Note: The existence of an unavoidable non-zero uncertainty $\Delta v(0)$ of the initial velocity is a purely quantum mechanical feature; its effect on the position uncertainty at large times can be understood classically.

For a macroscopic particle of mass, say, $m = 1g$, with an initial uncertainty of the position of its center of mass of order 10^{-13} cm (i.e. the size of a proton – the atomic nucleus of hydrogen) we find for the initial uncertainty of the velocity

$$\Delta v(0) \simeq \frac{\hbar}{\sqrt{2}\, m \Delta} \approx 10^{-16} \frac{m}{s}$$

For the position uncertainty to grow to 1 micron (still pretty small and only visible under a microscope) it would take 300 years! This is one of the reasons why Newtonian physics worked so well for almost 3 centuries, and why quantum mechanics was not discovered earlier.

Particle in a potential $V(x)$

$$\hat{H} = \frac{\hat{P}^2}{2m} + V(\hat{X})$$

$$\hat{H}|E\rangle = E|E\rangle \longrightarrow \int_{-\infty}^{\infty} \langle x | \frac{\hat{P}^2}{2m} + V(\hat{X}) | x' \rangle \langle x' | E \rangle = E \langle x | E \rangle$$

$$\Longrightarrow -\frac{\hbar^2}{2m} \frac{d^2 \psi_E(x)}{dx^2} + V(x)\psi_E(x) = E\psi_E(x)$$

$$\Rightarrow \boxed{\psi_E'' = -\frac{2m(E - V(x))}{\hbar^2} \psi_E}$$

If $V(x)$ is continuous, then ψ'' is continuous, and thus also (by integration) $\psi'(x)$ and $\psi(x)$.
But if $V(x)$ is discontinuous, then ψ'' jumps at the discontinuity. Still, ψ' will be continuous, as will $\psi(x)$. If $V(x)$ jumps by an infinite amount (infinitely high walls, δ-fct. potential), ψ' can jump, too (by a finite amount), and only $\psi(x)$ itself remains continuous:

$$\frac{\psi'(x+\Delta x)-\psi'(x)}{\Delta x} = -\frac{2m}{\hbar^2}\left[E-V(x)\right] \Rightarrow \psi'(x+\Delta x) = \psi'(x) + \frac{2m}{\hbar^2}V(x)\Delta x - \frac{2mE}{\hbar^2}\Delta x$$

$$= \psi'(x) + \frac{2m}{\hbar^2}\int_x^{x+\Delta x} dx'\, V(x') - \frac{2mE}{\hbar^2}\int_x^{x+\Delta x} dx'$$

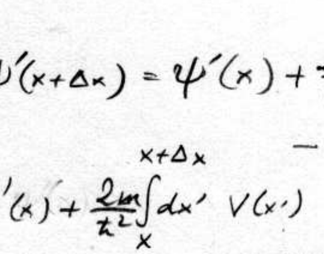
$$\xrightarrow{\Delta x\to 0} \psi'(x) + \lim_{\Delta x\to 0}\frac{2m}{\hbar^2}\int_x^{x+\Delta x} dx'\, V(x')$$

If $V(x') = V_0\,\delta(x'-x)$, or $V(x') = V_0\,\theta(x'-x_0)$ with $V_0\to\infty$, then $\psi'(x+\Delta x)$ and $\psi'(x)$ can differ.

5.2 Particle in a box

(give Exercise 5.2.6, square well potential, as homework)

Consider $V(x) = \begin{cases} 0 & |x| \le L/2 \\ \infty & |x| > L/2 \end{cases}$



The Schrödinger equation for this potential reads, in x-representation:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0$$

We solve this separately in regions I, II, and III, requiring continuity of ψ at the walls.

Start with region I, and let's begin by taking the potential finite, $V_0 > E$, there, taking $V_0 \to \infty$ later:

$$\frac{d^2\psi_I}{dx^2} = \frac{2m}{\hbar^2}(V_0 - E)\psi_I \quad \Rightarrow \quad \psi_I = Ae^{-\kappa x} + Be^{+\kappa x}$$

where $\kappa = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$ is real for $E < V_0$.

For $x \to -\infty$, $Ae^{-\kappa x}$ blows up. For ψ to be normalizable, ψ_I cannot blow up exponentially as $x \to -\infty$. $\Rightarrow$ $\boxed{A = 0}$

$$\Rightarrow \quad \psi_I(x) = Be^{\sqrt{\frac{2m}{\hbar^2}(V_0 - E)}\cdot x} \xrightarrow[\substack{V_0 \to \infty \\ x < -\frac{L}{2}}]{} 0$$

So for the box with infinitely high walls, ψ_I (and similarly ψ_{III}) vanish, $\boxed{\psi_I = \psi_{III} = 0}$

In region II, $V = 0$, so the solutions are those for a free particle:

$$\psi_{II}(x) = Ae^{i\sqrt{2mE}\,x/\hbar} + Be^{-i\sqrt{2mE}\,x/\hbar} = Ae^{ikx} + Be^{-ikx}$$

$$\left(k = \sqrt{2mE}/\hbar = p/\hbar\right)$$

Now, ψ has to be continuous, i.e. ψ_{II} must match ψ_I and ψ_{III} at $x = \pm L/2$. This boundary condition selects specific allowed values for E, turning the continuous energy spectrum of an unconfined free particle into a discrete spectrum:

Boundary conditions: $\psi_{II}(-\frac{L}{2}) = \psi_I(-\frac{L}{2}) = 0$

$$\psi_{II}(\tfrac{L}{2}) = \psi_{III}(\tfrac{L}{2}) = 0$$

$$\Rightarrow \begin{rcases} A e^{-ikL/2} + B e^{ikL/2} = 0 \\ A e^{ikL/2} + B e^{-ikL/2} = 0 \end{rcases} \underbrace{\begin{pmatrix} e^{-ikL/2} & e^{ikL/2} \\ e^{ikL/2} & e^{-ikL/2} \end{pmatrix}}_{M} \begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\Rightarrow \det M = e^{-ikL} - e^{ikL} = 0$$

$$\Rightarrow 2i \sin(kL) = 0 \quad \Rightarrow \boxed{k_n = \frac{n\pi}{L}, \; n = 0, \pm 1, \pm 2, \ldots}$$

$\Rightarrow$ energy quantization as a result of the boundary conditions!

Plugging the eigenvalues back into the boundary condition, we get

$$A_n e^{-in\pi/2} + B_n e^{+in\pi/2} = 0$$

(the other B.C gives the same!)

$$\Rightarrow \boxed{A_n = -e^{in\pi} B_n = (-1)^{n+1} B_n}$$

$\Rightarrow$ two sets of solutions (after normalization $\int |\psi|^2 dx = 1$)

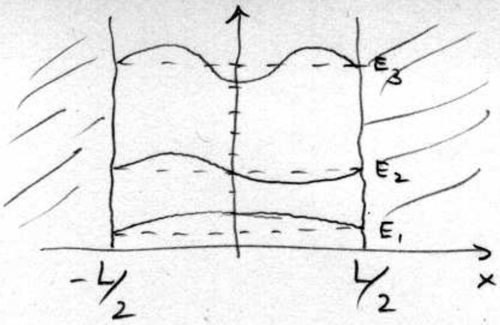
$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) & n \text{ even}, n \neq 0 \\ \sqrt{\frac{2}{L}} \cos\left(\frac{n\pi x}{L}\right) & n \text{ odd} \end{cases}$$

Since $\psi_{-n}(x) = (-1)^{n+1} \psi_n(x)$, negative n provide no independent solutions (they differ only by a constant phase factor)

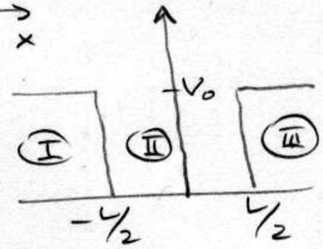
$$\Rightarrow \psi_n(x) = \begin{cases} \sqrt{\frac{2}{L}} \cos\left(n\pi \frac{x}{L}\right) & n = 1, 3, 5, \ldots \\ \sqrt{\frac{2}{L}} \sin\left(n\pi \frac{x}{L}\right) & n = 2, 4, 6, \ldots \end{cases}$$

$$\Rightarrow \boxed{E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2} n^2}$$

energy eigenvalues increase $\sim n^2$!



If V_0 is finite,



, the solutions do not vanish in regions (I) and (III), but decay exponentially there. In this case, the jump of V is finite at $x = \pm L/2$, so not only $\psi(x)$, but also $\frac{d\psi}{dx}(x)$ must be continuous.

In this case, we have 4 nonzero coefficients,

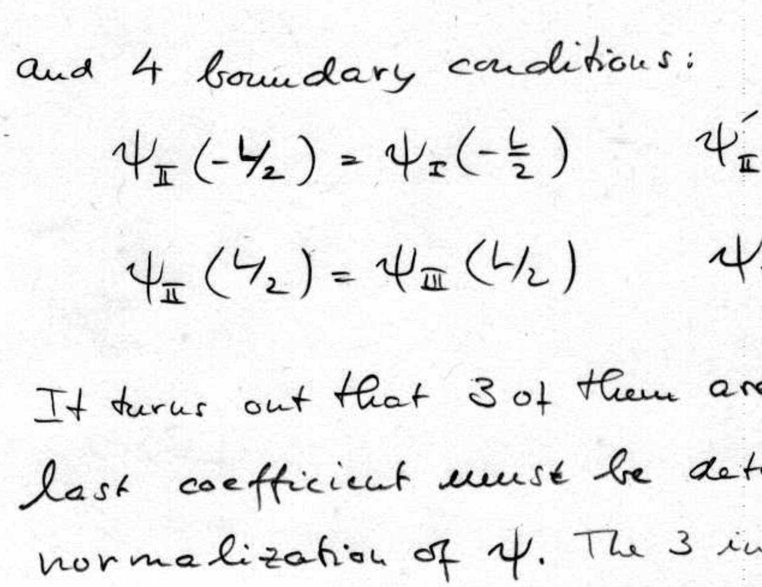
$$B_{I},\ A_{II},\ B_{II},\ A_{III}$$

and 4 boundary conditions:

$$\psi_{II}(-L/2) = \psi_{I}(-\tfrac{L}{2}) \qquad \psi'_{II}(-\tfrac{L}{2}) = \psi'_{I}(-\tfrac{L}{2})$$

$$\psi_{II}(L/2) = \psi_{III}(L/2) \qquad \psi'_{II}(L/2) = \psi'_{III}(L/2)$$

It turns out that 3 of them are independent, the last coefficient must be determined from the normalization of ψ. The 3 independent boundary conditions will select the allowed energy eigenvalues:



unless E is very carefully chosen, the matching at $x = \frac{L}{2}$ leads to both A_{III} and B_{III} non-zero $\longrightarrow$ ψ not normalizable!

So why is the lowest energy eigenvalue $E_1 \neq 0$?

Let's look at the expectation value of $\hat{H}$ in any of the eigenstates:

$$\langle \hat{H} \rangle = \frac{\langle \hat{P}^2 \rangle}{2m} + \langle V(\hat{X}) \rangle$$

Any bound state has $\langle \hat{P} \rangle = 0$ since for $\langle \hat{P} \rangle \neq 0$ the particle must drift on average either right or left, so it would eventually escape to infinity and wouldn't be bound.

So we can write

$$\langle \hat{H} \rangle = \frac{\langle (\hat{P} - \langle \hat{P} \rangle)^2 \rangle}{2m} + \langle \hat{V} \rangle = \frac{(\Delta P)^2}{2m} + \langle \hat{V} \rangle$$

If we use the uncertainty relation (see chapter 9 for proof)

$$\Delta P \cdot \Delta X \geq \hbar/2$$

this gives

$$\langle \hat{H} \rangle \geq \frac{\hbar^2}{8m(\Delta X)^2} + \langle \hat{V} \rangle$$

In our case x is strictly constrained to $|x| \leq L/2$ where

$$\hat{V} = 0 \implies \Delta X \leq \frac{L}{2} \implies \boxed{\langle \hat{H} \rangle \geq \frac{\hbar^2}{2mL^2}}$$

In an energy eigenstate $\langle H \rangle_n = E_n \implies \boxed{E_n \geq \frac{\hbar^2}{2mL^2}}$

So E_n can not be zero. In fact, E_1 is π^2 times this lower limit, showing that in the ground state ΔX is smaller than $\frac{L}{2}$.

The propagator for a particle in a box:

$$\hat{\mathcal{U}}(t) = \sum_{n=1}^{\infty} |n\rangle\langle n| e^{-i\frac{\hbar^2 n^2 \pi^2}{2mL^2} t/\hbar} = \hat{\mathcal{U}}(t,0)$$

In the x-basis:

$$\langle x|\hat{\mathcal{U}}(t,0)|x'\rangle = \mathcal{U}(x,t;x',0) = \sum_{n=1}^{\infty} \psi_n(x)\psi_n^*(x') e^{-\frac{i}{\hbar}\left(\frac{\hbar^2\pi^2 n^2}{2mL^2}\right)t}$$

$$\text{with } \psi_n = \begin{cases} \sin(n\pi \frac{x}{L}) & n \text{ even} \\ \cos(n\pi\frac{x}{L}) & n \text{ odd} \end{cases}$$

5.3 The continuity equation

We have already discussed that the quantum mechanical time evolution is unitary, such that the norm of the state of the system (i.e. the total probability to find the particle in any eigenstate of some observable) is conserved:

$$\langle\psi(t)|\psi(t)\rangle = \langle\psi(0)|\hat{\mathcal{U}}^+(t)\hat{\mathcal{U}}(t)|\psi(0)\rangle = \langle\psi(0)|\psi(0)\rangle = 1$$

$$\Rightarrow \int dx\,dy\,dz\ \langle\psi(t)|x,y,z\rangle\langle x,y,z|\psi(t)\rangle = \int d^3r\ |\psi(\vec{r},t)|^2$$

$$= \int d^3r\ \frac{dP(\vec{r},t)}{d^3r} = 1 = \text{constant}.$$

This is like charge conservation in E&M: $Q = \text{const} = \int \rho(\vec{r},t)\,d^3r$
independent of time

Let us study this a bit further. We start from the Schrödinger equation and its complex conjugate:

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

$$-i\hbar\frac{\partial\psi^*}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi^* + V\psi^* \quad (V \text{ is real!}) \qquad \Big|\cdot\psi$$

subtract

Multiply the first by ψ^*, the second by ψ, subtract:

$$i\hbar \frac{\partial}{\partial t} \underbrace{(\psi^* \psi)}_{\rho(\vec{r},t) = \frac{dP}{d^3r}(\vec{r},t)} = -\frac{\hbar^2}{2m} \left(\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^* \right)$$

$$\Rightarrow \boxed{\frac{\partial \rho}{\partial t} = -\frac{\hbar}{2mi} \vec{\nabla} \cdot \left(\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^* \right) \equiv -\vec{\nabla} \cdot \vec{J}}$$

continuity equation

where $\vec{J} = \frac{\hbar}{2mi} \left(\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^* \right)$

The continuity equation $\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0$ is a <u>local</u> <u>form of the law of conservation of probability</u>:

$$\int d^3r \, \frac{\partial \rho}{\partial t}(r,t) = \frac{d}{dt} \int \rho(\vec{r},t) \, d^3r = \frac{dP}{dt} = -\int d^3r \, \vec{\nabla} \cdot \vec{J}$$

$$= (\text{divergence theorem}) = -\oint_{S_\infty} \vec{J} \cdot d\vec{a} = 0$$

where $d\vec{a}$ is a surface normal vector on a surface S_∞ that encloses all of $\rho(\vec{r},t)$

For any wave function that is square integrable one can show that $r^{3/2} \psi \xrightarrow[r \to \infty]{} 0$ (otherwise $\int \psi^* \psi \, r^2 dr \, d\Omega$ is not bounded) such that $\vec{J}$ vanishes on S_∞, $\int_{S_\infty} \vec{J} \cdot d\vec{a} = 0$.

$\Rightarrow P = \text{constant}$ (probability is conserved)

An analogous equation holds in E&M, with ρ = charge density and $\vec{J}$ = electric current.