Expectation values (mean values)

$$P(\underbrace{q_1, \ldots, q_f}_{q}, t) = \psi^*(q_1, \ldots, q_f, t) \times \psi(q_1, \ldots, q_f, t)$$

$$P(q,t) = \psi^*(q,t)\psi(q,t) = |\psi|^2$$

$$\int_\Gamma P(q,t)\,d\tau = 1 \checkmark$$

$$\int_\Gamma F(q,t)P(q,t)\,d\tau = \langle F \rangle \checkmark$$

$$\langle \hat{F} \rangle = ?$$

$$P(q,t) = \psi^* \psi$$

Assume that $\hat{F}$ is multiplicative (e.g., $\hat{x}$, $\hat{V}$, ...)

$$\hat{F}\psi = F\psi$$

$$\langle \hat{F} \rangle = \int_\Gamma F \psi^* \psi \, d\tau$$

$$= \int_\Gamma \psi^* F \psi \, d\tau$$

$$= \int_\Gamma \psi^* (\hat{F} \psi) \, d\tau$$

In 1D:
$$\langle \hat{x} \rangle = \int_{-\infty}^{\infty} \psi^* \hat{x} \psi \, dx$$
$$= \int_{-\infty}^{\infty} \psi^* x \psi \, dx$$

What about $\hat{p}_\ell = \frac{\hbar}{i} \frac{\partial}{\partial q_\ell}$, $\hat{T} = -\frac{\hbar^2}{2m} \nabla^2$, etc. ?

$\boxed{\text{operators that are not multiplicative}}$

$$\langle \hat{T} \rangle = -\frac{\hbar^2}{2m} \int_{\mathbb{R}^3} \psi^* \nabla^2 \psi \, d\tau$$

$$\langle \hat{p}_x \rangle = \frac{\hbar}{i} \int_{\mathbb{R}^3} \psi^* \frac{\partial \psi}{\partial x} d\tau$$

$$\langle \hat{F} \rangle = \int_{\Gamma} \psi^* \hat{F} \psi \, d\tau$$

We will prove (later) that this definition is equivalent to

probability that F equals ω_n

$$\langle \hat{F} \rangle = \sum_n P(F = \omega_n)\, \omega_n$$

where

eigenvalue

eigenstate

$$\hat{F} u_n = \omega_n u_n$$

$$\psi = \sum_n c_n u_n$$

$$P(F = \omega_n) = |c_n|^2$$

If ψ is not normalized,

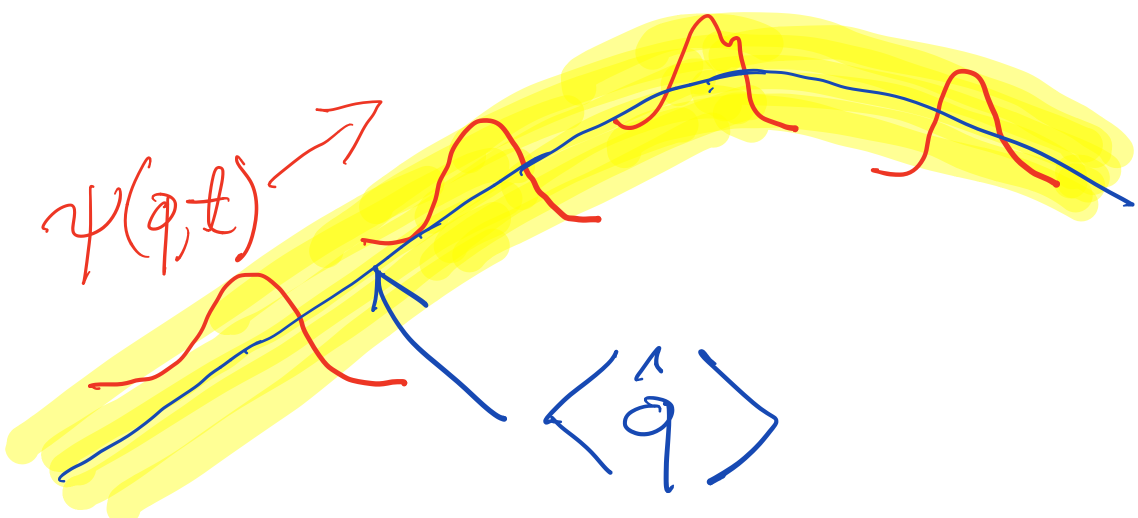
$$\langle \hat{F} \rangle = \frac{\int \psi^* \hat{F} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

$$\int \psi^* \psi \, d\tau = N$$

$$\psi' = \frac{\psi}{\sqrt{N}}$$

$$\langle \hat{F} \rangle = \int (\psi')^* \hat{F} \psi' \, d\tau$$

Ehrenfest theorems
(~1927)



Focus on one particle in 3D

$\psi(x,y,z,t)$.

In CM,

$$p_x = m\dot{x}$$

$$\frac{dx}{dt} = \frac{p_x}{m}$$

In QM,

$$\frac{d\langle \hat{x} \rangle}{dt} = \frac{1}{m}\langle \hat{p}_x \rangle$$

In CM,

$$\frac{dp_x}{dt} = F_x = -\frac{\partial V}{\partial x}$$

In QM,

$$\frac{d\langle \hat{p}_x \rangle}{dt} = -\left\langle \frac{\partial \hat{V}}{\partial x} \right\rangle$$

$$\frac{d}{dt}\langle \hat{p}_x \rangle = \frac{d}{dt}\int_{\mathbb{R}^3} \psi^* \hat{p}_x \psi \, d\tau$$

$$= -i\hbar \frac{d}{dt}\int_{\mathbb{R}^3} \psi^* \frac{\partial \psi}{\partial x} \, d\tau$$

$$= -i\hbar \int_{\mathbb{R}^3} \frac{\partial}{\partial t}\left(\psi^* \frac{\partial \psi}{\partial x}\right) d\tau$$

$$= -i\hbar \int_{\mathbb{R}^3} \psi^* \frac{\partial}{\partial x}\left(\frac{\partial \psi}{\partial t}\right) d\tau$$

$$- i\hbar \int_{\mathbb{R}^3} \frac{\partial \psi^*}{\partial t} \frac{\partial \psi}{\partial x} \, d\tau$$

$$i\hbar\frac{\partial\psi}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\psi+V\psi$$

$$-i\hbar\frac{\partial\psi^*}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\psi^*+V\psi^*$$

$(V=V^*)$

$$\frac{d\langle\hat{p}_x\rangle}{dt}=$$

$$=-\int_{\mathbb{R}^3}\psi^*\frac{\partial}{\partial x}\left(\underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi}_{1}+\underbrace{V\psi}_{3}\right)d\tau$$

$$+\int_{\mathbb{R}^3}\left(\underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi^*}_{2}+\underbrace{V\psi^*}_{4}\right)\frac{\partial\psi}{\partial x}d\tau$$

$$=-\frac{\hbar^2}{2m}\left[\underbrace{\int_{\mathbb{R}^3}(\nabla^2\psi^*)\frac{\partial\psi}{\partial x}\,d\tau}_{2}\right.$$

$$-\int_{\mathbb{R}^3} \psi^* \nabla^2 \left(\frac{\partial \psi}{\partial x}\right) d\tau \Big]$$

①

$$-\int_{\mathbb{R}^3} \Big[\psi^* \frac{\partial}{\partial x}(V\psi) - \quad ③$$

$$- \psi^* V \frac{\partial \psi}{\partial x} \Big] d\tau \quad ④$$

?

$$① \int_{\mathbb{R}^3} \psi^* \boxed{\nabla^2} \frac{\partial \psi}{\partial x} d\tau = $$

$$= \int_{\mathbb{R}^3} (\nabla^2 \psi^*) \frac{\partial \psi}{\partial x} d\tau$$

②

$$\frac{\partial \psi}{\partial x} = \varphi$$

$$\forall \ \psi, \varphi$$

$$\int_{\mathbb{R}^3} \psi^* \nabla^2 \varphi \, d\tau \overset{?}{=} \int_{\mathbb{R}^3} (\nabla^2 \psi^*) \varphi \, d\tau$$

$$\int_{\mathbb{R}^3} (\nabla^2 \psi^*) \varphi \, dx\,dy\,dz$$

$$= \int_{\mathbb{R}^3} \frac{\partial^2 \psi^*}{\partial x^2} \varphi \, dx\,dy\,dz$$

$$+ \int_{\mathbb{R}^3} \frac{\partial^2 \psi^*}{\partial y^2} \varphi \, dx\,dy\,dz$$

$$+\int_{\mathbb{R}^3} \frac{\partial^2 \psi^*}{\partial z^2}\varphi\, dx\,dy\,dz$$

$$\int_{\mathbb{R}^3} \frac{\partial^2 \psi^*}{\partial x^2}\varphi\, dx\,dy\,dz$$

$$= \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} \frac{\partial^2 \psi^*}{\partial x^2}\varphi\, dx$$

$$\int_{-\infty}^{\infty} \frac{\partial^2 \psi^*}{\partial x^2}\varphi\, dx \;\frac{\text{by}}{\text{parts}}$$

$$= \cancel{\frac{\partial \psi^*}{\partial x}\varphi\Big|_{x=-\infty}^{x=+\infty}} \quad 0$$

$$-\int_{-\infty}^{\infty} \frac{\partial \psi^*}{\partial x}\frac{\partial \varphi}{\partial x}\,dx$$

$$\underset{\text{parts}}{\overset{\text{by}}{=}} -\left(\cancel{\psi^* \frac{\partial \varphi}{\partial x}\Big|_{x=-\infty}^{x=+\infty}}^{\,0} - \int_{-\infty}^{\infty} \psi^* \frac{\partial^2 \varphi}{\partial x^2}\,dx \right)$$

$$\int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} \frac{\partial^2 \psi^*}{\partial x^2}\varphi\,dx$$

$$= \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} \psi^* \frac{\partial^2 \varphi}{\partial x^2}\,dx$$

$$\int_{\mathbb{R}^3} \frac{\partial^2 \psi^*}{\partial x^2} \varphi \, d\tau$$

$$= \int_{\mathbb{R}^3} \psi^* \frac{\partial^2 \varphi}{\partial x^2} \, d\tau$$

$$\int_{\mathbb{R}^3} (\nabla^2 \psi^*) \varphi \, d\tau$$

$$= \int_{\mathbb{R}^3} \psi^* \nabla^2 \varphi \, d\tau$$

∇^2 - hermition

$$\frac{d\langle \hat{p}_x \rangle}{dt} =$$

$$= -\int_{\mathbb{R}^3} \psi^* \left[\frac{\partial}{\partial x}(V\psi) - V\frac{\partial \psi}{\partial x} \right] d\tau$$

$$= -\int_{\mathbb{R}^3} \psi^* \left[\frac{\partial V}{\partial x}\psi + \cancel{V\frac{\partial \psi}{\partial x}} - \cancel{V\frac{\partial \psi}{\partial x}} \right] d\tau$$

$$= -\underbrace{\int_{\mathbb{R}^3} \psi^* \frac{\partial V}{\partial x} \psi \, d\tau}_{\left\langle \frac{\partial \hat{V}}{\partial x} \right\rangle}$$

$$\frac{d\langle \hat{p}_x \rangle}{dt} = -\left\langle \frac{\partial \hat{V}}{\partial x} \right\rangle$$

In CM,

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \{F, H\}$$

In QM

$$\frac{d\langle \hat{F} \rangle}{dt} = \left\langle \frac{\partial \hat{F}}{\partial t} \right\rangle + \frac{1}{i\hbar} \langle [\hat{F}, \hat{H}] \rangle$$

Ex.:

$$\hat{F} = \hat{p}_x, \quad \hat{H} = \frac{\hat{p}_x^2}{2m} + \hat{V}(x)$$

$$\frac{d}{dt}\langle \hat{p}_x \rangle = \cancel{\left\langle \frac{\partial \hat{p}_x}{\partial t} \right\rangle} \to 0$$

$$+ \frac{1}{i\hbar} \langle \underbrace{[\hat{p}_x, \hat{H}]}_{= -i\hbar \frac{\partial \hat{V}}{\partial x}} \rangle$$

Boundary and continuity conditions, bound & unbound (scattering) states

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi$$

- 1st-order PDE with respect to t
- 2nd-order PDE with respect to q's.

(initial conditions)

→ we must know $\psi(q, t_0)$ for some t_0 and all q's.

(boundary conditions)

→ we must know $\psi(q', t)$ and $\frac{\partial \psi}{\partial q_i}(q', t)$ for all values of t for $q' \in A$ → boundary

ψ and $\dfrac{\partial \psi}{\partial q_\ell}$ (or $\nabla \psi$) are continuous, finite, single-valued

continuity conditions

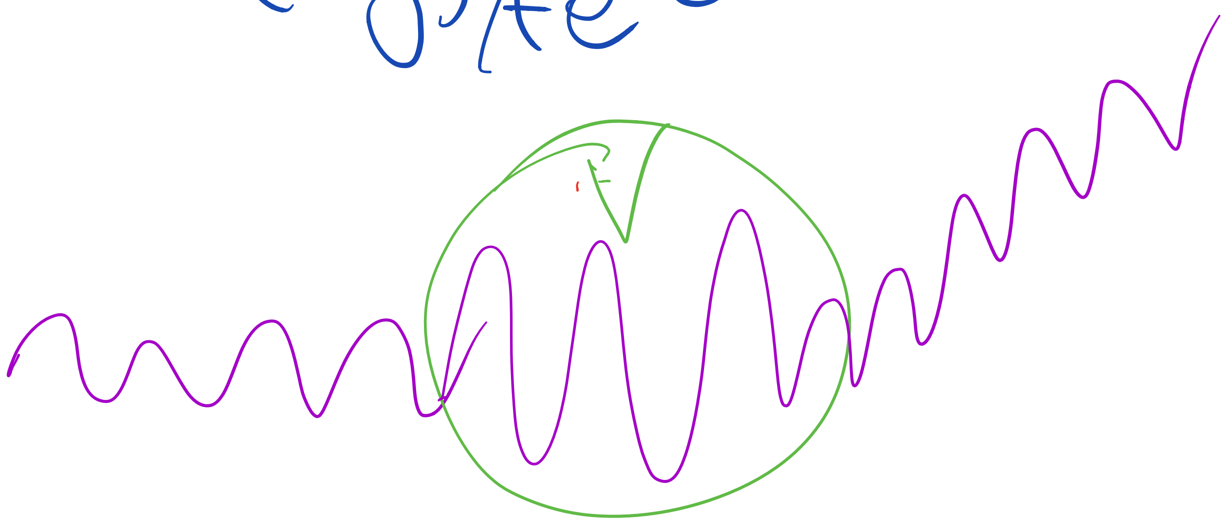
Two types of physical boundary conditions:

- ψ is such $\int |\psi|^2 d\tau < \infty$

($\psi \longrightarrow 0$ at large distances)

$\longrightarrow$ BOUND STATES (localized)

- ψ is such that it remains finite at large distances (e.g., $Ae^{i(\vec{k}\cdot\vec{r}-\omega t)}$)



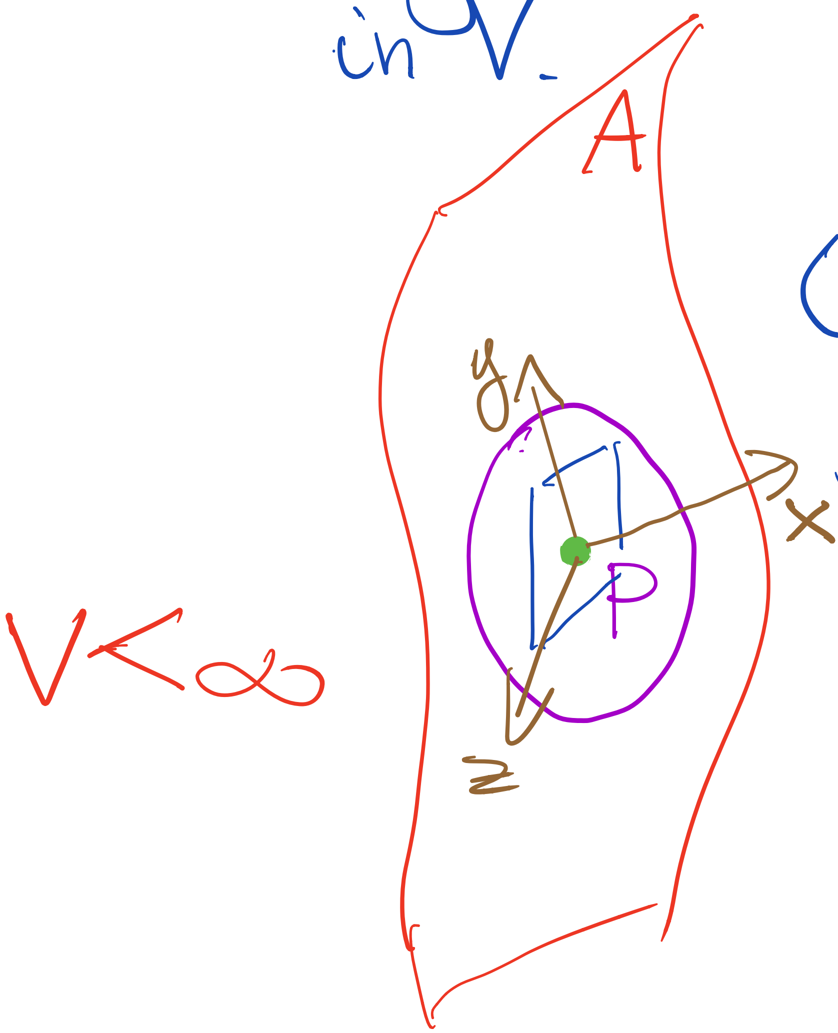
UNBOUND STATES (scattering)

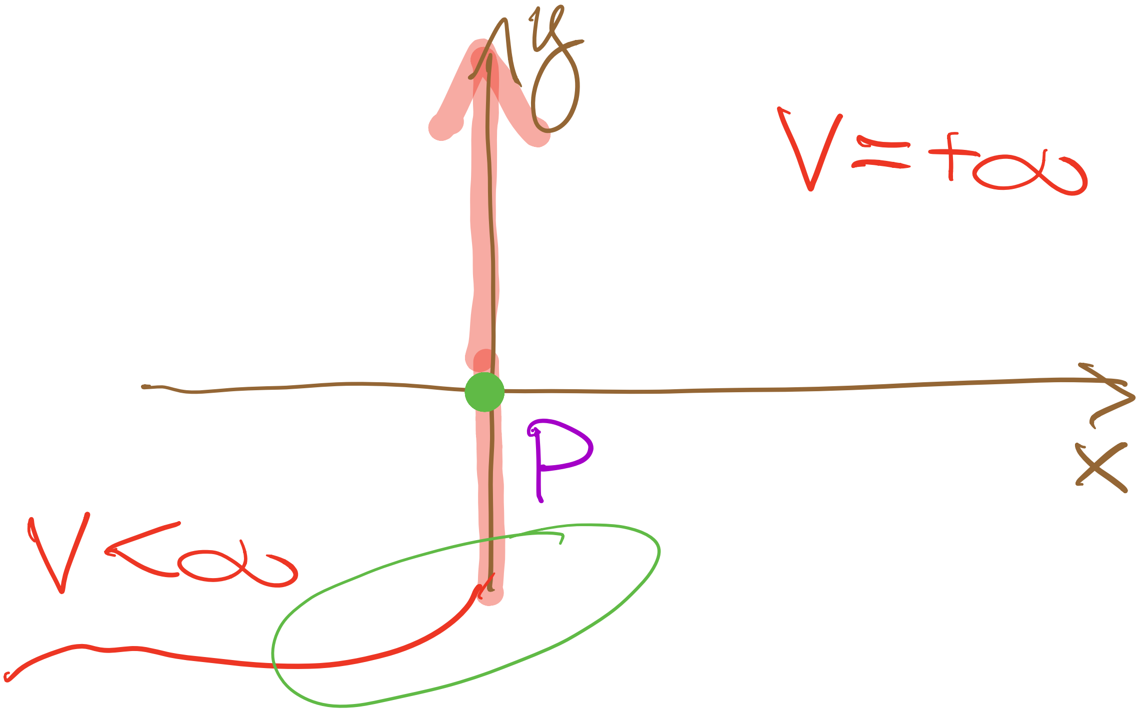
- ~~ψ is such that~~ (unphysical) ~~$|\psi| \longrightarrow \infty$ at large distances~~

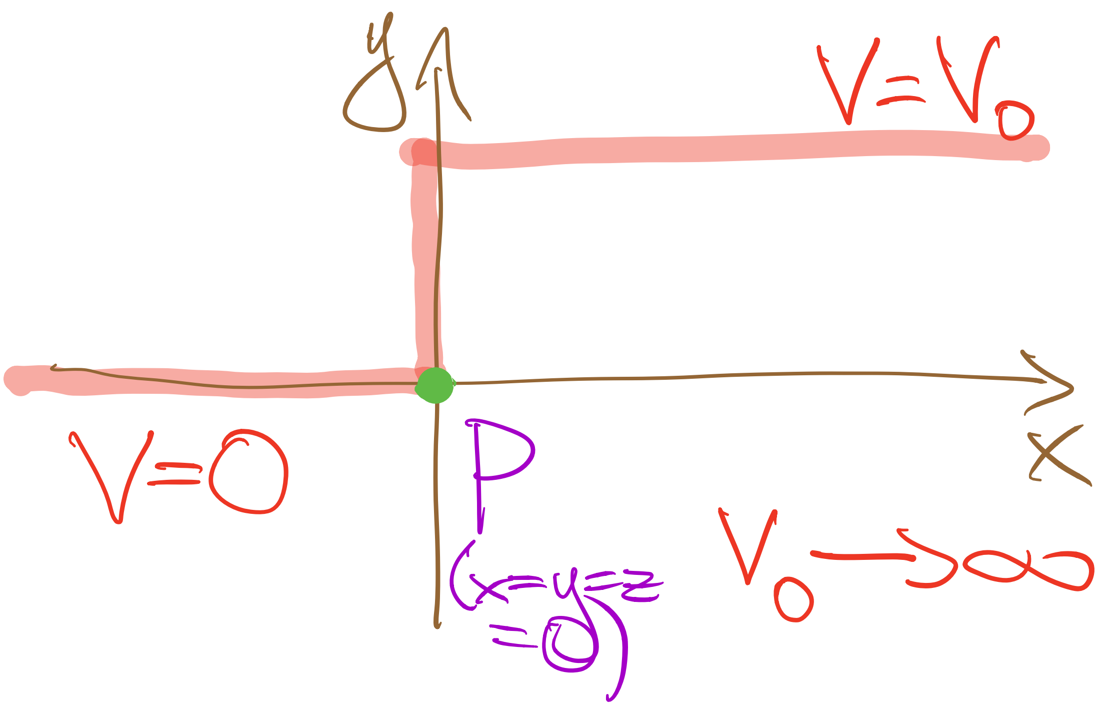
Relationship between the nature of ψ (bound / scattering) and V

I. Infinite discontinuity in V.

$V = +\infty$ (classically forbidden)







$$Hu = Eu$$

$$u = u(x, y, z)$$

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dx^2} + V(x)u = Eu$$

$$V(x) = 0 \text{ for } x < 0$$

$$V(x) = V_0 \text{ for } x > 0$$

Assume that

$E < V_0$ (because we will study $V_0 \to \infty$)

$x<0$

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dx^2} = Eu$$

$$u(x) = A\sin\alpha x + B\cos\alpha x$$

$$\alpha = \sqrt{\frac{2mE}{\hbar^2}}$$

$x>0$

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dx^2} + V_0 u = Eu$$

$$u(x) = Ce^{-\beta x} + De^{\beta x}$$

$$\beta = \sqrt{\frac{2m(V_0-E)}{\hbar^2}} \quad (V_0-E_0 > 0)$$

1. $u(x)$ must be finite for $x \to +\infty$

$\Rightarrow \underline{D = 0}$.

2. u must be continuous at $x=0$

$B = C + D = C$

$\underline{B = C}$

3. $\frac{du}{dx}$ must be continuous at $x=0$

$x<0 \quad \frac{du}{dx} = \alpha A \cos \alpha x$
$\qquad - \alpha B \sin \alpha x$

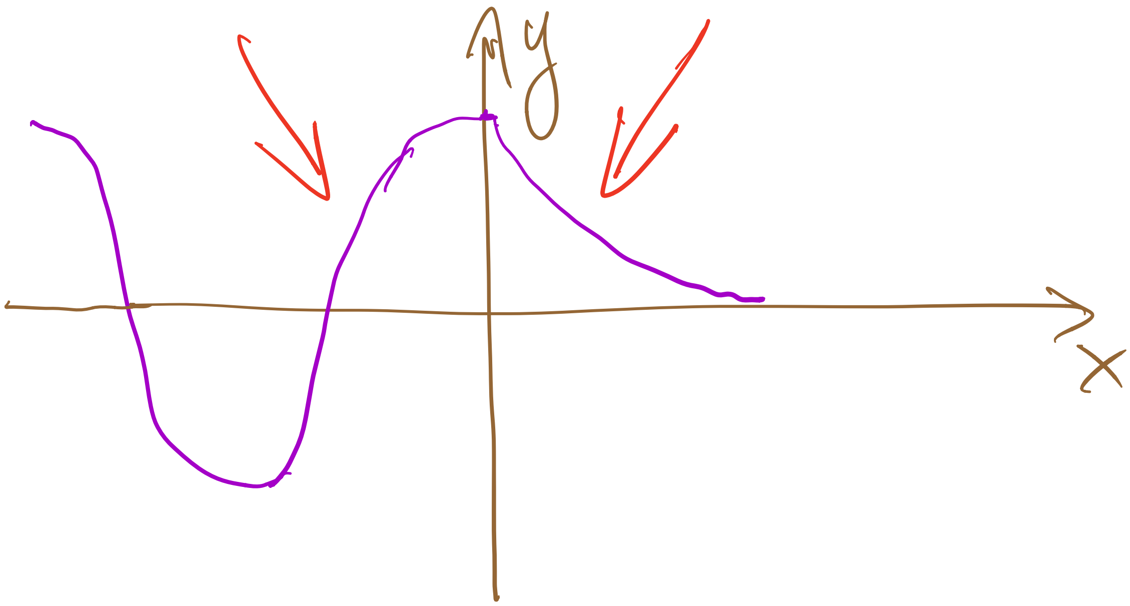
$x>0 \quad \frac{du}{dx} = -\beta C e^{-\beta x}$

At $x=0$

$$\underline{\alpha A = -\beta C}$$

$$u(x) = \begin{cases} x<0 & A \sin \alpha x + B \cos \alpha x \\ x \geq 0 & B e^{-\beta x} \end{cases}$$

$$\underline{\alpha A = -\beta B}$$



$V_0 \to \infty$

$\Rightarrow \beta \to \infty$

$\Rightarrow B = 0$

$\boxed{\alpha A = -\beta B}$

$\Rightarrow u(x) = 0$ for $x \geq 0$

In the region of $V=\infty$,

$u=0$.