PHY127 FS2023

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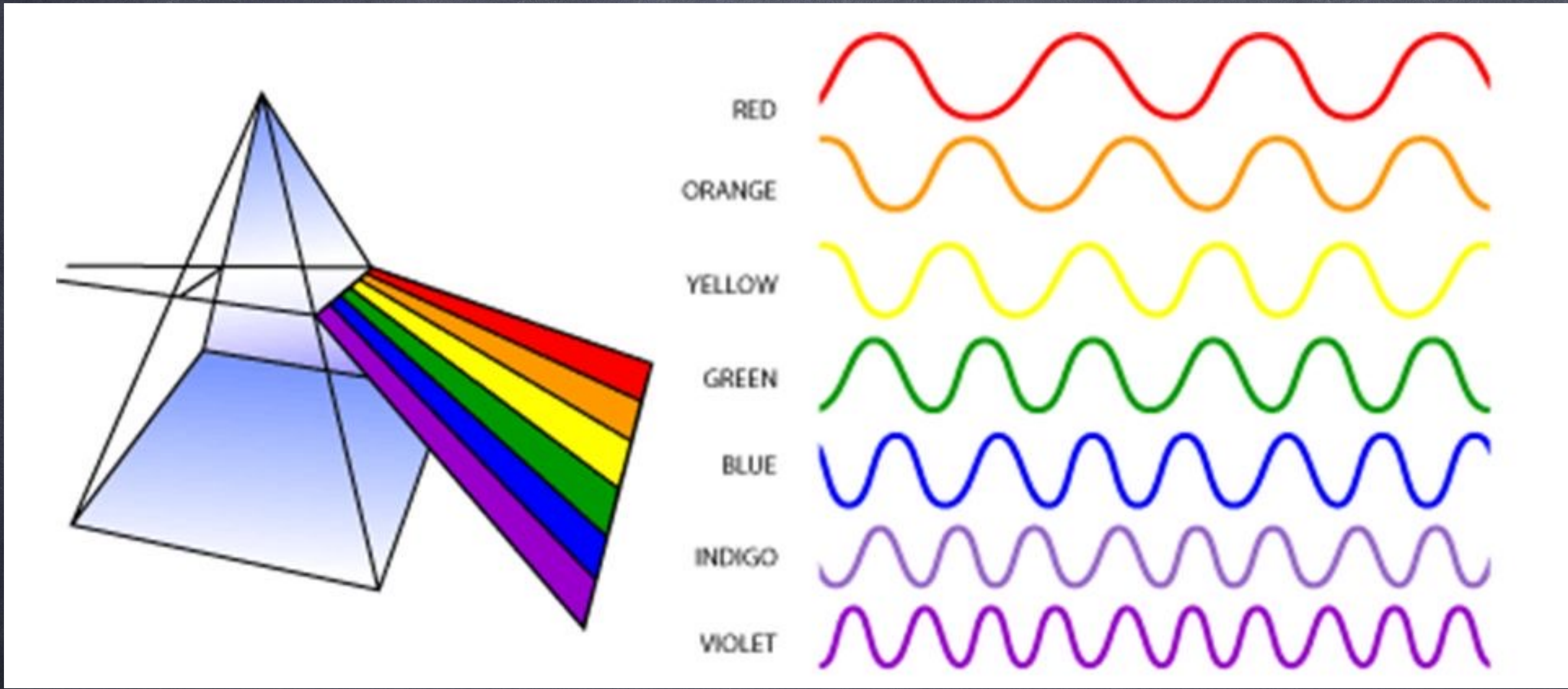
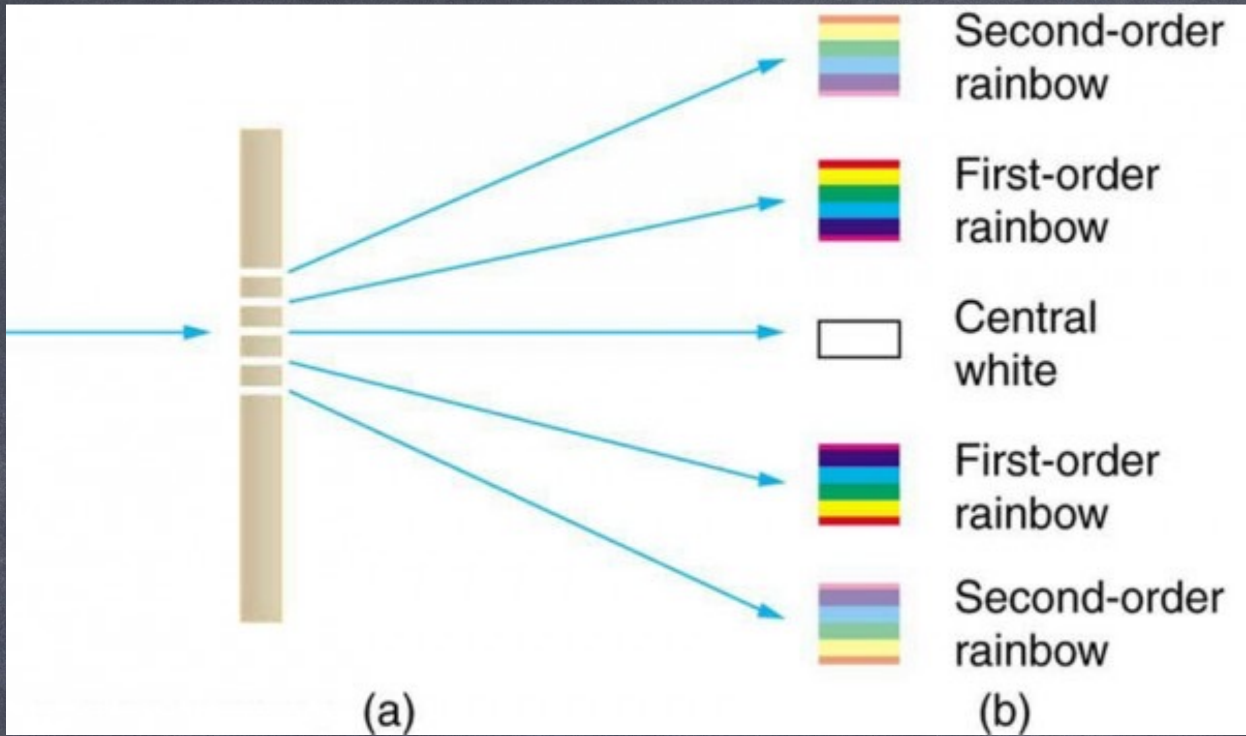
Lecture 6

March 31st, 2023

we observe that white light generated from a blackbody can be split into a spectrum of frequencies.




Second-order
rainbow
First-order
rainbow
Central
white
First-order
rainbow
Second-order
rainbow
(a)
(b)

Make a model of the light coming from an atom.

Empirically, light (visible) from hydrogen atom,

Balmer series: $$\lambda = 364.6 \text{ nm} \left(\frac{m^2}{m^2-4}\right)$$ for $m = 3, 4, 5, \ldots$

Extended to other atoms ⓪

$$\boxed{\frac{\nu}{c} = \frac{1}{\lambda} = R Z^2 \left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)}$$

n_1, n_2: integers

$n_1 > n_2$

R: Rydberg constant

$R = 10.97373 \ \mu m^{-1}$

Z: charge of atom

Bohr: hypothesis that violates classical physics.

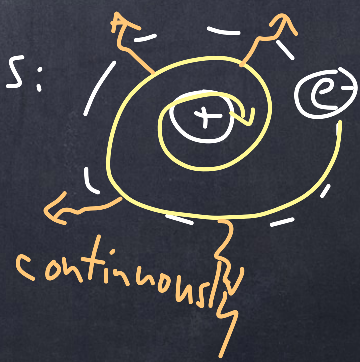
There are allowed transitions in energy such that

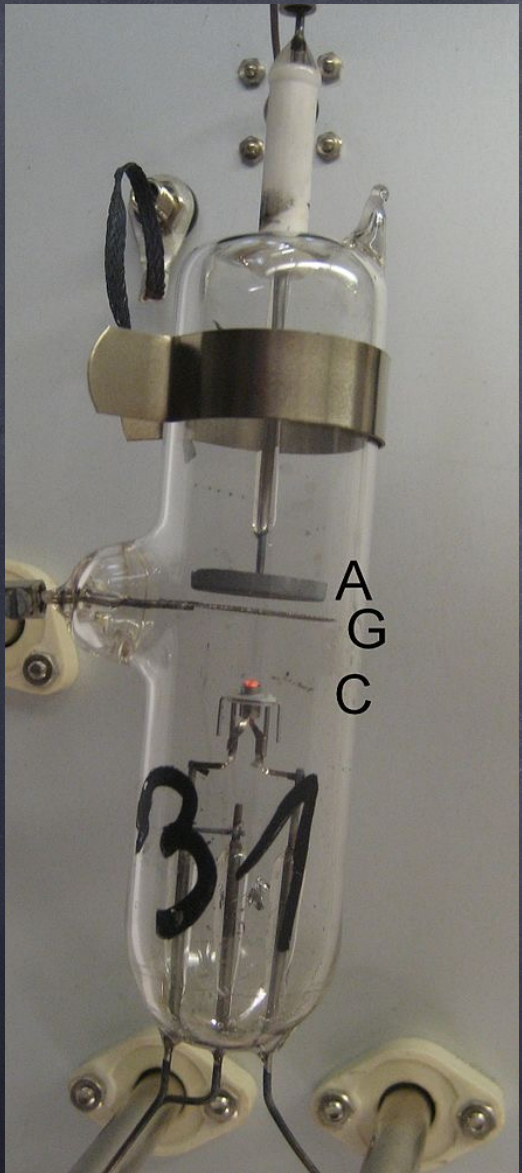
$$\boxed{\nu = \frac{\epsilon_i - \epsilon_f}{h}} \quad ①$$

ϵ_i, ϵ_f: initial + final energies.

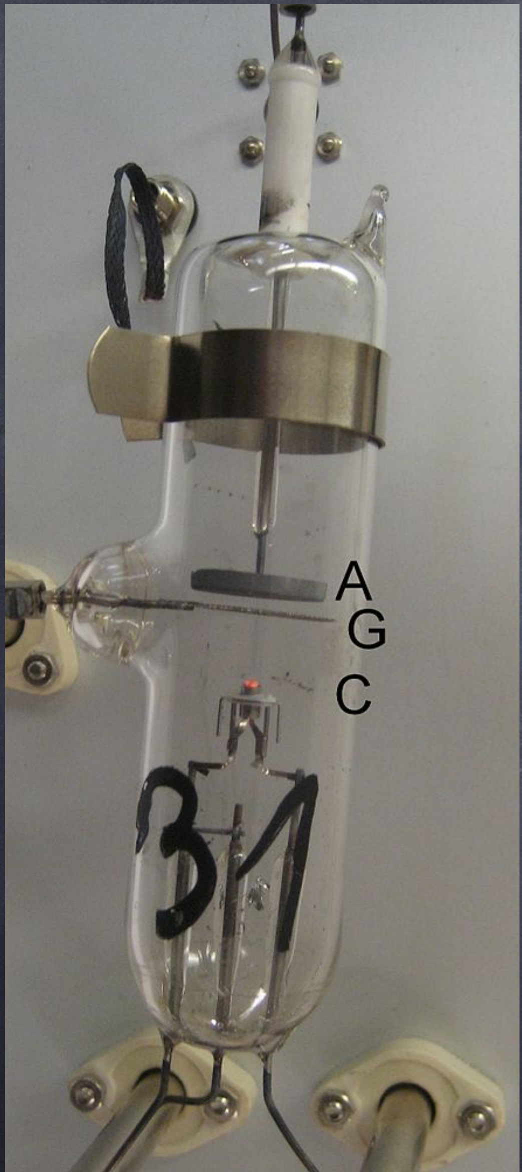
Bohr:

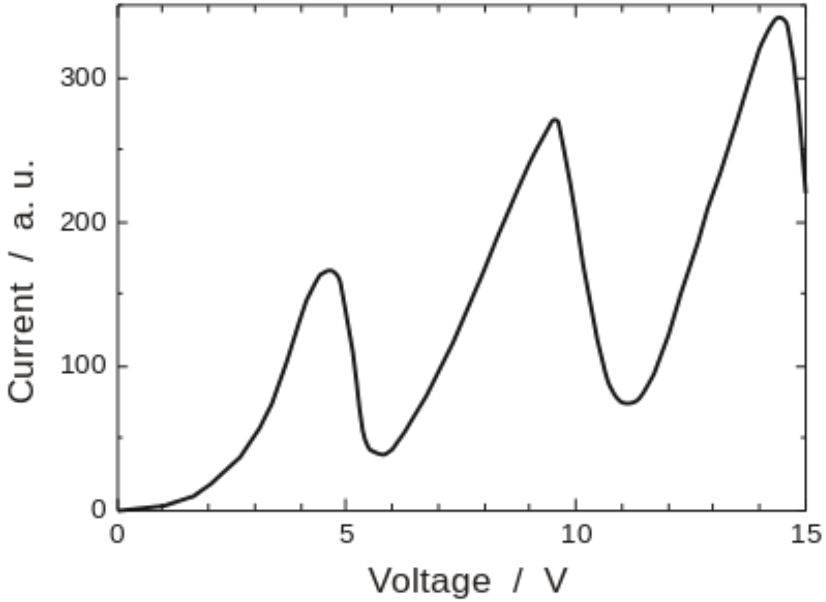
Classical physics:

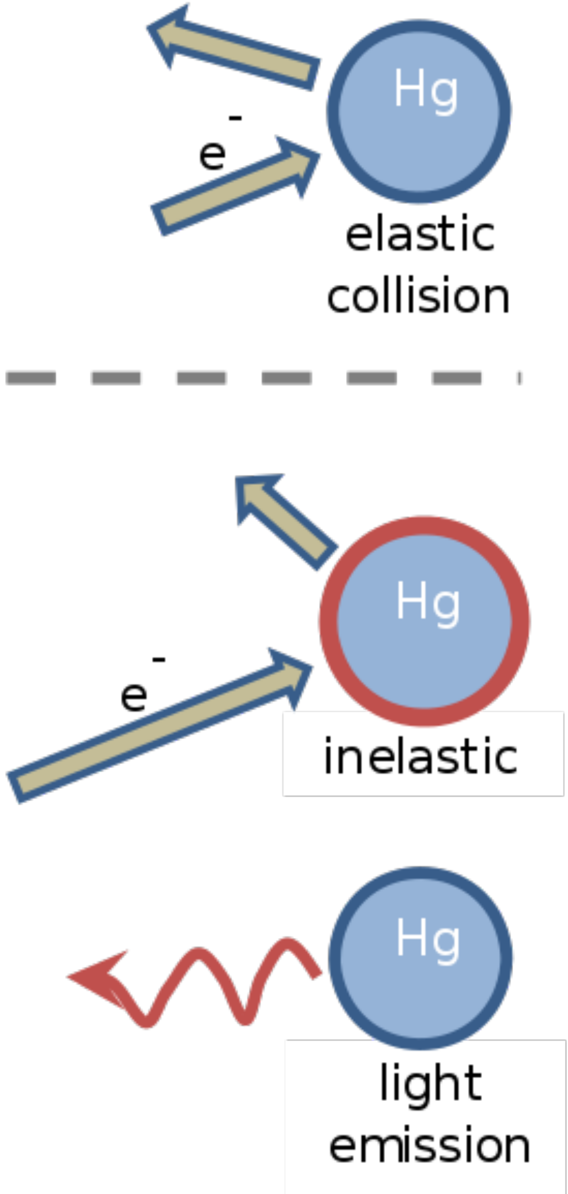


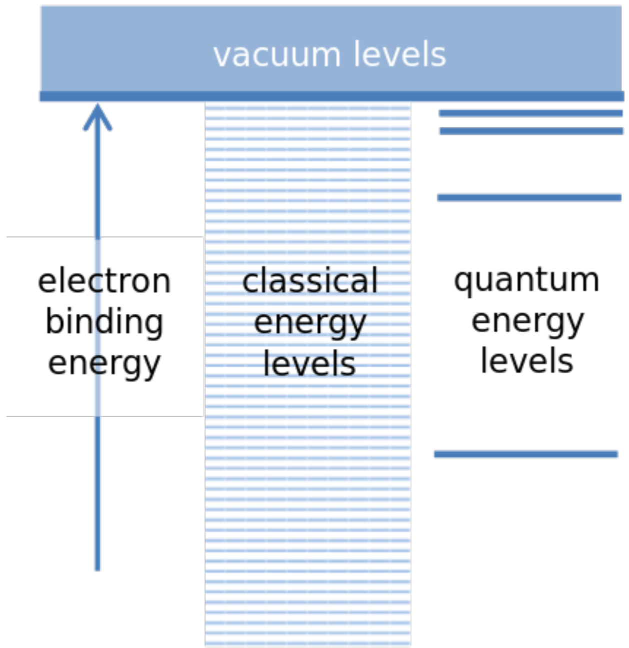

A
G
C

Franck-Hertz eperiment: shows quantum aspects of atom









In Coulomb field, $U = -\frac{kZe^2}{r}$ k: Boltzmann constant

For an electron bound to an atom

$$\epsilon = \underbrace{K}_{\text{kinetic energy}} + U = \frac{1}{2}mv^2 - \underbrace{\frac{kZe^2}{r}}_{\text{energy}}$$

In a circular orbit: $F = ma = \frac{mv^2}{r}$ $\frac{v^2}{r}$: centripetal acceleration

$$\underbrace{\frac{mv^2}{r}}_{\text{centripetal force}} = \underbrace{\frac{kZe^2}{r^2}}_{\text{Coulomb force}} \Longrightarrow \boxed{\underbrace{\frac{1}{2}mv^2}_{K} = \frac{1}{2}\frac{kZe^2}{r}} \quad (2a)$$

So $$\boxed{\epsilon_r = -\frac{1}{2}\frac{kZe^2}{r}} \quad (2)$$

Energy is a function of r.
Different radii → different energies.

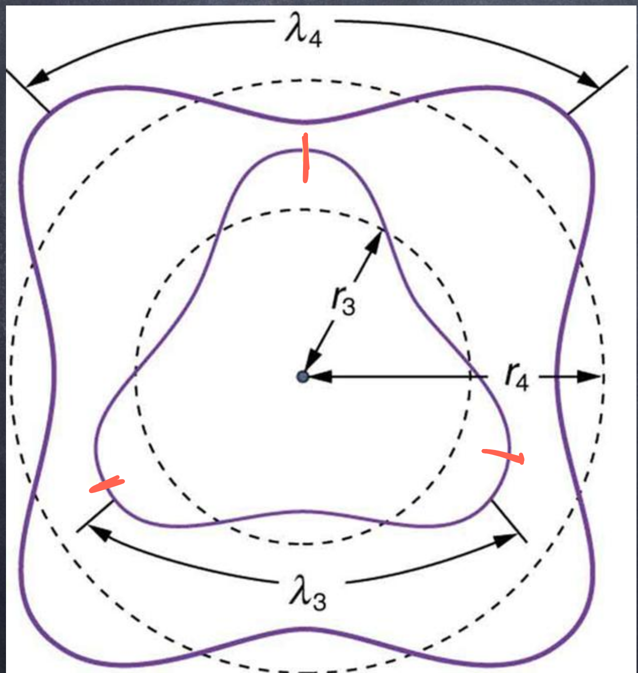
using (1) + (2):

$$\boxed{\nu = \frac{\epsilon_i - \epsilon_f}{h} = \frac{\frac{1}{2}kZe^2}{h}\left(\frac{1}{r_2} - \frac{1}{r_1}\right)} \quad (3)$$

r_2, r_1: two different radii

Comparing ③ theory with ⓪ expt.,
we see that the radii r_1, r_2 must be proportional to integers squared.

de Broglie considered that an electron orbit around an atom was like standing waves. $\left(\lambda = \frac{h}{p}\right)$



$n\lambda$ = circumference of a circle $= 2\pi r$
for n: integers $= 1, 2, 3, \ldots$

If we take $p = \frac{h}{\lambda}$ (p: momentum)

$\lambda = \frac{h}{p}$ $\left(\hbar = \frac{h}{2\pi}\right)$

$$n\lambda = \frac{nh}{p} = 2\pi r \Rightarrow n\hbar = rp = \underbrace{rmv}_{\text{angular momentum.}}$$

PHY 117:
$\bar{L} = m\bar{v} \times \bar{r}$
$L = mvr$ for a circle

we see that angular momentum (of electron in atom) is quantized as a result of the standing wave condition:

$$\boxed{n\hbar = mvr} \quad (4)$$

Take (4), square it: $v^2 = \frac{n^2\hbar^2}{m^2r^2}$, substitute it into (2a)

$$\frac{1}{2}m\left(\frac{n^2\hbar^2}{m^2r^2}\right) = \frac{kZe^2}{r}$$

solve for r

$$\boxed{r = \frac{n^2\hbar^2}{mkZe^2}} \quad (5)$$

we see that r is quantized.
we define a constant

$$a_0 = \frac{\hbar^2}{mke^2} \approx 0.0529 \text{ nm}$$

which is called the Bohr radius.

Substitute (5) $\rightarrow$ (3):

$$\nu = \frac{\frac{1}{2}kZe^2}{h}\left(\frac{1}{\frac{n_2^2\hbar^2}{mkZe^2}} - \frac{1}{\frac{n_1^2\hbar^2}{mkZe^2}}\right) \Rightarrow \boxed{\nu = \frac{Z^2mke^4}{4\pi\hbar^3}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)} \quad (6)$$

Compare our theory 6 to our empirical formula 0, the formulas agree, and this constant R is related to other constants, $R = \frac{mk^2e^4}{4\pi c \hbar^3}$

Substitute 5 → 2 :
radius energy

$$E_n = -\frac{1}{2}\frac{kZe^2}{r} = \frac{-k^2e^4mZ^2}{2\hbar^2}\frac{1}{n^2}$$

n: integer

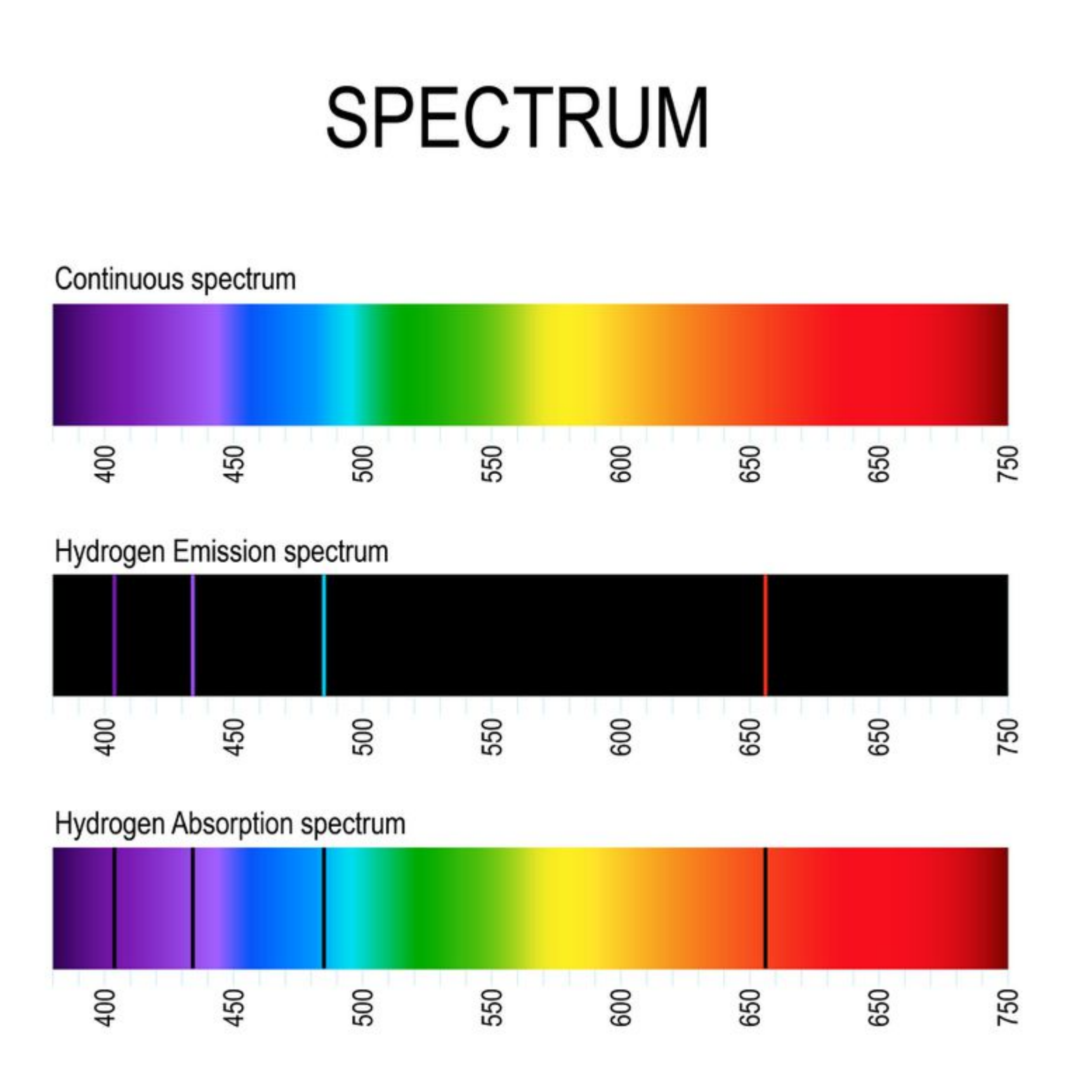
we define ground state energy E_0

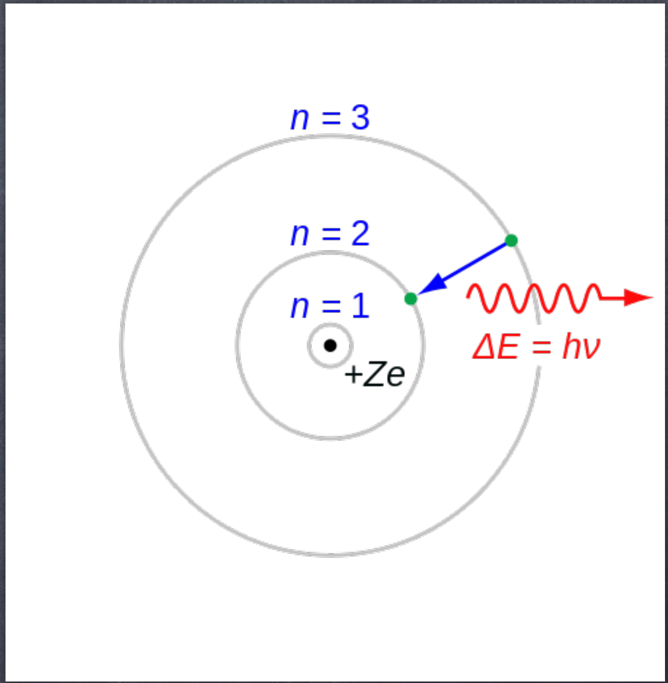
$$\boxed{E_0 = \frac{k^2e^4m}{2\hbar^2} \approx 13.6\,\text{eV}} \quad (7)$$

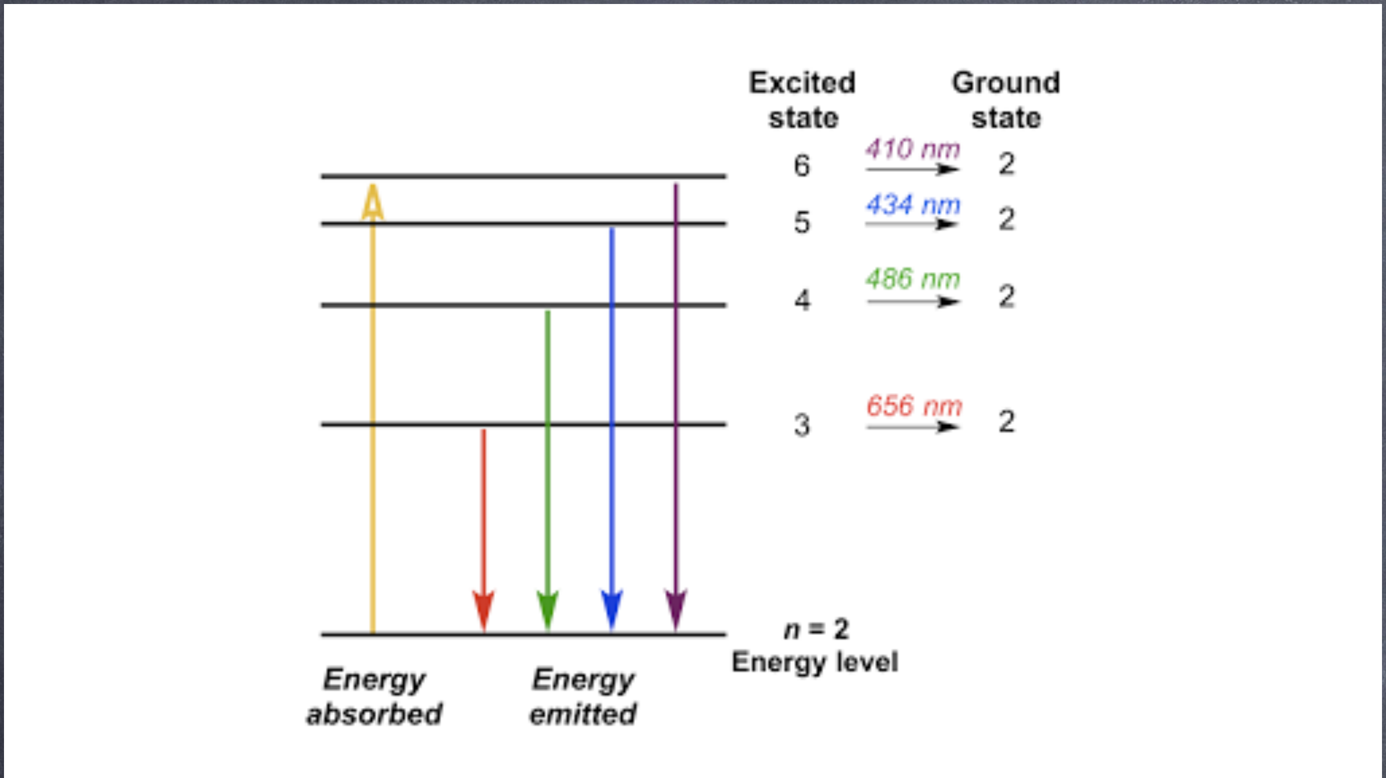
Then

$$\boxed{E_n = -\frac{Z^2}{n^2}E_0} \quad (8)$$

These are the allowed energy levels of the hydrogen atom ($Z=1$)

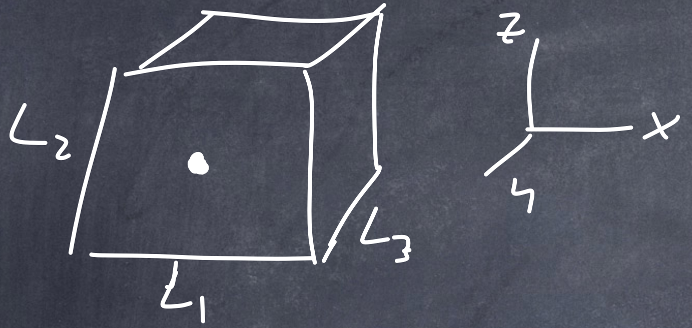

SPECTRUM
Continuous spectrum
400
450
500
550
600
650
650
750
Hydrogen Emission spectrum
400
450
500
550
600
650
650
750
Hydrogen Absorption spectrum
400
450
500
550
600
650
650
750


n = 3
n = 2
n = 1
+Ze
ΔE = hν



Balmer series

A particle trapped in a 3-D box. (extension of our 1-D box)



we use the 3-D Schroedinger equation.

$$\boxed{\frac{-\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+U\psi=E\psi} \quad ①$$

Here, $U=0$ inside the box, outside $U=\infty$

the wave functions that solve the ① Factorize:

$$\psi(x,y,z)=\psi(x)\,\psi(y)\,\psi(z)$$

The solution is

$$\boxed{\psi(x,y,z)=A(\sin k_1x)(\sin k_2y)(\sin k_3z)} \quad ②$$

k_1, k_2, k_3 are related to wavelength of our standing waves in each dimension.

A is the constant that is determined by normalizing $1=\int_0^{L_3}\int_0^{L_2}\int_0^{L_1}\psi^2(x,y,z)\,dx\,dy\,dz \Rightarrow A$

Insert ② into ①, we find that

$$\epsilon = \frac{\hbar^2}{2m}\left(k_1^2 + k_2^2 + k_3^2\right)$$

+ since $p_x = \hbar k_1$

$p_y = \hbar k_2$

$p_z = \hbar k_3$

$$\epsilon = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$$

Look at ②, we need $\psi(x,y,z) = 0$ on the boundaries of our box, when $x = L_1$, $y = L_2$, or $z = L_3$

$x = L_1$: $\sin(k_1 L_1) \overset{\text{must}}{=} 0 \Rightarrow$ true if $k_1 L_1 = n_1 \pi$

so $k_1 = \frac{n_1 \pi}{L_1}$ n_1 : integer

Likewise: for $y = L_2$: $k_2 = \frac{n_2 \pi}{L_2}$

$z = L_3$: $k_3 = \frac{n_3 \pi}{L_3}$

These are allowed energies of a ptcl in a 3-D box

Finally, we see that $\epsilon_{n_1,n_2,n_3} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2}\right)$

integers n_1, n_2, n_3

If $L_1 = L_2 = L_3$, energies are "degenerate"

$\epsilon_{2,2,1} = \epsilon_{2,1,2} = \epsilon_{1,2,2}$ ——— $9\epsilon_1$

$\epsilon_{1,1,2} = \epsilon_{1,2,1} = \epsilon_{2,1,1}$ ——— $6\epsilon_1$

$\epsilon_{1,1,1}$ ——— $3\epsilon_1$

But if $L_1 \neq L_2 \neq L_3$, then these energies would be split:

$\epsilon_{2,1,2}$

$\epsilon_{2,2,1}$

$\epsilon_{1,2,2}$

$\epsilon_{1,1,2}$

$\epsilon_{1,2,1}$

$\epsilon_{2,1,1}$

$\epsilon_{1,1,1}$

Now, we consider a 3D atom, which has a potential:

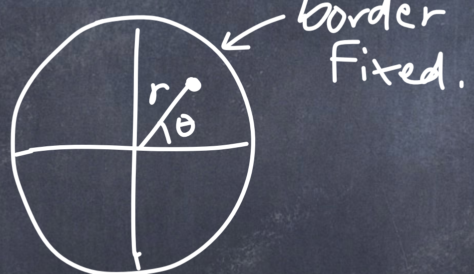
$$U = \frac{-kZe^2}{r}$$

This is a spherical potential of Coulomb field of a atom of charge Z with one electron.

First consider a 2D sphere.

Because particles behave as waves, to solve where the particle is, & its energies, we have to consider standing wave problem for different boundary conditions.

Drum



2-D membrane
(circular)

we have 2 degrees of freedom.

2 "quantum" numbers
$m = 0, 1, 2, \ldots$
$n = 0, 1, 2, \ldots$

solutions to 2D circle: Bessel functions

Here Ψ is height of drum membrane

$$\Psi(r,\theta) = \Psi(r)\,\Psi(\theta)$$

If we add time,

$$\Psi(r,\theta,t) = \Psi(r)\,\Psi(\theta)\,\Psi(t)$$