E kinetic energy of the ejected electron

When copper is bombarded with high-energy electrons, X rays are emitted. Calculate the energy (in joules) associated with the photons if the wavelength of the X rays is 0.154 nm.

$$E = h \times \nu$$

$$E = h \times c / \lambda$$

$$E = 6.63 \times 10^{-34}\ (\text{J}\cdot\cancel{\text{s}}) \times 3.00 \times 10^{8}\ (\cancel{\text{m}}/\cancel{\text{s}}) / 0.154 \times 10^{-9}\ (\cancel{\text{m}})$$

$$E = 1.29 \times 10^{-15}\ \text{J}$$

Dual Nature of Light

Energy – Mass relationship :

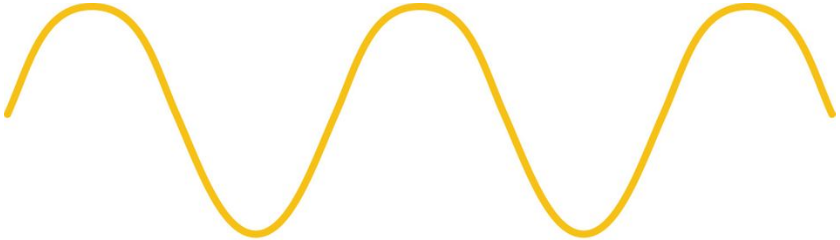
A particle but also a wave :

$$E = mc^2$$

$$m = \frac{E}{c^2}$$

Summary :

- Energy is quantized
- Only discrete units of energy (quanta) could be transferred
- Dual nature of light



Light as a wave phenomenon

Light as a stream of photons

De Broglie 1924

λ Proportional to h/mv

$$\lambda = h/mv$$

H :Planck Constant
M : masse
V : velocity

Diffraction

<u>What is the wavelength for an electron?</u>

Me = 9.11×10^{-31} kg
Ve = 1.0×10^{7} m/s

$$\lambda_e = \frac{cc}{cc}$$

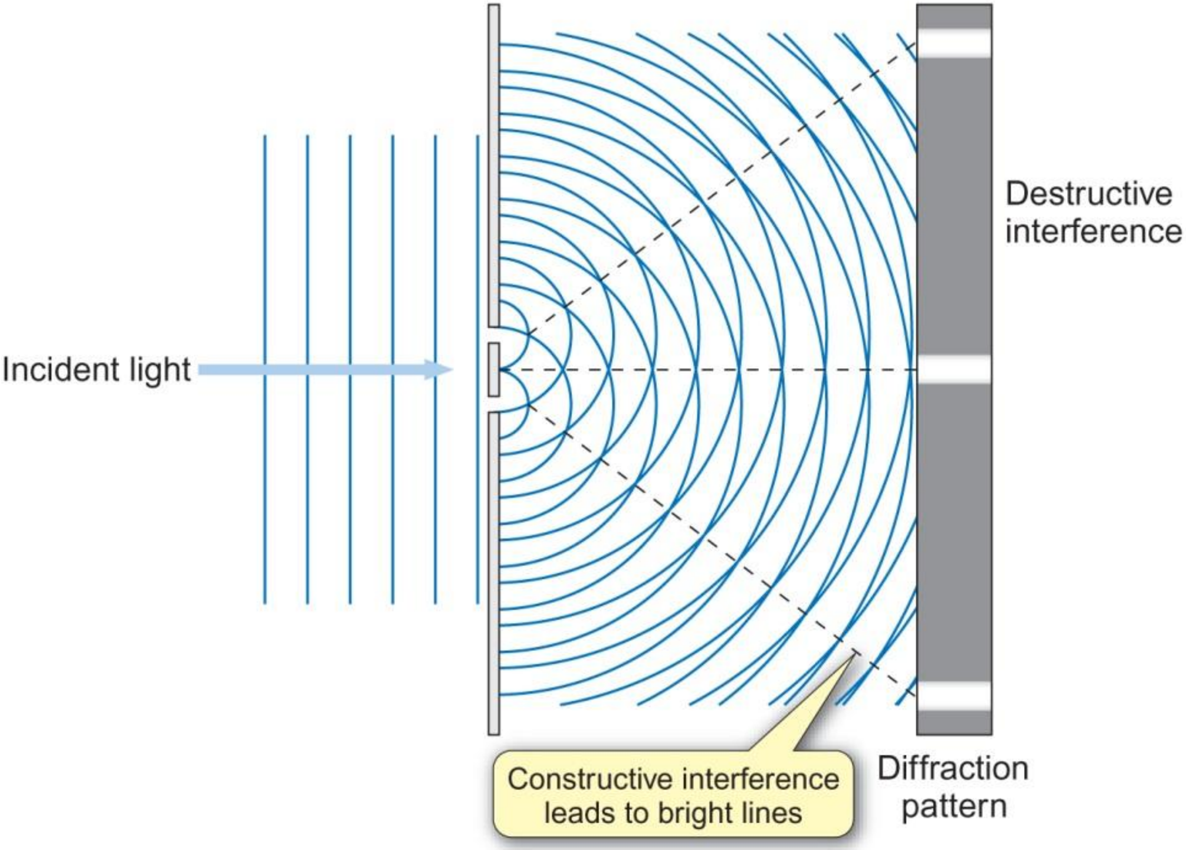
1 J = 1 kg.m^2/s^2
6.626×10^{-34}Js

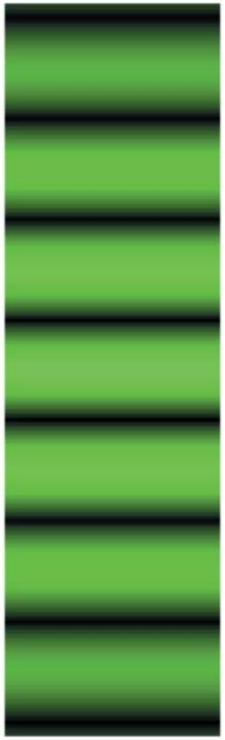
$$\lambda_e = \frac{6.626x10^{-34}\,\frac{kgm^2}{s}}{\left(9.11x10^{-31}kg\right)\left(1.0x10^{7}m/s\right)} = 7.3x10^{-11}m$$

The electron has a WL similar to the spacing of atoms in a crystal. Confirmed for Ni crystal.

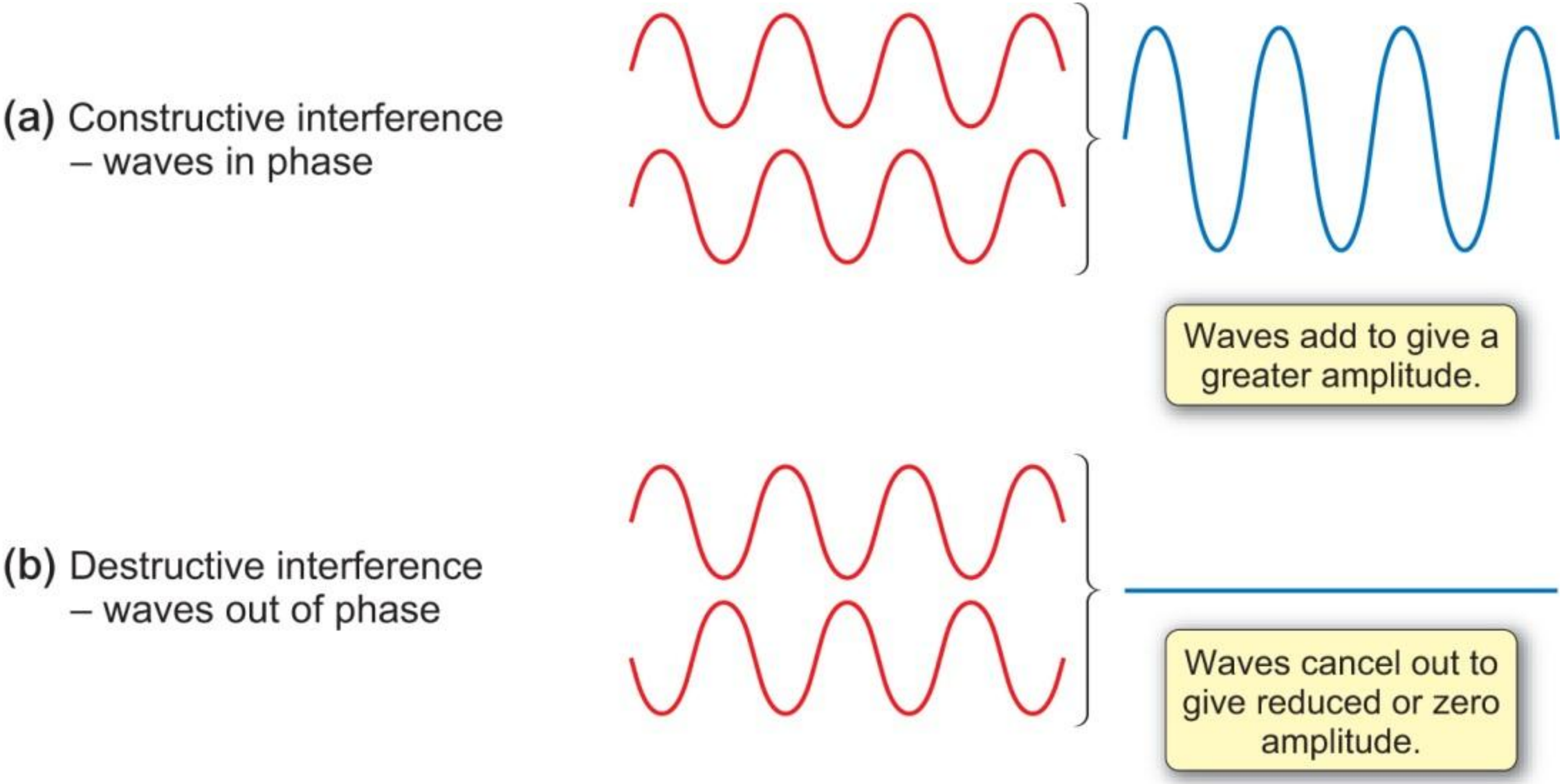
<u>Diffraction</u> : result of light scattered from a regular array of points or lines.

How to test the wave properties of an electron?





How to test the wave properties of an electron?



(a) Constructive interference
– waves in phase

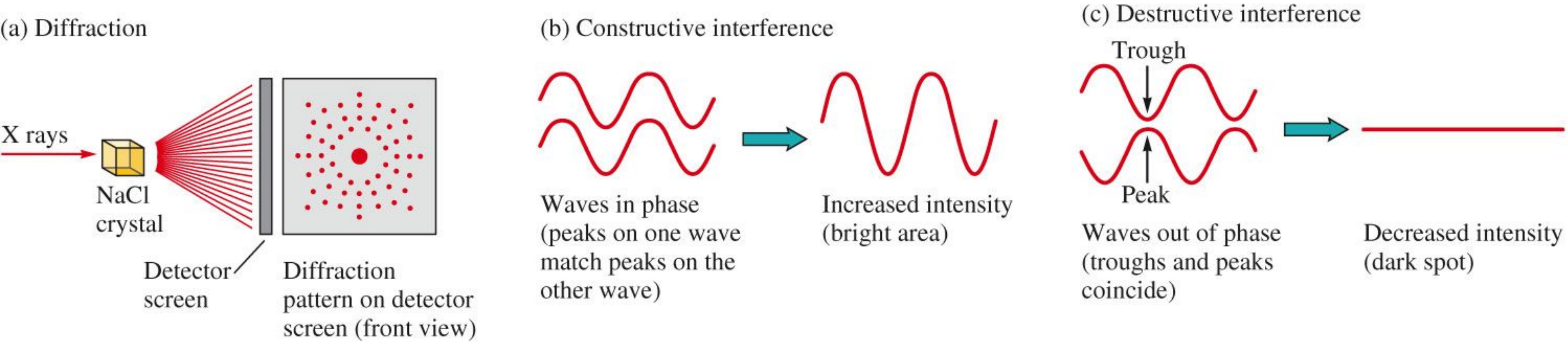
Waves add to give a greater amplitude.

(b) Destructive interference
– waves out of phase

Waves cancel out to give reduced or zero amplitude.

Diffraction

When X-rays are scattered by ordered atoms □ Diffraction pattern.



Conclusion

All matter exhibits both particulate and wave properties.

Large particles : mainly particle
Small particles : mainly wave
Intermediate particles (electron) : both

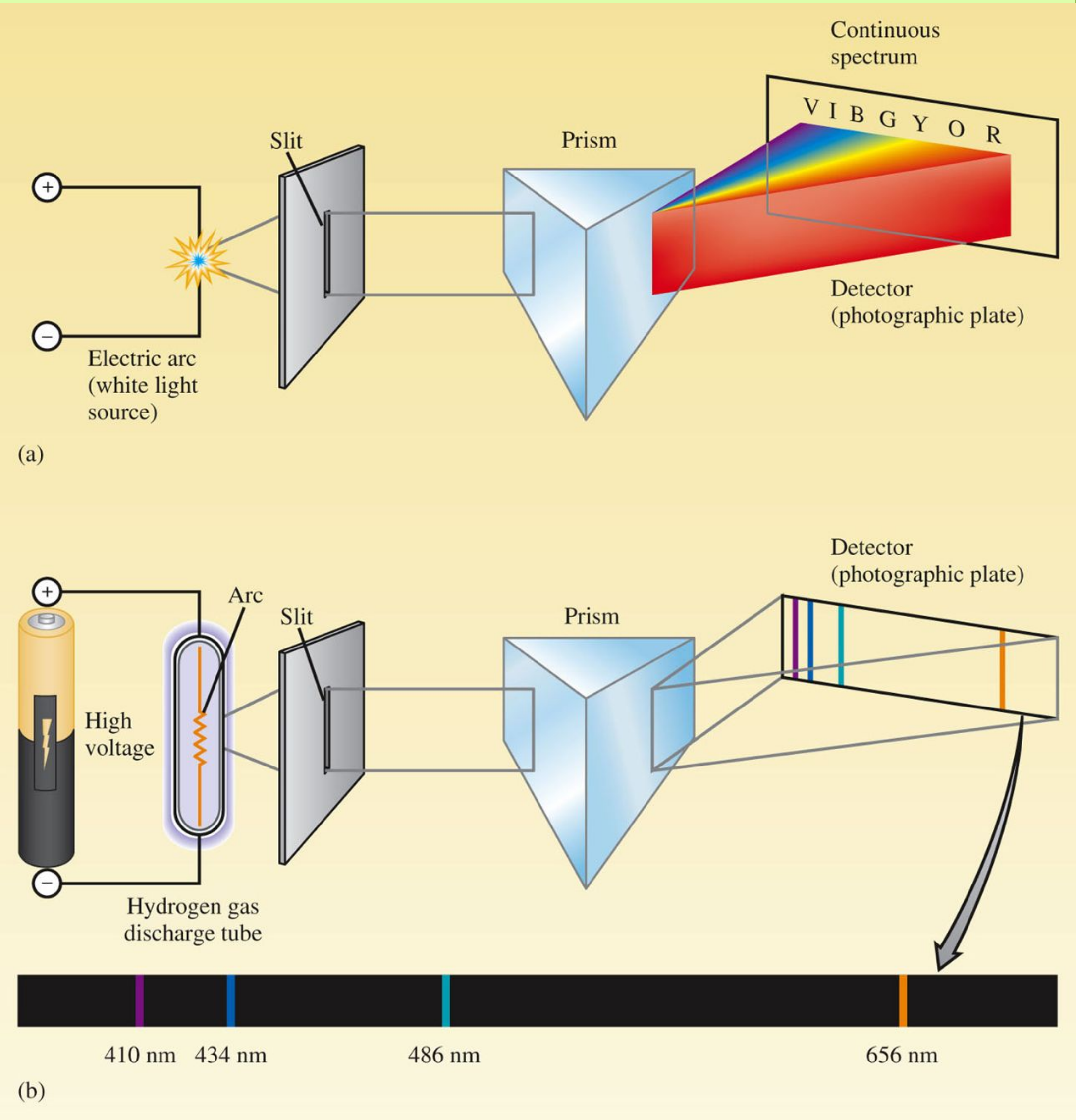
Atomic Spectrum of Hydrogen

When a high energy discharge is passed through H_2 □ H-H breaks □ excited H atoms.

Release of energy □ Emission spectrum.

$$\vartheta \propto \frac{1}{4} - \frac{1}{n^4} \quad n = 3, 4, 5, \dots.$$

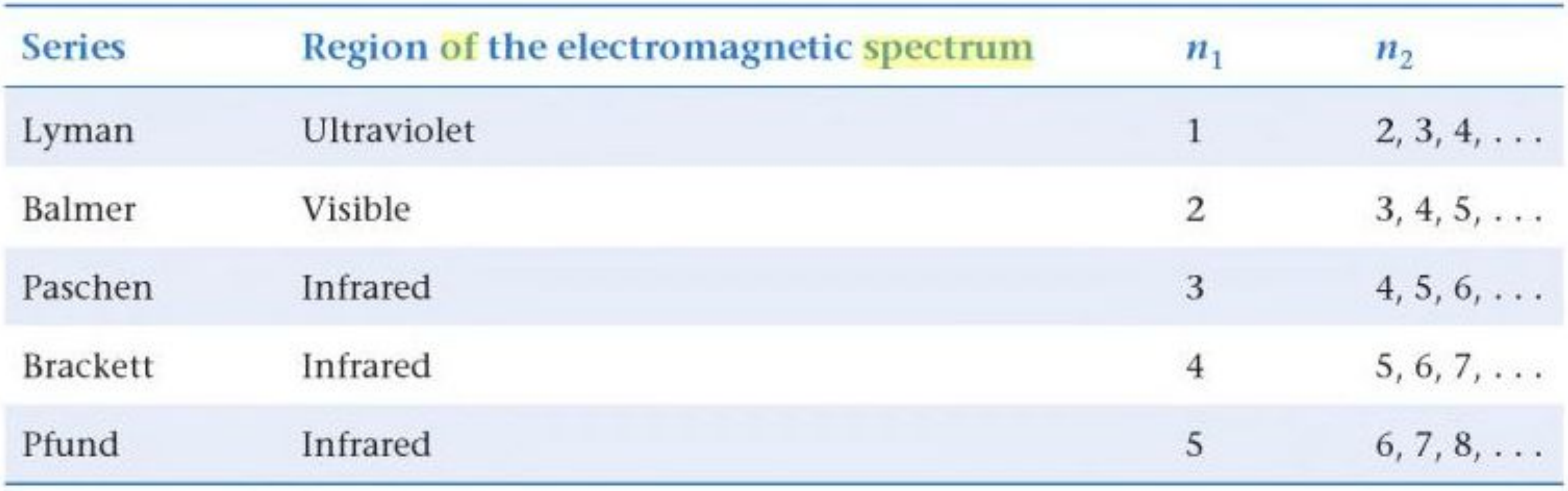
Balmer Series (visible lines)



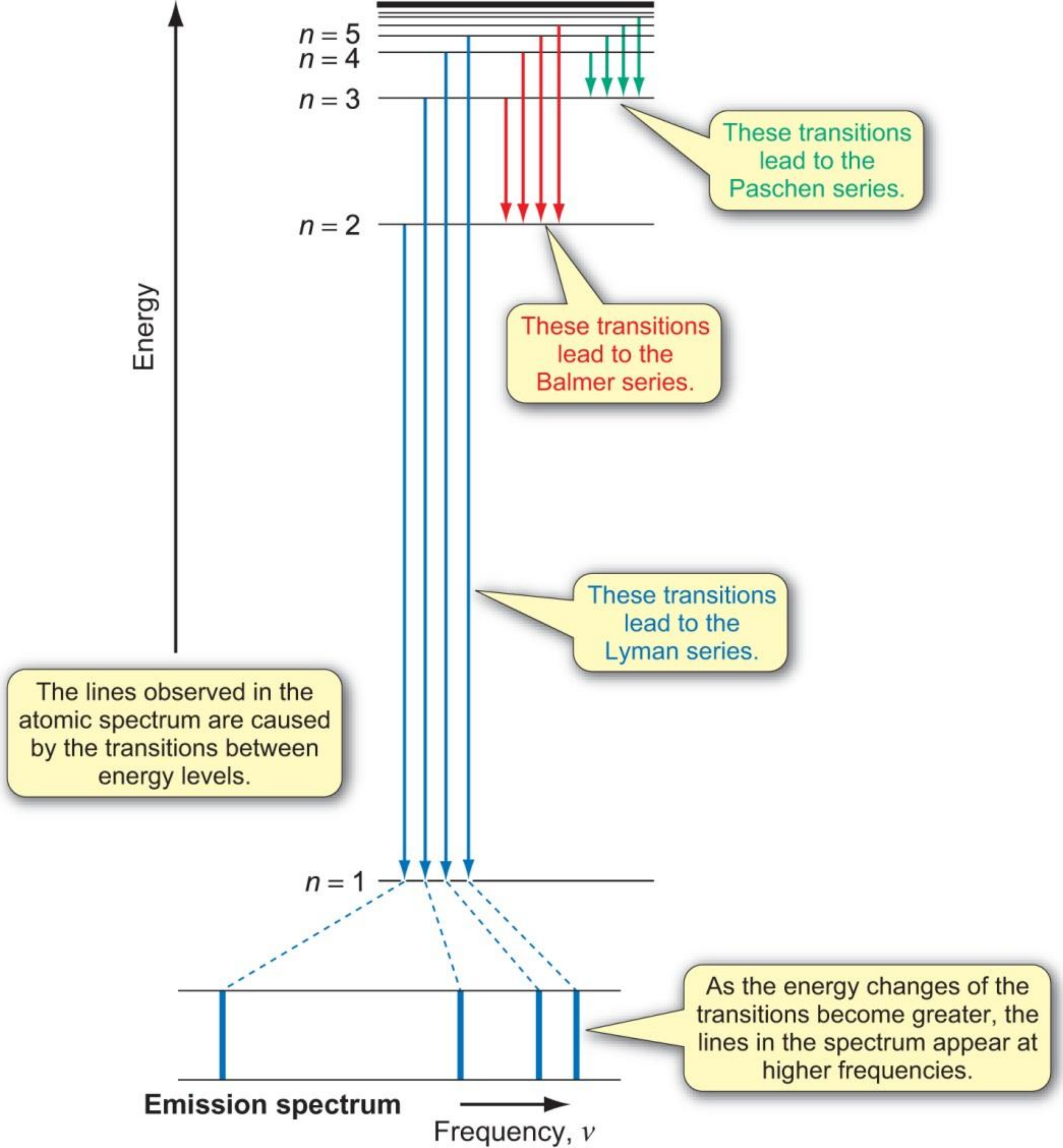
$$\boxed{\vartheta = R_H \left[\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right] \; Rydberg\ Equation}$$

$$n_2 > n_1 \qquad R_H = 3.29.10^{15}\,Hz$$

Table 3.4. The atomic spectrum of hydrogen



Series	Region of the electromagnetic spectrum	n_1	n_2
Lyman	Ultraviolet	1	2, 3, 4, . . .
Balmer	Visible	2	3, 4, 5, . . .
Paschen	Infrared	3	4, 5, 6, . . .
Brackett	Infrared	4	5, 6, 7, . . .
Pfund	Infrared	5	6, 7, 8, . . .



These transitions lead to the Paschen series.

These transitions lead to the Balmer series.

These transitions lead to the Lyman series.

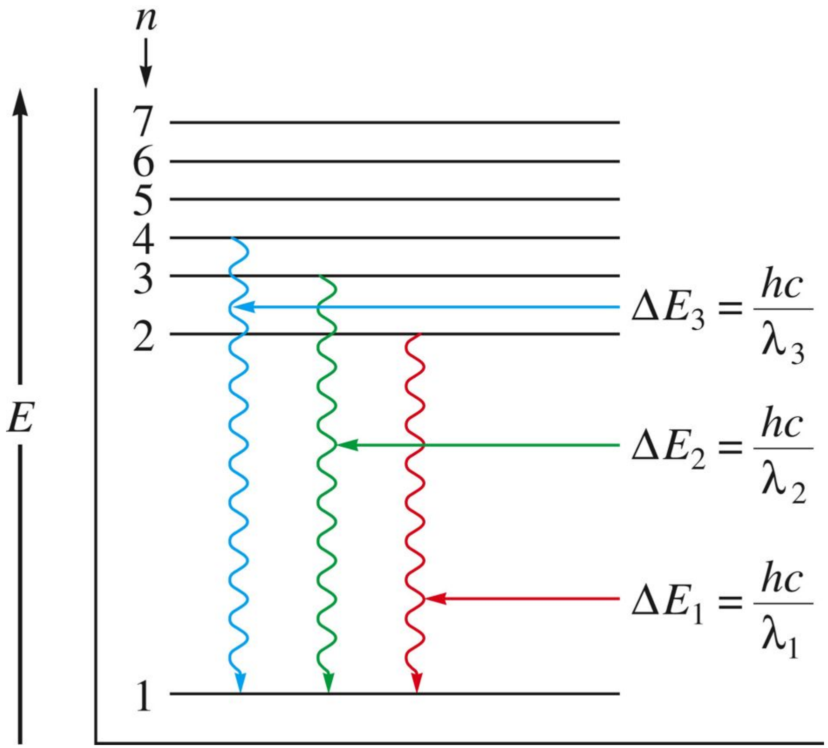
The lines observed in the atomic spectrum are caused by the transitions between energy levels.

As the energy changes of the transitions become greater, the lines in the spectrum appear at higher frequencies.

Atomic Spectrum of Hydrogen

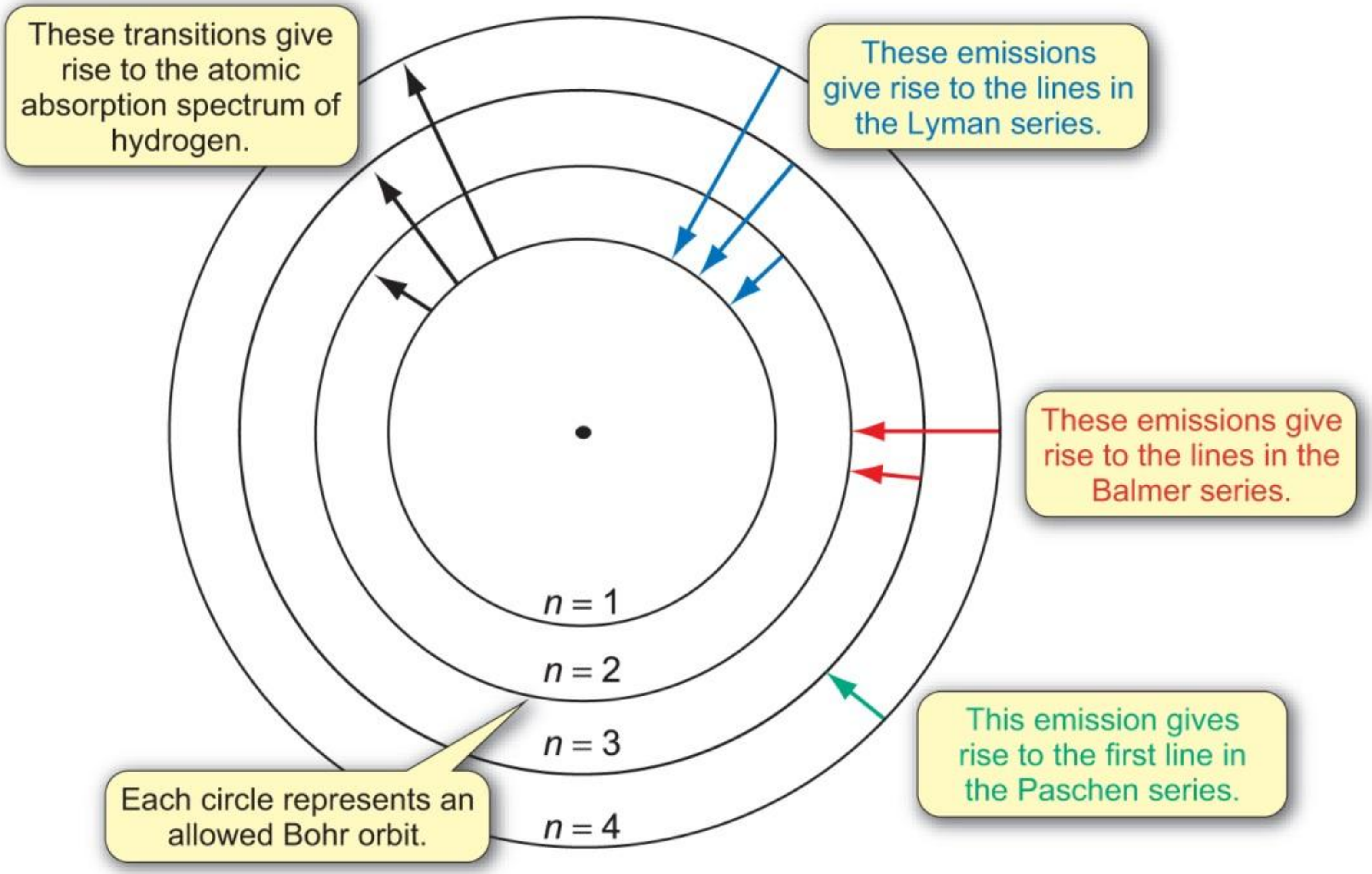
Why do we have a line spectrum for H ?

Only certain energies are allowed for the electron in the hydrogen atom. Energy is quantized!



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

3.3.2: The Bohr Model



These transitions give rise to the atomic absorption spectrum of hydrogen.

These emissions give rise to the lines in the Lyman series.

These emissions give rise to the lines in the Balmer series.

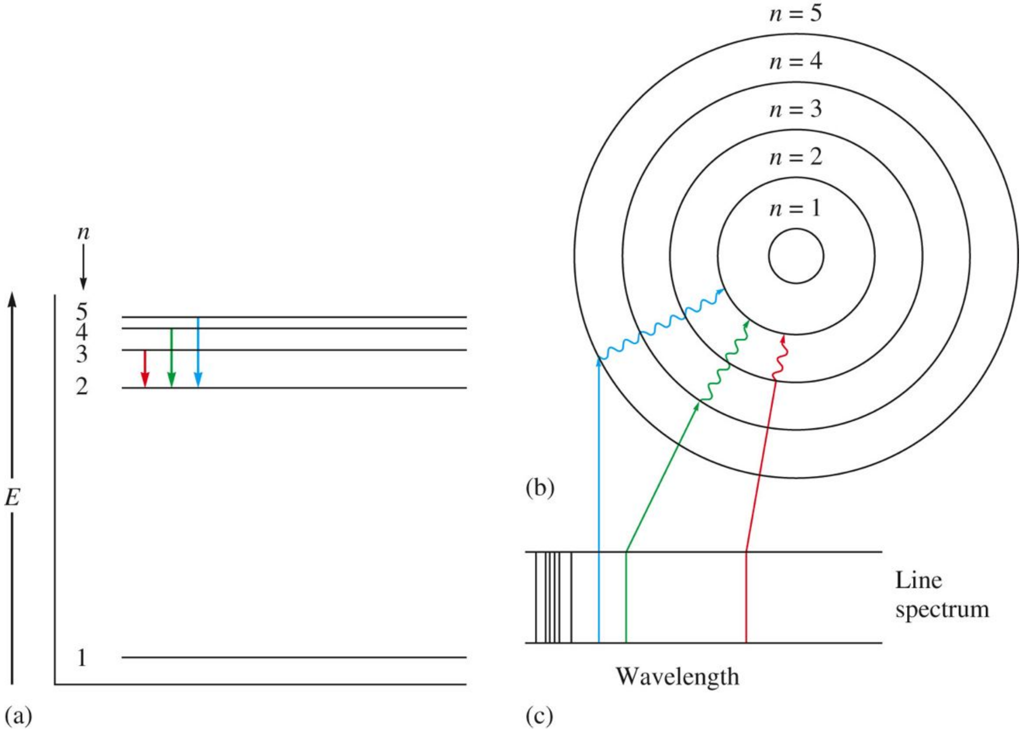
This emission gives rise to the first line in the Paschen series.

Each circle represents an allowed Bohr orbit.

The Bohr Model

General Idea :
The electron in a hydrogen atom moves around the nucleus only in certain allowed circular obits.

Bohr used classical physics to calculate the radii of these orbits.
At an infinite distance E=0 (n=∞)



$$E = -2.178x10^{-18}\,J\left(\frac{Z^2}{n^2}\right)$$

The Bohr Model

Example : Energy emitted from n=6 to ground state :

$$E_6 = -2.178x10^{18}J\left(\frac{1^2}{6^2}\right) = -6.05x10^{-20}J$$

$$E_1 = -2.178x10^{18}J\left(\frac{1^2}{1^2}\right) = -2.178x10^{-18}J$$

$$\Delta E = -2.118x10^{-18}J$$

The negative sign means that the electron is more tightly bound when n=1 than when n=6

$$\Delta E = h\frac{c}{\lambda_{emitted}} \rightarrow \lambda_{emitted} = \frac{hc}{\Delta E}$$

$$= \frac{\left(6.626x10^{-34}Js\right)\left(3.000x10^{8}m/s\right)}{2.18x10^{-18}J} = 9.379x10^{-8}m$$

Wave Function and Atomic Orbitals

3.5.1 Wave properties of matter, Heisenberg uncertainty principle

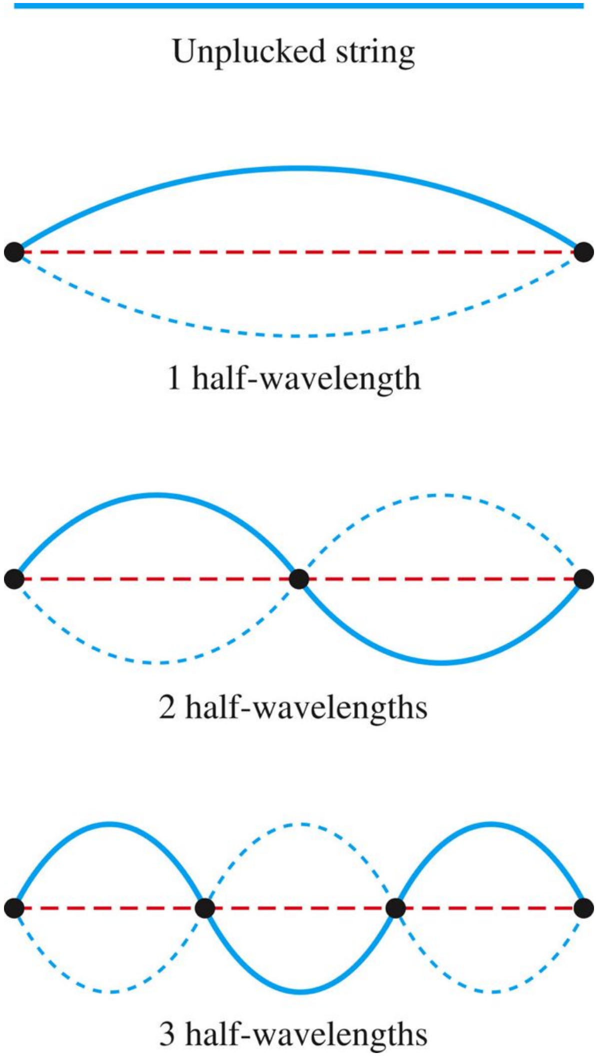
3.5.2 Wave-functions and Schrödinger equation

3.5.3 Shapes of atomic orbitals

De Broglie

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

λ = Wavelength
h = Planck Constant
m = Mass
u = Velocity of the particle



All moving particles have wave properties

The electron bound to the nucleus is similar to a standing wave.
The waves do not travel.
Node = no displacement of the wave = each end.
□ Always a whole number of half-WL.

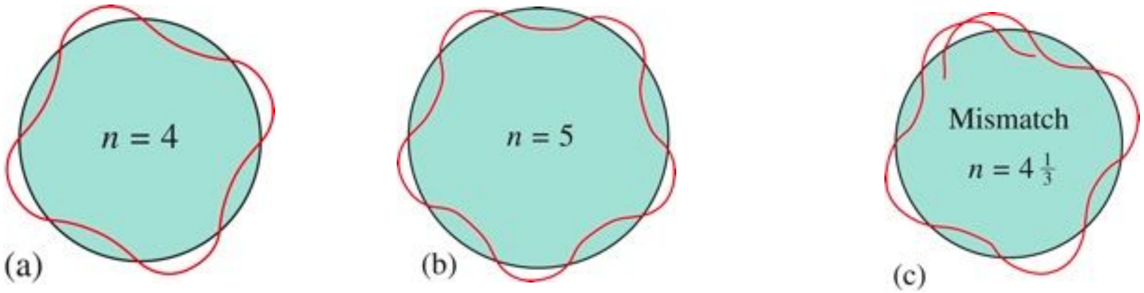
Enter

2.2 SCHRONDINGER EQUATION

Quantum Mechanical Description of the Atom

Heisenberg – de Broglie – Schrödinger

Only certain circular orbits have a circumference into which a whole number of wavelength of the standing electron will fit.



$$\hat{H}\psi = E\psi$$

ψ = wave function : describes x, y, z of the electron
H = Hamiltonian operator
E = Total Energy of the atom (E_p e-p + E_k e)

– probability of finding an electron at some point is proportional to Ψ Ψ *. Ψ * is the complex conjugate

The Schrödinger equation

The probability distributions and allowed energy levels for electrons in atoms and molecules can be calculated using the Schrödinger equation

– second order differential equation

$$H\Psi = E\Psi$$

H - is Hamiltonian operator
E - is energy of solution ψ
ψ - is wavefunction

– equation has a large number of different solutions
» each corresponds to a different possible probability distribution for the electron

– probability of finding an electron at some point is proportional to $\Psi \Psi^*$. Ψ^* is the complex conjugate

Schrodinger Wave Equation

Wavefunction (ψ) for an electron can be calculated be **Schrodinger equation:**

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi + E_{PE}\psi = E\psi$$

Kinetic energy

Potential energy

Total energy

A partial differential shows how a function depends on one variable when several are changing

Hamiltonian for one Electron

$$H = \frac{-h^2}{8\pi^2 m}\underbrace{\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)}_{} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0\sqrt{x^2+y^2+z^2}}}_{}$$

Kinetic Energy of the Electron Motion

Potential Energy of the Electron. The result of electrostatic attraction between the electron and the nucleus. It is commonly designated as V

h = planck Constant
m = mass of the electron
e = charge of the electron
Z = charge of the nucleus
$\sqrt{x^2+y^2+z^2}$ =r = distance from the nucleus
$4\pi\epsilon_0$ = permittivity of vacuum

$$\hat{H}\psi = E\psi$$

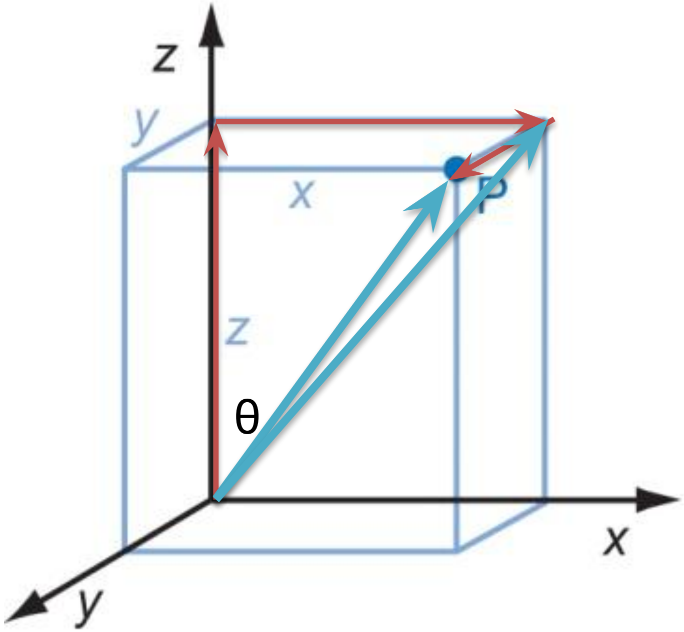
$$\underbrace{\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)}_{\text{Kinetic Energy}} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0\sqrt{x^2 + y^2 + z^2}}}_{\text{Potential Energy}}$$

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - V(x, y, z)\right]\psi(x, y, z) = E\psi(x, y, z)$$

Where $V = \frac{Ze^2}{4\pi\epsilon_0 r} = \frac{Ze^2}{4\pi\epsilon_0\sqrt{x^2+y^2+z^2}}$

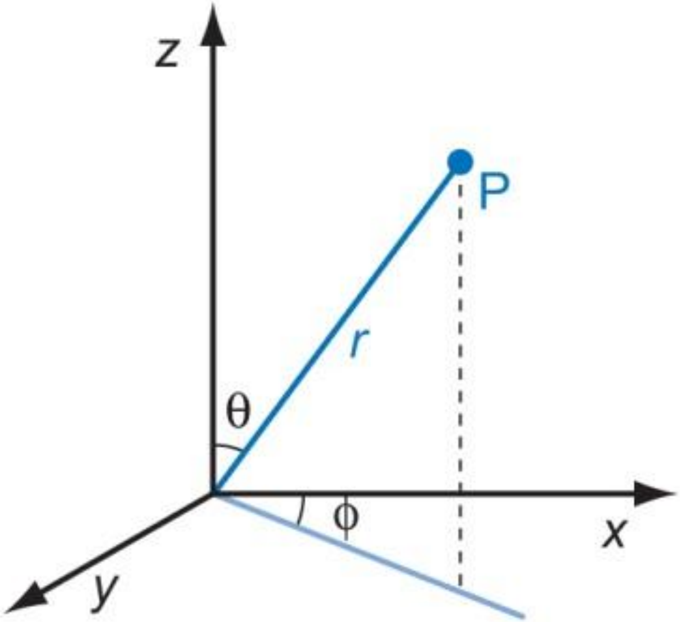
Cartesian and Spherical Coordinate

Cartesian coordinates



The position of the point P is defined in terms of *x*, *y*, and *z*

Spherical coordinates



The position of the point P is defined in terms of the distance *r* and the angles θ and ϕ

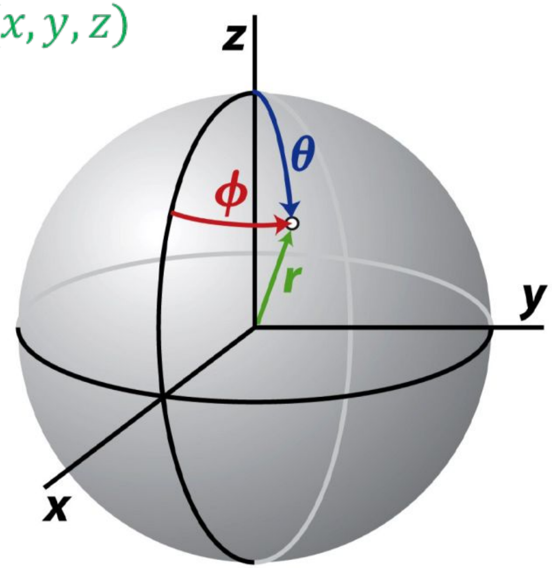
Quantum Numbers and Atomic Wavefunctions

- Atomic wavefunctions are usually expressed in spherical polar coordinates – give value of Ψ at any point in space specified by r, θ and φ

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)-V(x,y,z)\Big]\psi(x,y,z) = E\psi(x,y,z)$$

The wavefunction

x = rsinθcosφ
y = rsinθsinφ
z = rcosθ



- Can write Ψ(r, θ, φ)=R(r) Y(θ, φ)
  – R(r) is radial part of wavefunction
  – Y(θ, φ) is angular part of wavefunction

https://www.youtube.com/watch?v=sT8JIn7Q_Fo
https://www.youtube.com/watch?v=NpgKGIaE9Zc

Homework-2

- Please solve problems ;

Chapter 3

6, 9, 10, 12, 14, 16 and 17

Due on Wednesday. Recitation time

Wave Equation for the Hydrogen Atom

$$\Psi(x, y, z) = \Psi(r, \theta, \varphi) = R(r)\, Y(\theta, \varphi)$$

– R(r) is radial part of wavefunction

Describes electrons density at different distances from the nucleus

– Y(θ, φ) is angular part of wavefunction

Describes the shape of the orbitals and its orientation in space.

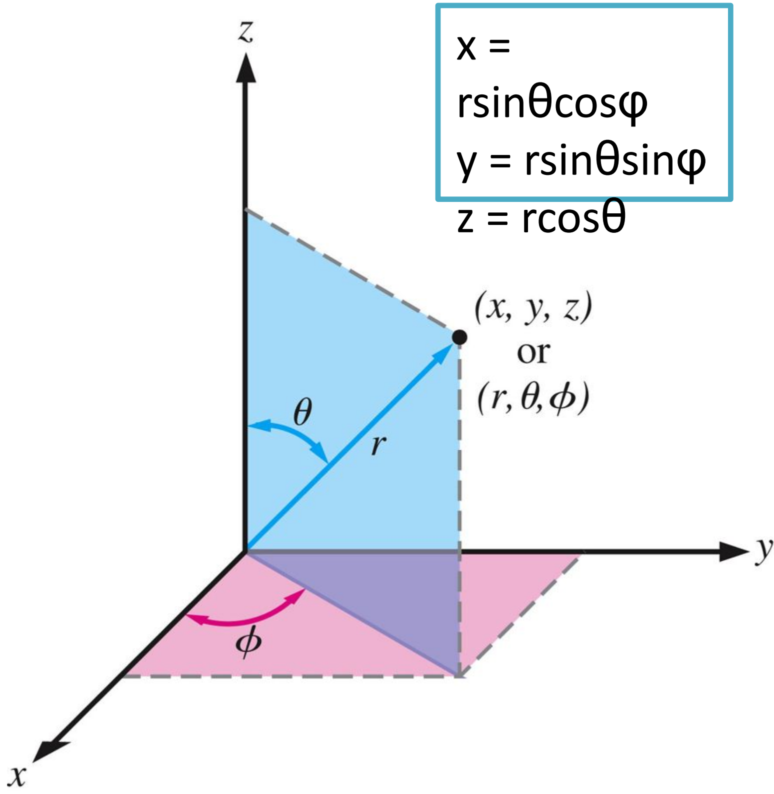
In other words:

How the probability changes from point to point at a given distance from the center of the atom.

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

$y = r\sin\theta\sin\varphi$

$z = r\cos\theta$



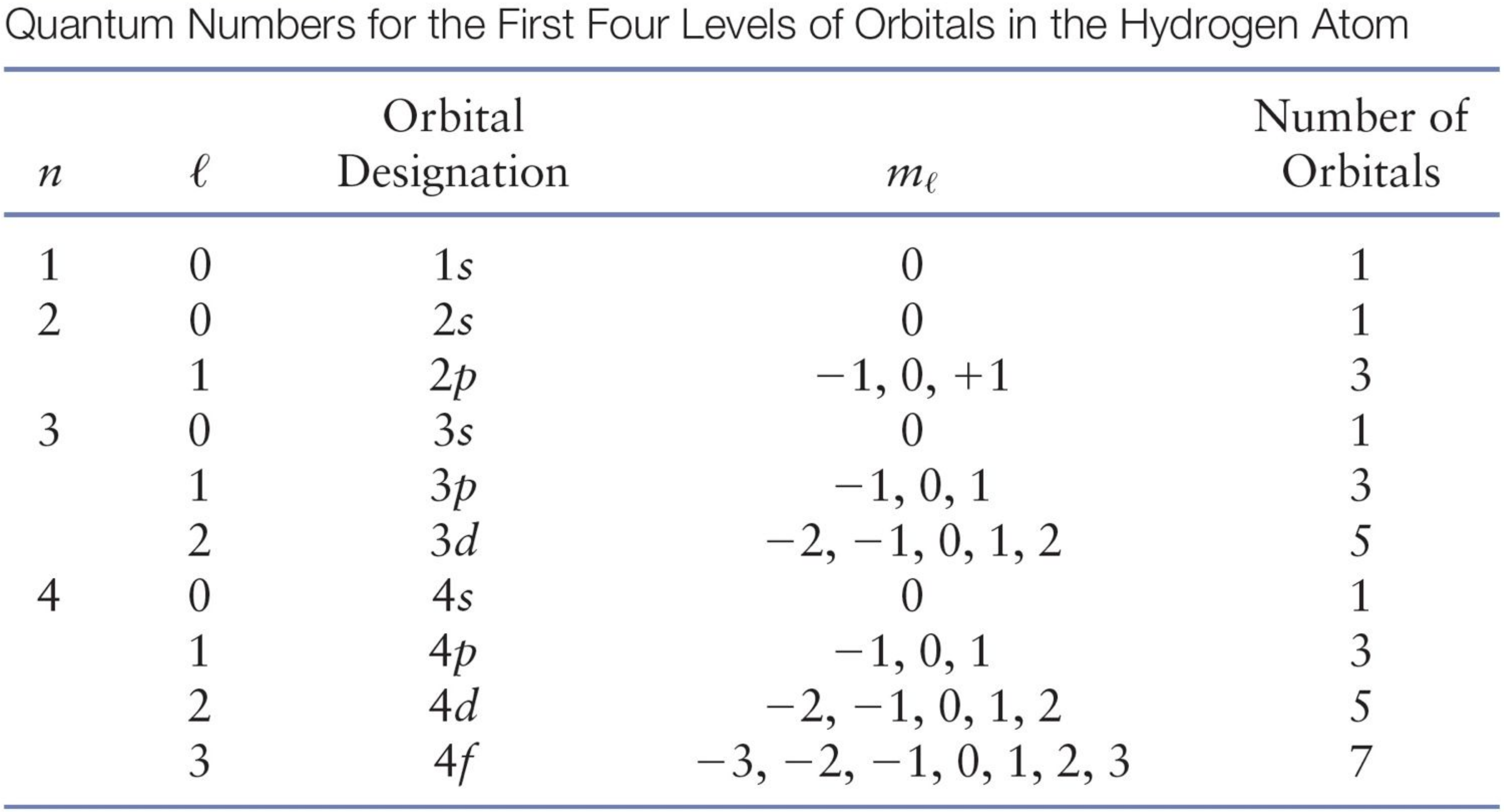
Quantum numbers :

Quantum numbers :

n = principal quantum number : size and energy of the orbital

l = angular momentum quantum number : 0 to n-1 : shape of the orbital

m_l = magnetic quantum number : -l to +l : orientation in space of the angular momentum

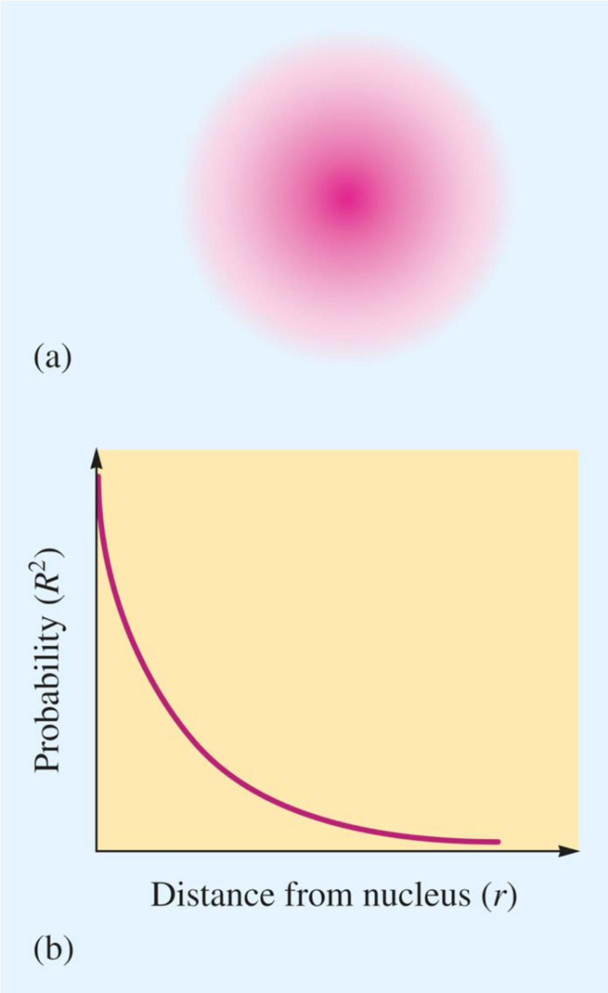


Quantum Numbers for the First Four Levels of Orbitals in the Hydrogen Atom

n	ℓ	Orbital Designation	m_ℓ	Number of Orbitals
1	0	1*s*	0	1
2	0	2*s*	0	1
	1	2*p*	−1, 0, +1	3
3	0	3*s*	0	1
	1	3*p*	−1, 0, 1	3
	2	3*d*	−2, −1, 0, 1, 2	5
4	0	4*s*	0	1
	1	4*p*	−1, 0, 1	3
	2	4*d*	−2, −1, 0, 1, 2	5
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7

Radial and Angular Wave Function for 1s derived from Schrodinger Equation

$$\Psi(r, \theta, \phi) = R(r) \times \theta Ø(\theta, Ø)$$

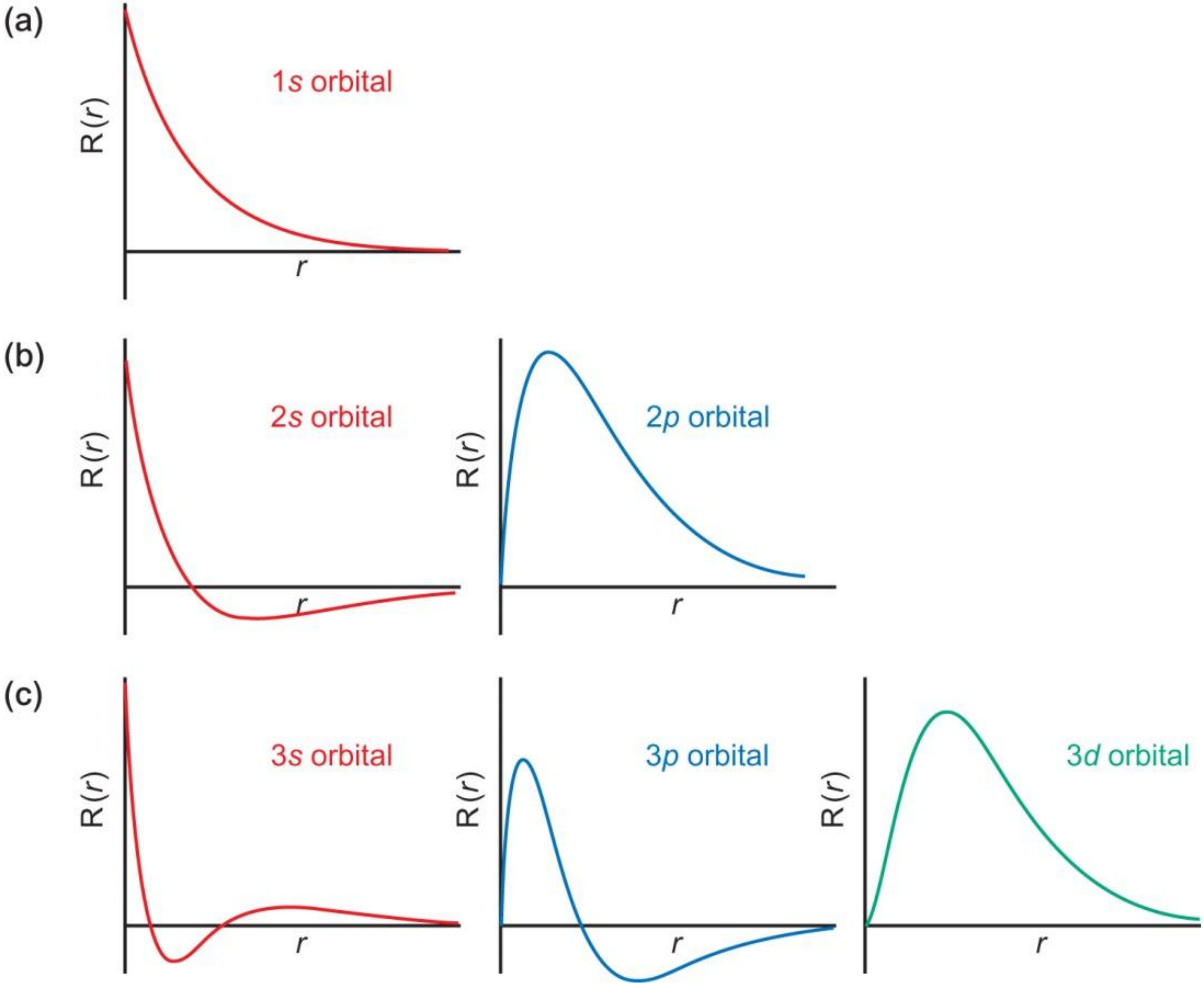


$$\left[\frac{4}{a_0{}^3}\right]^{\frac{1}{2}} e^{-\frac{r}{a_0}} \times \left[\frac{1}{4\pi}\right]^{\frac{1}{2}} = \left[\frac{1}{\pi a_0{}^3}\right]^{\frac{1}{2}} e^{-\frac{r}{a_0}}$$

$$R(r) = \left[\frac{1}{\pi a_0{}^3}\right]^{\frac{1}{2}} e^{-\frac{r}{a_0}}$$

$$a_0 = \frac{\varepsilon_0 h^2}{\pi m_e e^2} = 52.9 \text{ pm (Bohr Radius)}$$

Plot of Radial Wave Function = f(r)

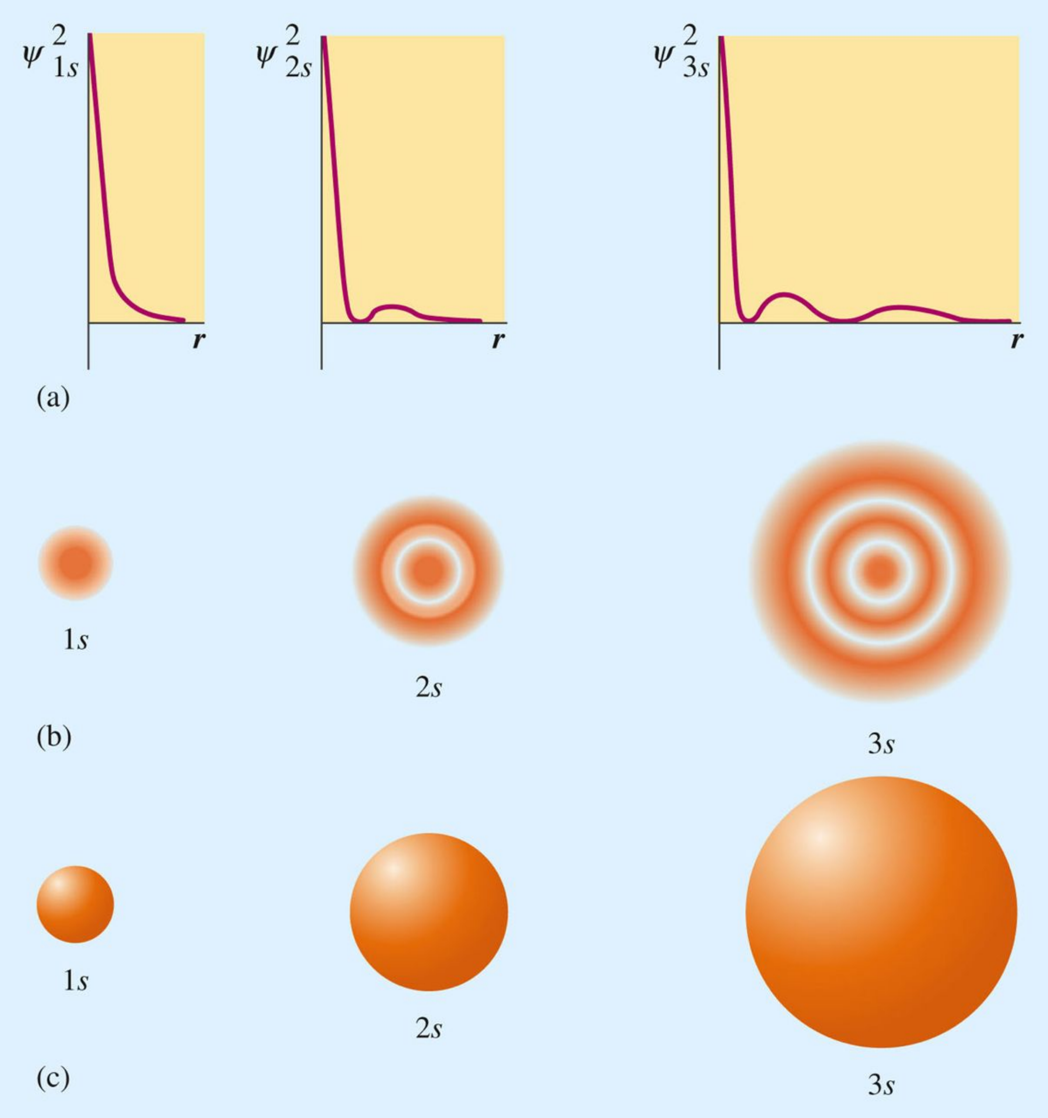


s orbitals

Size : 1s<2s<3s.
Energy : 1s<2s<3s.

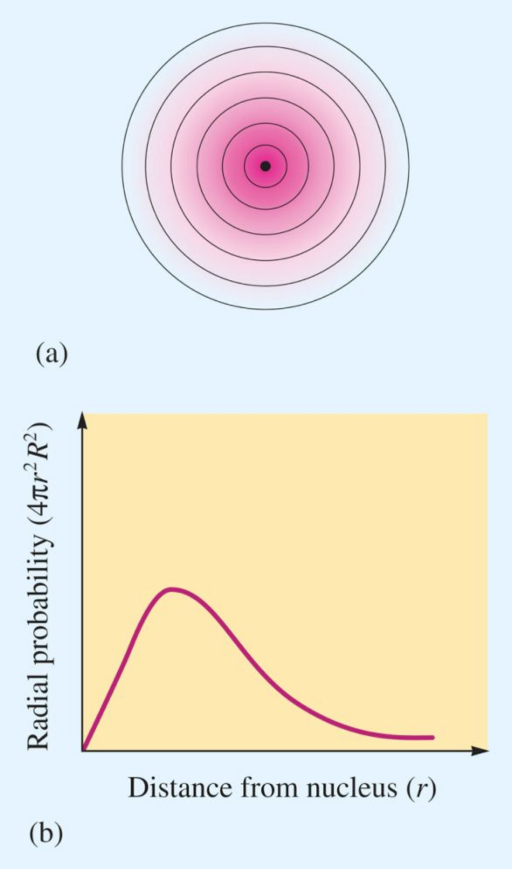
Surface of 0 probability = nodal surface / node.

Number of node = n-1 for s orbitals.



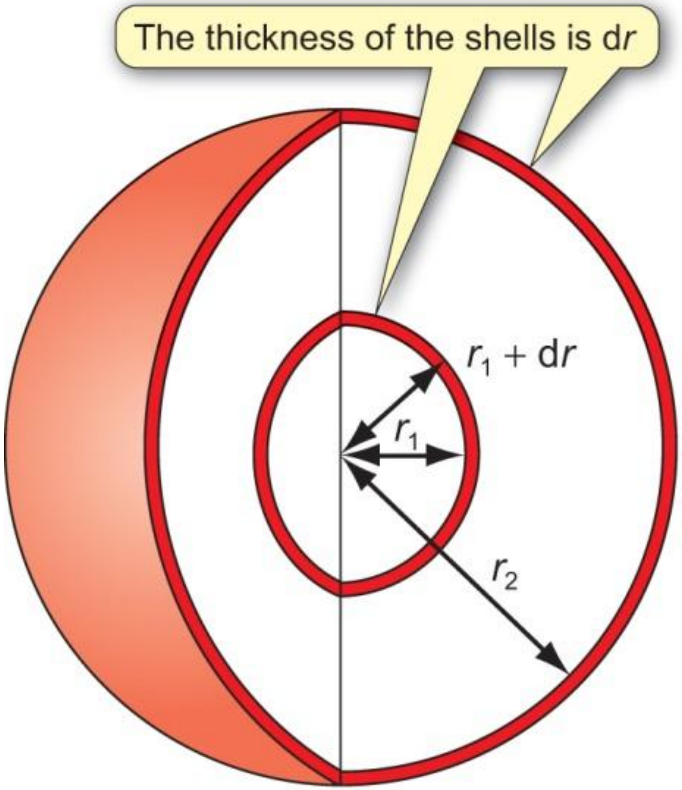
Physical Meaning of Orbitals

The wave function has no easy physical meaning.
The square of the WV at a certain point in space = probability to find an electron near that point = probability distribution.



For 1s orbital : arbitrary accepted size = radius of the sphere that encloses 90% of total electron probability.

Radial Probability Distribution : $4\pi r^2 R(r)^2 = f(r)$



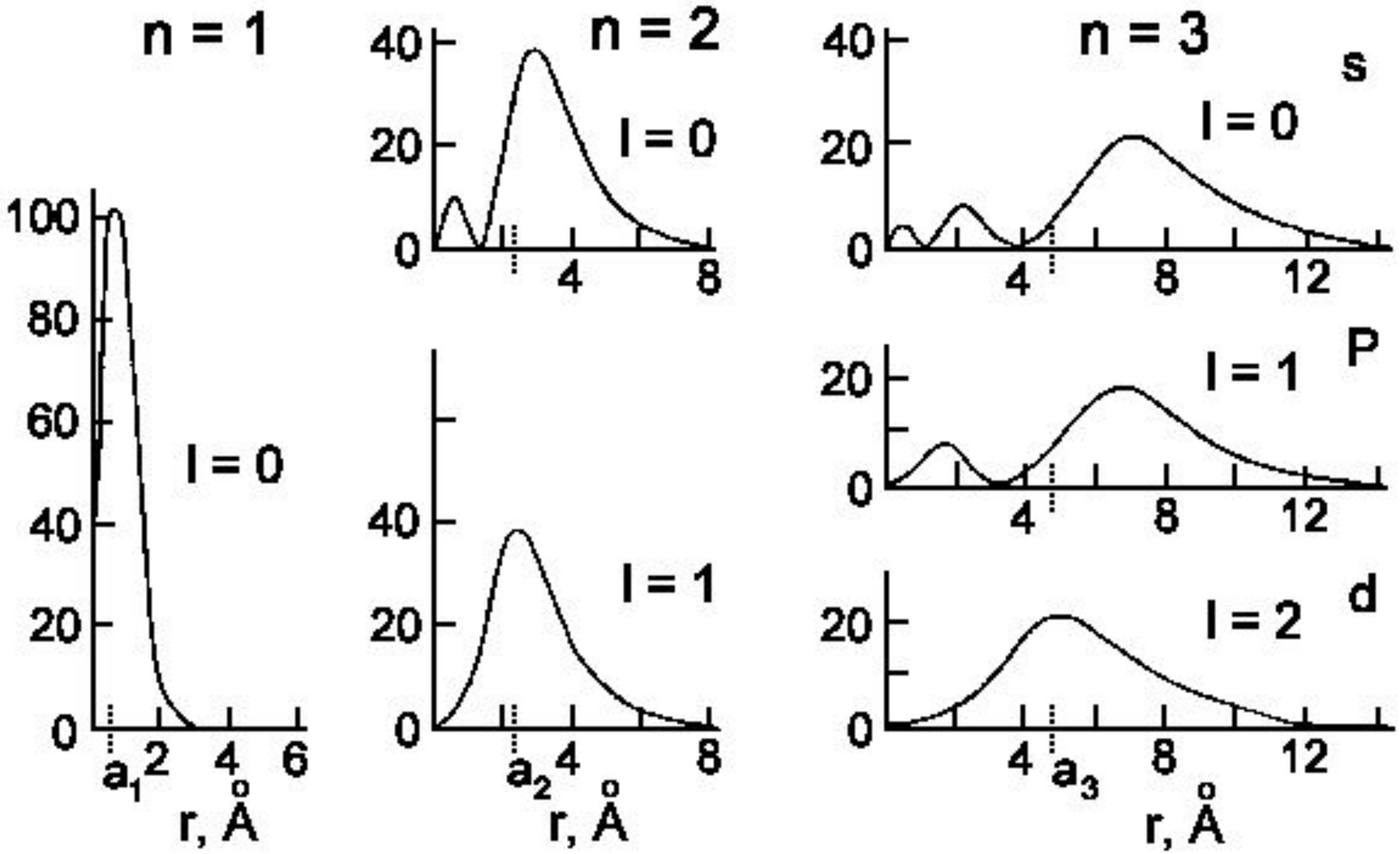
Volume of a thin shell of thickness dr at a radius r

$= $ area of surface of sphere × dr

$= 4\pi r^2 \mathrm{d}r$

a_1 = 52.9pm radius at n =1 for hydrogen

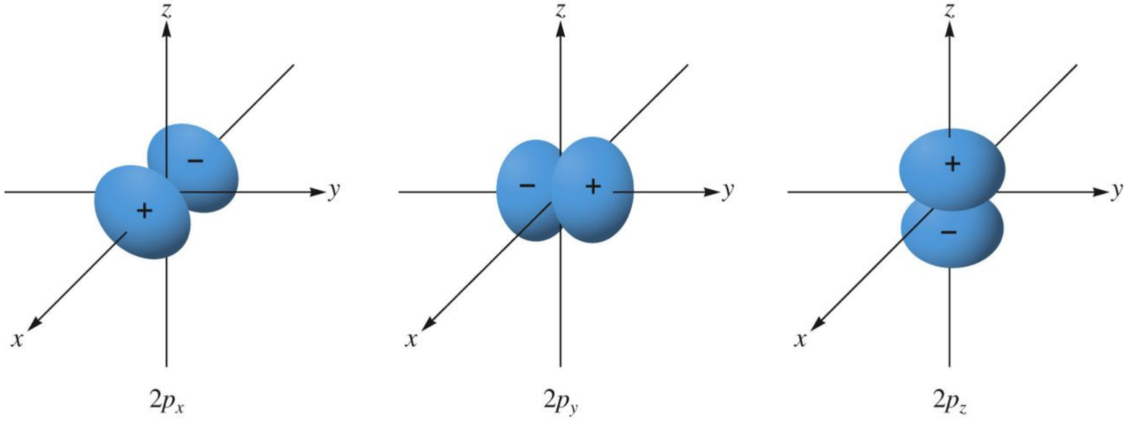
Radial Probability Distribution : $4\pi r^2 R^2 = \mathrm{f}\,(\mathrm{r})$



a_1 = 52.9pm radius at n =1 for hydrogen

p orbitals

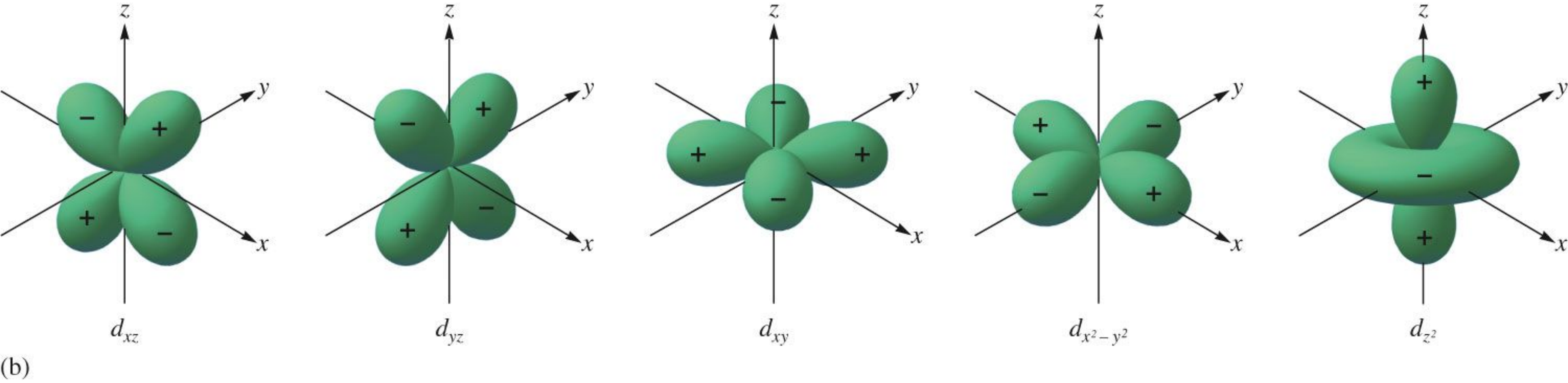
Two lobes separated by a node.
Sine function : + and - □ same for the orbital.
Px, Py, Pz following their orientation



(b)

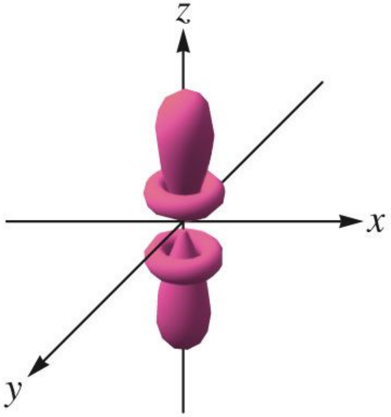
d orbitals

2 different shapes : $d_{xz,}d_{yz,}d_{xy}$, $d_{x2\text{-}y2}$ and d_{z2}

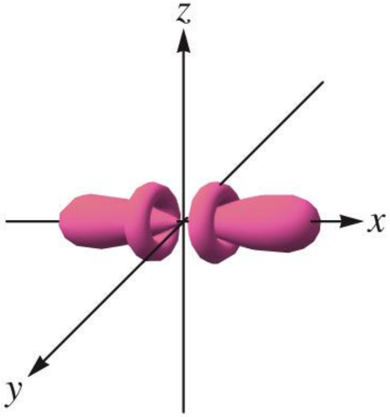


f orbitals

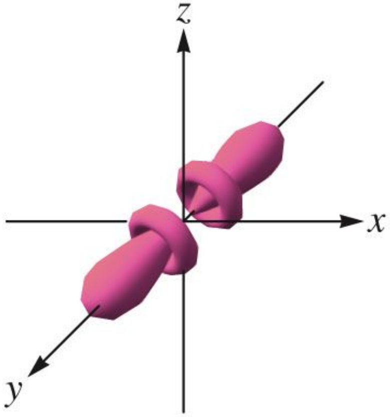
Very complex shapes



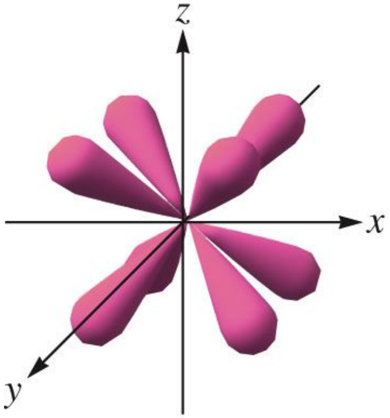
$f_{z^3 - \frac{3}{5}zr^2}$



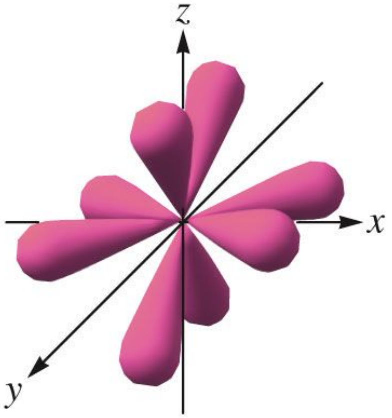
$f_{x^3 - \frac{3}{5}xr^2}$



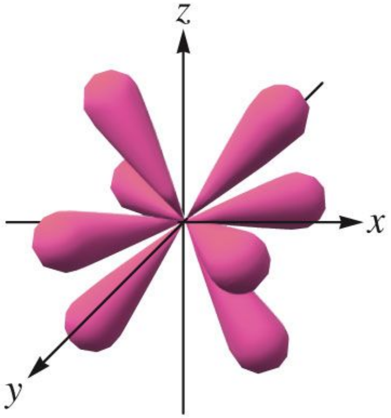
$f_{y^3 - \frac{3}{5}yr^2}$



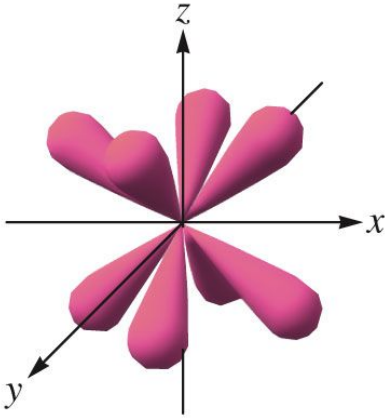
f_{xyz}



$f_{y(x^2 - z^2)}$



$f_{x(z^2 - y^2)}$



$f_{z(x^2 - y^2)}$

Schrödinger Equation

Each solution ψ of the Schrödinger equation has a specific value for E.
A specific wave function for a given electron = **orbital**

An orbital ≠ orbit.

How does an electron move in an orbit? We don’t know!

Heisenberg uncertainty principle

There is a fundamental limitation to just how precisely we can know both the position and the momentum of a particle at a given time.

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

$$\hbar = \frac{h}{2\pi} \rightarrow \Delta x \Delta p \geq \frac{h}{4\pi}$$

Negligible for macro particles (ball, etc.) but not for small particles!

The Hydrogen Atom : summary

1. The quantum mechanical model : electron = wave
   Series of wave function (orbitals) that describe the possible energies and spatial distributions available to the electrons.

2. Heisenberg : the electron motion can't be defined.
   The square of the WF = probability distribution of the electron in an orbital.

3. The size of the orbital is arbitrarily defined .
   Surface that contains 90% of the total electron probability.

4. The H atom has many orbitals.
   In the ground state : e- in 1s.

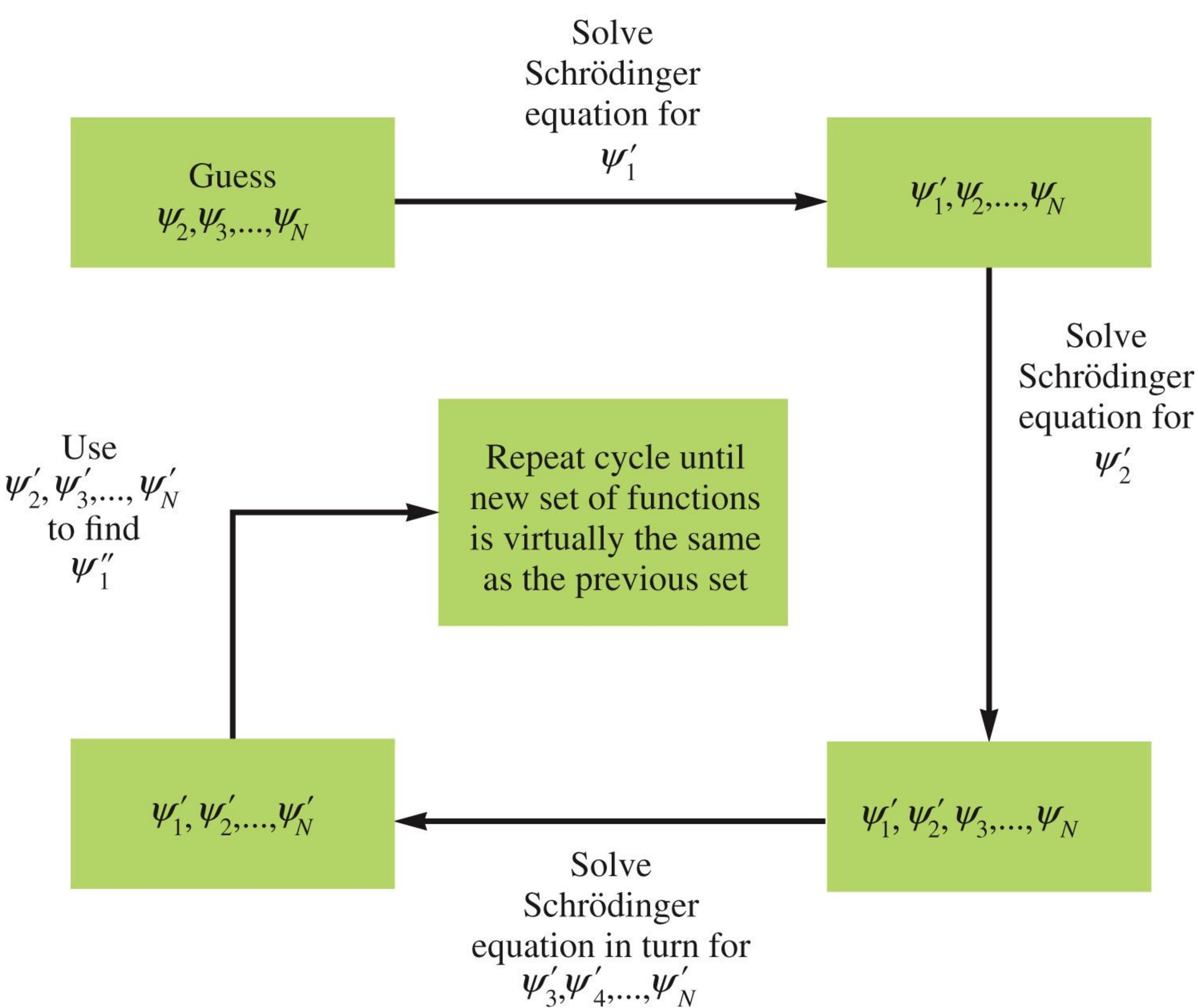
Polyelectronic Model

Schrödinger equation can be solved exactly only for hydrogen.
Schrödinger equation cannot be solved exactly for polyelectronic atoms.

It has to be approximated : SCF : Self-Consistent Field by Hartree.

1- A WF (orbital) is guessed for each electron except for electron 1.
2- Schrödinger equation is solved for electron 1
3- The repulsion between 1 and the others electrons are computed
4- ψ_1 is found
5- $\psi_{2,}$ etc. are computed
6- The entire process start again until a self-consistent field is obtained

Self-Consistent Field Method



Guess $\psi_2, \psi_3, \ldots, \psi_N$

Solve Schrödinger equation for ψ'_1

$\psi'_1, \psi_2, \ldots, \psi_N$

Solve Schrödinger equation for ψ'_2

$\psi'_1, \psi'_2, \psi_3, \ldots, \psi_N$

Solve Schrödinger equation in turn for $\psi'_3, \psi'_4, \ldots, \psi'_N$

$\psi'_1, \psi'_2, \ldots, \psi'_N$

Use $\psi'_2, \psi'_3, \ldots, \psi'_N$ to find ψ''_1

Repeat cycle until new set of functions is virtually the same as the previous set

http://www.youtube.com/watch?v=UVkTuOwfOh0

Review this link at home

https://www.youtube.com/watch?v=A6DiVspoZ1E

Many Electron Atoms

Part V

Electron spin,
Aufbau principle,
Anomalies in electronic configuration,
Structure of Periodic table

Electron Spin and Pauli Principle

A 4th quantum number describe the electron : m_s : electron spin quantum number.

The electron doesn’t really “spin” = name for the intrinsic angular moment.

m_s = +1/2 or -1/2

<u>Pauli exclusion principle </u>: in a given atom no two electrons can have the same set of four quantum numbers.
– An orbital can hold only two electrons and they must have opposite spin.

History of the Periodic Table

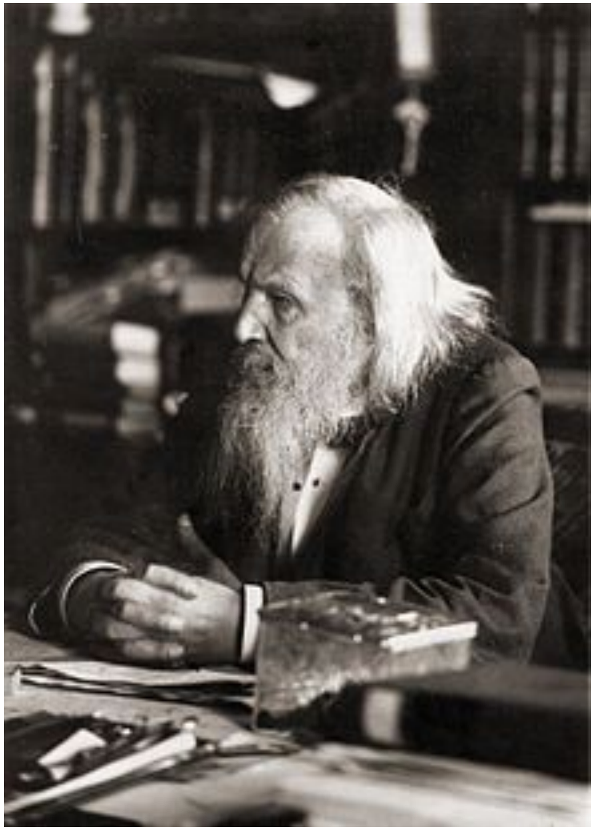
Dmitri Mendeleev : ми́трий Менделе́ев

One of first to arrange known elements into a chart

Allowed prediction of element properties

Arranged known elements according to increasing atomic masses

Mendeleev first stated the periodic law
"The properties of the elements are a periodic function of their atomic masses"

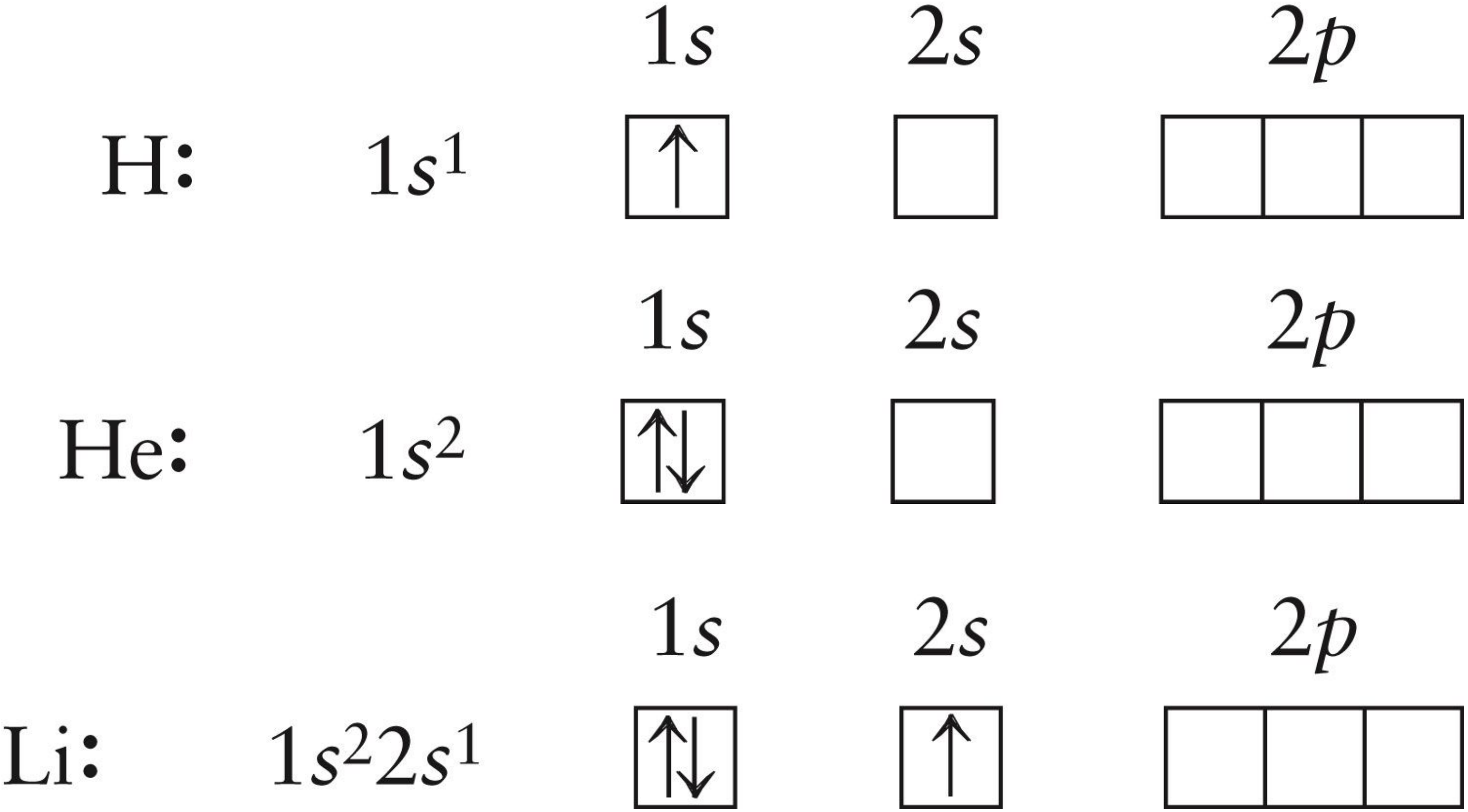


1834 – 1907
Saint Petersburg - Russia

Later, after more observations, the table was correctly arranged in ORDER OF INCREASING ATOMIC NUMBER

The Aufbau Principle

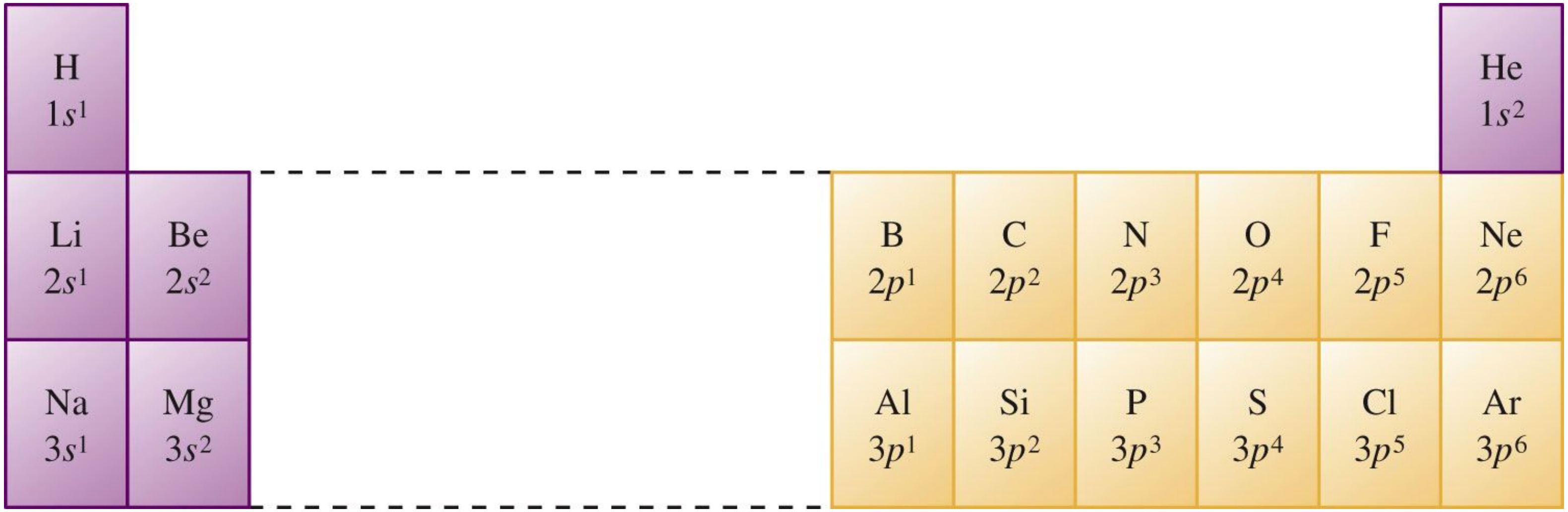
Principle to populate orbitals.



Valence electrons

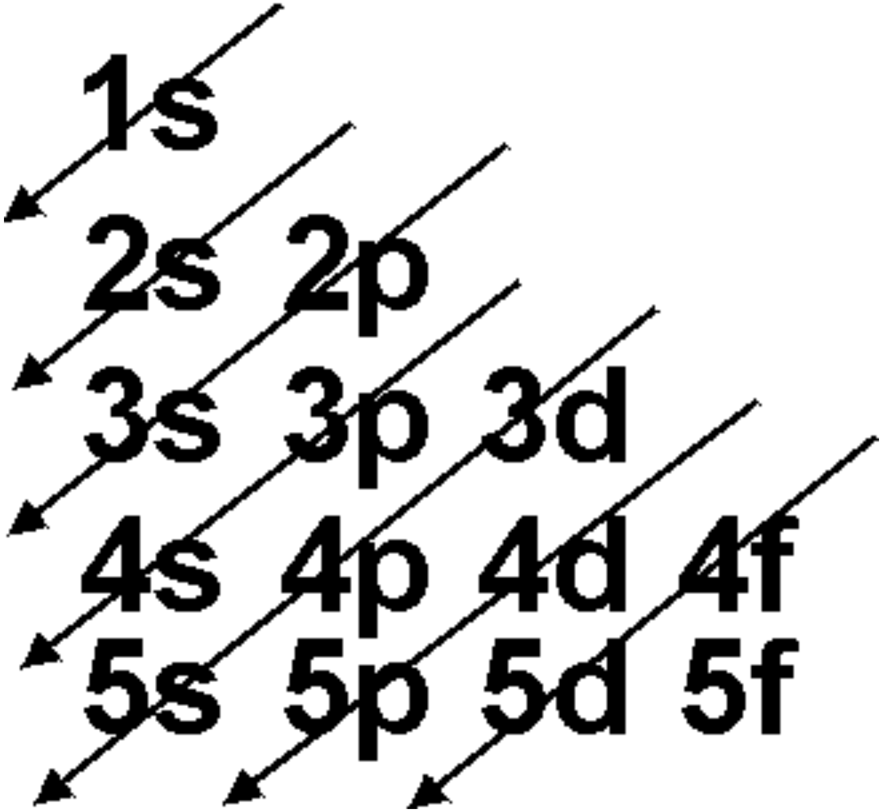
Valence electrons = electrons from the outermost principal quantum level of an atom.

Group : Elements in a column : Same valence configuration



H $1s^1$								He $1s^2$
Li $2s^1$	Be $2s^2$		B $2p^1$	C $2p^2$	N $2p^3$	O $2p^4$	F $2p^5$	Ne $2p^6$
Na $3s^1$	Mg $3s^2$		Al $3p^1$	Si $3p^2$	P $3p^3$	S $3p^4$	Cl $3p^5$	Ar $3p^6$

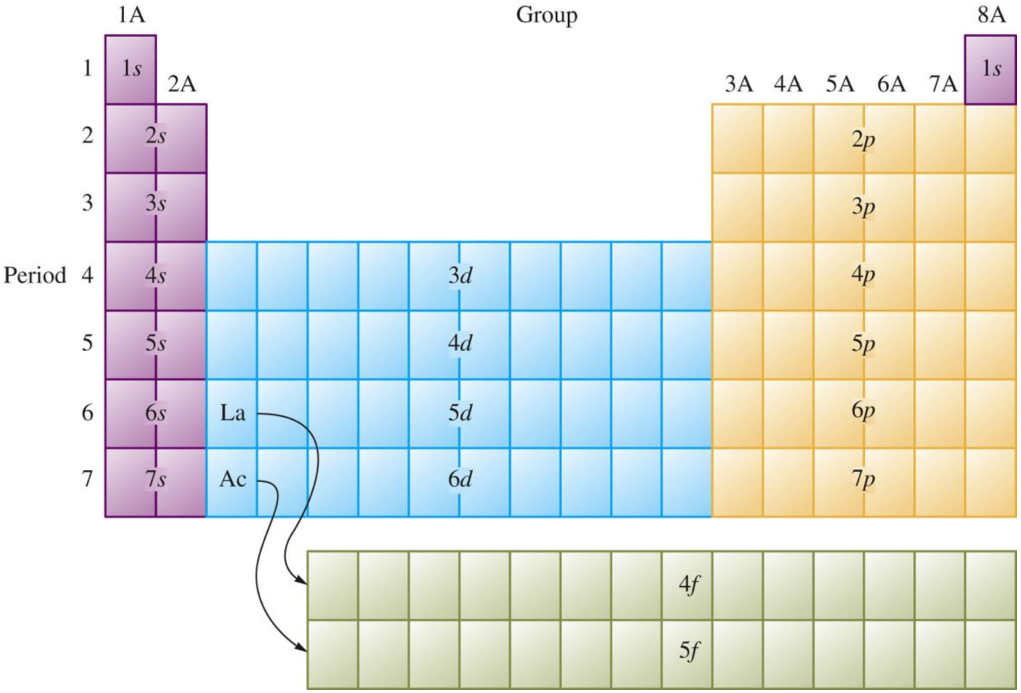
Rules



Rules

After $4s^2$, we fill 3d.

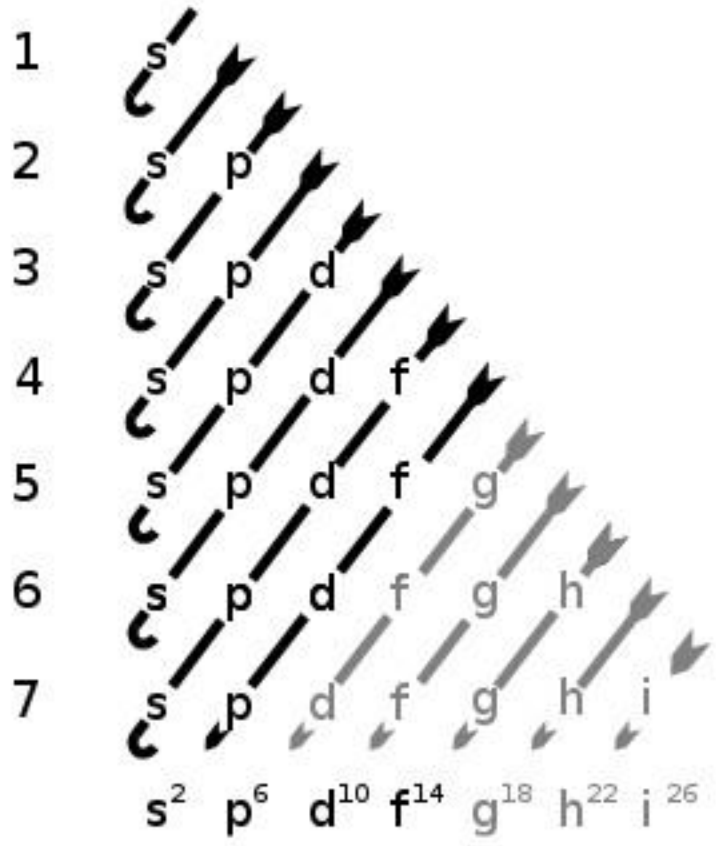
Mn : $[Ar]4s^2 3d^5$ – Fe $[Ar]4s^2 3d^6$



Additional Rules:

- The (n+1) orbitals always fill before the nd orbitals.
- After lanthanum, the lanthanide series occur. □ filling of 4f instead of 5d
- After actinium, the actinide series occur. □ filling 5f instead of 6d
- Groups 1A□8A indicate the total number of valance electrons.
- Groups 1A□8A are main group elements.

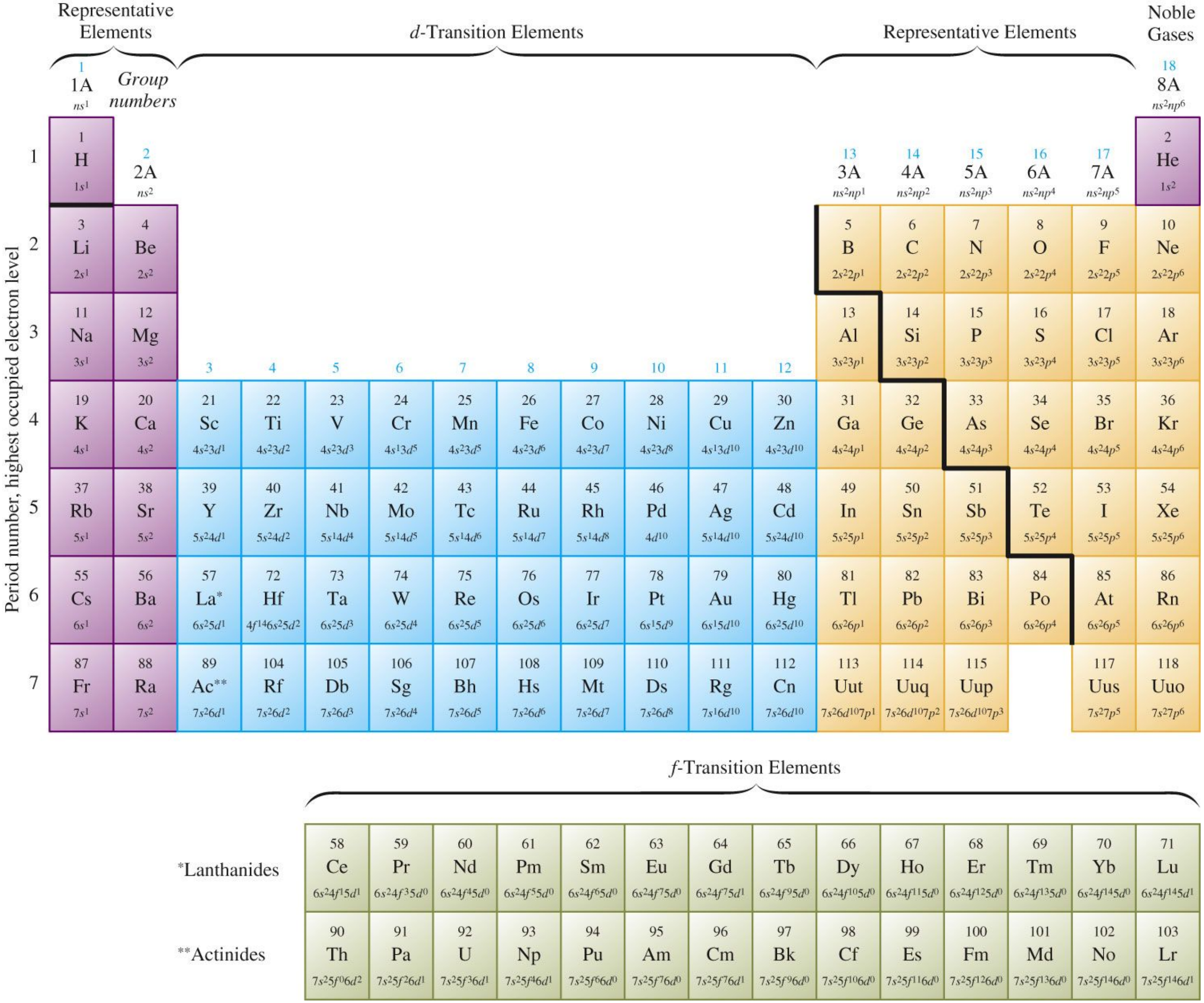
Rules



Element above 118
are generally unstable

G contain 9 orbitals l = n-1 = 4 so -4,-3,-2, -1, 0, 2, 3, 4 each

Rules



Representative Elements | *d*-Transition Elements | Representative Elements | Noble Gases

Group numbers

Period number, highest occupied electron level

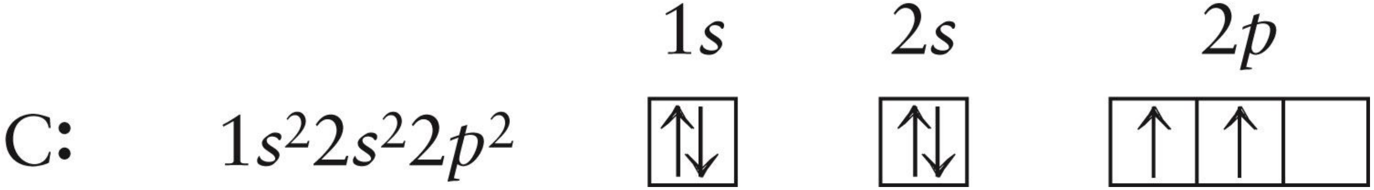
	1 1A ns^1	2 2A ns^2	3	4	5	6	7	8	9	10	11	12	13 3A ns^2np^1	14 4A ns^2np^2	15 5A ns^2np^3	16 6A ns^2np^4	17 7A ns^2np^5	18 8A ns^2np^6
1	1 H $1s^1$																	2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $4s^23d^1$	22 Ti $4s^23d^2$	23 V $4s^23d^3$	24 Cr $4s^13d^5$	25 Mn $4s^23d^5$	26 Fe $4s^23d^6$	27 Co $4s^23d^7$	28 Ni $4s^23d^8$	29 Cu $4s^13d^{10}$	30 Zn $4s^23d^{10}$	31 Ga $4s^24p^1$	32 Ge $4s^24p^2$	33 As $4s^24p^3$	34 Se $4s^24p^4$	35 Br $4s^24p^5$	36 Kr $4s^24p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $5s^24d^1$	40 Zr $5s^24d^2$	41 Nb $5s^14d^4$	42 Mo $5s^14d^5$	43 Tc $5s^14d^6$	44 Ru $5s^14d^7$	45 Rh $5s^14d^8$	46 Pd $4d^{10}$	47 Ag $5s^14d^{10}$	48 Cd $5s^24d^{10}$	49 In $5s^25p^1$	50 Sn $5s^25p^2$	51 Sb $5s^25p^3$	52 Te $5s^25p^4$	53 I $5s^25p^5$	54 Xe $5s^25p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La* $6s^25d^1$	72 Hf $4f^{14}6s^25d^2$	73 Ta $6s^25d^3$	74 W $6s^25d^4$	75 Re $6s^25d^5$	76 Os $6s^25d^6$	77 Ir $6s^25d^7$	78 Pt $6s^15d^9$	79 Au $6s^15d^{10}$	80 Hg $6s^25d^{10}$	81 Tl $6s^26p^1$	82 Pb $6s^26p^2$	83 Bi $6s^26p^3$	84 Po $6s^26p^4$	85 At $6s^26p^5$	86 Rn $6s^26p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac** $7s^26d^1$	104 Rf $7s^26d^2$	105 Db $7s^26d^3$	106 Sg $7s^26d^4$	107 Bh $7s^26d^5$	108 Hs $7s^26d^6$	109 Mt $7s^26d^7$	110 Ds $7s^26d^8$	111 Rg $7s^16d^{10}$	112 Cn $7s^26d^{10}$	113 Uut $7s^26d^{10}7p^1$	114 Uuq $7s^26d^{10}7p^2$	115 Uup $7s^26d^{10}7p^3$		117 Uus $7s^27p^5$	118 Uuo $7s^27p^6$

f-Transition Elements

*Lanthanides	58 Ce $6s^24f^15d^1$	59 Pr $6s^24f^35d^0$	60 Nd $6s^24f^45d^0$	61 Pm $6s^24f^55d^0$	62 Sm $6s^24f^65d^0$	63 Eu $6s^24f^75d^0$	64 Gd $6s^24f^75d^1$	65 Tb $6s^24f^95d^0$	66 Dy $6s^24f^{10}5d^0$	67 Ho $6s^24f^{11}5d^0$	68 Er $6s^24f^{12}5d^0$	69 Tm $6s^24f^{13}5d^0$	70 Yb $6s^24f^{14}5d^0$	71 Lu $6s^24f^{14}5d^1$
**Actinides	90 Th $7s^25f^06d^2$	91 Pa $7s^25f^26d^1$	92 U $7s^25f^36d^1$	93 Np $7s^25f^46d^1$	94 Pu $7s^25f^66d^0$	95 Am $7s^25f^76d^0$	96 Cm $7s^25f^76d^1$	97 Bk $7s^25f^96d^0$	98 Cf $7s^25f^{10}6d^0$	99 Es $7s^25f^{11}6d^0$	100 Fm $7s^25f^{12}6d^0$	101 Md $7s^25f^{13}6d^0$	102 No $7s^25f^{14}6d^0$	103 Lr $7s^25f^{14}6d^1$

Hund’s Rule

The lowest energy configuration for an atom is the one having the maximum number of unpaired electrons allowed by the Pauli Principle.



Configuration of Ne? $1s^2 2s^2 2p^6$
Configuration of Na? $[Ne]3s^1$

Pauli Exclusion Principle

Pauli Exclusion principle ; no two electrons in an atom can have the same quantum numbers n, l, ml, and ms – this means that an orbital can never have more than two electrons in it

Hund’s Rule

Hund’s rule of maximum multiplicity requires that electrons be placed in orbitals to give the maximum total spin possible (the maximum number of parallel spin)

Penetration Effect

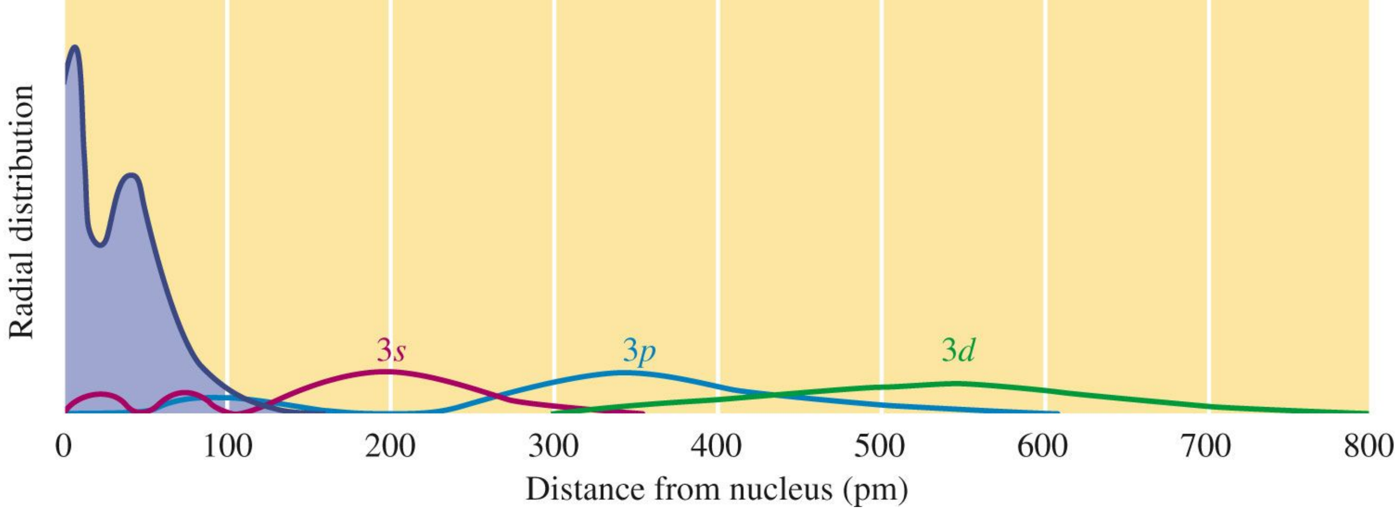
Why do we fill s, p and then d?.

Core electrons : 1s, 2s and 2p are shielding 3s, 3p, 3d from the nuclear charge.

Even if 3s has a max around 200pm, it has a small/significant prob. of being quite close to the nucleus □ Penetration effect.

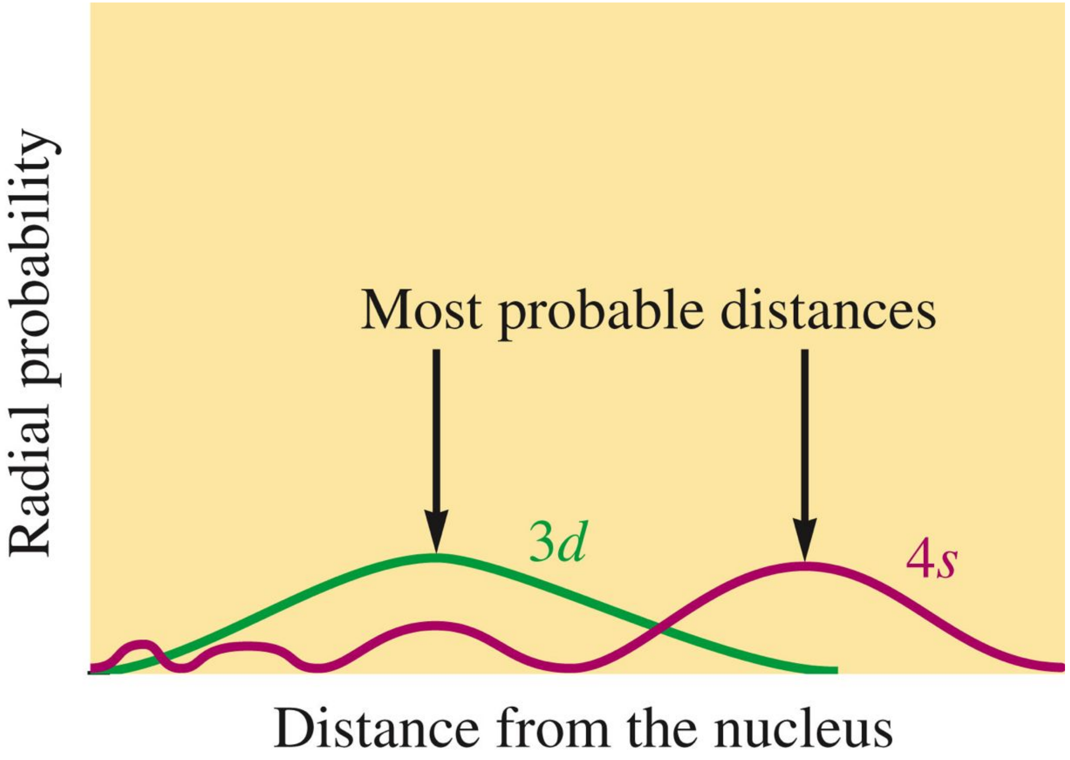
3p has less chance to be near the nucleus

3d shows much less penetration than 3p. $\mathbf{E_{3s} < E_{3p} < E_{3d}}$



Penetration Effect

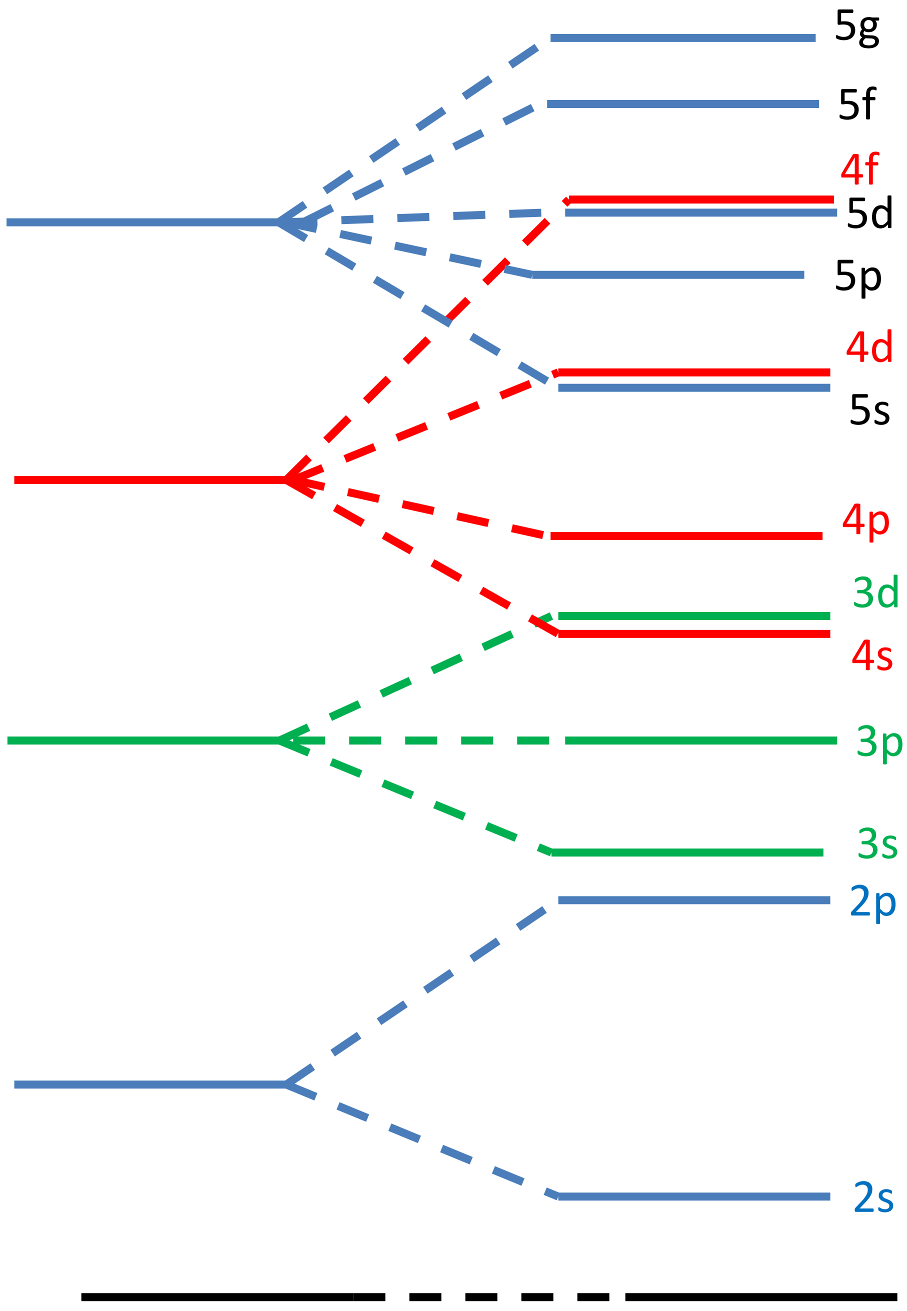
The penetration effect also explains why 4s is filled before 3d.

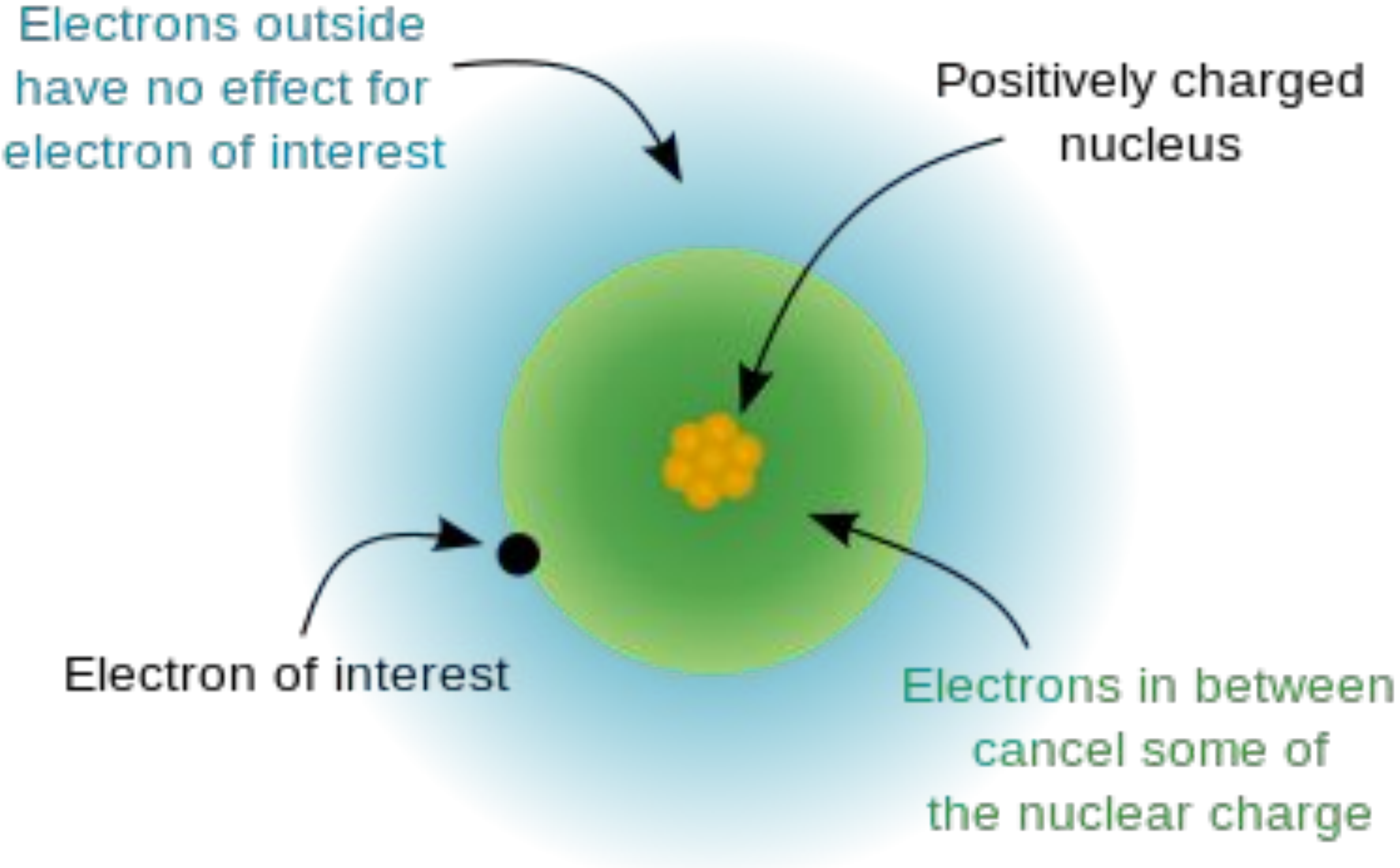


Potassium : $1S^2 2S^2 2P^6 3S^2 3P^6 4S^1$ rather than $1S^2 2S^2 2P^6 3S^2 3P^6 3d^1$

An electron in a 4S penetrate much more than an electron in a 3d orbital, as shown Graphically. (qualitative explanation)

Slater rules provide an approximate Guide explain why certain orbitals fill before others.





https://en.wikipedia.org/wiki/Effective_nuclear_charge

Slater's Rules

The rules were devised semi-empirically by John C. Slater and published in 1930

- Identify Z_{eff} (as a measure of attraction) for any electron

$$Z^* = Z - S$$

Where Z = nuclear charge

S = shielding constant

Rule-1. The atoms electronic structure is written in order of increasing quantum numbers n and l grouped as follows:

(1s) (2s,2p) (3s,3p) (3d) (4s,4p) (4d) (4f) (5s, 5p) (5d) etc.

Rule-2. Each group to the right do not shield electrons to their left.

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https://www.youtube.com/watch?v=5flvrGhT40U & https://www.youtube.com/watch?v=9mXQJUrOhxk
https://www.youtube.com/watch?v=RSf98oxyVm8

Slater's Rules

The rules were devised semi-empirically by John C. Slater and published in 1930

- Rules for determining S

S = shielding constant

Rule-1. The atoms electronic structure is written in order of increasing quantum numbers n and l grouped as follows:

(1s) (2s,2p) (3s,3p) (3d) (4s,4p) (4d) (4f) (5s, 5p) (5d) etc.

Rule-2. Each group to the right do not shield electrons to their left.

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https://www.youtube.com/watch?v=5flvrGhT40U & https://www.youtube.com/watch?v=9mXQJUrOhxk
https://www.youtube.com/watch?v=RSf98oxyVm8

Slater's Rules for determining *S* for a specific electron

The shielding constant (S) ***ns*** and ***np*** valence electrons:

3a) Each electron in the same (ns, np) group contributes 0.35 to the value of S for each other electron in the group.

Except. *A 1s electron contributes 0.30 to S of another 1s electron***.**

EXAMPLE: $2s^2p^5$, in a particular 2p electron has 6 other electron in (2s, 2p) group. Each of these contribute 0.35 to the value of S, for a total contribution to S of $6\times0.35=2.10$

Slater's Rules for determining *S* for a specific electron

Rule -3b: **Each electron in *n-1* group contribute 0.85 to S**

Rule -3c: **Each electron in *n-2* group or lower shells contribute 1.00 to S**

EXAMPLE: 3s electrons of sodium ($1s^2 2s^2 p^6 3S^1$) , there are 8 electrons in n-1 (2s, 2p) group, each of these contribute 0.85 to the value of S, for a total contribution to S of 8×0.85=6.80. There are two electrons in n-2(1S) 2 ×1 = 2, S = 8.80

Z^* for Na = $Z - S = 11 - 8.8$

$= 2.2$

Slater’s Rules for determining *S* for a specific electron

a) **Rule -4a**: Each electron in ***nd and nf*** valence

Each electron in the same group (nd) or (nf) group contribute **0.35 to the value of S** to each other electron in the group (same rule as 3a)

a) **Rule -4b**:

Each electron in groups to the left contribute **1 to the value of S.**

Nickel

Use slater rules to calculate the shielding constant S and effective nuclear charge of 3d and 4s electrons. Compare

Explain why the most common oxidation state of Ni have [Ar]$3d^8$

Solution

- Rule-1 : the electron configuration is written using slater's groupings:

  $(1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(3d^8)(4s^2)$

To calculate **S** for 3d valence electron:

Rule 4a : each electron in the group $(3d^8)$ contributes 0.35 to S. Total contribution = 7×0.35=2.45

Rule 4b : each electron in the group to the left of *$(3d^8)$ Contribute 1 to S*. Total contribution = 18×1=18.00

Total S = 2.45 +18.00= 20.45

The effective nuclear charge Z*=28-20.45=7.55

Solution

- Rule-1 : the electron configuration is written using slater's groupings:

  $(1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(3d^8)$ $(4s^2)$

To calculate S for 4s valence electron:

Rule 3a : each electron in the 4s group contribute 0.35 1× 0.35

Rule 3b : each electron in the n-1 group contribute 0.85 (0.85.16) = 13.60

Rule 3c : each electron on the left of *n-1* *Contribute 1 to S.* Total contribution = 10×1=10.00

Total S = 0.35 + 13.60 + 10.00= 23.95

The effective nuclear charge Z*=28-23.95=4.05

Comparison of The effective nuclear charge

- 3d electrons

The effective nuclear charge

Z*=28-20.45=7.55

- 4s electrons

Z*=28-23.95=4.05

- Ni : [Ar]$3d^8$
- **All transition Metals loose *ns* electrons more readily than *(n-1) d* electrons**

Periodic Properties of Atoms : Ionization Energy

Ionization Energy : Energy required to remove an electron from a gaseous atom or ion. IE in kJ **or** eV (1 eV = 1.602×10^{-19}J)

$$X_{(g)} \;\square\; X^{+}_{(g)} + e^{-}$$

Koopmans' theorem : IE of an electron = energy of the orbital from which it came. (Approx because it doesn't take into account a reorganization)

$Al_{(g)} \;\square\; Al^{+}_{(g)} + e^{-}$ $\quad I_1 = 580$ kJ/mol

$Al^{+}_{(g)} \;\square\; Al^{2+}_{(g)} + e^{-}$ $\quad I_2 = 1815$ kJ/mol

$Al^{2+}_{(g)} \;\square\; Al^{3+}_{(g)} + e^{-}$ $\quad I_3 = 2740$kJ/mol

$Al^{3+}_{(g)} \;\square\; Al^{4+}_{(g)} + e^{-}$ $\quad I_4 = 11\ 600$kJ/mol

$[Ne]3s^{2}3p^{1}$: First e^{-} come from 3p, second from 3s

$I_1<I_2<I_3$ □ Why? Positive charge increases □ Electron more and more tightly bound.

I_4 is very high : Al^{3+} : $1s^{2}2s^{2}2p^{6}$: core electrons are bound very tight!

Trend in Atomic Properties : Ionization Energy

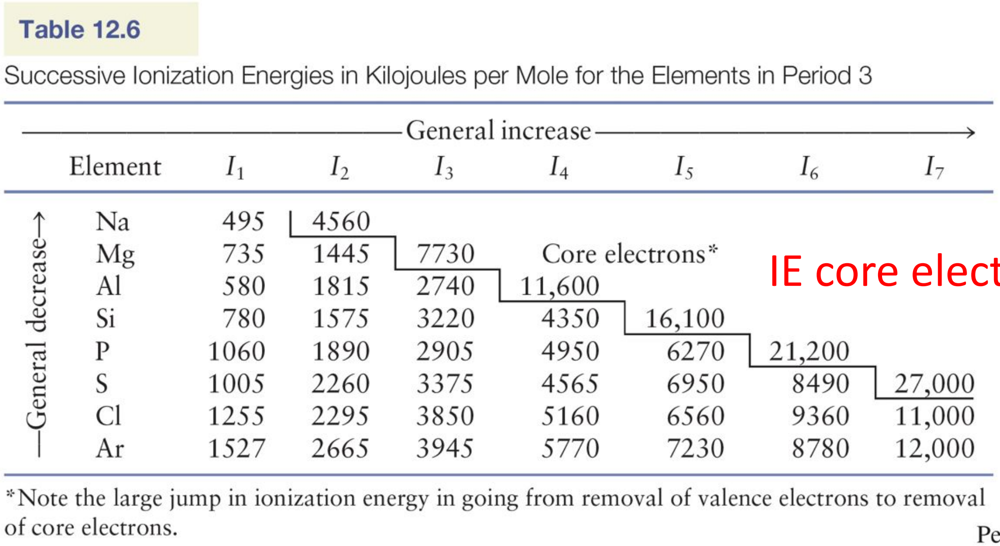


Table 12.6

Successive Ionization Energies in Kilojoules per Mole for the Elements in Period 3

General increase →

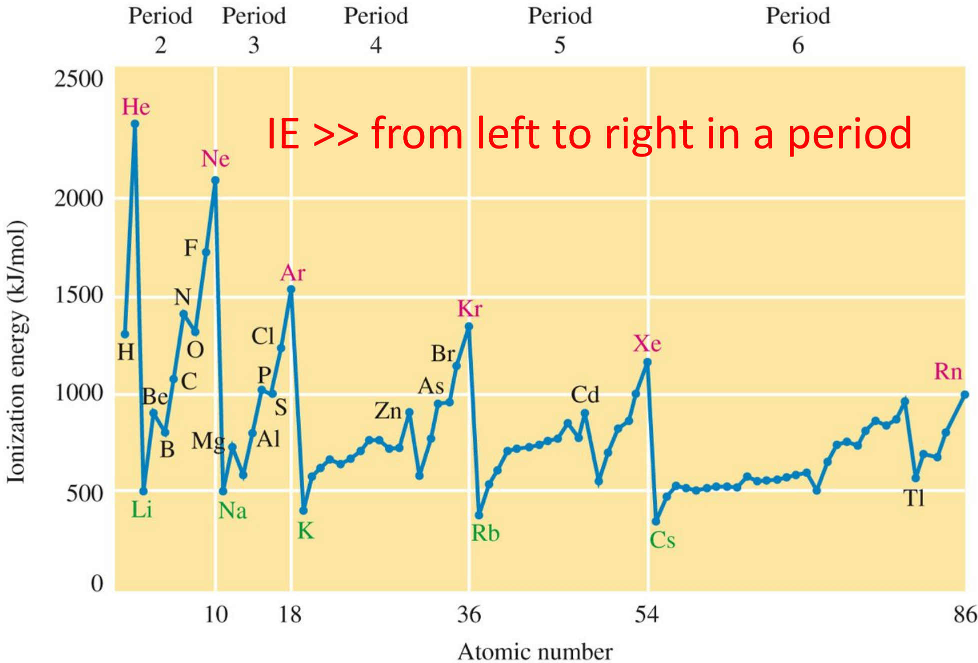
↑ General decrease

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4560					
Mg	735	1445	7730	Core electrons*			
Al	580	1815	2740	11,600			
Si	780	1575	3220	4350	16,100		
P	1060	1890	2905	4950	6270	21,200	
S	1005	2260	3375	4565	6950	8490	27,000
Cl	1255	2295	3850	5160	6560	9360	11,000
Ar	1527	2665	3945	5770	7230	8780	12,000

*Note the large jump in ionization energy in going from removal of valence electrons to removal of core electrons.

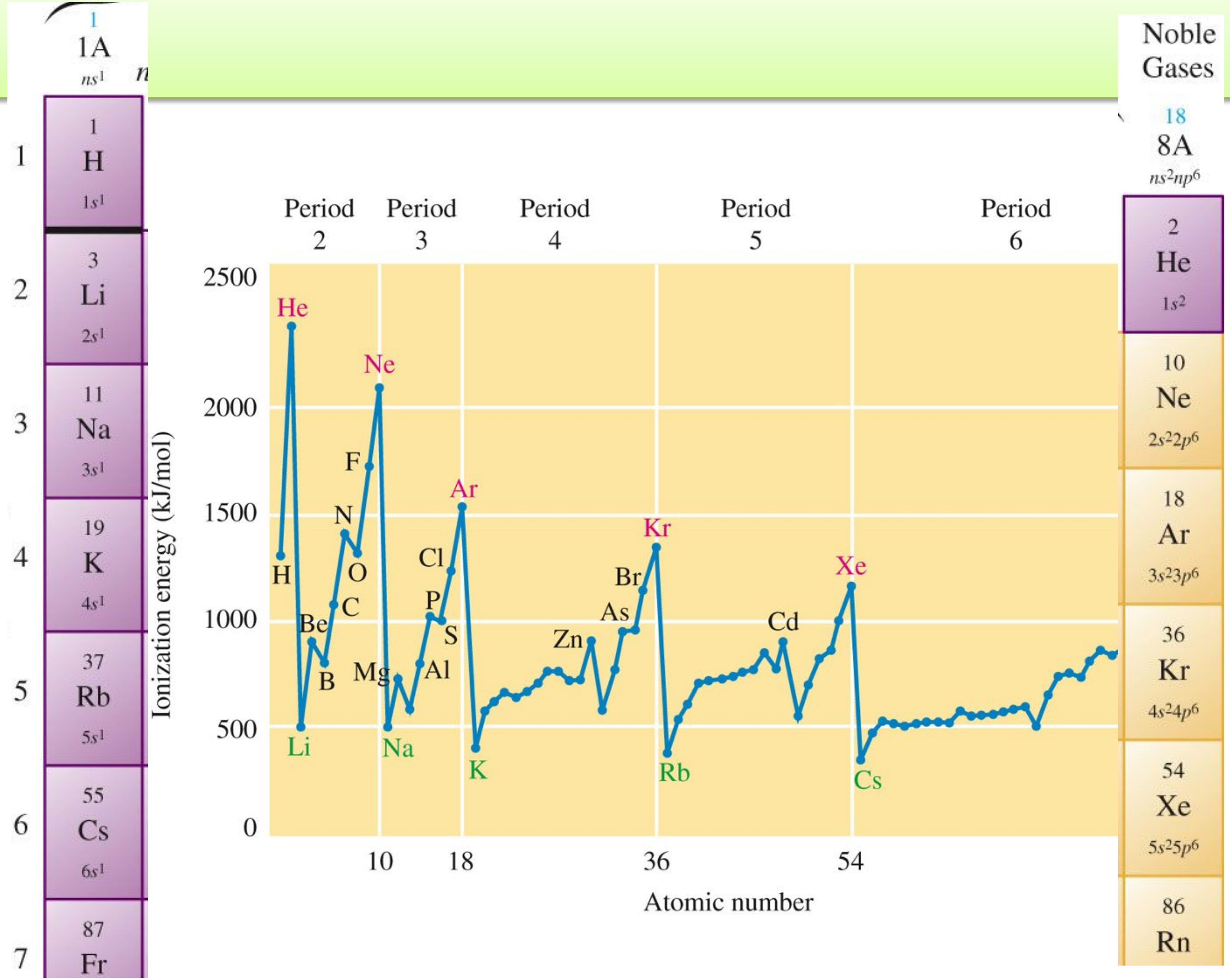
IE core electrons >>

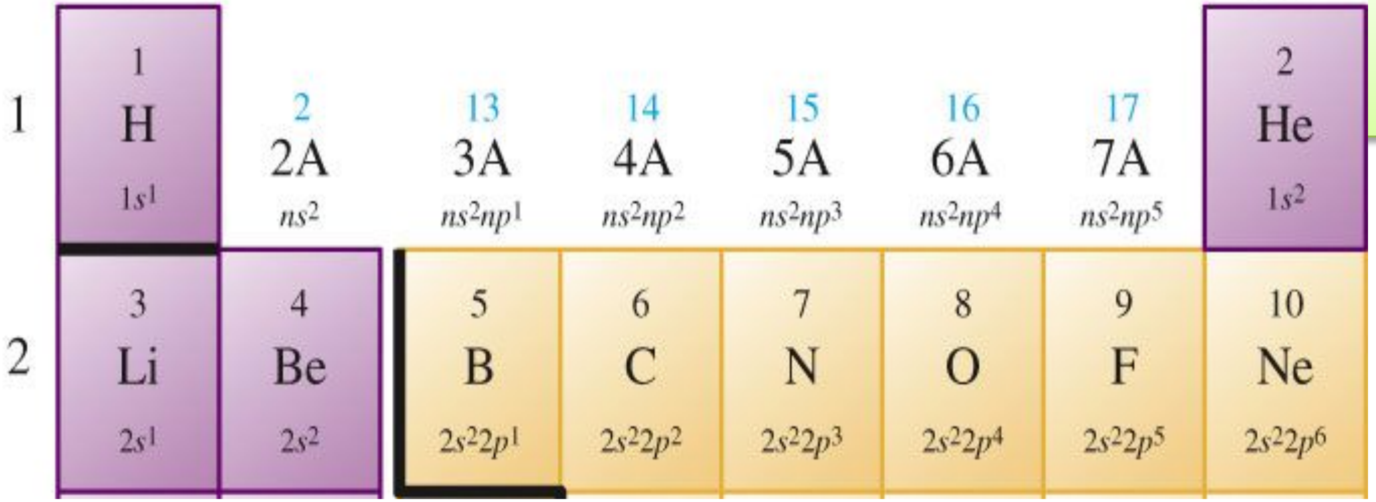
$X(g) \longrightarrow X^{+}(g) + 1e^{-}$



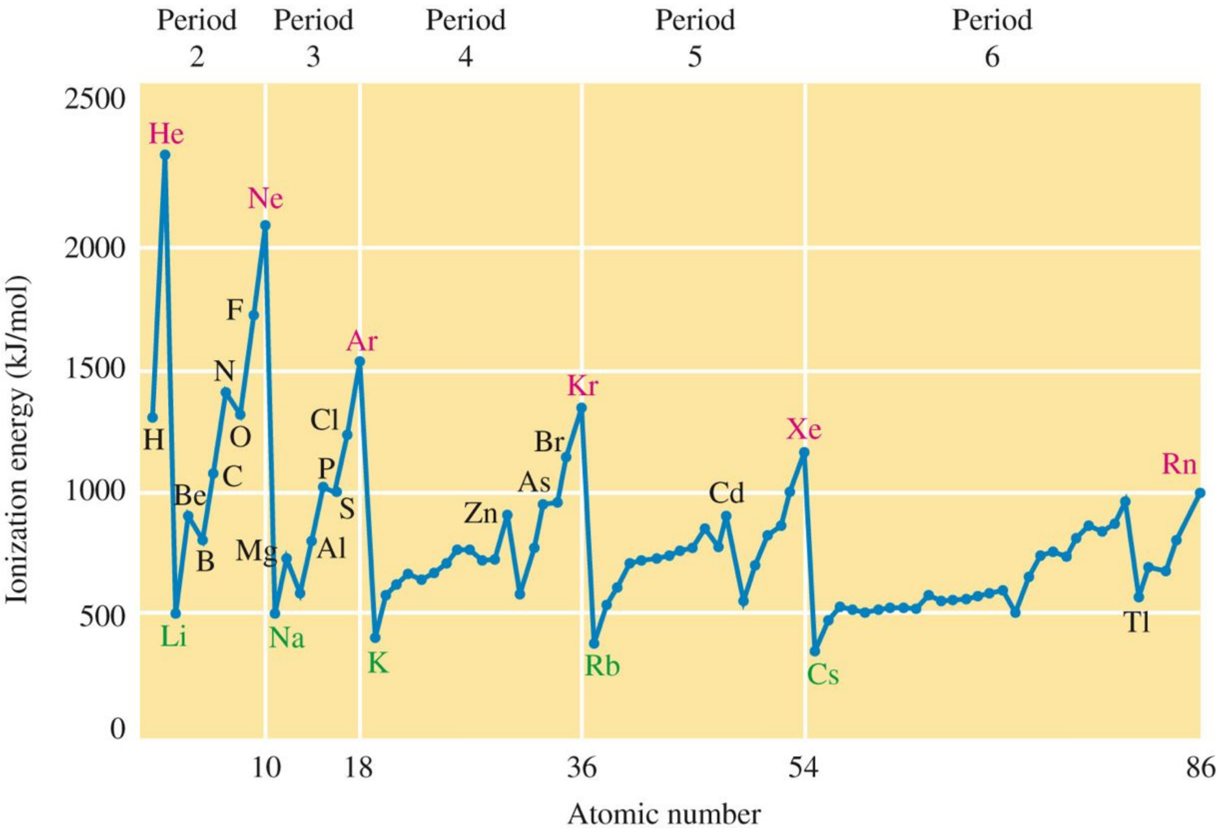
IE >> from left to right in a period

The first ionization energy increases across a period and decreases down a group

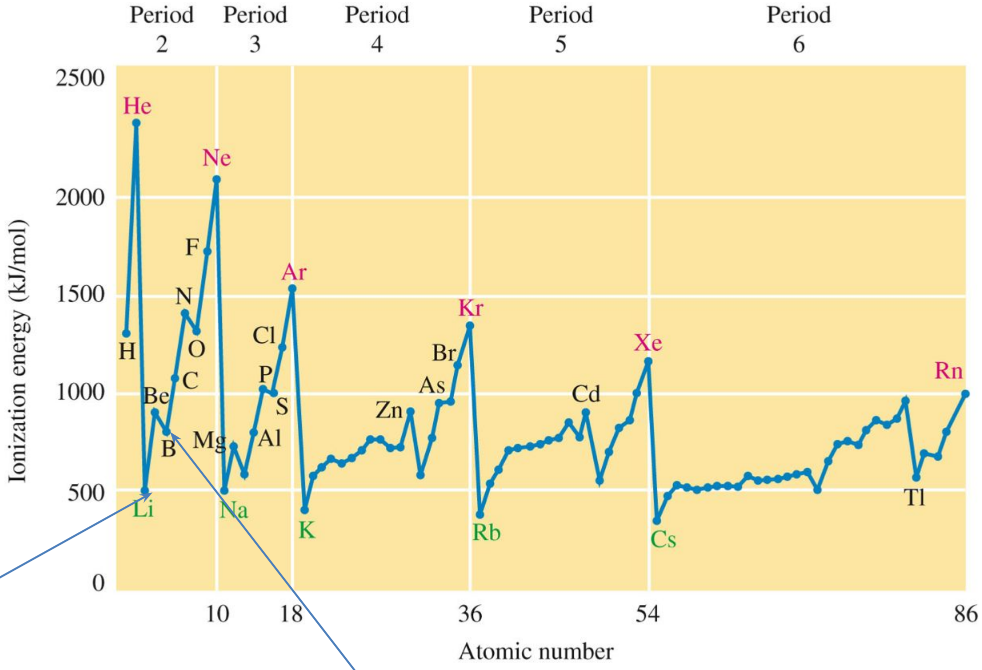

1
1A
ns^1
1
H
$1s^1$
3
Li
$2s^1$
11
Na
$3s^1$
19
K
$4s^1$
37
Rb
$5s^1$
55
Cs
$6s^1$
87
Fr
1
2
3
4
5
6
7
Noble Gases
18
8A
ns^2np^6
2
He
$1s^2$
10
Ne
$2s^22p^6$
18
Ar
$3s^23p^6$
36
Kr
$4s^24p^6$
54
Xe
$5s^25p^6$
86
Rn
Period 2
Period 3
Period 4
Period 5
Period 6
Ionization energy (kJ/mol)
2500
2000
1500
1000
500
0
He
H
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
P
S
Cl
Ar
K
Zn
As
Br
Kr
Rb
Cd
Xe
Cs
10
18
36
54
Atomic number



1	1 H $1s^1$	2 2A ns^2	13 3A ns^2np^1	14 4A ns^2np^2	15 5A ns^2np^3	16 6A ns^2np^4	17 7A ns^2np^5	2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$	5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$



Trend in Atomic Properties : Ionization Energy



Li: $1s^22s^1$ (3 electrons)
Be: $1s^22s^2$ (3 electrons)
Expected since Be electrons do shield each other completely

Be: $1s^22s^2$ (3 electrons)
B: $1s^22s^22p^1$ (3 electrons)
Expected since 2s electrons do shield each 2p electrons effectively

Trend in Atomic Properties : Ionization Energy

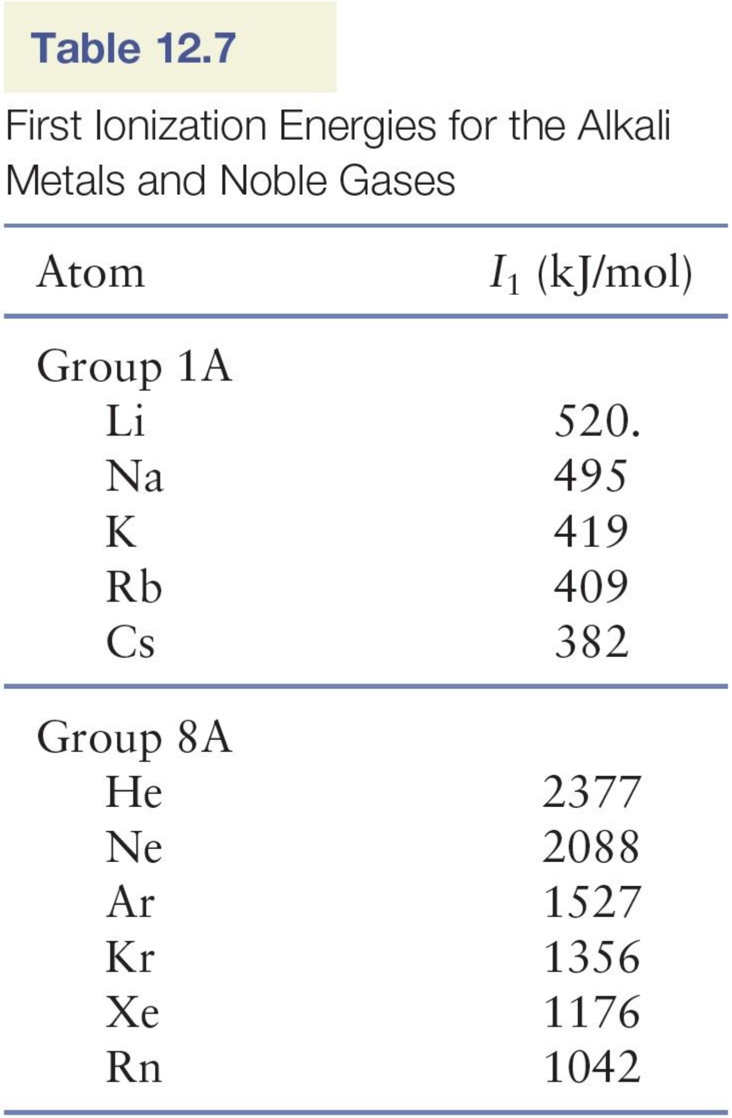


Table 12.7

First Ionization Energies for the Alkali Metals and Noble Gases

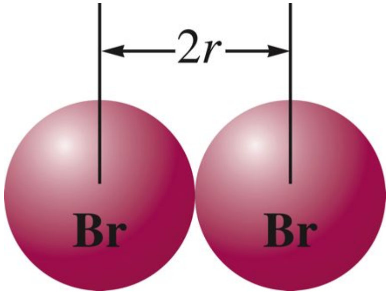
Atom	I_1 (kJ/mol)
Group 1A	
Li	520.
Na	495
K	419
Rb	409
Cs	382
Group 8A	
He	2377
Ne	2088
Ar	1527
Kr	1356
Xe	1176
Rn	1042

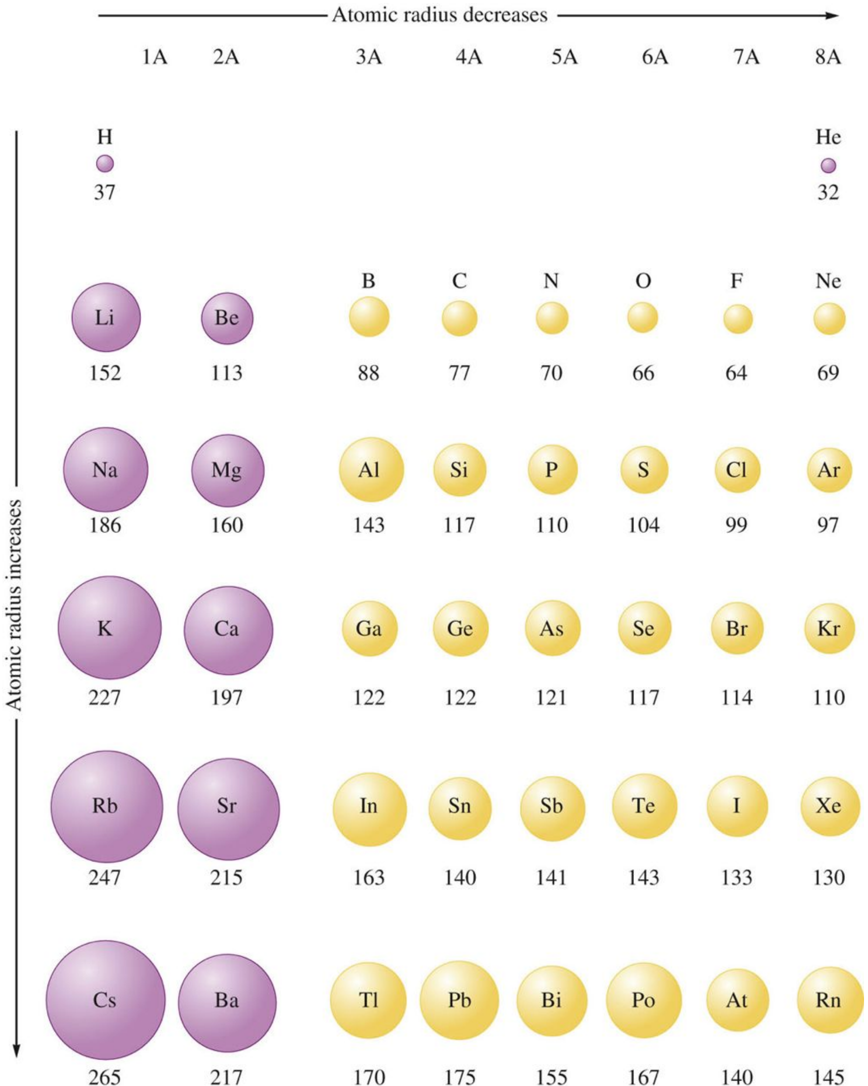
IE goes down along a group.

The removed electron is away from the core

Trend in Atomic Properties : Atomic Radius

Atomic Radius: half the distance between the nuclei in a molecule consisting of identical atoms.





END

END

Alkali Metals – 1A

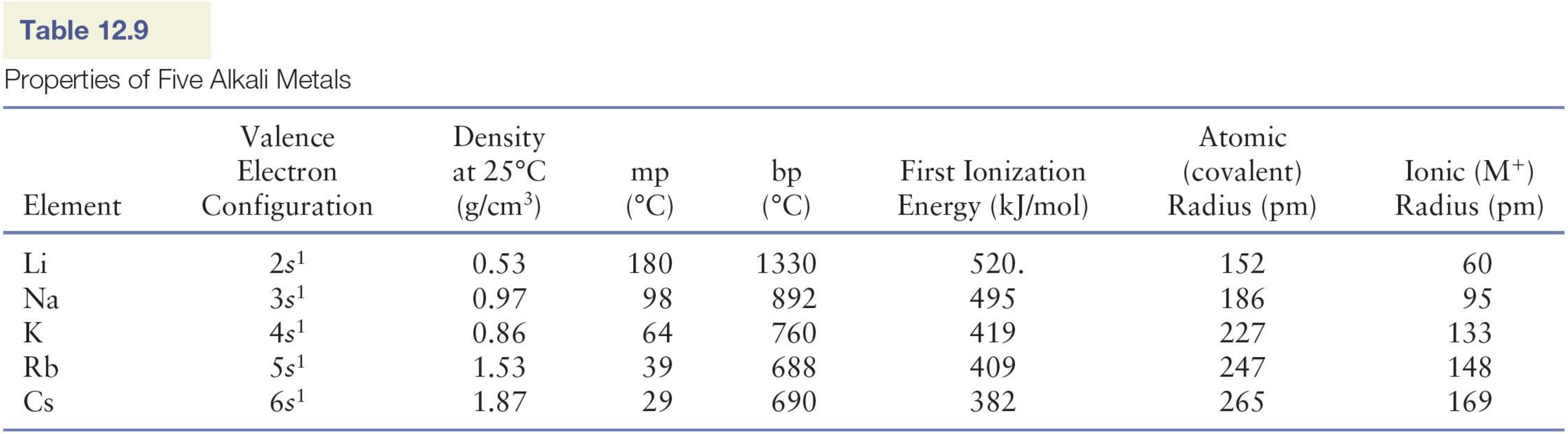


Table 12.9

Properties of Five Alkali Metals

Element	Valence Electron Configuration	Density at 25°C (g/cm^3)	mp (°C)	bp (°C)	First Ionization Energy (kJ/mol)	Atomic (covalent) Radius (pm)	Ionic (M$^+$) Radius (pm)
Li	$2s^1$	0.53	180	1330	520.	152	60
Na	$3s^1$	0.97	98	892	495	186	95
K	$4s^1$	0.86	64	760	419	227	133
Rb	$5s^1$	1.53	39	688	409	247	148
Cs	$6s^1$	1.87	29	690	382	265	169

Low melting point

Lose easily an electron

Strong reducer

Li > K > Na

Abnormal: Order is due to the hydration energies.

Na and K react more violently with water than Li due to its high melting point.

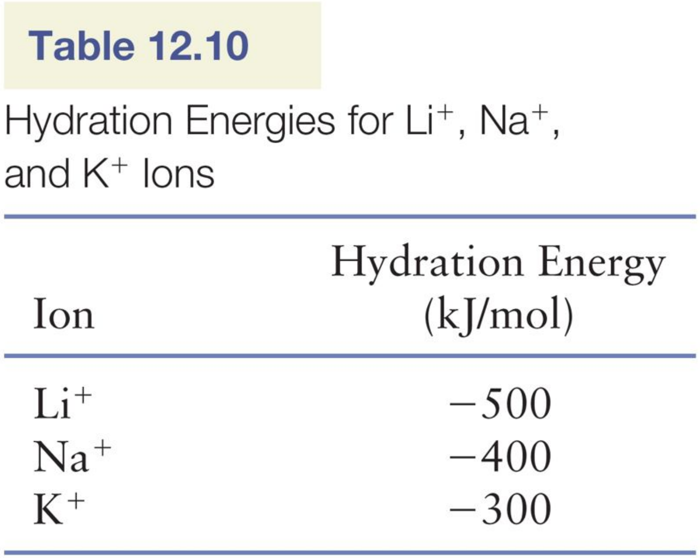
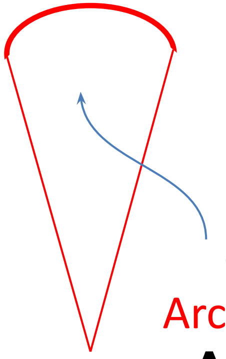


Table 12.10

Hydration Energies for Li$^+$, Na$^+$, and K$^+$ Ions

Ion	Hydration Energy (kJ/mol)
Li$^+$	−500
Na$^+$	−400
K$^+$	−300

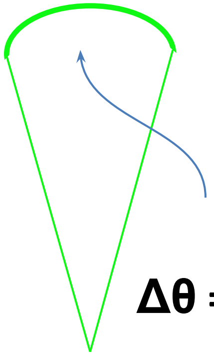


ρΔφ

Arc Length = **ρΔφ**

$$\Delta\varphi = \frac{\text{Arc Length}}{\text{radius of the circle}}$$

$$\text{Angle} = \frac{\text{Arc Length}}{\text{radius of the circle}}$$

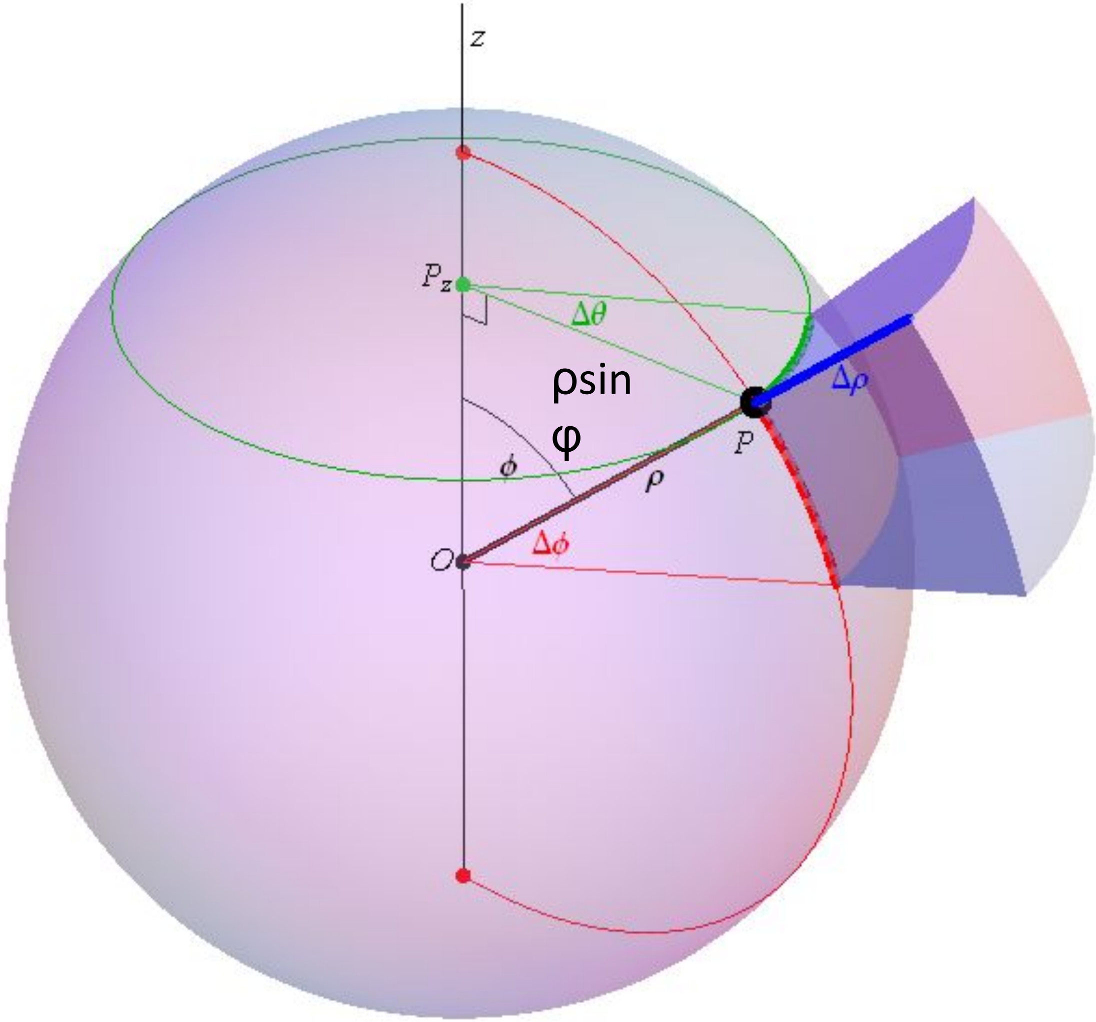


ρsinφΔθ

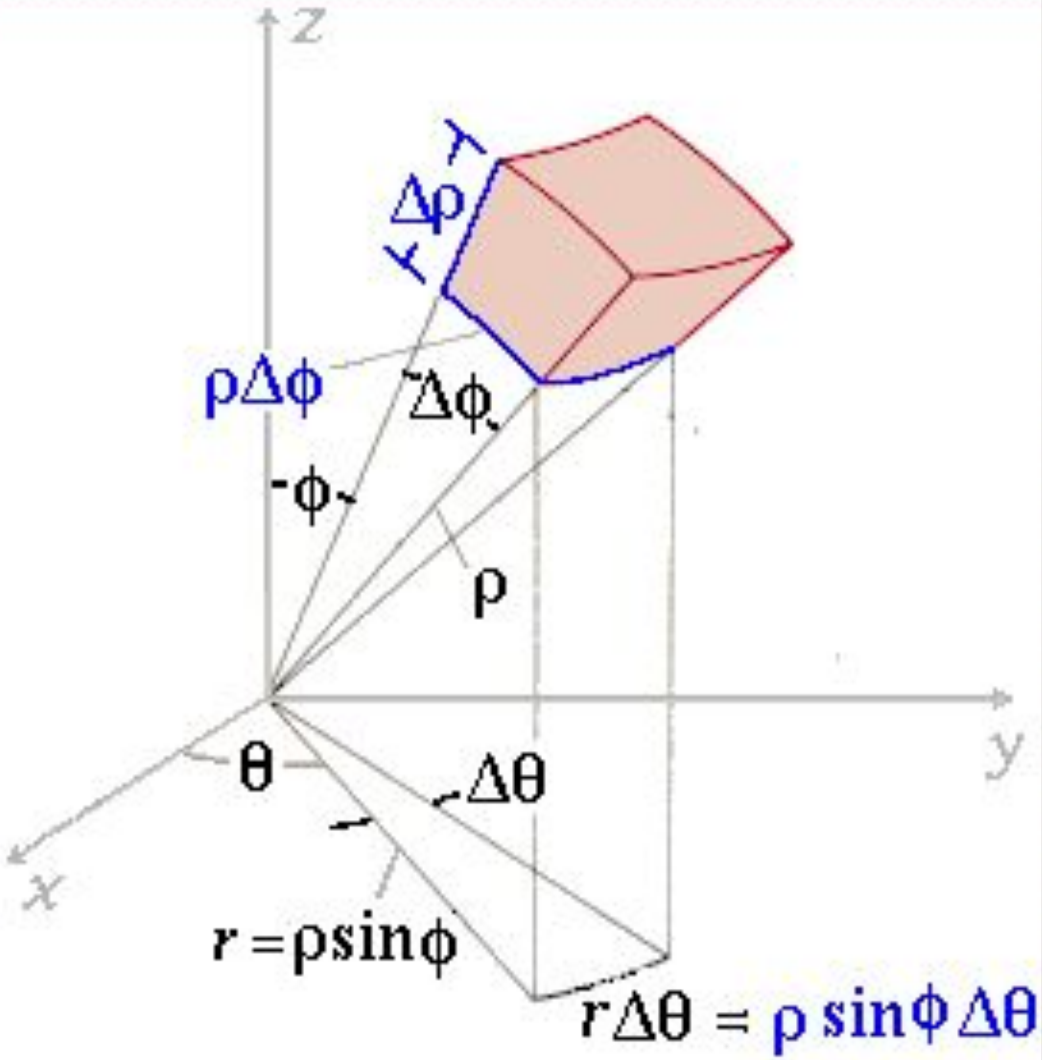
$$\Delta\theta = \frac{\text{Arc Length}}{\text{radius } (\rho\sin\varphi)}$$

Arc Length = **ρsinφΔθ**

Δρ



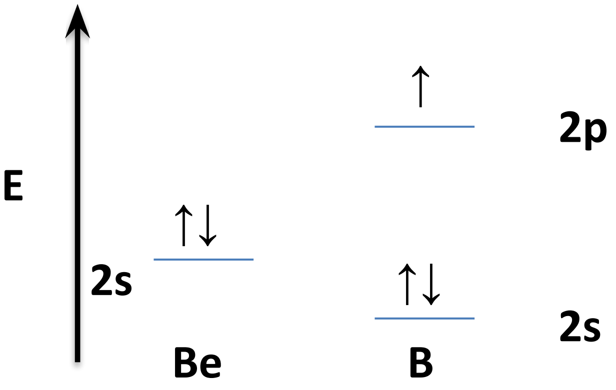
ρsin φ

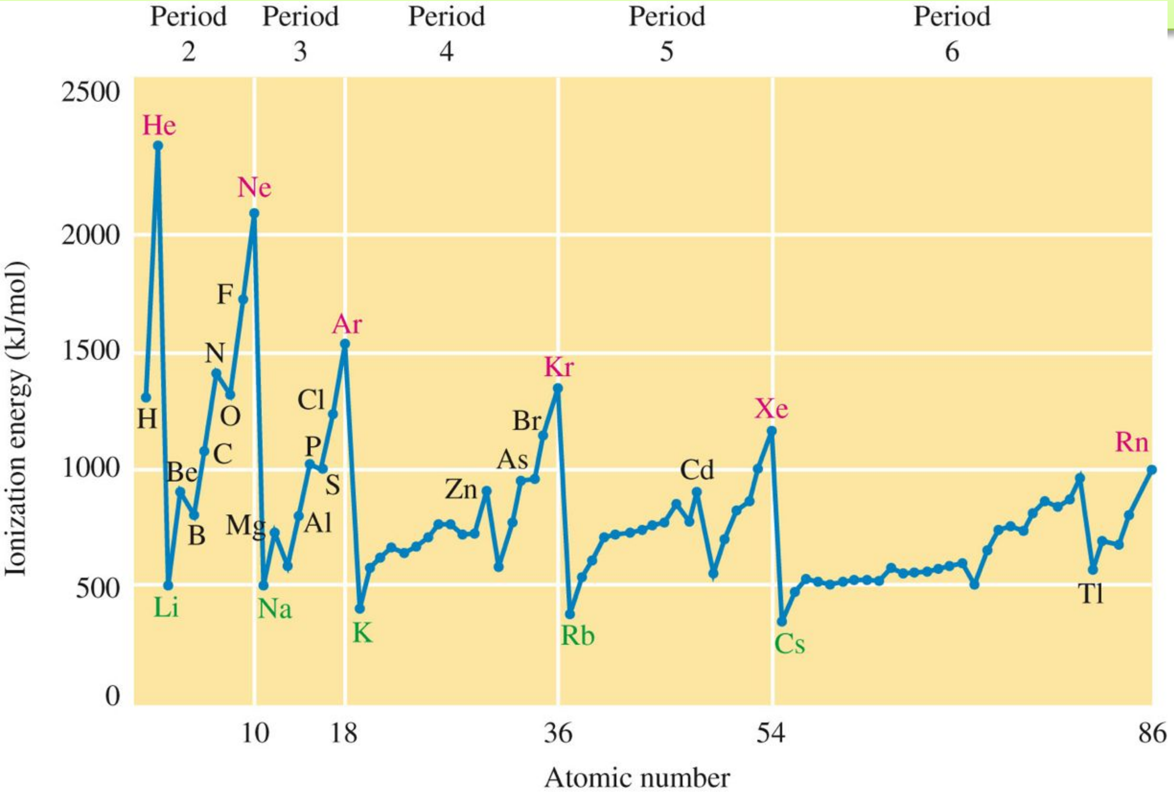


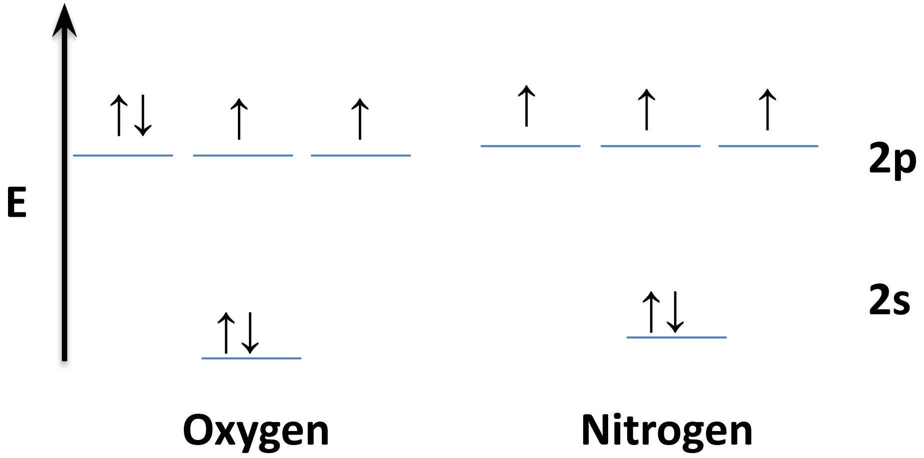
$$\Delta V = (\Delta\rho)(\rho\Delta\phi)(\rho\sin\phi\,\Delta\theta)$$

$$\Rightarrow \quad dV = \rho^2 \sin\phi\, d\rho\, d\phi\, d\theta$$

Trend in Atomic Properties : Ionization Energy







Oxygen has lower ionization energy than nitrogen