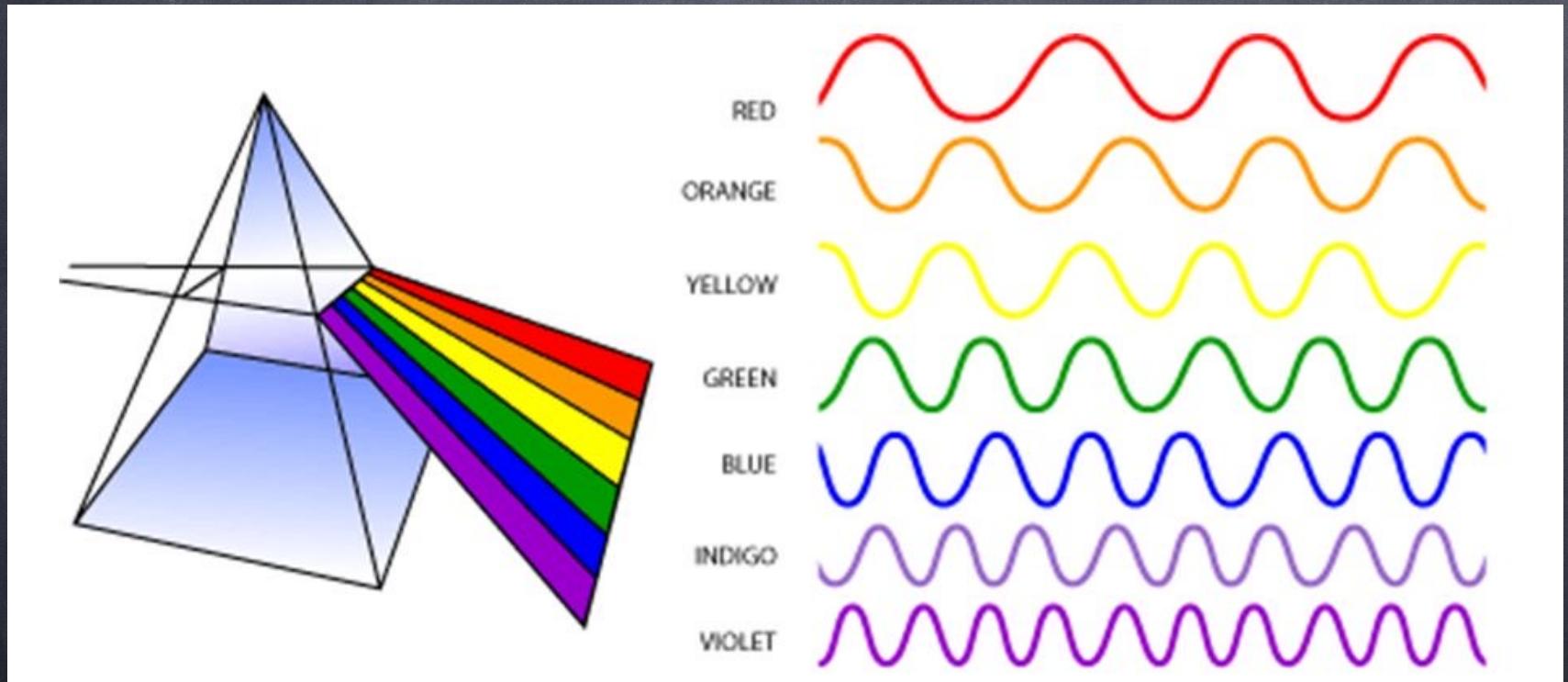


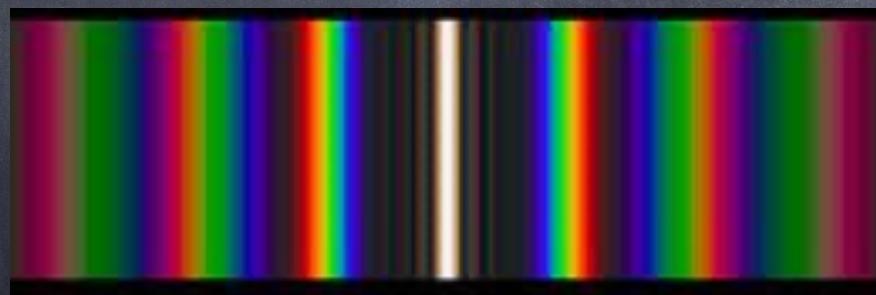
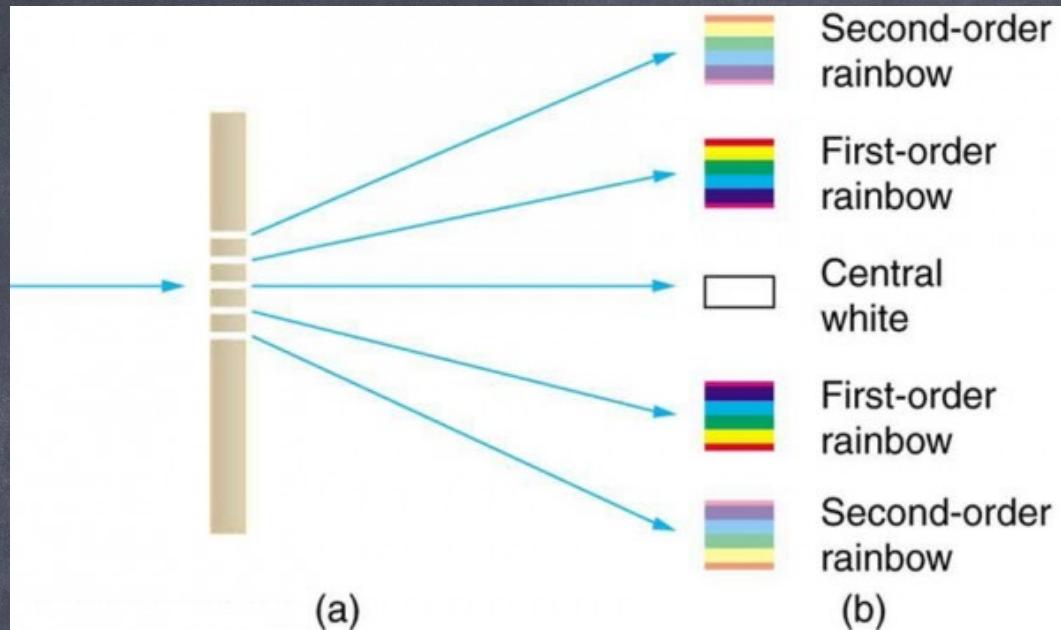
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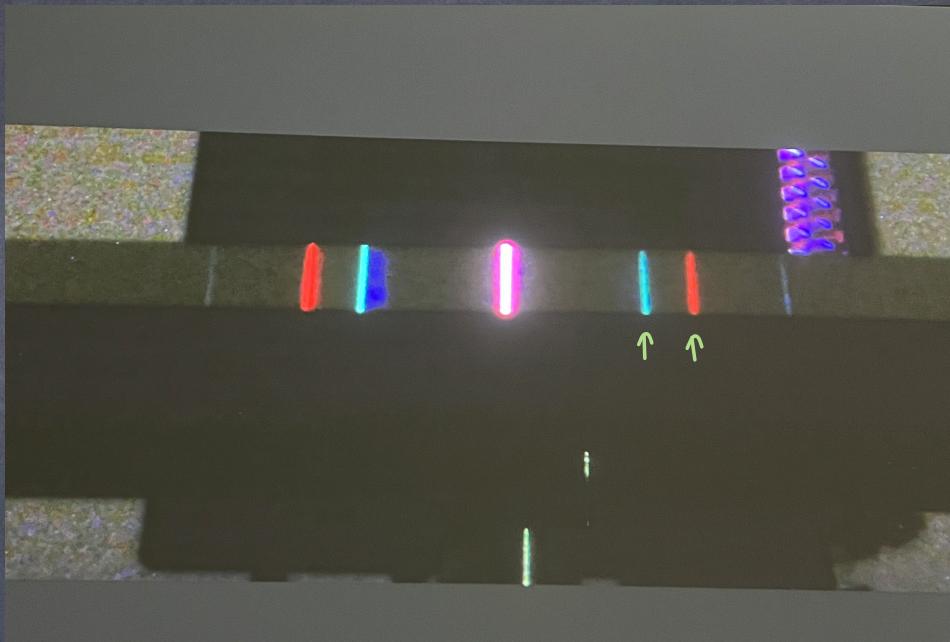
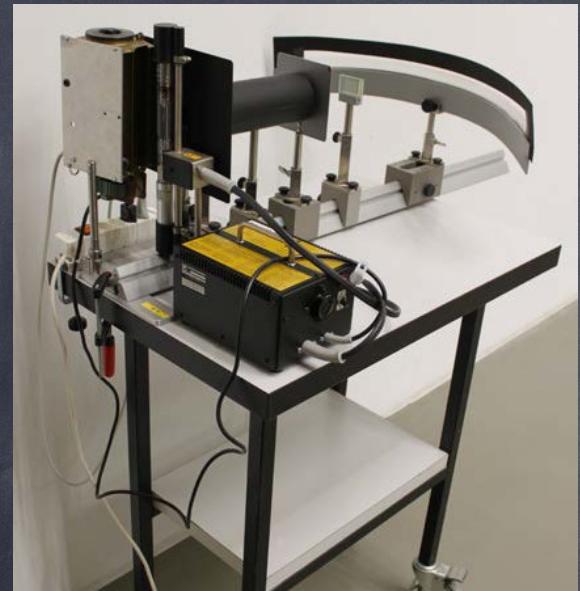
Prof. Ben Kilminster
Lecture 6
April 12th, 2024

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



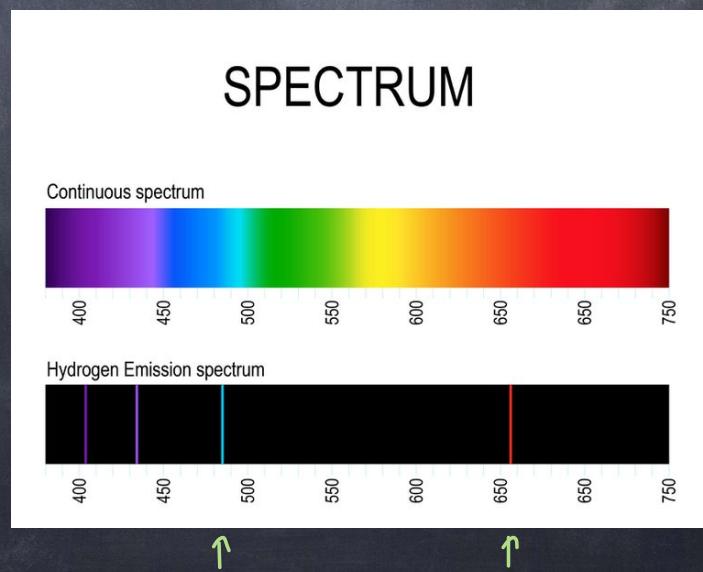
diffraction grating splits light into wavelengths





using a diffraction grating,
we split light from
hydrogen gas

we observe that
hydrogen emits light
of specific wavelengths.



Make a model of the light coming from an atom.

Empirically, light (visible) from hydrogen atom,
Balmer (1885) Balmer series: $\lambda = 364.6 \text{ nm} \left(\frac{m^2}{m^2 - 4} \right)$ for $m = 3, 4, 5, \dots$

Extended to other atoms
Rydberg (1888)

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

n_1, n_2 : integers
 $n_1 > n_2$

R: Rydbers constant
 $R = 10.97373 \mu\text{m}^{-1}$

After advent of Einstein,
 $E = \frac{hc}{\lambda} = h\nu$, and quantum mechanics,
Bohr (1913) realized these described energy levels ($E = h\nu$),

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

n_1, n_2 : integers
 $n_1 > n_2$
Z: charge of atom

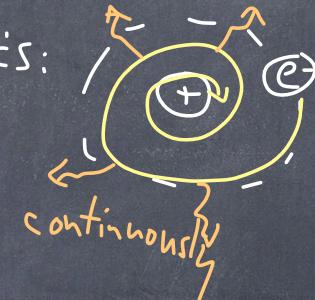
Bohr: hypothesis that violates classical physics.

There are allowed transitions in energy such that

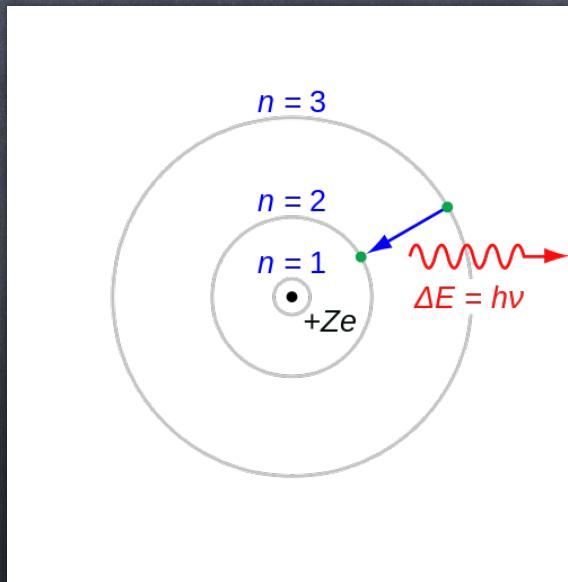
$$V = \frac{E_i - E_f}{\hbar} \quad ①$$

E_i, E_f : initial + final energies.

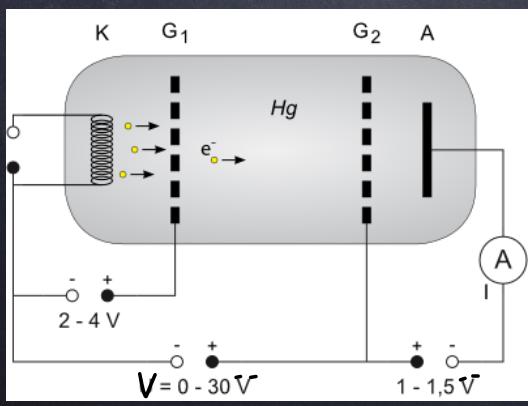
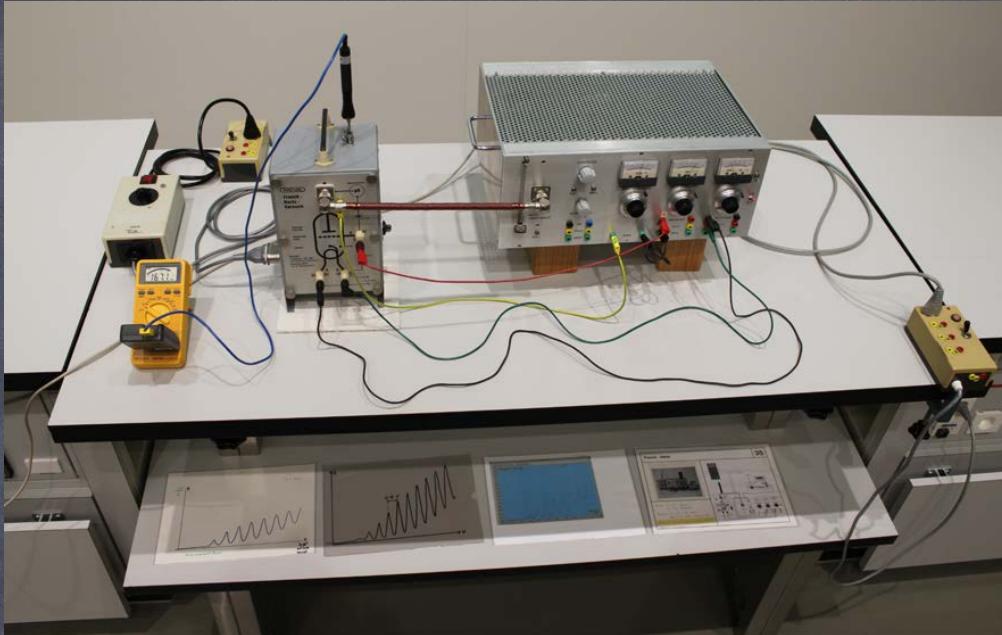
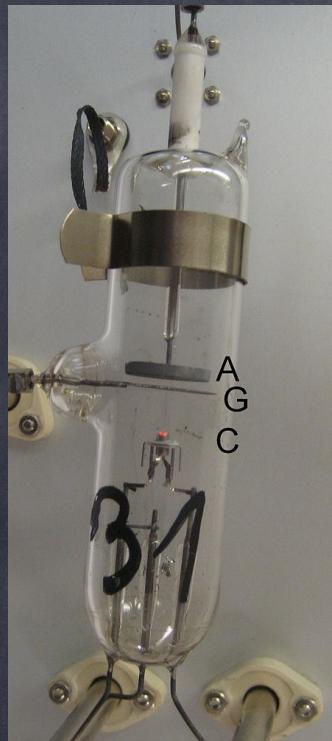
Classical physics:



Bohr:
(1913)

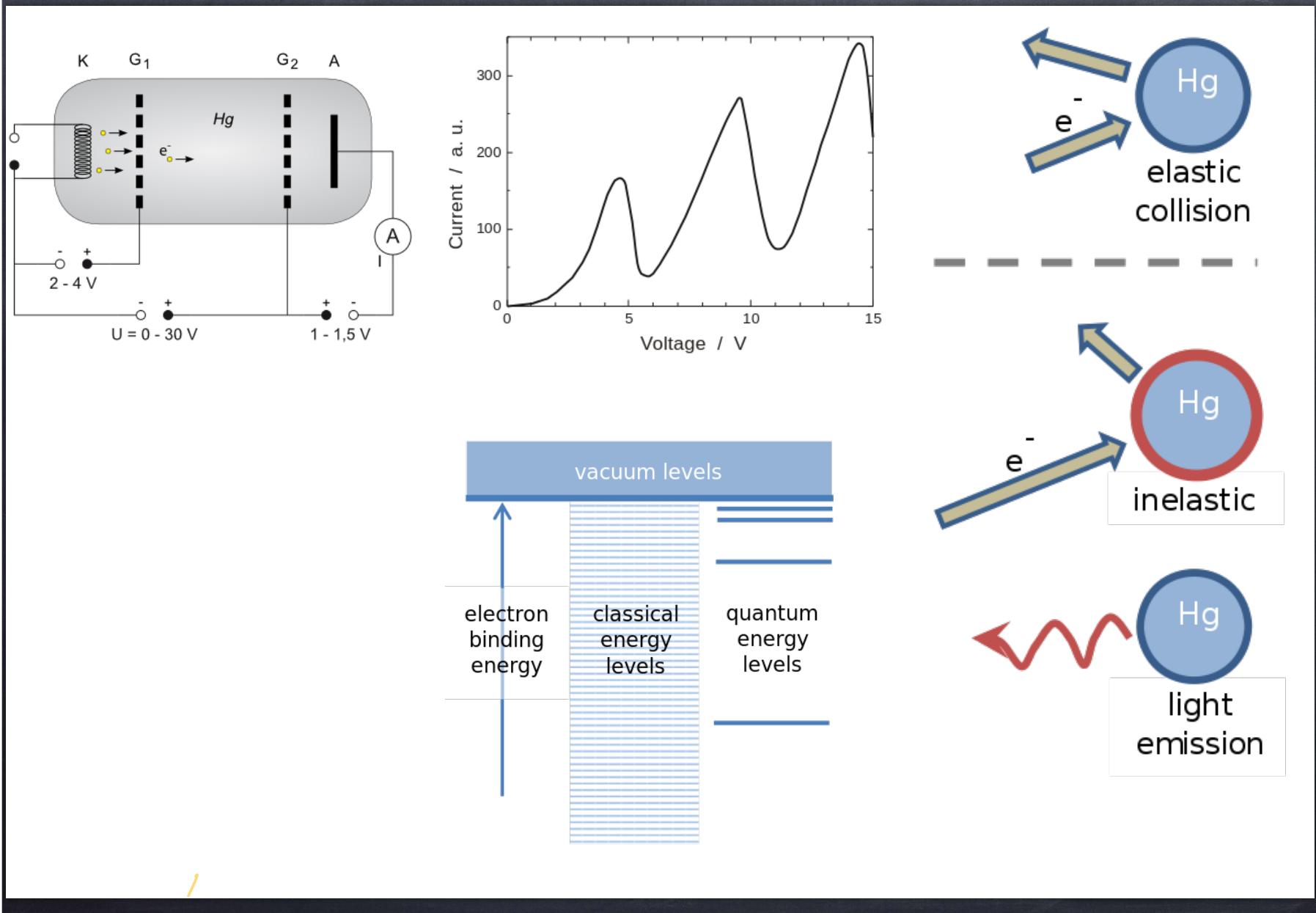


Franck - Hertz experiment (1914) validated the quantum nature theory of atoms

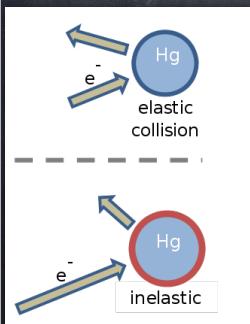
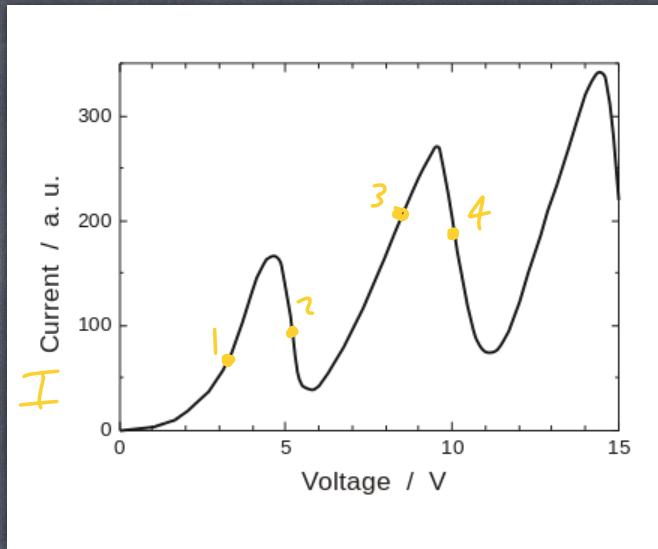
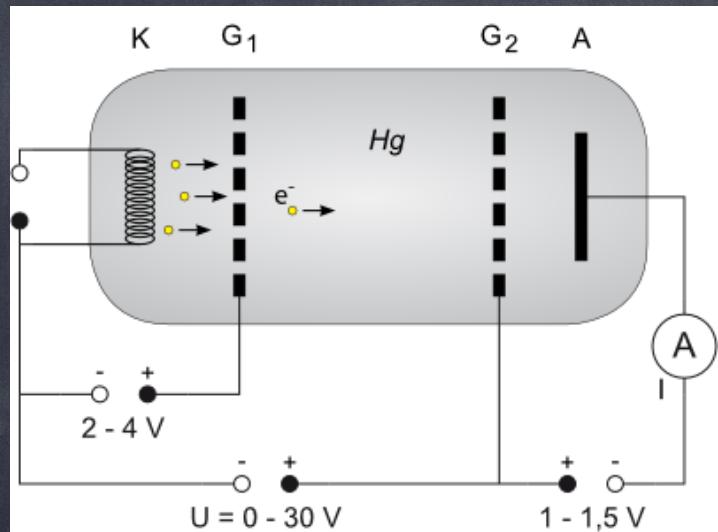


- tube filled with heated mercury vapor.
 - electrons accelerated through tube:
 $eV = \frac{1}{2}mv^2$ where V changes
 - If electrons have at least $(1.5V)e = K$ when passing G_2 they reach the collector and current will be measured in \textcircled{A}
- $I = eAnv$
- n : charge/volume
 A : cross-section area
 e : electron charge

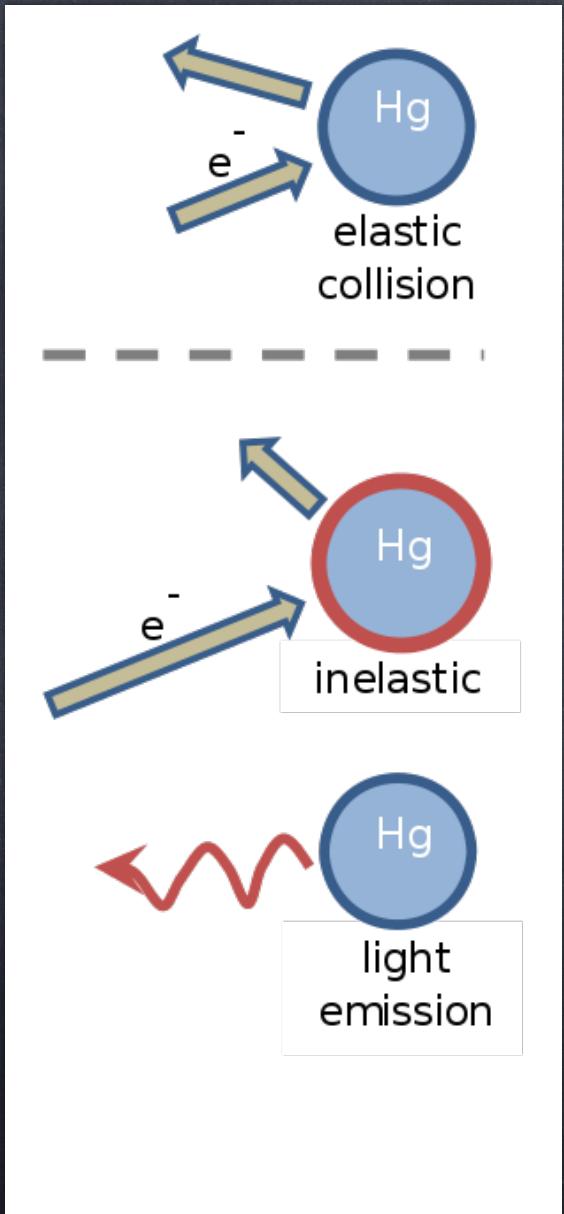
Franck-Hertz experiment : shows quantum aspects of atom



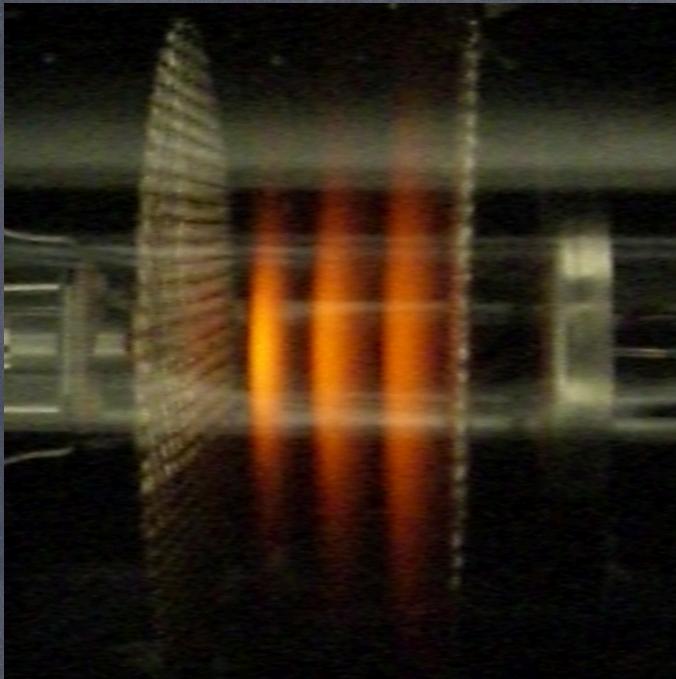
Franck-Hertz experiment: shows quantum aspects of atom



- 1: V increases $\rightarrow N$ increases \rightarrow Current increases
- 2: Above 4.9 V , atoms can absorb 4.9 eV of electron energy, decreasing $N \rightarrow$ decreases I
- 3: Electron has interacted once, but gains N
 $\rightarrow I$ increases.
- 4: Above $2 \cdot 4.9\text{ V} = 9.8\text{ V}$, electron scatters inelastically a second time and loses velocity,
 $\rightarrow I$ decreases



IF instead of mercury , we would use neon, the



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

For an electron bound to an atom

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

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

$$\frac{mv^2}{r} = \frac{kZe^2}{r^2} \Rightarrow$$

$\underbrace{\frac{1}{2}mv^2}_{\text{centripetal force}} = \underbrace{\frac{kZe^2}{r}}_{\text{Coulomb force}}$

$$\boxed{\frac{1}{2}mv^2 = \frac{kZe^2}{r}} \quad (2)$$

$K = \uparrow$

So

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

Energy is a function of r .

Different radii \rightarrow different energies.

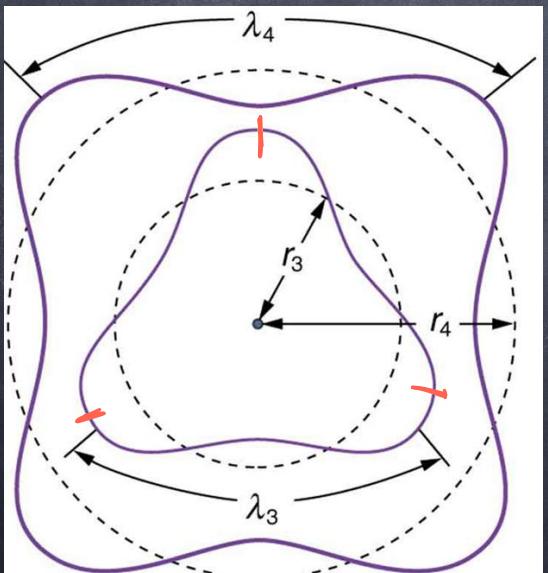
Using ① + ② :

$$\boxed{V = \frac{E_i - E_f}{h} = \frac{1}{2} \frac{kZe^2}{h} \left(\frac{1}{r_2} - \frac{1}{r_1} \right)} \quad (3)$$

r_2, r_1 : two different radii

Comparing ③ theory with ⑥ 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. ($\lambda = \frac{h}{p}$)



$$n\lambda = \text{circumference of a circle} = 2\pi r$$

for n : integers = 1, 2, 3, ...

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

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

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

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

$p \parallel \lambda$

$$\vec{L} = \vec{m}\vec{v} + \vec{r}$$

$$L = mvr \text{ for a circle}$$

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

$$n\hbar = mv r \quad (4)$$

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

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

solve for r

$$r = \frac{n^2 \hbar^2}{m k Z e^2} \quad (5)$$

We see that r is quantized.
We define a constant

$$a_0 = \frac{\hbar^2}{m k e^2} \approx 0.0529 \text{ nm}$$

which is called the Bohr radius.

Substitute (5) \Rightarrow (3):

$$v = \frac{1}{2} k Z e^2 \left(\frac{1}{n_1^2 \hbar^2} - \frac{1}{n_2^2 \hbar^2} \right)$$

$$v = \frac{Z^2 m k e^4}{4 \pi \hbar^3} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \quad (6)$$

Compare our theory ⑥ to our empirical formula ⑦,
 the formulas agree, and this constant R is related
 to other constants, $R = \frac{mk^2e^4}{4\pi c\hbar^3}$

Substitute ⑤ \rightarrow ② :
 radius Energy

$$E_n = -\frac{1}{2} \frac{kze^2}{r} = -\frac{k^2 e^4 m z^2}{2\hbar^2} \frac{1}{n^2} \quad n: \text{integer}$$

we define
 ground state
 energy E_0

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

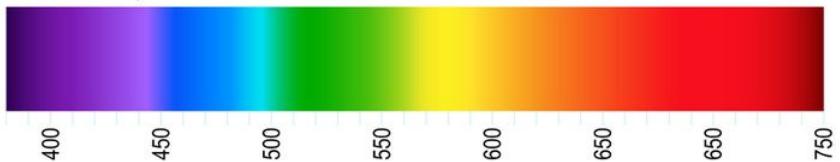
Then

$$E_n = -\frac{z^2}{n^2} E_0 \quad ⑧$$

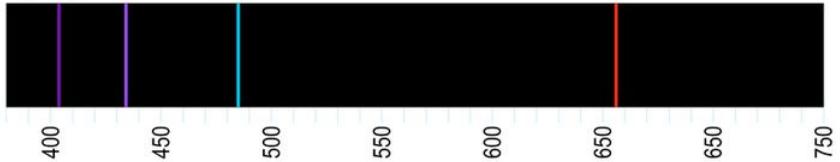
These are the allowed
 energy levels of the hydrogen
 atom ($z=1$)

SPECTRUM

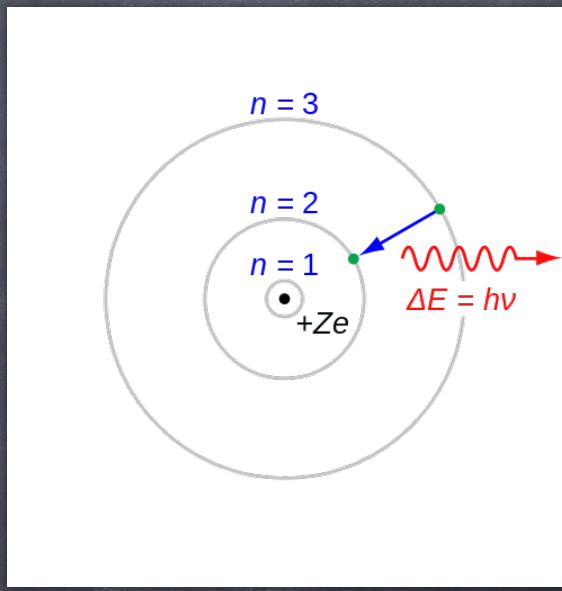
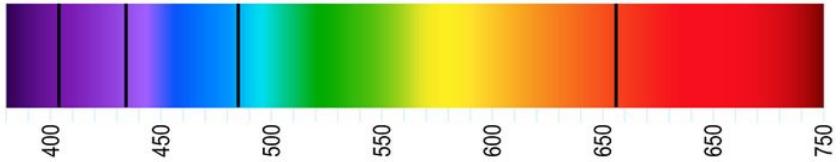
Continuous spectrum



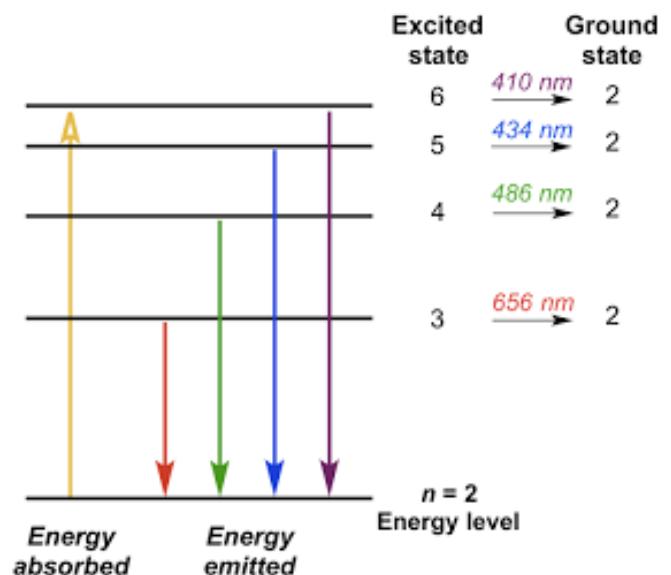
Hydrogen Emission spectrum

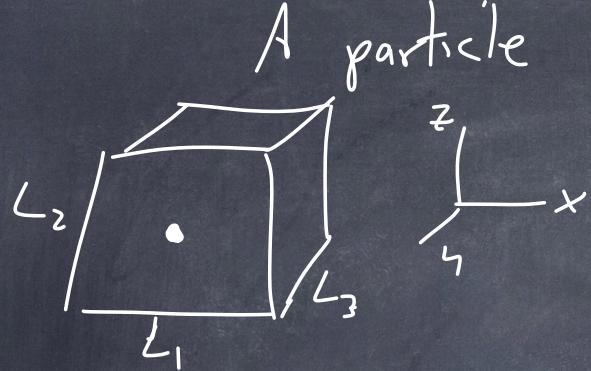


Hydrogen Absorption spectrum



Balmer series





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

We use the 3-D Schrödinger equation.

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

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

$$\boxed{\Psi(x, y, z) = A (\sin k_1 x) (\sin k_2 y) (\sin k_3 z)} \quad (2)$$

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 $|A| = \iiint_{000}^{L_1 L_2 L_3} \Psi^2(x, y, z) dx dy dz \Rightarrow A$

Insert ② into ①, we find that

$$E = \frac{\hbar^2}{2m} (k_1^2 + k_2^2 + k_3^2) + \text{since } p_x = \hbar k_1$$

$$p_y = \hbar k_2$$

$$p_z = \hbar k_3$$

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

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

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

$$\text{Likewise: for } y = L_2 : k_2 = \frac{n_2 \pi}{L_2} \quad \text{so } k_1 = \frac{n_1 \pi}{L_1} \quad n_i : \text{integer}$$

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

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

Finally, we see that integers n_1, n_2, n_3

$$E_{n_1, n_2, n_3} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right)$$

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

$$\epsilon_{2,2,1} = \epsilon_{3,1,2} = \epsilon_{1,3,2}$$

$$9\epsilon_1$$

$$\epsilon_{1,1,2} = \epsilon_{1,2,1} = \epsilon_{2,1,1}$$

$$6\epsilon_1$$

$$\epsilon_{1,1,1} \quad 3\epsilon_1$$

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

$$\begin{array}{c} \epsilon_{2,2,1} \\ \epsilon_{1,2,2} \end{array}$$

$$\begin{array}{c} \epsilon_{1,1,2} \\ \epsilon_{1,2,1} \\ \epsilon_{2,1,1} \end{array}$$

$$\epsilon_{1,1,1}$$

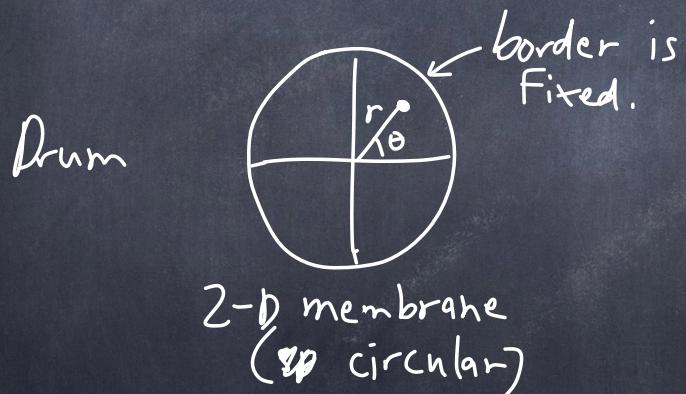
Now, we consider a 3D atom, which has a potential:

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

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.



we have 2 degrees of freedom.

2 "quantum" numbers

$$m = 0, 1, 2, \dots$$

$$n = 0, 1, 2, \dots$$

Solutions to 2D circle: Bessel Functions

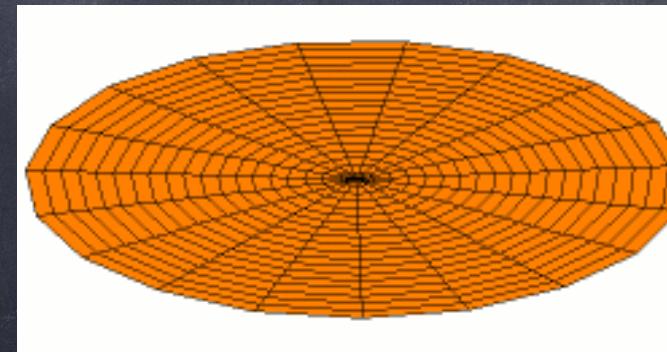
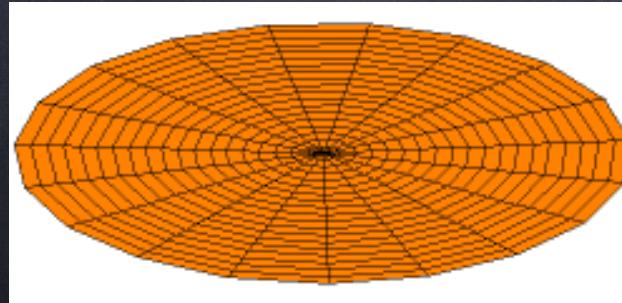
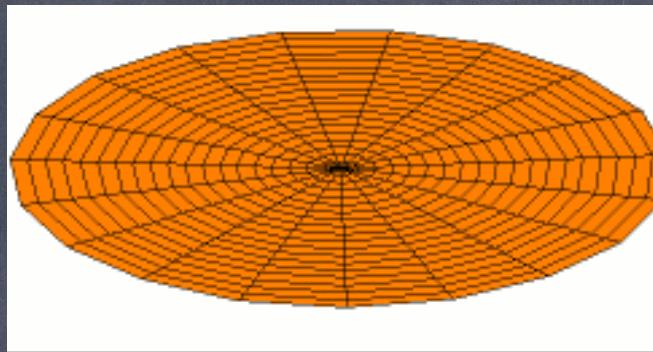
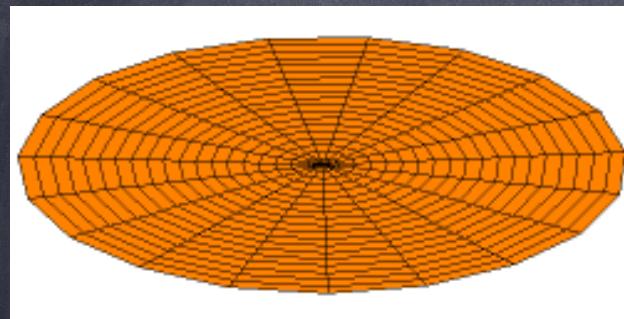
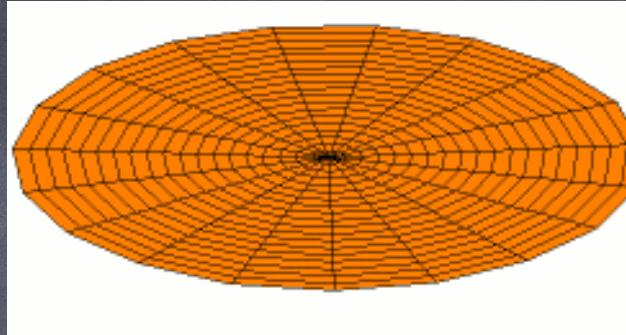
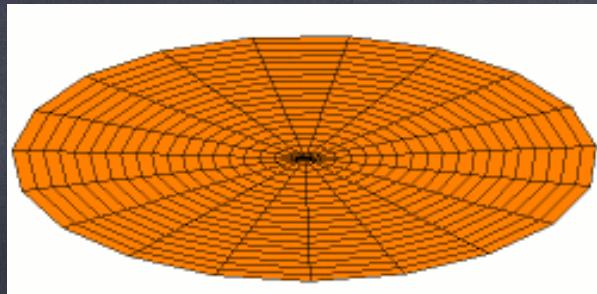
Here Ψ is height of drum membrane

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

If we add time,
 $\Psi(r, \theta, t) = \Psi(r) \Psi(\theta) \Psi(t)$



Grundschwingung bei ca. 31Hz



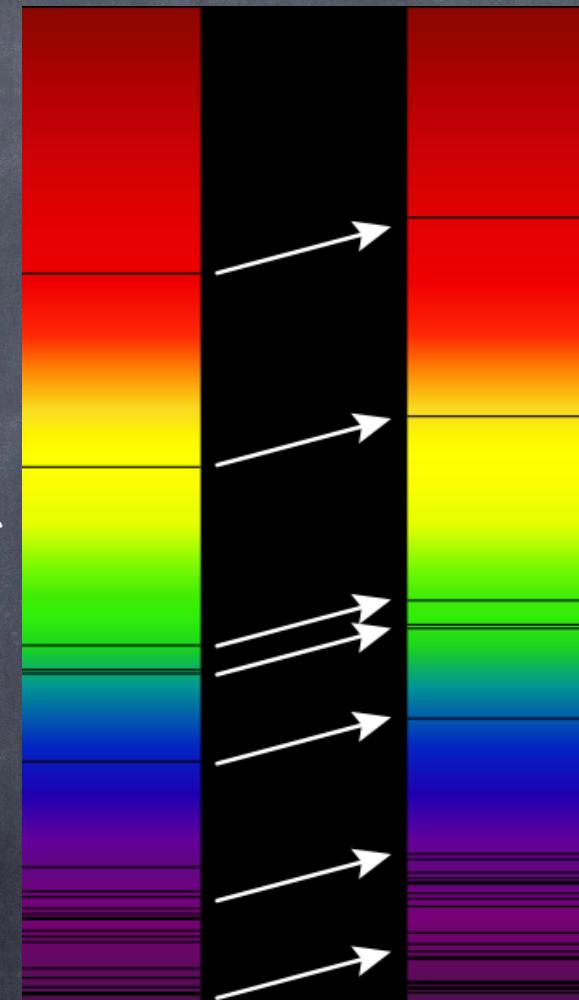
IF time, "red shift" of absorption lines

The same spectral lines are shifted due to the relativistic Doppler effect.

This is a shift of $\lambda \cdot v$ due to the velocity of an object wrt to us.

Allows scientists to measure speed of distant objects.

Let's us observe that the universe is expanding (accelerating!)

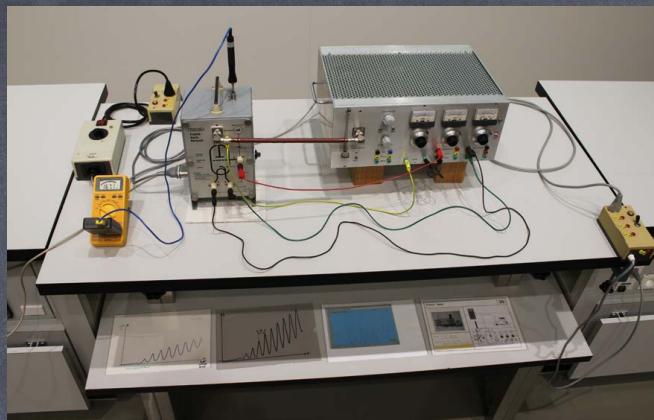


↑
sun

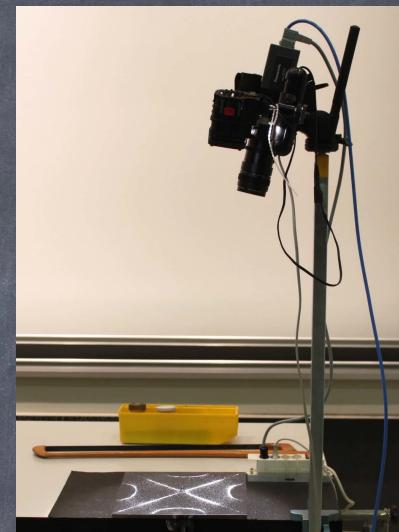
↑
distant galaxy



A6



A35



W22



Grundschwingung bei ca. 31Hz

A58



W23