I/ Review of Quantum mechanics

1) The crisis of classical mechanics

a) Blackbody radiation : (1901) planck (Nobel 1918)

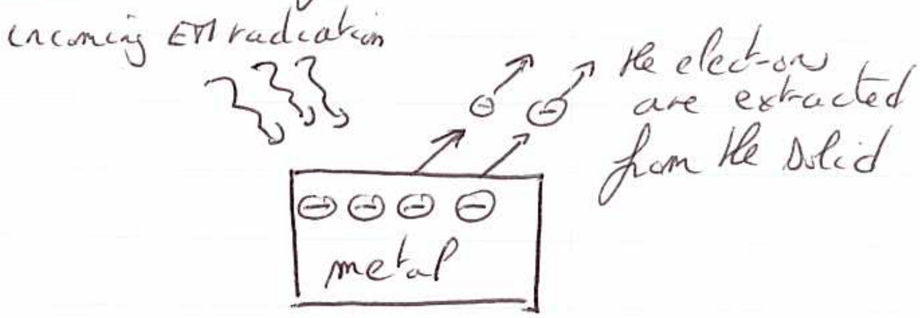
classical mechanics fails to explain the ~~spe~~ energy spectrum of a blackbody.

→ Electromagnetic energy could be emitted only in quantized form.

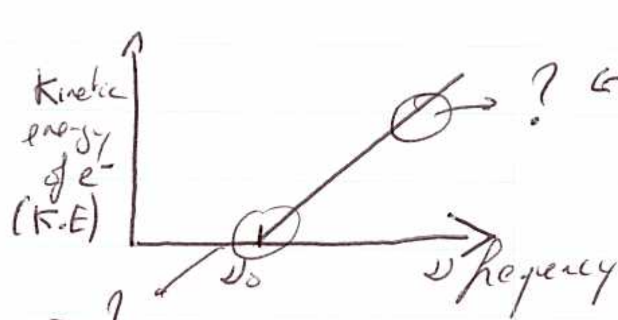
h: planck constant = 6.62618×10^{-34} J.s

$E = h\nu$ ν: frequency (s^{-1})

b) Photoelectric effect : hitting a solid with light



experiment



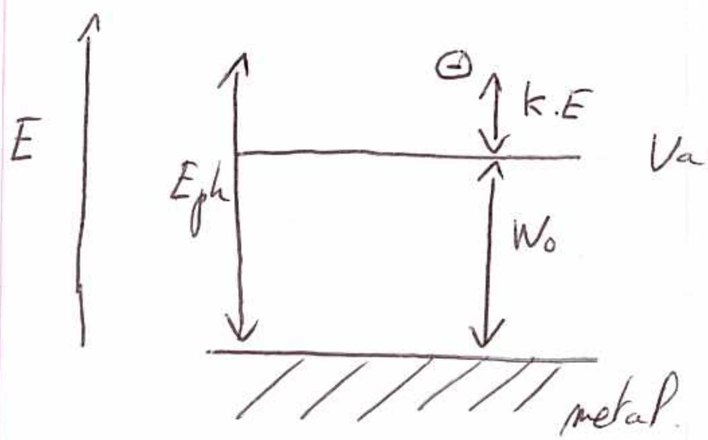
? ⟷ in EM theory, the energy should be proportional to the intensity of the light, it should not depend on the frequency ??

? ⟷ nothing happen below a certain threshold (?)

Einstein Explanation : (1905) (Nobel 1921).

$E = h\nu$ has a physical meaning, it is the energy of a 'light quanta', particle that is called "photon" ($E = E_{ph}$)

$\Rightarrow$ photoelectric effect can then be explained using inelastic collision.



So $E_{ph} = W_0 + KE$ where W_0 is the workfunction, the energy that is required by $1e^-$ to leave the metal. [potential barrier]

it comes $E_{ph} = h\nu = W_0 + KE$

for $K.E = 0 \Rightarrow h\nu_0 = W_0$

So $\boxed{KE = h(\nu - \nu_0)}$ that confirms the experimental data.

Q: Is light a wave or a particle?

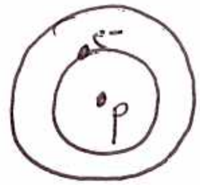
A: Both (!!)

(c) Hydrogen atom ($1e^-$, $1p$)

Experimental Results: spectrum of EM radiation from an excited hydrogen gas is discrete (?)

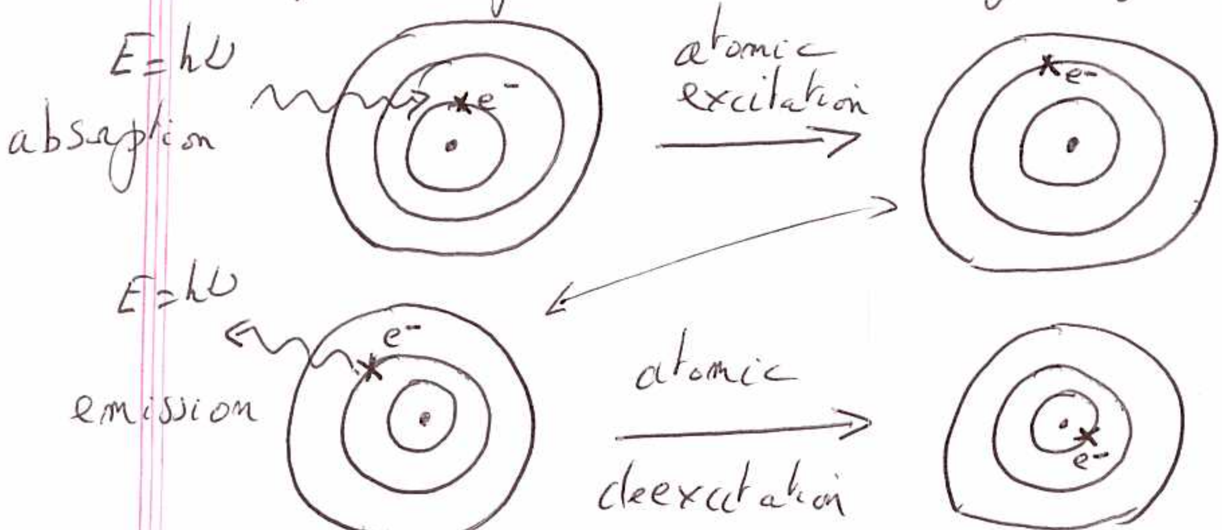
Bohr explanation (1913) (Nobel 1922).

starting point "Planetary model of the atom" of Rutherford



But now orbits are quantized! (if not $\bar{e}$ should fall into the nuclei)

e^- can make transition between the orbits within excitation and deexcitation processes resp. by absorption or emission of light (photon)



Bohr model provides the correct electron energies.

$$\boxed{E_n\,(eV) = -\frac{R_y}{n^2}}$$

$$R_y = \frac{m q^4}{(4\pi\varepsilon_0)^2\, 2\hbar^2}$$

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

R_y is a Rydberg.

$\hbar = \frac{h}{2\pi} = 1.054 \times 10^{-34}$ J.s

$1\,eV \longleftrightarrow 1.602 \times 10^{-19}\ (\equiv q)$ Joules we get $E_n(eV) = -\frac{13.6}{n^2}$

and a discrete spectrum.

Also for $n=1$, the Bohr radius is

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{mq^2} \simeq 0.529\,\mathring{A} \quad (1\,\mathring{A} \equiv 10^{-10}\,m)$$

$\Rightarrow$ the Bohr model leaves many unanswered questions and it does not provide a general framework for solving problem of this type.

2 Quantum mechanics = fundamental

a Generalization of duality wave-particle for all form of matter

De broglie (1924) (Nobel 1929).

$\Rightarrow$ it was an assumption that was not based on experiments

- For a given particle with momentum $\vec{p}$ and energy E we associate a plane wave with wave vector $\vec{k}$ and "angular" frequency $\omega (= 2\pi\nu)$

such as

$$\boxed{\vec{p} = \hbar \vec{k}} \qquad \boxed{E = \hbar \omega}$$

Also $\vec{p} = m\vec{v}$ (particle with mass m and velocity v)

$\|\vec{k}\| = \dfrac{2\pi}{\lambda}$ (λ is the wavelength)

duality wave-particle $\boxed{\lambda = \dfrac{h}{p}}$

we can write this wave under "a plane wave" form

$$\boxed{\Psi(\vec{r}, t) = A \exp i(\vec{k}.\vec{r} - \omega t)}$$

3) Schrödinger equation. (1926) [Nobel 1933]

starting point : classical description of the energy E

$$E = T + U \equiv \frac{p^2}{2m} + U$$

K.E potential energy.

Schrödinger converted this equation to a wave equation by defining a wave function Ψ such as.

$$\frac{p^2}{2m}\Psi + U\Psi = E\Psi$$

* if we suppose that $\Psi = A e^{i(\vec{k}.\vec{r} - \omega t)}$, we can show that

$$\vec{\nabla}\Psi = i\vec{k}\Psi \qquad \vec{\nabla} \equiv \begin{vmatrix} \partial/\partial x \\ \partial/\partial y \\ \partial/\partial z \end{vmatrix}$$

using $p = \hbar k$ $\Rightarrow$ $\vec{p}\Psi = -i\hbar\vec{\nabla}\Psi$

p becomes the operator $-i\hbar\nabla$

so $p^2\Psi = -\hbar^2\Delta\Psi$ $\left(\Delta \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$

* we can also show that $\frac{\partial\Psi}{\partial t} = -i\omega\Psi$

using $E = \hbar\omega$ $\Rightarrow$ $E\Psi = i\hbar\frac{\partial\Psi}{\partial t}$

E is the operator $i\hbar\frac{\partial}{\partial t}$

The Schrodinger equation finally becomes.

$$\boxed{H\,\Psi(\vec{r},t) = i\hbar\,\frac{\partial\Psi(\vec{r},t)}{\partial t}}$$

where H is the operator Hamiltonian.

$$\boxed{H = -\frac{\hbar^2}{2m}\Delta + U(\vec{r},t).}$$

- if now we suppose that H is time independent $[U(\vec{r},t) \equiv U(\vec{r})]$, we set $\Psi(\vec{r},t) = \varphi(\vec{r})e^{-i\omega t}$

and it comes the time independent Schrodinger equation

$$\boxed{H\varphi(\vec{r}) = E\,\varphi(\vec{r})}$$

* <u>Physical meaning of Ψ</u>

$P(\vec{r},t) = |\Psi(\vec{r},t)|^2 dr$ represent the probability density to find an "electron" in a volume dr at time t.

<u>Remarks</u>:

(i) for time independent problem

$$|\Psi(\vec{r},t)|^2 = |\varphi(\vec{r})|^2 \qquad (\underline{Rq}: |a|^2 = a\,a^*).$$

(ii) $\varphi(\vec{r}) = A\,e^{i\varphi}$ only $|A|^2$ (amplitude) has a physical meaning, φ (phase) does not have one.

→ However the phase relative to the superposition of waves may affect the amplitude [interference effect]

To obtain the energy spectrum of a system, In general, one must solve the following PDE (partial differential equation):

$$\boxed{-\frac{\hbar^2}{2m}\Delta \psi(\vec{r}) + U(\vec{r})\,\psi(\vec{r}) = E\,\psi(\vec{r})} \quad \text{for } \vec{r} \in \Omega$$

[one needs to know $U(\vec{r})$ and the boundary conditions of $\psi(\vec{r})$ on the frontier $\partial\Omega$]

- analytical solution exists if $U(\vec{r})$ has simple forms: (does not depend on r, depends linearly on r, r^2, $\frac{1}{r}$ ...)
- In realistic system, $U(\vec{r})$ has a very complex dependency on $\vec{r}$ $\Rightarrow$ one needs to resort to numerical methods.