Lecture #6: 3-D Box and Separation of Variables

Last time:

Build up to **Schrödinger Equation:** some wonderful surprises

* operators
* eigenvalue equations
* operators in quantum mechanics – especially $\hat{x} = x$ and $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$
* non-commutation of $\hat{x}$ and $\hat{p}_x$: related to uncertainty principle
* wavefunctions: probability amplitude, continuous! therefore no perfect localization at a point in space
* expectation value (and normalization)

$\widehat{H}\psi = E\psi$

* Free Particle
* Particle in 1-D Box (first viewing)

Today:

1. Review of Free Particle
   some simple integrals

2. Review of Particle in 1-D "Infinite" Box
   boundary conditions
   pictures of $\psi_n(x)$, Memorable Qualitative features

3. Crude uncertainties, Δx and Δp, for Particle in Box

4. 3-D Box
   separation of variables
   Form of E_{n_x,n_y,n_z} and ψ_{n_x,n_y,n_z}

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1. Review of Free particle: $V(x) = V_0$

$\psi_{|k|}(x) = ae^{+ikx} + be^{-ikx}$ complex oscillatory (because $E > V_0$)

$$E_k = \frac{(\hbar k)^2}{2m} + V_0 \qquad k \text{ is not quantized}$$

$$\int_{-\infty}^{\infty}\left|\psi_{|k|}(x)\right|^2 dx = \int_{-\infty}^{\infty}\left[|a|^2 + |b|^2 + a^*be^{-2ikx} + ab^*e^{2ikx}\right]dx$$

$$= |a|^2\infty + |b|^2\infty + a^*b0 + ab^*0$$

(Note what happens to the product $e^{-ikx}e^{+ikx}$)

can't normalize $\psi = ae^{ikx}$ to 1.

$$\int_{-\infty}^{\infty} dx|a|^2 e^{-ikx}e^{+ikx} = \int_{-\infty}^{\approx} dx|a|^2$$

which blows up. Instead, normalize to specified # of particles between x_1 and x_2.

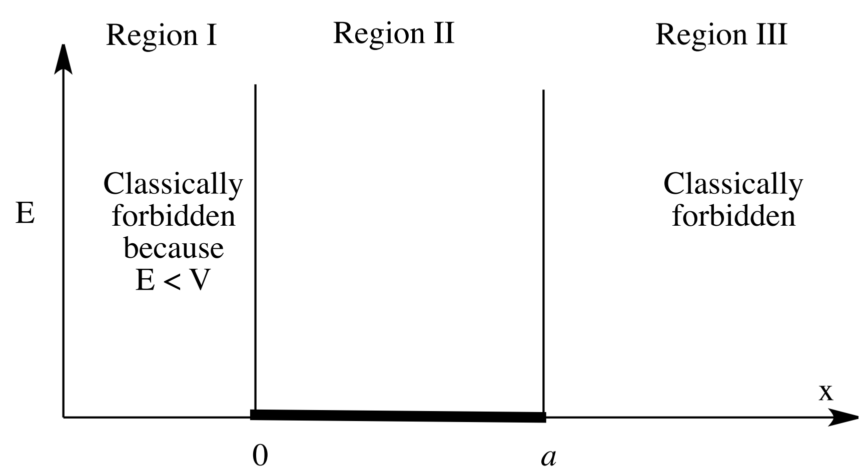
Questions: Is $\psi_k(x) = ae^{ikx} + be^{-ikx}$ an eigenfunction of $\hat{p}_x$? $\widehat{p_x^2}$? What do your answers mean?
Is e^{ikx} eigenfunction of $\hat{p}_x$? What eigenvalue?

2. <u>Review of Particle in 1-D Box of length *a*, with infinitely high walls</u>

"infinite box" or "PIB"

In view of its importance in starting you out thinking about quantum mechanical particle in a well problems, I will work through this problem again, carefully.

$$V(x) = 0 \qquad 0 \le x \le a$$
$$V(x) = \infty \qquad x < 0, x > a$$



Consider regions I and III.
E < V(x)

$$\widehat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \infty$$

$$\underbrace{\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}}_{\text{finite}} = \underbrace{(\infty - E)\psi}$$

no matter what finite value we choose for E, the Schrödinger equation can only be satisfied by setting $\psi(x) = 0$ throughout regions I and III.

So we know that $\psi(x) = 0 \quad x < 0, x > a$.

But $\psi(x)$ must be continuous everywhere, thus $\psi(0) = \psi(a) = 0$.
These are b*oundary conditions*.

Note, however, that for finite barrier height and width, we will eventually see that it is possible for $\psi(x)$ to be nonzero in a classically forbidden [$E < V(x)$] region. "Tunneling." (There will be a problem on Problem Set #3 about this.)

So we solve for $\psi(x)$ in Region II, which looks exactly like the free particle because $V(x) = 0$ in Region II. Free particle solution are written in sin, cos form rather than $e^{\pm ikx}$ form, because application of boundary conditions is simpler. [This is an example of finding a general principle and then trying to find a way to violate it.]

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

Apply boundary conditions

$$\psi(0) = 0 = 0 + B \rightarrow B = 0$$

$$\psi(a) = 0 = A\sin ka \Rightarrow ka = n\pi, \qquad \boxed{k_n = \frac{n\pi}{a}}$$

Normalize: $1 = \int_{-\infty}^{\infty} dx\psi^*\psi = A^2\int_0^a dx \sin^2\frac{n\pi x}{a} \rightarrow A = \left(\frac{2}{a}\right)^{1/2}$ (Picture of normalization integrand suggests that the value of the normalization integral = $a/2$)

Non-Lecture

Normalization integral for particle-in-a-box eigenfunctions

$$\psi_n(x) = A\sin\left(\frac{n\pi}{a}x\right)$$

Normalization (one particle in the box) requires $\int_{-\infty}^{\infty} dx\psi^*\psi = 1$.

For V(x) = 0, $0 \le x \le a$ infinite wall box:

$$1 = \int_{-\infty}^{0} dx\psi^*\psi + \int_{0}^{a} dx\psi^*\psi + \int_{a}^{\infty} dx\psi^*\psi = 0 + |A|^2 \int_0^a dx \sin^2\frac{n\pi}{a}x + 0$$

$$1 = |A|^2 \int_0^a dx \sin^2\frac{n\pi}{a}x$$

Definite integral

$$\int_0^{\pi} dy \sin^2 y = \pi/2$$

change variable: $y = \frac{n\pi}{a}x$

$$dy = \frac{n\pi}{a}dx \Rightarrow dx = \frac{a}{n\pi}dy$$

limits of integration:

$x = 0 \Rightarrow y = 0$
$x = a \Rightarrow y = n\pi$

$$\int_0^a dx \sin^2\frac{n\pi}{a}x = \int_0^{n\pi}\left(\frac{a}{n\pi}\right)dy \sin^2 y = \frac{a}{n\pi}n\left(\frac{\pi}{2}\right) = \frac{a}{2}$$

$1 = |A|^2\frac{a}{2}$, thus $A = \left(\frac{2}{a}\right)^{1/2}$

$$\psi_n(x) = \left(\frac{2}{a}\right)^{1/2}\sin\left(\frac{n\pi}{a}x\right)$$

(A very good equation to remember!)

End of Non-Lecture

Find E_n. These are *all* of the allowed energy levels.

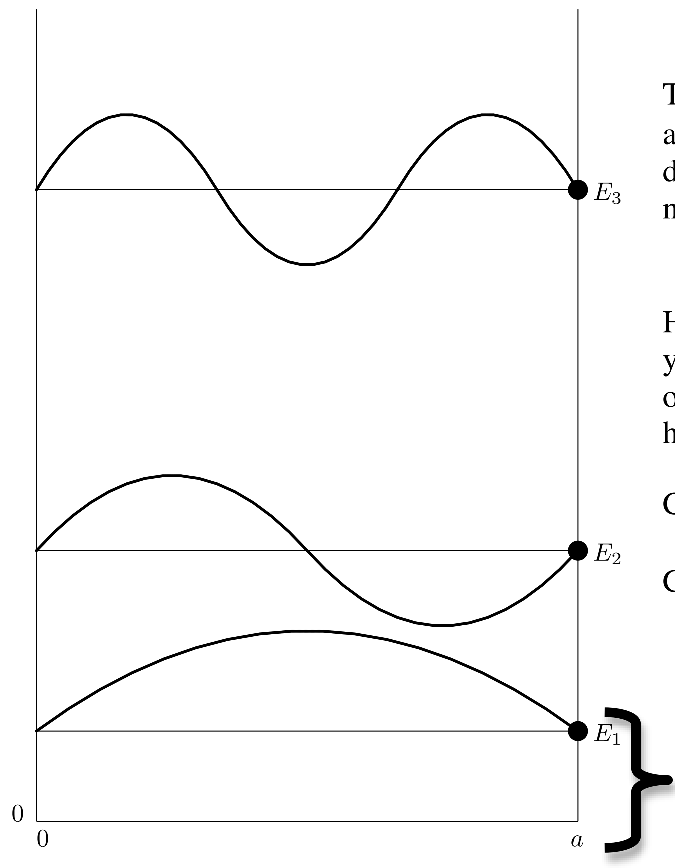
$$\widehat{H}\psi_n = E_n\psi_n$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_n = E_n\psi_n$$

$$+\frac{\hbar^2}{2m}\underbrace{(k_n)^2}_{\frac{n^2\pi^2}{a^2}} = E_n = \frac{h^2}{4\pi^2}\frac{1}{2m}\frac{n^2\pi^2}{a^2} = n^2\underbrace{\left(\frac{h^2}{8ma^2}\right)}_{E_1}$$

n = 1, 2, …
n = 0 would correspond to empty box

Energy levels are integer multiples of a common factor, $E_n = E_1n^2$. (This will turn out to be of special significance when we look at solutions of the time-dependent Schrödinger equation (Lecture #13).



These are "stationary states". You are not allowed to ask, if the system is in ψ_3, how does the particle get from one side of a node to the other.

How would you sample ψ_3? What would you measure? [Quantum Mechanics is full of what/how is "in principle" measurable, hence knowable.]

Could you measure ψ_3?

Could you measure $|\psi_3|^2$?

All *bound* systems have their lowest energy level at an energy greater than the energy of the bottom of the well: "zero-point energy"

This zero-point energy is a manifestation of the uncertainty principle. Why? What is the momentum of a state with zero kinetic energy? Is this momentum perfectly specified? What does that require about position?

3. <u>Crude estimates of Δx, Δp</u> (we will make a more precise definition of uncertainty in the next lecture)

$\Delta x = a$ for all n (the width of the well)

$$\Delta p_n = \underbrace{+\hbar k_n}_{\vec{p}\text{ to right}} - \underbrace{(-\hbar k_n)}_{\vec{p}\text{ to left}} = 2\hbar|k_n| = 2\hbar\left(\frac{n\pi}{a}\right)$$

$$= \frac{2}{2\pi}h\left(\frac{n\pi}{a}\right) = hn/a$$

The joint uncertainty is

$$\Delta x_n \Delta p_n = (a)\frac{hn}{a} = hn \text{ which increases linearly with } n.$$

$n = 0$ would imply $\Delta p_n = 0$ and the uncertainty principle would then require $\Delta x_n = \infty$, which is impossible! This is an indirect reason for the existence of zero-point energy.

Since the uncertainty principle is

$$\Delta x \Delta p_x = h$$

it appears that the $n = 1$ state is a minimum uncertainty state. It will be generally true that the lowest energy state in a well is a minimum uncertainty state.

4. Use the 3-D box to illustrate a very convenient general result: *separation of variables*.

Whenever it is possible to write $\widehat{H}$ in the form:

$$\widehat{H} = \hat{h}_x + \hat{h}_y + \hat{h}_z \qquad \text{(provided that the additive terms are mutually commuting)}$$

$$\frac{\hat{p}_x^2}{2m} + V_x(\hat{x}) + \text{etc.}$$

it is possible to obtain ψ and E in separated form (which is exceptionally convenient!):

$$\psi(x,y,z) = \psi_x(x)\psi_y(y)\psi_z(z)$$

$$E = E_x + E_y + E_z.$$

Or, more generally, when

$$\widehat{H} = \sum_{i=1}^{n} \hat{h}_i(q_i)$$

then

$$\psi = \prod_{i=1}^{n} \psi_i(q_i)$$

$$E = \sum_{i=1}^{n} E_i$$

Consider the specific example of the 3-D box with edge lengths a, b, and c.

V(x,y,z) = 0 $\quad$ $0 \le x \le a$, $0 \le y \le b$, $0 \le z \le c$, otherwise V = ∞.

This is a special case of $V(x,y,z) = V_x + V_y + V_z$.

$$T\left(\hat{p}_x, \hat{p}_y, \hat{p}_z\right) = \frac{-\hbar^2}{2m}\underbrace{\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]}_{\nabla^2 \text{ “Laplacian”}}$$

$$\begin{aligned}\widehat{H}(x,y,z) &= \left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_x(\hat{x})\right] + \left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + V_y(\hat{y})\right] + \left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial z^2} + V_z(\hat{z})\right] \\ &= \hat{h}_x + \hat{h}_y + \hat{h}_z\end{aligned}$$

Schrödinger Equation

$$\left[\hat{h}_x + \hat{h}_y + \hat{h}_z\right]\psi(x,y,z) = E\psi(x,y,z)$$

try $\psi(x,y,z) = \psi_x(x)\psi_y(y)\psi_z(z)$,

where $\hat{h}_i$ operates only on ψ_i,

and $\hat{h}_i\psi_i = E_i\psi_i$ are the solutions of the 1-D problem.

$$\hat{h}_x\psi(x,y,z) = \psi_y\psi_z\hat{h}_x\psi_x = \psi_y\psi_z E_x\psi_x = E_x\psi_x\psi_y\psi_z = E_x\psi(x,y,z)$$

↑ (does not operate on y,z)

$$\hat{h}_y\psi = E_y\psi_x\psi_y\psi_z$$

$$\hat{h}_z\psi = E_z\psi_x\psi_y\psi_z$$

$$\hat{h}_x\psi + \hat{h}_y\psi + \hat{h}_z\psi = \widehat{H}\psi = \left(E_x + E_y + E_z\right)\psi.$$

So we have shown that, if $\widehat{H}$ is separable into *additive* (commuting) terms, then ψ can be written as a product of *independent* factors, and E will be a sum of *separate* subsystem energies. Convenient!

So, for the *a,b,c* box

$$\psi_{n_x} = (2/a)^{1/2} \sin\frac{n_x \pi x}{a}\,, \qquad E_{n_x} = n_x^2 \frac{h^2}{8ma^2}$$

$$\int_0^a dx\psi_{nx}^2 = 1$$

$$\psi_{n_y} = (2/b)^{1/2} \sin\frac{n_y \pi}{b}, \quad \text{normalized}, E_{n_y} = n_y^2 \frac{h^2}{8mb^2}$$

$$\psi_{n_z} = (2/c)^{1/2} \sin\frac{n_z \pi}{c}, \quad \text{normalized}, E_{n_z} = n_z^2 \frac{h^2}{8mc^2}$$

$$E_{n_x, n_y, n_z} = \frac{h^2}{8m}\left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right]$$

$$\psi_{n_x n_y n_z} = \left(\frac{8}{abc}\right)^{1/2} \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{b} \sin\frac{n_z \pi z}{c}.$$

If each of the factors of ψ_{n_x, n_y, n_z} is normalized, it's easy to show that

$$\int dx\,dy\,dz \left|\psi_{n_x n_y n_z}\right|^2 = 1$$

because each of the integrations acts on only one separable factor.

This looks like a lot of algebra, but it really is an important, convenient, and frequently encountered simplification.

We use this separable form for ψ and E all of the time, even when $\widehat{H}$ is *not exactly* separable (for example, a box with slightly rounded corners).

$$\widehat{H} = \widehat{H}^{(0)} + \widehat{H}^{(1)}$$

$\widehat{H}^{(0)}$: a separable Hamiltonian that we use to define a complete set of "basis functions" and "zero-order energies."

$\widehat{H}^{(1)}$: a correction term that contains what we would like to leave out.

This is the basis for our intuition, names of things, and approximate energy level formulas.

$\widehat{H}^{(1)}$ contains small inter-sub-system coupling terms that are dealt with by perturbation theory (Lectures #15, #16 and #19).

You should look at some properties of a particle in a box. Some of these properties are based on simple insights, while others are based on actually evaluating the necessary integrals.

$\langle x \rangle$

$\langle x^2 \rangle$

$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$ "variance"

$\langle p_x \rangle$

$\langle p_x^2 \rangle$

σ_{p_x}

$\sigma_x \sigma_{p_x}$

FWHM

Gaussian $G(x - x_0, \sigma_x)$ $[x_0$ is "center", σ_x is "width"$]$

Lorentzian $L(x - x_0, \sigma_x)$

Minimum Uncertainty Wavepacket