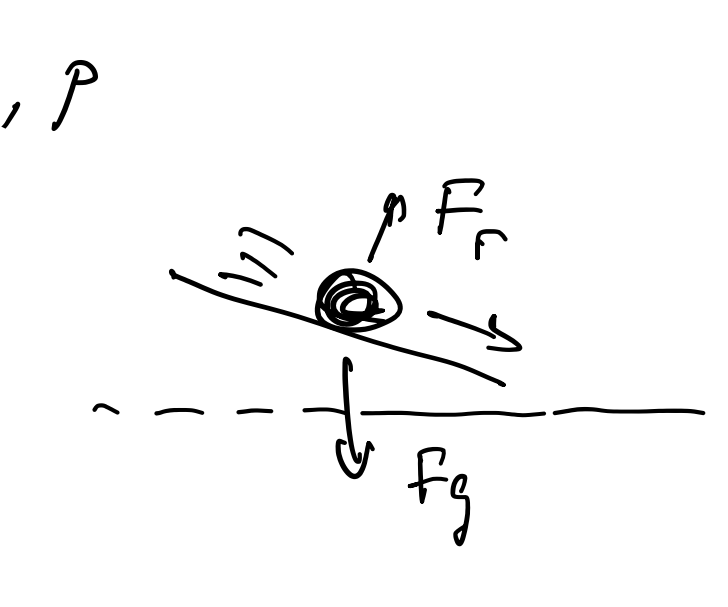
Wavefunction and quantum version of Newton second law of mechanics

Classical

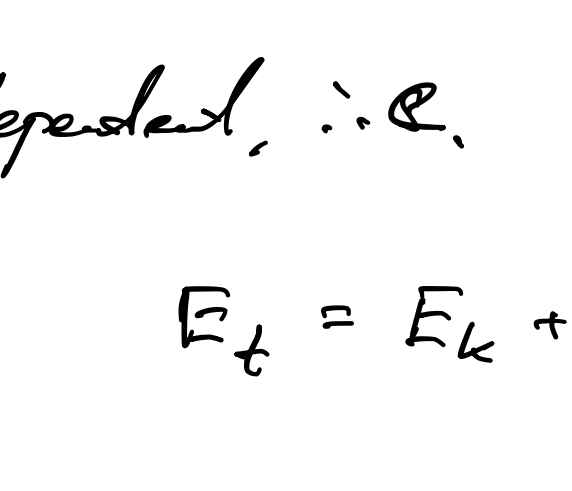
$x \to E, p$



$F = ma = \sum F$

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

$E_t = E_k + E_p$



$v = const$

Quantum

$x \to \Psi$

What is it wavefunction?

The units of $[h]$ allowed us to introduce λ:

$\lambda = \frac{h}{p}$ - de Broglie wavelength

m

particle — wave

E, p — ν, λ

Ψ - is a wave of probability

$\Psi(x) \to \Psi(\bar{r}) = \Psi(x, y, z)$

Physical meaning:

$P(x) = |\Psi(x)|^2 = \Psi^*(x)\Psi(x)$ ← complex conjugate

$P(a \leq x \leq b) = \int_a^b P(x)\,dx$

What mathematical form wavefunction can have?

Obviously harmonic monochromatic wave:

$$\Psi = \Psi_0 \sin(\bar{k}\bar{r} - \omega t) = \Psi_0 e^{i(kx - \omega t)}$$

Time independence:

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

Time-independent second Newton's law:

$$\boxed{\hat{H}\Psi = E\Psi}$$ Shrödinger equation

How we can understand it

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

Why? Very simple:

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

But how we can extract p from Ψ?

de Broglie wavefunction:

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

$\bar{k} = \frac{\bar{p}}{\hbar} \quad \omega = \frac{E}{\hbar}$

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

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

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

⇓

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

In a sense:

$\hat{E}_k\Psi + \hat{E}_p\Psi = E\Psi$

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

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.

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

① Free particle in 1D

Let's take simple case — free particle

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

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

What will be the solution?

We are looking for Ψ, that is

$A\Psi'' = -B\Psi$?

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

But we need $-B$

2) $\Psi = A\sin kx \Rightarrow \Psi'' = -k^2 \underbrace{A\sin kx}_{\Psi}$

If we to put this solution back:

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

⇓

If you solve this, then

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

So, what we found is

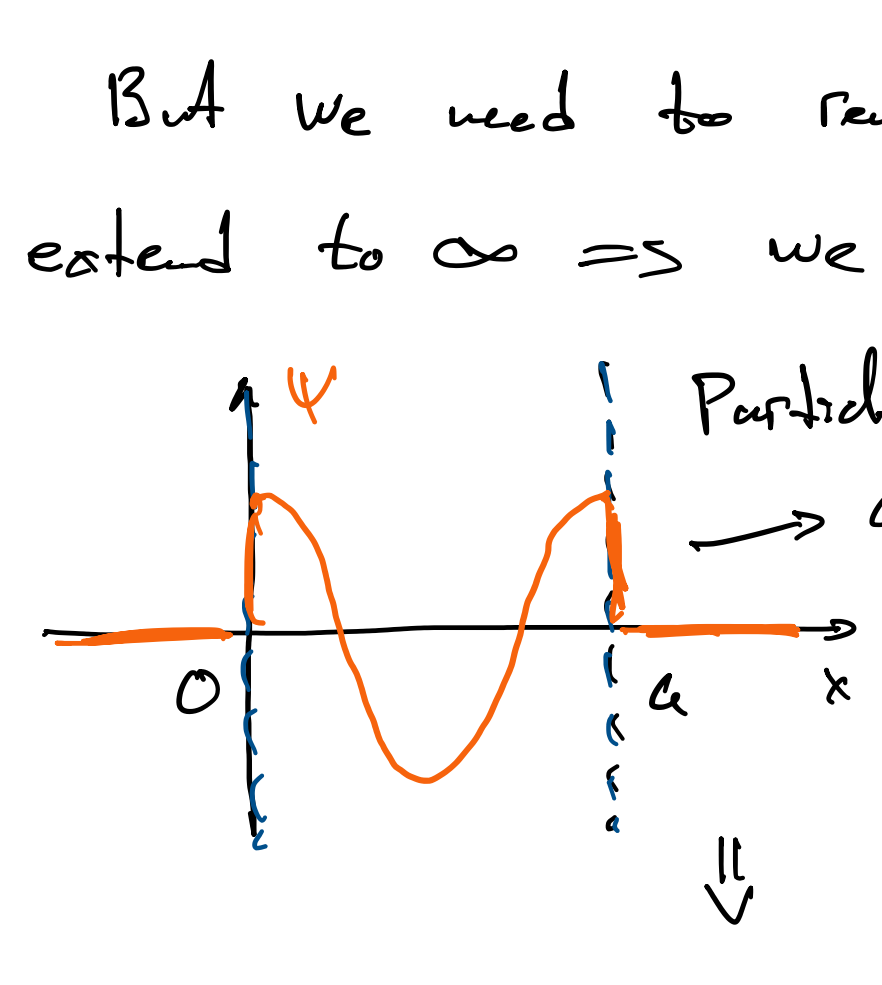
$\Psi = A\sin kx$ solves SE, with $E = \frac{h^2}{8\pi^2 m}k$

Other solutions will be:

$\Psi = A\cos kx$

$\Psi = Ae^{ikx}$

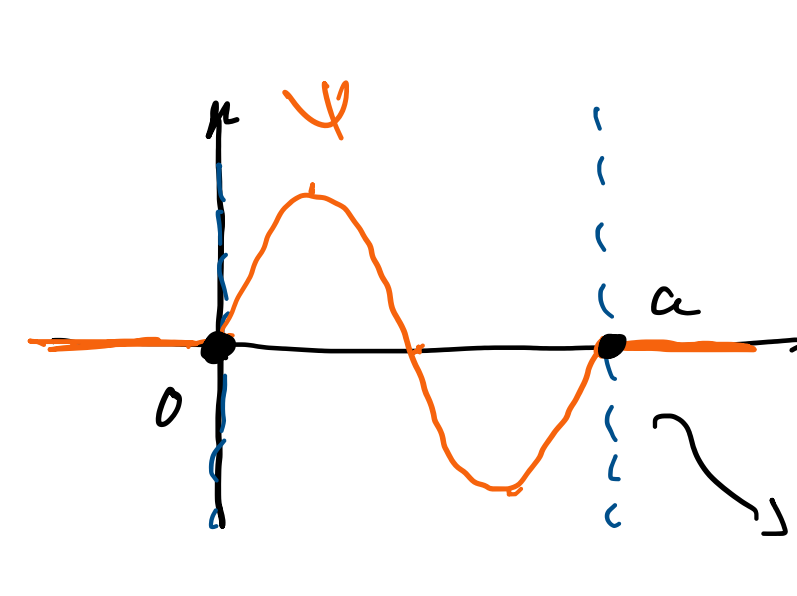
But there is a problem with it!



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

As long as $A > 0$ this $\int P\,dx \to \infty$!

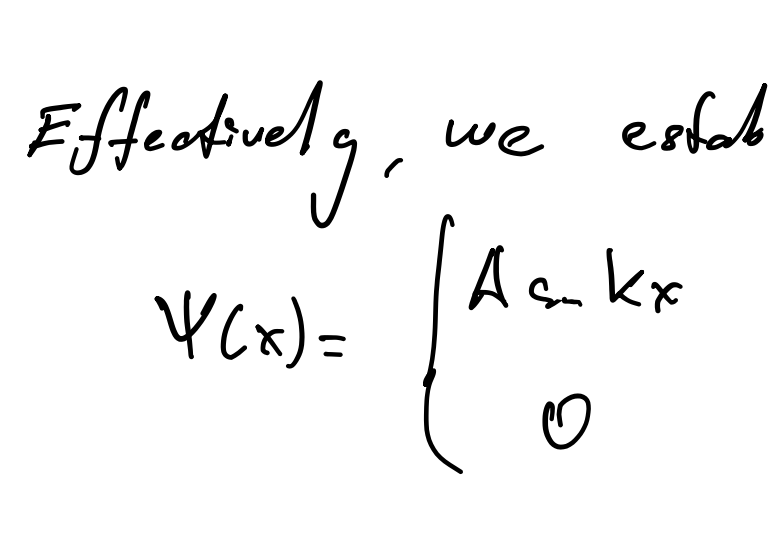
But we need to remember, particle cannot extend to ∞ ⇒ we need to confine it.



Particle in a box!

→ cannot be as it is not continuous function

⇓



allowed!

↳ idea of a string

Effectively, we established border conditions

$$\Psi(x) = \begin{cases} A\sin kx & 0 \leq x \leq a \\ 0 & -\text{"}- \end{cases}$$

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

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

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

The final solution then will be:

$$\Psi_n(x) = \begin{cases} A\sin\frac{n\pi x}{a}, & 0 \leq x \leq a \\ 0, & -\text{"}- \end{cases}$$

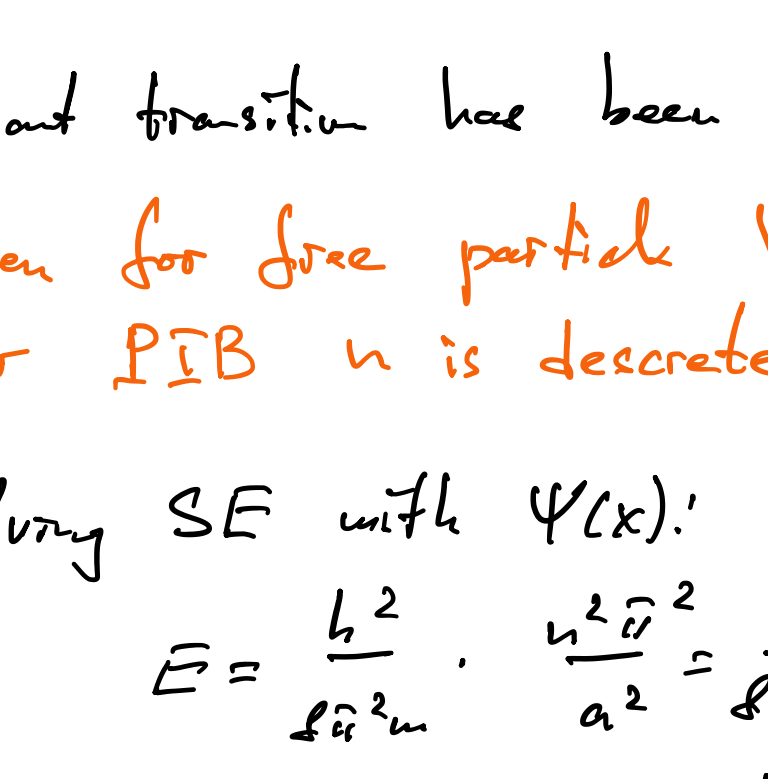
Important transition has been made:

when for free particle ∀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!

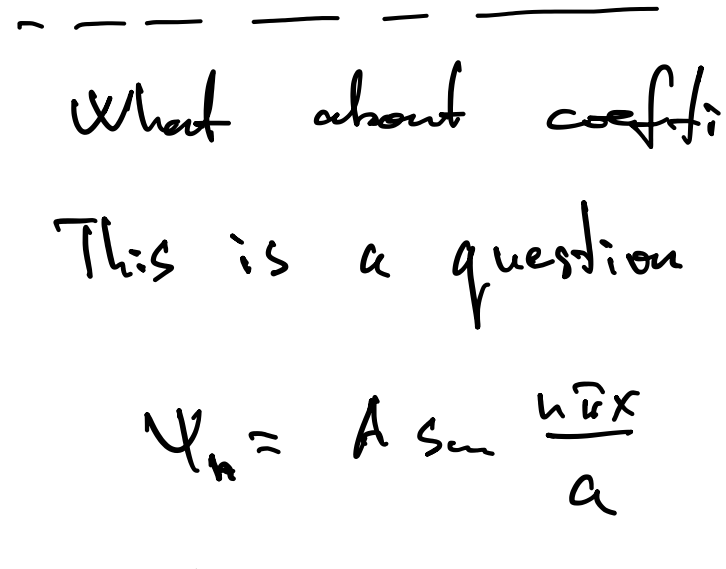


$E_n \sim n^2$

What about coefficient A?

This is a question of normalization

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



$P = |\Psi|^2$

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

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

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

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

$\underbrace{\qquad}_{\frac{n\pi}{2}}$

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

Final $\Psi = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}$

② Free particle in 3D

What about more realistic thing → 3D

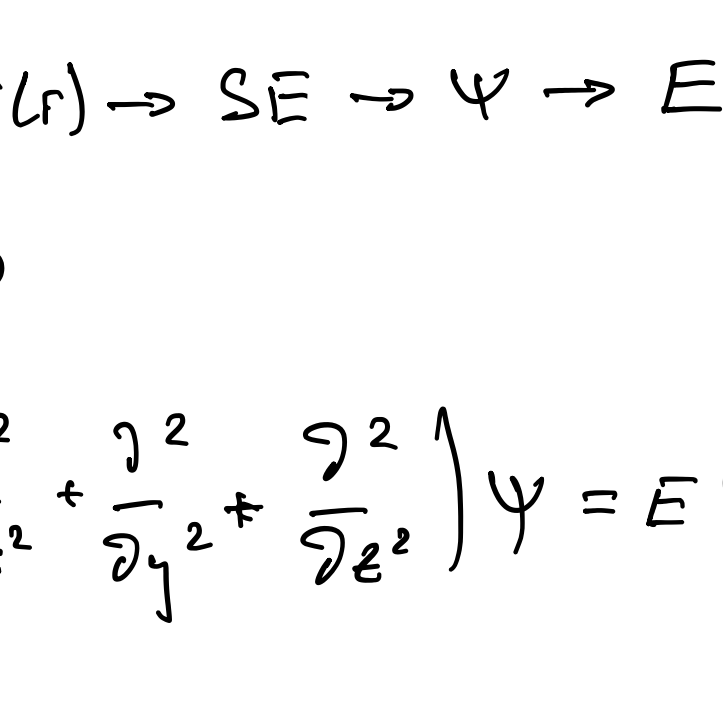
Again, similar recepie:

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

1) $V(r) = 0$

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

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

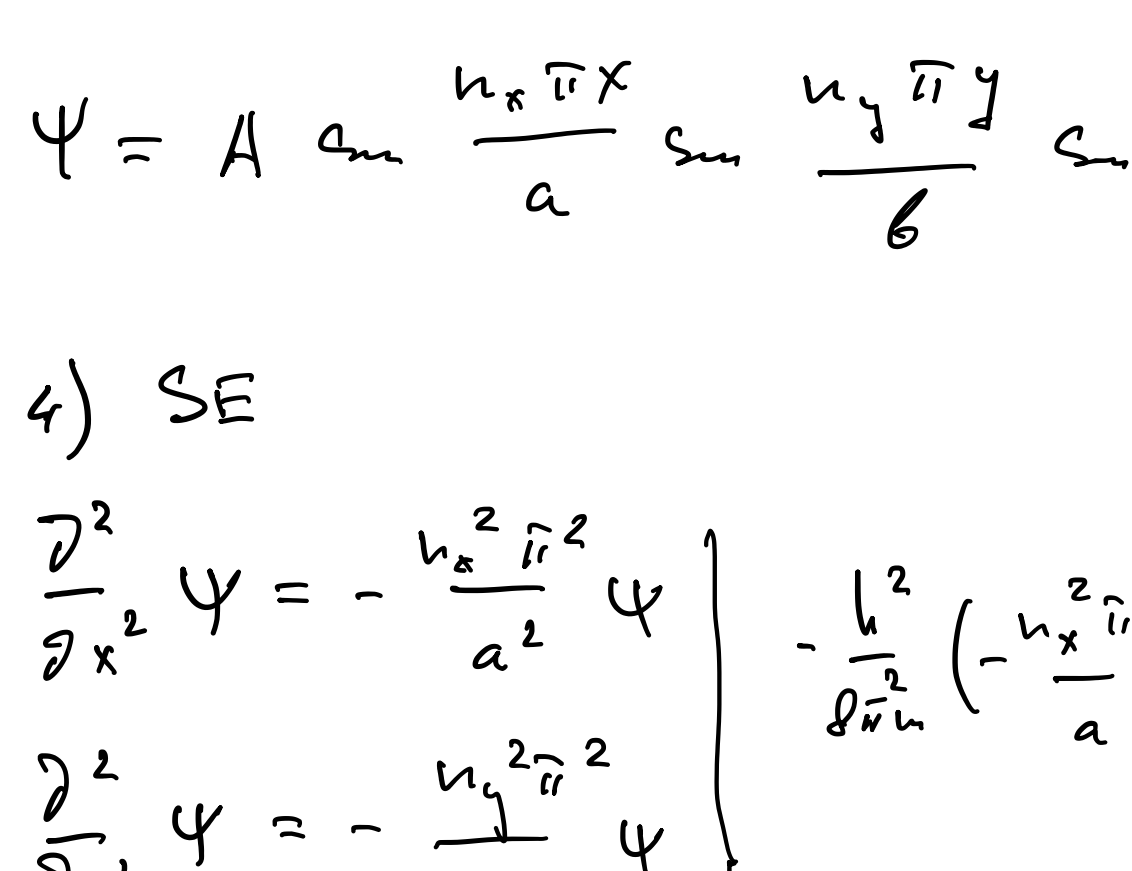
$$\left.\begin{aligned} \frac{\partial^2}{\partial x^2}\Psi &= -\frac{n_x^2\pi^2}{a^2}\Psi \\ \frac{\partial^2}{\partial y^2}\Psi &= -\frac{n_y^2\pi^2}{b^2}\Psi \\ \frac{\partial^2}{\partial z^2} &= -\frac{n_z^2\pi^2}{c^2}\Psi \end{aligned}\right| \quad -\frac{h^2}{8\pi^2 m}\left(-\frac{n_x^2\pi^2}{a^2} - \frac{n_y^2\pi^2}{b^2} - \frac{n_z^2\pi^2}{c^2}\right)\Psi = E\Psi$$

⇓

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

Let's summarize:



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

$E \sim n^2$

Numbers?

Visible photon:

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

Thermal energy:

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

Translational eigen state:

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

$\sim 10^{-24}\,J \to$ really tiny!

So, if visible photon is 600 nm translation will have resonance ~ 6 cm

Demonstration