Chemistry 3830

Periodic Table

and

Atomic Structure

Periodic Table of the Elements

Group

Period	1	2	3															4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																															2 He
2	3 Li	4 Be																									5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg																									13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc															22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y															40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

Main group — s block — p block

Transition Metals — d block

Lanthanides and Actanides — f block

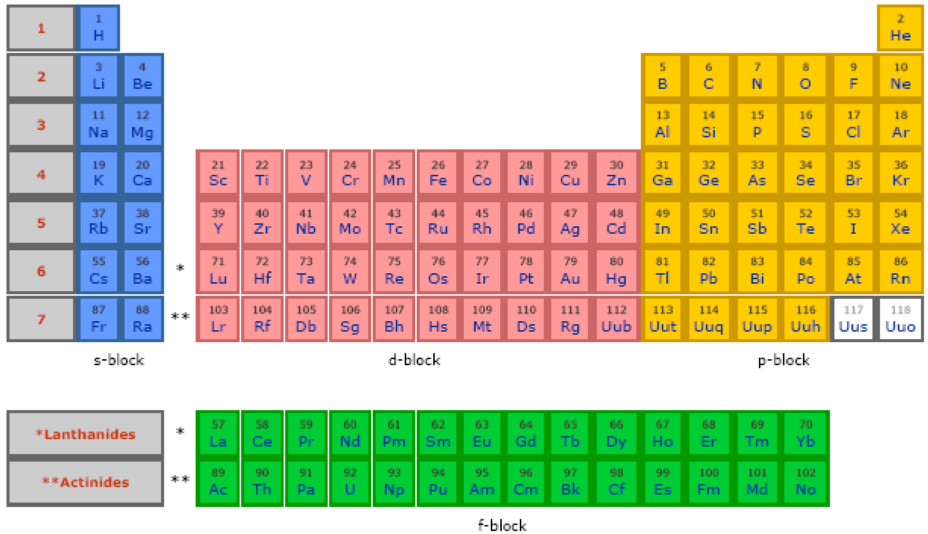
Periodic Table of the Elements

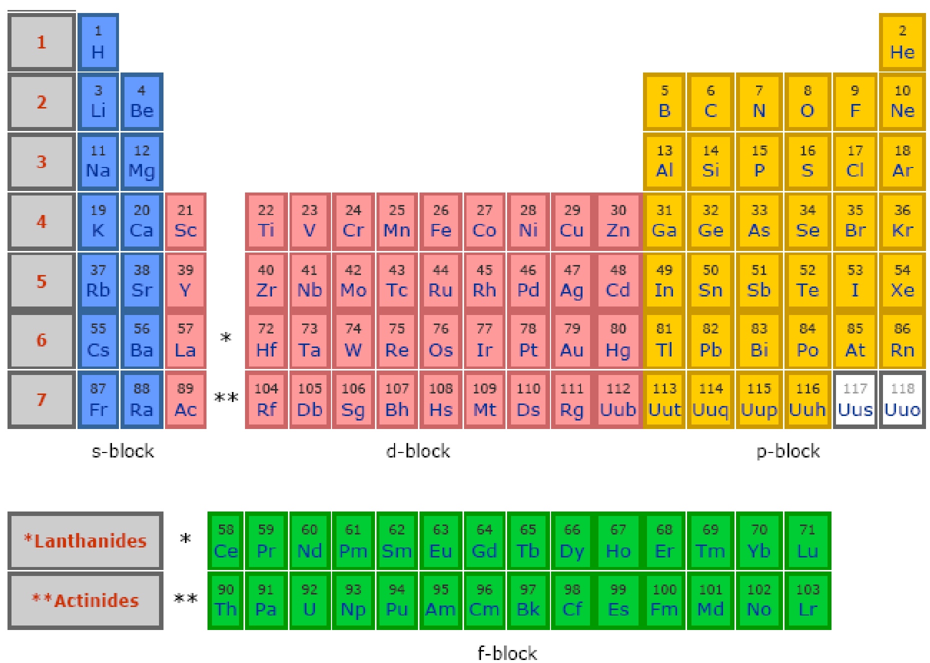
Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
	s-block						d-block									p-block			

*Lanthanides	*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
**Actinides	**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

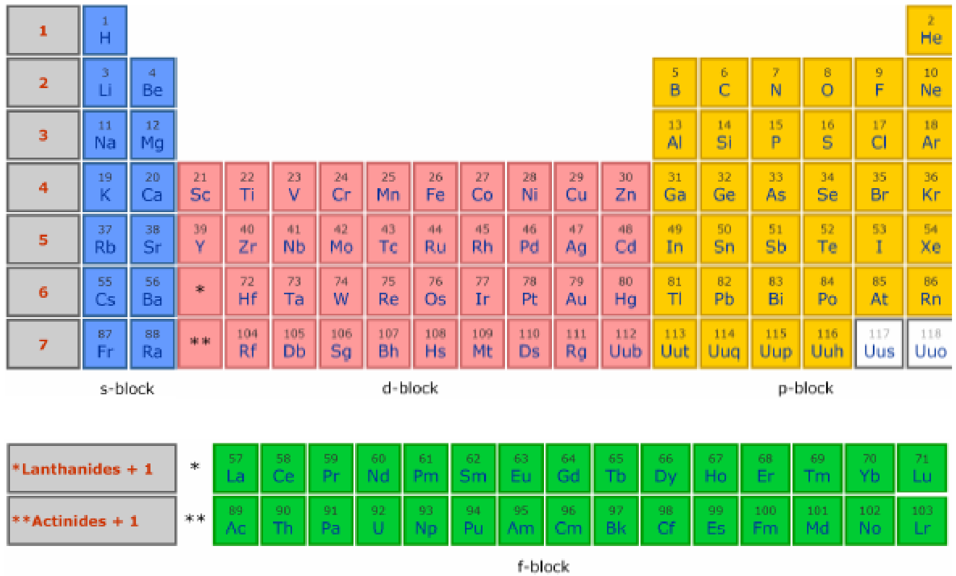
f-block

Three Different Periodic Tables





Three Different Periodic Tables



Introduction to *d* and *f*-Block Chemistry

Abundances of the elements in the earth's crust:

% abundance	elements
>10	O, Si
10^{-1}	Al, Fe, Ca, Na, K, Mg
$1\text{-}10^{-1}$	H, Ti, Cl, P
$10^{-1}\text{-}10^{-2}$	Mn, F, Ba, Sr, S, C, N, Zr, V, Cr
$10^{-2}\text{-}10^{-3}$	Rb, Ni, Zn, Ce, Cu, Y, La, Nd, Co, Sc, Li, Nb, Ga, Pb, Th, B
$10^{-3}\text{-}10^{-4}$	Pr, Br, Sm, Gd, Ar, Yb, Cs, Dy, Hf, Er, Be, Xe, Ta, Sn, U, As, W, Mo, Ge, Ho, Eu
$10^{-4}\text{-}10^{-5}$	Tb, I, Tl, Tm, Lu, Sb, Cd, Bi, In
$10^{-5}\text{-}10^{-6}$	Hg, Ag, Se, Ru, Te, Pd, Pt
$10^{-6}\text{-}10^{-7}$	Rh, Os, Ne, He, Au, Re, Ir
$10^{-7}\text{-}10^{-9}$	Kr
$10^{-9}\text{-}10^{-20}$	Ra, Pa, Ac, Po, Rn, Np, Pu, Pm
$< 10^{-20}$	Fr, At, transplutonium elements

Blue = 1st row TM, Red = 2nd row TM, Green = 3rd row TM

- In general, 1st row TMs are more abundant than 2nd or 3rd row TMs.

Introduction to *d* and *f*-Block Chemistry

Mineral sources and methods of recovery for some commercially important d-block metals:

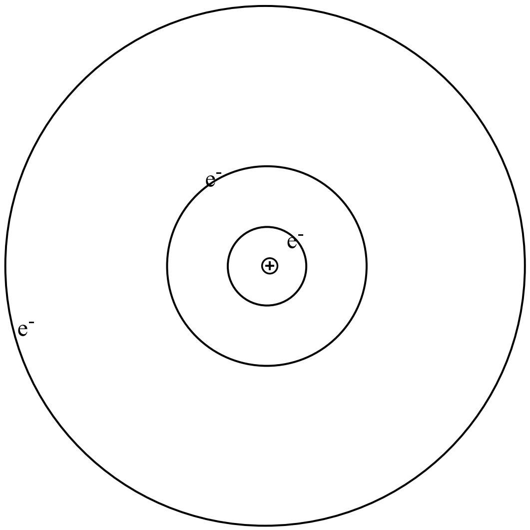
Metal	**Principal minerals**	**Method of recovery**
Titanium	Ilmenite, $FeTiO_3$ Rutile, TiO_2	$TiO_2 + 2C + 2Cl_2 \rightarrow TiCl_4 + 2CO$ followed by reduction of $TiCl_4$ with Na or Mg
Vanadium	Vanadinite, $Pb_5(VO_4)_3Cl$	
Chromium	Chromite, $FeCr_2O_4$	$FeCr_2O_4 + 4C \rightarrow Fe + 2Cr + 4CO$
Molybdenum	Molybdenite, MoS_2	$2MoS_2 + 7\ O_2 \rightarrow 2MoO_3 + 4SO_2$ followed by either: $MoO_3 + 2Fe \rightarrow Mo + Fe_2O_3$ or $MoO_3 + 3H_2 \rightarrow Mo + 3H_2O$
Tungsten	Scheelite, $CaWO_4$ Wolfamite, $FeMn(WO_4)_2$	$CaWO_4 + 2HCl \rightarrow WO_3 + CaCl_2 + H_2O$ followed by $2WO_3 + 6H_2 \rightarrow 2W + 6H_2O$
Manganese	Pyrolusite, MnO_2	$MnO_2 + C \rightarrow Mn + CO_2$
Iron	Hematite, Fe_2O_3 Magnetite, Fe_3O_4 Limonite, FeO(OH)	$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
Cobalt	Cobaltite, CoAsS Smaltite, $CoAs_2$ Linnaeite, Co_3S_4	byproduct of copper and nickel production
Nickel	Pentlandite, $(Fe,Ni)_6S_8$	$2NiS + 2O_2 \rightarrow 2Ni + 2SO_2$
Copper	Chalcopyrite, $CuFeS_2$ Chalcocite, Cu_2S	$2CuFeS_2 + 2SiO_2 + 5O_2 \rightarrow 2Cu + 2FeSiO_3 + 4SO_2$

- **Oxides** preferred for 1st row and early TMs
- **Sulfides** preferred for 2nd/3rd row and late TMs

Atomic Structure

Atoms consist of
(i) a nucleus (containing protons and neutrons)
(ii) Electron shell

Planetary Model



(i) Nucleus:

Positively charged (because of protons)

Very small, 10^{-15} m = 1 fm

Number of protons define the element

(ii) Electron shell:

Negatively charged (because of electrons)

Electron shell will define the size of the atom (10^{-10} m = 100 pm = 1 Å)

Electrons are extremely small (estimated as 10^{-18} m)

Atoms are mainly empty space!

In chemistry (NOT nuclear chemistry),
only electrons are involved in chemical reactions

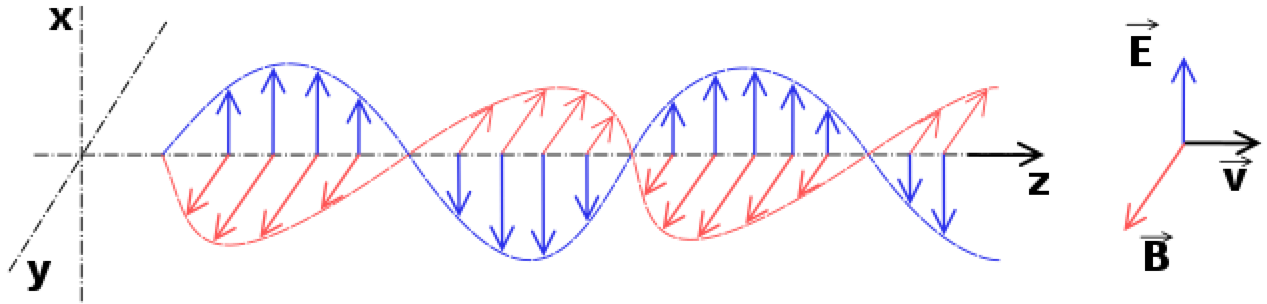
Electronic Structure of an Atom

How can we study the electronic structure of the atom?

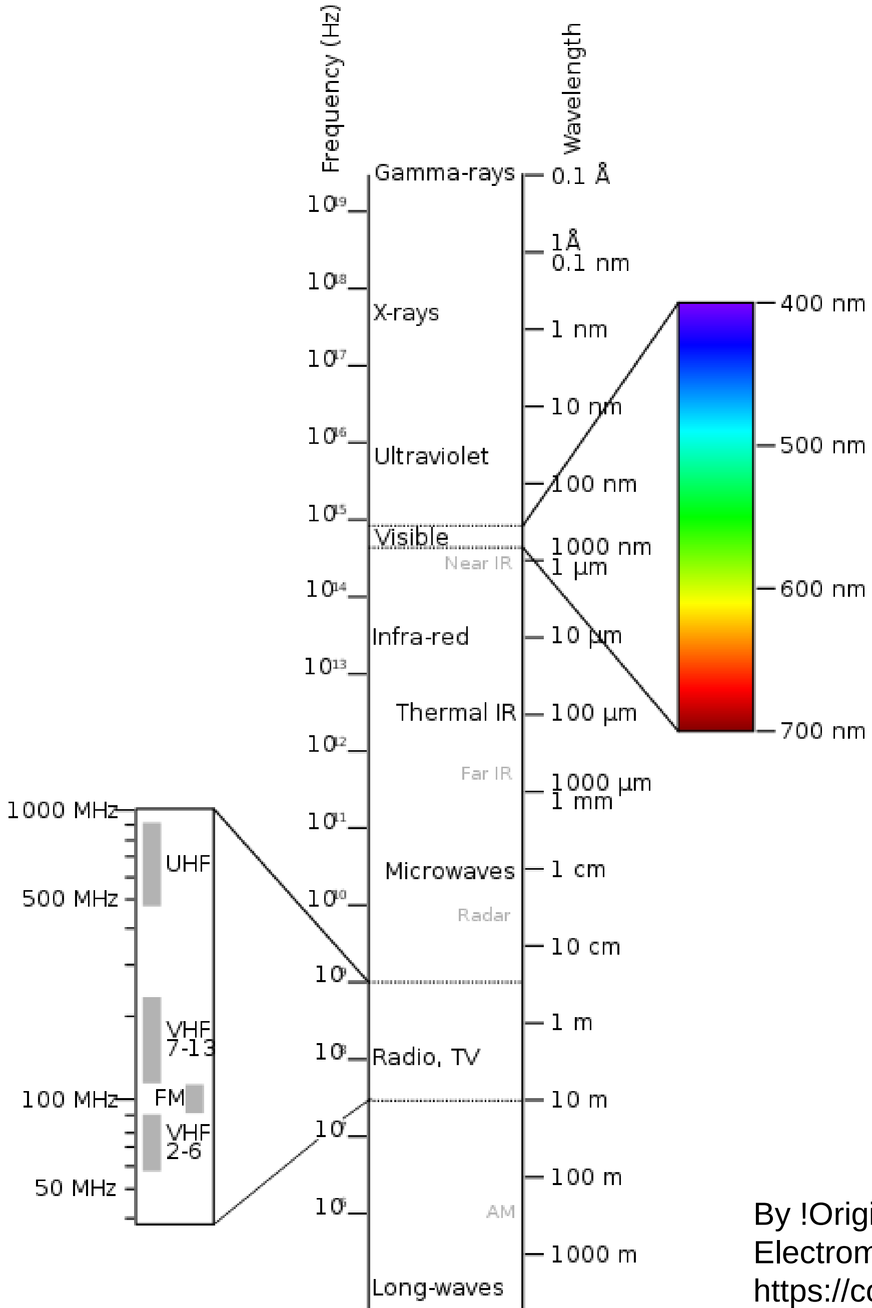
Answer: Through interaction of electromagnetic radiation with matter!

What is electromagnetic radiation?

Electric and magnetic components (mathematical description: Maxwell's equations)



Electromagnetic radiation



$$Speed\ of\ light = c = \lambda \nu$$

$$Units: \frac{m}{s} = m \times \frac{1}{s} \lambda \nu$$

Wave Description

Wave Particle Duality of Electromagnetic Radiation

wave

Wavelength and frequency

$$c = \lambda \nu$$

c = speed of light in the vacuum
= 2.997925×10^{8} m/s

Diffraction experiment
for example: X-ray crystallography

particle

Photon of a particular energy

Energy of a photon: $E = h\nu$

h = Planck's constant
= 6.62607×10^{-34} Js

Photoelectric effect (Einstein)

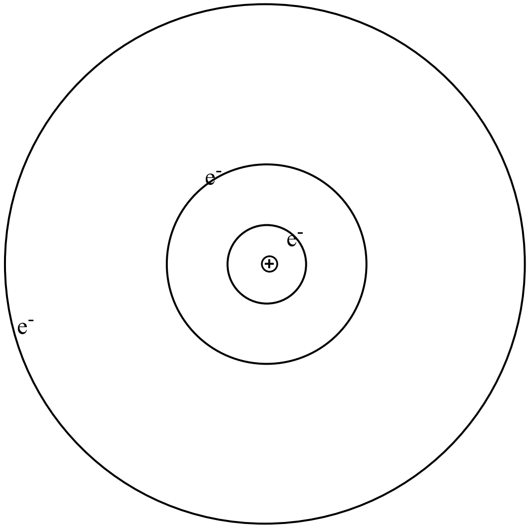
Absorption and emission spectra

Bohr Model of the Atom

Two postulates:

(i) In the absence of radiation absorption or emission, electrons stay in a stationary state.

(ii) Absorption occurs only in discrete amounts, corresponding to a change in energy between two stationary states of the electron.



Electronic energies are quantized
(n = principle quantum number)

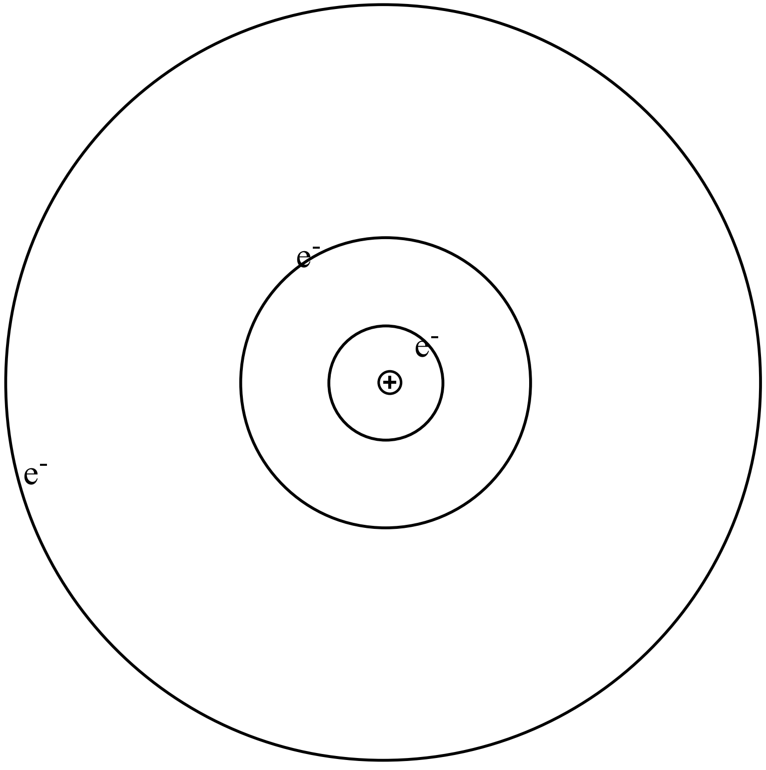
Energy of an electron in the state n:

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2}\left(\frac{Z^2}{n^2}\right) = -R_H\left(\frac{Z^2}{n^2}\right);\ R_H = 2.149 \times 10^{-18} J$$

$$|E_n - E_m| = h\nu = \frac{Z^2 m_e e^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_n^2} - \frac{1}{n_m^2}\right)$$

Bohr Model of the Atom

$$r_n = \frac{\varepsilon_0 h^2}{Z\pi m e^2} n^2 = a_0 \frac{n^2}{Z};\ a_0 = \ Bohr\ radius = 52.9\ pm$$



Wave Particle Duality of Subatomic Particles

particle

wave

Electrons, protons, neutrons

?

Certain mass and size

Diffraction experiment

for example: neutron

or electron diffraction

De Broglie equation

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

Wavelength of electrons

(and neutrons, protons and any matter)

Diffraction Experiment

Light can be diffracted using a grid or a lattice (crystal lattice in X-ray crystallography)

A diffraction experiment is using the wave description.

Particles (neutrons and electrons) can be diffracted.

Electron diffraction through a sheet of
crystalline aluminium (historic experiment)

The Schröderinger Wave Equation

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

Hamiltonian (operator)

Energy

Wavefunction

$$\hat{A}\Psi = c\Psi$$

Operator

Eigenvalue

Wavefunction
(Eigenfunction)

Electronic Wavefunctions?

We want to know the electronic wavefunctions

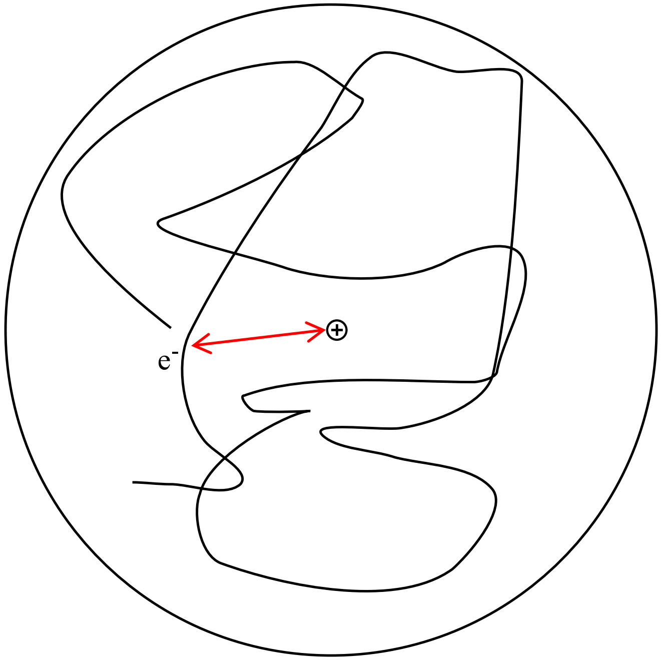
$$\hat{H}\Psi = E\Psi$$

We can describe the Hamiltonian (energy) operator

Kinetic energy of nucleus

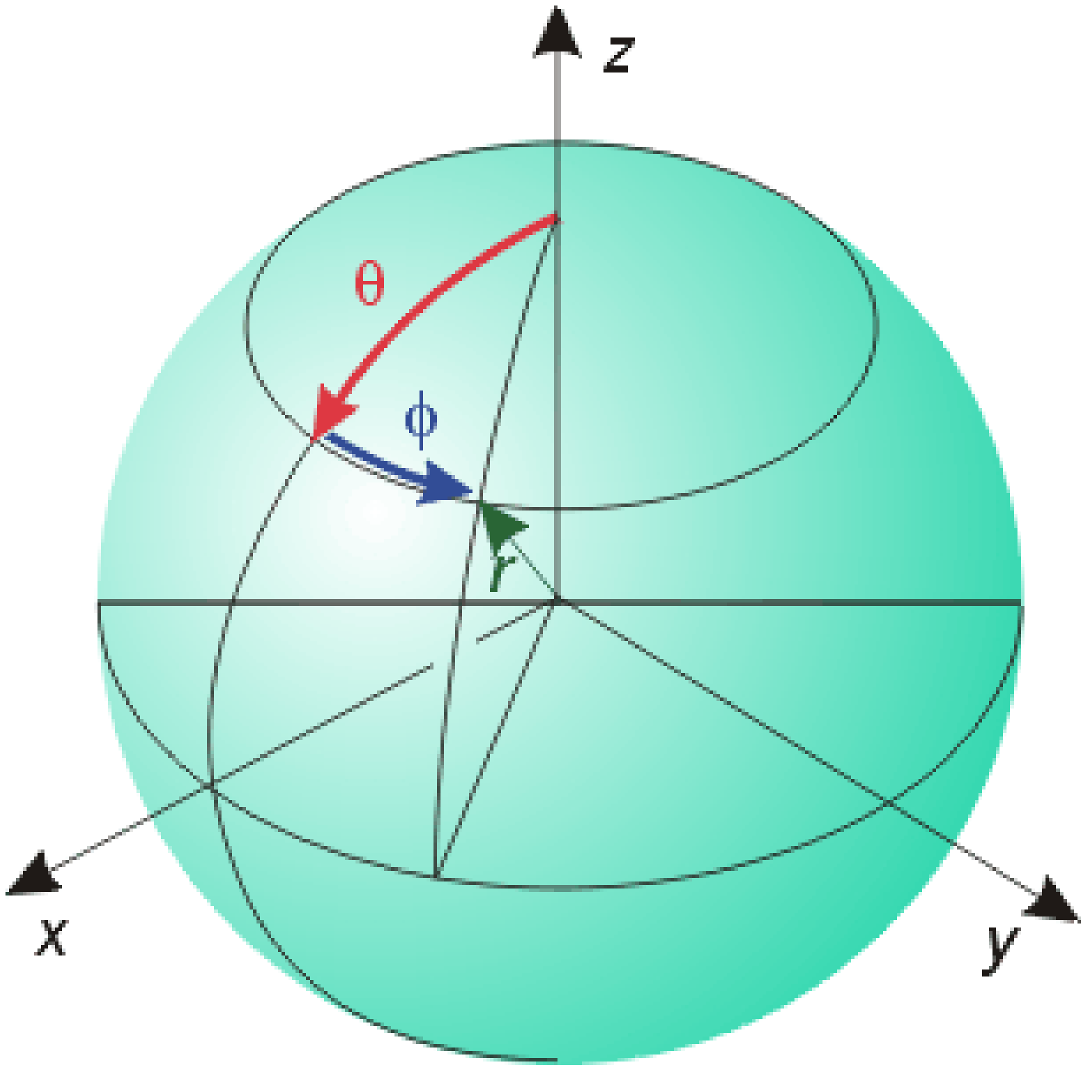
Kinetic energy of electron

Potential energy:
Electron-nucleus attraction



We need to “solve Schrödinger’s equation” to get the allowed wavefunctions

Spherical Polar Coordinate System



Spherical polar coordinates

r is the radius

θ is the colatitude

φ is the azimuth

In this coordinate system, the equation describing a spherical surface is simply $f(r, \theta, \phi) = r$

i.e., if $r = 3$, a sphere of radius 3

Solving Schröderinger's Equation

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

1. Conversion from Cartesian Coordinates (xyz) to
Spherical Polar Coordinates (r, θ {theta}, φ{phi})

2. Separation of variables, three different subfunctions:

$$\Psi = R(r)\Theta(\theta)\Phi(\varphi)$$

↓ "solving Schrödinger's equation"

$$\frac{1}{\mathrm{R}}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{8\pi^2 m}{h^2} + \left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)r^2 = \mathrm{u} \quad (R \text{ subfunction})$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(sin\theta\frac{d\Theta}{d\theta}\right) - \frac{v^2}{sin^2\theta} + u\Theta = 0 \quad (\Theta \text{ subfunction})$$

$$\frac{1}{\Phi}\frac{d^2}{d\varphi^2} = -v^2 \quad (\Phi \text{ subfunction})$$

Quantum numbers: $u = l(l+1)$; $v = m_l$

Solving Schröderinger’s Equation

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

$$\Psi = R(r)\Theta(\theta)\Phi(\varphi) = R(r)Y(\theta, \varphi)$$

radial wavefunction angular wavefunction

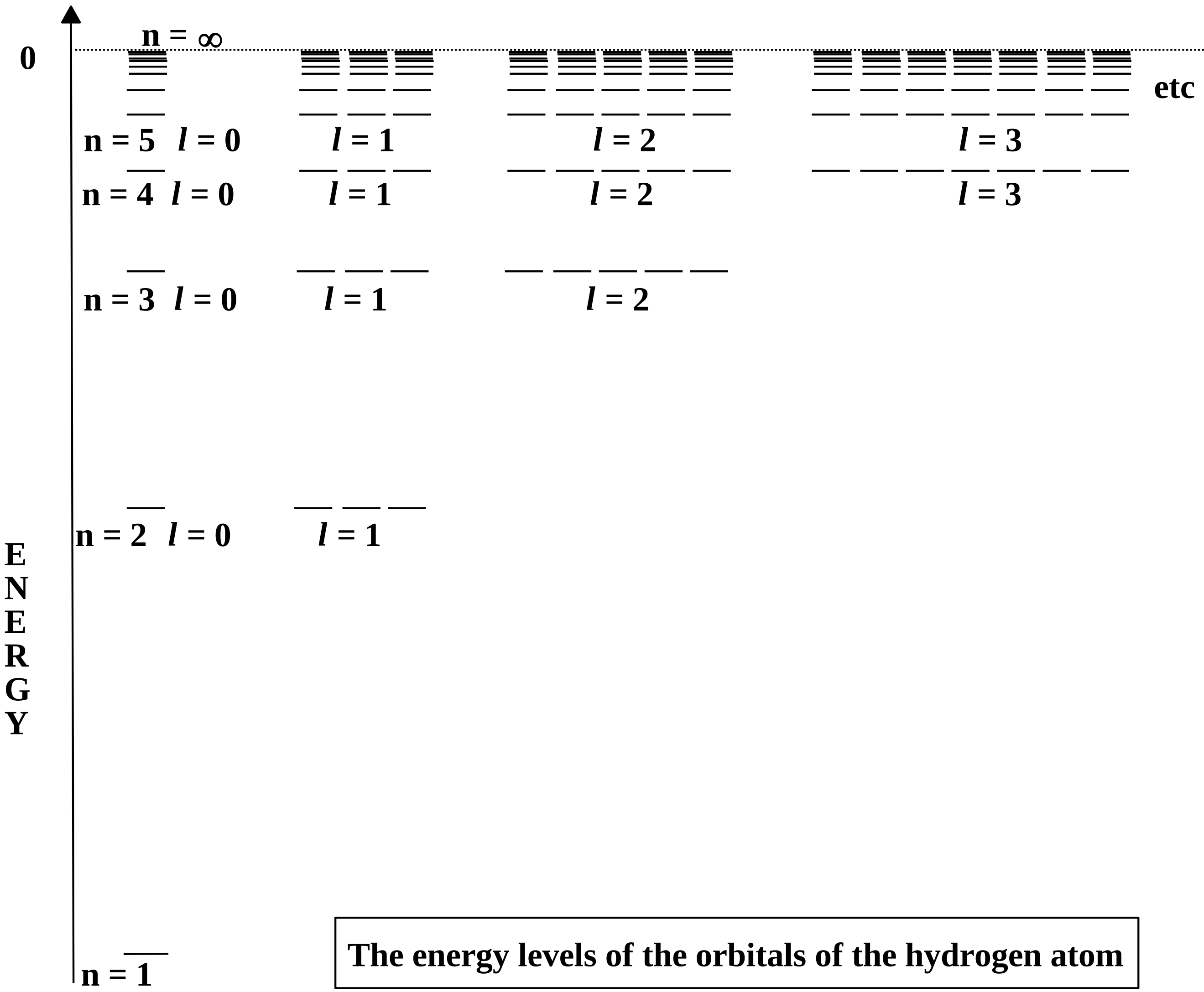
“solving Schrödinger’s equation”

$$\Psi = R_{n,l}(r)Y_{l,m_l}(\theta, \varphi)$$

Only certain wavefunctions are allowed!
Only certain quantum numbers are allowed!

Quantum Numbers

n = <u>principle quantum number </u>(information about the shell, information about energy)
n = 1, 2, 3, 4, …..



The energy levels of the orbitals of the hydrogen atom

Quantum Numbers

l = <u>angular momentum quantum number</u> (information about the subshell,
type of orbital,
and angular momentum)

l = 0, 1, 2, 3, ….. (n-1)

angular momentum of an electron in an orbital: $\hat{L}^2\Psi = l(l+1)\hbar^2\Psi$

$$|L| = \sqrt{l(l+1)}\hbar$$

Orbital names assigned to values of *l*

l	0	1	2	3	4	5
orbital label	*s* *(sharp)*	*p* *(principal)*	*d* *(diffuse)*	*f* *(fundamental)*	g	*h*

Quantum Numbers

m_l = magnetic quantum number (information about the orientation of the orbital, or the z-component of the angular momentum)

$m_l = 0, \pm 1, \pm 2, \pm 3, \ldots\ldots \pm l$

z-component of the angular momentum of an orbital: $\hat{L}_z \Psi = m_l \hbar \Psi$

$$\Psi = R_{n,l}(r) Y_{l,m_l}(\theta, \varphi)$$

Quantum Numbers

m_s = electron spin quantum number

Orbitals defined by the quantum numbers n, l and m_l may contain up to two electrons

Each of the electrons has a unique “electron spin” and is usually denoted as “spin up” ↑ and “spin down” ↓

$m_s = +½, –½$