Energy Eigenvalue Problem

As we derived for the position representation, our energy eigenvalue problem is now a differential equation,

$$\boxed{\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\varphi_E(x)=E\,\varphi_E(x)}$$

To solve this equation we need to find both the eigenvalues, E, and eigenfunction, $\varphi_E(x)$.

We cannot do this in general. We need to know $V(x)$, the potential energy of the system, to develop any solutions.

We start our investigation with the Infinite Square Well.

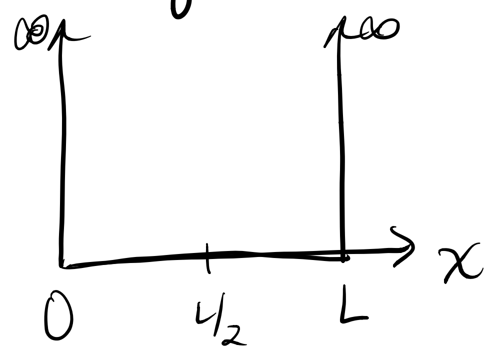
The Infinite Square Well

- The infinite square well (aka 1D particle in a box) is the canonical example of solving the energy eigenvalue problem using the position representation.
- Starting from 3 assumptions, we can construct a mathematical model of the potential.
    1) there's zero force on the particle between the walls ($V_x = \text{const}$)
    2) infinte force at the walls (dV_x/dx is discontinuous)
    3) infinite potential outside ($V_x \to \infty$ outside)

We are free to choose $V_x = \text{const}$ to be zero. So

$$V(x) = \begin{cases} +\infty & x < 0 \\ 0 & 0 < x < L \\ +\infty & x > L \end{cases}$$

We represent that infinite square well visually like so, (3)



Derivation: Finding φ_E & E

So the potential is piecewise defined, so that is how we will start and then patch the solution together as needed.

Outside the well: $V(x) = \infty$

$$\underbrace{\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \infty\right)}_{\text{oof. "infinite" operator}} \varphi_E(x) = E\,\varphi_E(x)$$

but these have to be finite

$$\varphi_E(x) = 0 \quad \text{for } x<0 \;\&\; x>L$$

this makes sure that E is still finite.

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Ultimately, we will force $\varphi_E(x)$ for $0<x<L$ to match at the walls to force continuity. that is $\varphi_E(0)=0$ & $\varphi_E(L)=0$.

Inside the well: $V(x)=0$

$$\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}+0\right)\varphi_E(x)=E\,\varphi_E(x)$$

$$\frac{d^2}{dx^2}\varphi_E(x)=\underbrace{\frac{-2mE}{\hbar^2}}\,\varphi_E(x)$$

all positive quantities

define $k^2 \equiv \frac{2mE}{\hbar^2}$

$\Leftarrow$ k is the "wavevector" as we will see soon it is related closely to λ

$$\boxed{\frac{d^2}{dx^2}\varphi_E(x)=-k^2\varphi_E(x)}$$

You have solved eqn's like this one before in classical mechanics: $\underline{\frac{d^2}{dt^2}x(t)=-\omega^2x(t)}$

$x(t)=A\sin(\omega t)+B\cos(\omega t) \Leftarrow$

The general solution to this equation is the sum of sinusoidal functions, 5

$$\varphi_E(x) = A\sin(kx) + B\cos(kx)$$

Notice that $\varphi_E(x)$ is a continuous function.

Note: A, B, k are unknown still. k is related to the energy eigen values, E

Impose Boundary Conditions

$\varphi_E(x)$ is a continuous function so,

$\varphi_E(0) = \varphi_E(L) = 0$ to match outside.

1 $\varphi_E(0) = A\sin(0) + B\cos(0) = 0$

2 $\varphi_E(L) = A\sin(kL) + B\cos(kL) = 0$

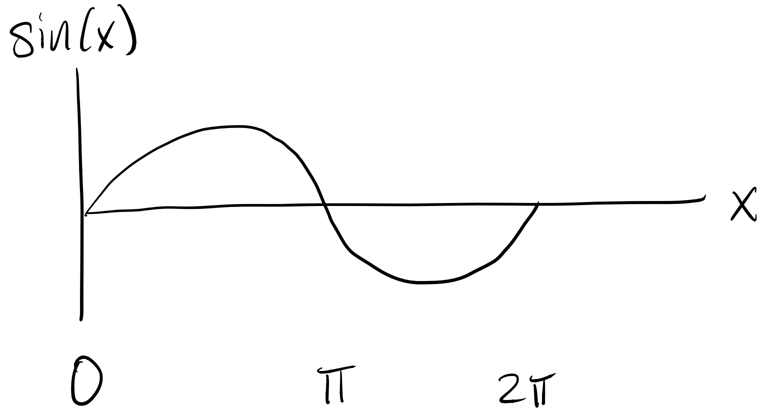
From 1, $\varphi_E(0) = 0 = B$

$\therefore$ for 2 $\varphi_E(L) = A\sin(kL) = 0$

If $A=0$ then $\varphi_E = 0$ for all space

So let's instead see what happens if $\sin(kL) = 0$.

sin(x) looks like this,



we see that it vanishes (goes to zero) at regular intervals, every $\underline{\underline{n\pi}}$.

This sets the quantization condition!
Remember $\langle x|\psi\rangle$ is continuous but energy is quantized so $\underline{k}$ must be quantized!

$\sin(kL) = 0$ if $kL = n\pi$ for $\underline{n > 0}$

so $k \rightarrow \boxed{k_n = \frac{n\pi}{L}}$ Wave vector is quantized!

Moreover, $k_n^2 \equiv \frac{2mE_n}{\hbar^2}$ so,

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

Energy is quantized!

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We are left with,

$$|E_n\rangle \doteq \varphi_n(x) = \begin{cases} 0 & x<0 \\ A\sin\left(\frac{n\pi x}{L}\right) & 0<x<L \\ 0 & x>L \end{cases}$$

A is still undetermined, but recall,

$\langle E_n|E_n\rangle = 1 \rightarrow$ so we have the probabilistic interpretation we need

$$\langle E_n|E_n\rangle \doteq \int_{-\infty}^{\infty} \varphi_n^*(x)\varphi_n(x)\,dx = \int_{-\infty}^{\infty} |\varphi_n(x)|^2 dx = 1$$

φ_n is nonzero only from 0 to L and is completely real so,

wolframed

$$\int_{-\infty}^{\infty} |\varphi_n(x)|^2 dx = \int_0^L |A|^2 \sin^2\left(\frac{n\pi x}{L}\right) dx \doteq |A|^2 \frac{L}{2} = 1$$

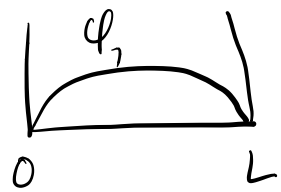
So, $A = \sqrt{\frac{2}{L}}$

infinite square well wave functions

$$\boxed{\varphi_n(x) = \begin{cases} 0 & x<0 \\ \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) & 0<x<L \\ 0 & x>L \end{cases}}$$

Finally, if we sketch the first few wavefunctions we start to see the role of $k_n = \frac{n\pi}{L}$. 8

$$\varphi_1(x) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{\pi x}{L}\right)$$

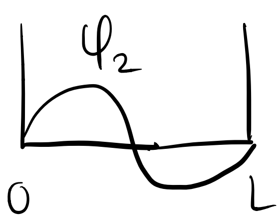


notice that the wavelength for φ_1 is,

$$\lambda_1 = 2L \implies k_1 = \pi/L \quad \text{so that } \lambda_1 = \frac{2\pi}{k_1}$$

(like in wave mech.) $\left(\text{wavelength} = \frac{2\pi}{\text{wavenumber}}\right)$

$$\varphi_2(x) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{2\pi x}{L}\right)$$

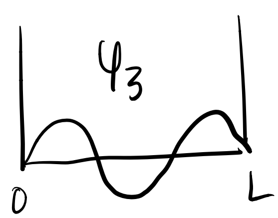


notice

$$\lambda_2 = L \Rightarrow k_2 = \frac{2\pi}{L} \quad \text{and } \lambda_2 = \frac{2\pi}{k_2}$$

again!

$$\varphi_3(x) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{3\pi x}{L}\right)$$



$$\lambda_3 = \frac{2}{3}L \Rightarrow k_3 = \frac{3\pi}{L} \quad \text{and } \lambda_3 = \frac{2\pi}{k_3}$$

again

The eigenstates are those that fit an integer number of nodes in the box,

$$k_n = \frac{n\pi x}{L} \qquad \text{so } \lambda_n = \frac{2\pi}{k_n} = \frac{2L}{nx}$$

So inside the box we can write,

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$$|E_n\rangle \doteq \varphi_n(x) = \sqrt{\frac{2}{L}}\sin(k_n x) = \sqrt{\frac{2}{L}}\sin\left(\frac{2\pi x}{\lambda n}\right)$$

These wavefunctions are representing orthonormal eigenstates. So just like $|+\rangle$ & $|-\rangle$ in spin 1/2 these wavefunctions are,

(1) normal

$$\langle E_n|E_n\rangle \doteq \int_{-\infty}^{\infty} |\varphi_n(x)|^2 dx = 1$$

(2) orthogonal

$$\langle E_m|E_n\rangle \doteq \int_{-\infty}^{\infty} \varphi_m^*(x)\,\varphi_n(x) = 0$$

and

(3) complete

$$|\psi\rangle = \sum_n c_n|E_n\rangle$$

$$\psi(x) = \sqrt{\frac{2}{L}}\sum_n c_n \sin(k_n x)$$