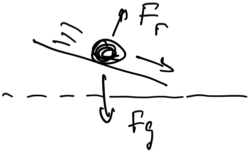
Translation: particle in a box approach

Classical

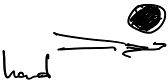
$X \rightarrow E, p$



$$F = ma = \sum F$$

But that is time-dependent. What about time independent, i.e. $\sum F = 0$

$$E_t = E_k + E_p$$



$V = const$

Quantum

Energy conservation (time-independent second Newton law)

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

How we can understand it

$\hat{H} = \hat{E}_k + \hat{E}_p$ we deal with operators.

Why? Very simple!

$$E_k = \frac{1}{2} m v^2 \Rightarrow [E_k] = \frac{[m]\cdot[v]^2\cdot[m]}{[m]} =$$

$$= \frac{[p]^2}{[m]}$$

But how we can extract p from Ψ?

de Broglie wavefunction!

$$\Psi(x,t) = \Psi_0 e^{i(kx-\omega t)}$$

$$\bar{k} = \frac{\bar{P}}{\hbar} \qquad \omega = \frac{E}{\hbar}$$

$$\Psi(x,t) = \Psi_0 e^{\frac{i}{\hbar}(px-Et)}$$

$$\frac{\partial\Psi}{\partial x} = \Psi_0 \frac{ip}{\hbar} e^{\frac{i}{\hbar}(px-Et)} = \frac{ip}{\hbar}\Psi$$

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}$$ – momentum operator

$$\Downarrow$$

$$\frac{\hat{p}\cdot\hat{p}}{2m} = -\frac{\hbar^2}{2m}\nabla^2 = -\frac{h^2}{8\pi^2 m}\nabla^2 = \hat{E}_k$$

$$\hat{H}\Psi = -\frac{h^2}{8\pi^2 m}\nabla^2\psi(x) + V(r)\Psi(x) = E\Psi(x)$$

The recipe is very simple then:

1) We need to determine $E_p = V(r)$ the particle is in.
2) Finalize SE (shrödinger equation)
3) Solve SE to find Ψ
4) Find E.

$$\boxed{V(r) \longrightarrow SE \rightarrow \Psi(r) \rightarrow E}$$

Let's take simple case — free particle

$V(r) = 0$ $\qquad$ $r \rightarrow x$ (one dimension)

$$-\frac{h^2}{8\pi m}\nabla^2\psi = E\psi$$

What will be the solution?

$$A\psi'' = B\psi \ ?$$

1) $\psi = e^{kx}$ $\quad \psi' = ke^{kx}$ $\quad \psi'' = k^2 e^{kx}$

But we need „$-$"B

2) $\psi = A\sin kx \Rightarrow \psi = -Ak^2\sin kx$

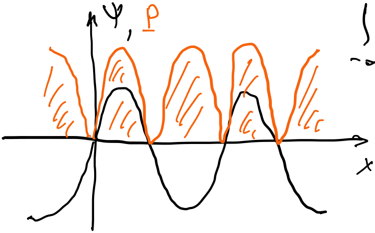
$$-\frac{h^2}{8\pi^2 m}\left(-k^2 A \sin kx\right) = EA\sin kx$$

$$\Downarrow$$

If you solve this, then

$$E = \frac{h^2}{8\pi^2 m} k^2$$

But there is a problem with it!

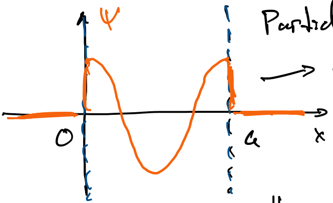


$$\int_{-\infty}^{+\infty} P(x)\,dx = 1$$

As long as $A>0$

this $\int P\,dx \to \infty$

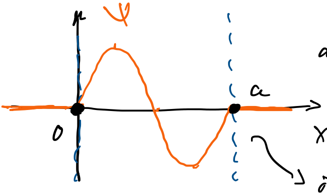
But we need to remember, particle cannot extend to ∞ $\Rightarrow$ we need to confine it.



Particle in a box!

→ cannot be as it is not continuous f

$$\Downarrow$$



allowed!

idea of a string

Effectively, we established border conditions

$$\psi(x)=\begin{cases} A\sin kx & 0\le x\le a \\ 0 & -''- \end{cases}$$

$$\psi(a)=0 \Rightarrow \sin ka=0 \Rightarrow ka=n\pi$$

So, what k's will be allowed in a box?

$$\boxed{k=\frac{n\pi}{a}}$$

The final solution then will be:

$$\psi_n(x)=\begin{cases} A\sin\frac{n\pi x}{a}, & 0\le x\le a \\ 0, & -''- \end{cases}$$

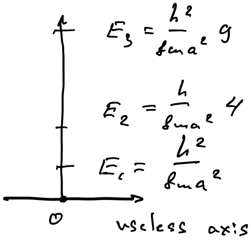
Important transition has been made:

when for free particle $\forall k$
for PIB n is descrete!

Solving SE with $\Psi(x)$:

$$E = \frac{h^2}{8\pi^2 m}\cdot\frac{n^2\pi^2}{a^2} = \frac{h^2}{8ma^2}n^2$$

descrete spectrum!



$$E_3 = \frac{h^2}{8ma^2}9$$

$$E_2 = \frac{h}{8ma^2}4 \qquad E_n \sim n^2$$

$$E_1 = \frac{h^2}{8ma^2}$$

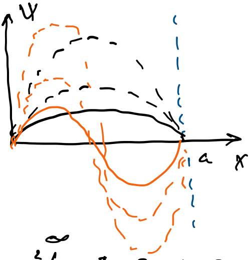
* * *

What about coefficient A?

$$\Psi_n = A\sin\frac{n\pi x}{a}$$

$$P = |\psi|^2$$

$$\int_{-\infty}^{+\infty} P(x)dx = 1$$



$$1 = A^2\int_{-\infty}^{\infty}\sin^2\frac{n\pi x}{a}dx =$$ changing $\frac{n\pi x}{a} = m$

$$dm = \frac{n\pi}{a}dx$$

$$= A^2\int_0^a \sin^2\frac{n\pi x}{a}dx = A^2\cdot\frac{a}{n\pi}\cdot\underbrace{\int_0^{n\pi}\sin^2 m\,dm}_{\frac{n\pi}{2}} = A^2\frac{a}{2}$$

$A = \sqrt{\frac{2}{a}}$ – normalization coefficient.

* * *

What about more realistic thing → 3D

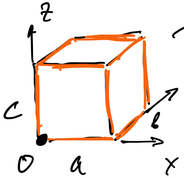
Again, similar recepie:

$$V(r) \to SE \to \Psi \to E$$

1) $V(r) = 0$

2) $-\frac{\hbar^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi = E\Psi$

3) $\Psi(x, y, z) = A \sin k_x x \sin k_y y \sin k_z z$



→ now actual box

The same idea of boundary conditions:

$$\begin{cases} \Psi(0) = \Psi(a) = 0 \\ \Psi(0) = \Psi(b) = 0 \\ \Psi(0) = \Psi(c) = 0 \end{cases}$$

$$\Psi = A \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{b} \sin\frac{n_z \pi z}{c}$$

4) SE

$$\frac{\partial^2}{\partial x^2}\psi = -\frac{n_x^2\pi^2}{a^2}\psi$$

$$\frac{\partial^2}{\partial y^2}\psi = -\frac{n_y^2\pi^2}{b^2}\psi$$

$$\frac{\partial^2}{\partial z} = -\frac{n_z^2\pi^2}{c^2}\psi$$

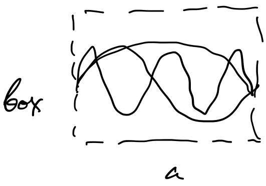
$$-\frac{h^2}{8\pi^2 m}\left(-\frac{n_x^2\pi^2}{a^2} - \frac{n_y^2\pi^2}{b^2} - \frac{n_z^2\pi^2}{c^2}\right)\psi = E\psi$$

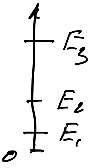
$$\Downarrow$$

non-cubic: $E_{n_x, n_y, n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$

cubic: $E_{cubic} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$

Let's summarize!





$E_n = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$

$E \sim n^2$

Numbers?

$E = h\nu \approx 6.63 \cdot 10^{-34}\, J \cdot s \cdot 10^{15}\, \frac{1}{s} \approx 10^{-19}\, J$

$kT = 1.38 \cdot 10^{-23} \cdot \frac{J}{K} \cdot 300\, K \sim 10^{-21}\, J$

$$E_1 = \frac{\left(6.63 \cdot 10^{-34}\, J \cdot s\right)^2}{8 \cdot 0.028\, \frac{kg}{mol} \cdot \frac{mol}{6 \cdot 10^{23}} \cdot \left(10^{-9}\, m\right)^2} \sim \frac{36 \cdot 10^{-68}}{3 \cdot 10^{-2} \cdot 10^{-23} \cdot 10^{-18}} \sim$$

$\sim 10^{-24}\, J$ — really tiny!