Lecture #5: Begin Quantum Mechanics: Free Particle and Particle in a 1D Box

Last time:

1-D Wave equation $\frac{\partial^2 u}{\partial x^2} = \frac{1}{\mathrm{v}^2}\frac{\partial^2 u}{\partial t^2}$

- $u(x,t)$: displacements as function of x,t
- 2nd-order: solution is sum of 2 linearly independent functions
- *general* solution by separation of variables
- boundary conditions give *specific* physical system
- "normal modes" — octaves, nodes, Fourier series, "quantization"
- The pluck: superposition of normal modes, time-evolving wavepacket
  Problem Set #2: time evolution of plucked system
- More complicated for separation of 2-D rectangular drum. Two separation constants.

Today: Begin Quantum Mechanics

The 1-D Schrödinger equation is very similar to the 1-D wave equation. It is a postulate. Cannot be derived, but it is motivated in Chapter 3 of McQuarrie. *You can only determine whether it fails to reproduce experimental observations*. This is one of the weirdnesses of Quantum Mechanics.

We are always trying to break things (story about the Exploratorium in San Francisco).

1. Operators: Tells us to do something to the function on its right.

Examples: $\hat{A}f = g$, operator denoted by $\hat{A}$ ("^" hat)

* take derivative $$\begin{cases} \frac{d}{dx} f(x) = f'(x) \\ \frac{d}{dx}\left(af(x)+bg(x)\right) = \underbrace{af'(x)+bg'(x)}_{\text{linear operator}} \end{cases}$$

* integrate $$\int dx\left(af(x)+bg(x)\right) = \underbrace{a\int dxf + b\int dxg}_{\text{linear operator}}$$

* take square root $$\sqrt{\left(af(x)+bg(x)\right)} = \underbrace{\left[af(x)+bg(x)\right]^{1/2}}_{\text{NOT linear operator}}$$

We are interested in *linear operators* in Quantum Mechanics. (part of McQuarrie's postulate #2)

2. Eigenvalue equations

$\hat{A}f(x) = af(x)$

a is an eigenvalue of the operator $\widehat{\mathrm{A}}$.

f(x) is a specific eigenfunction that "belongs" to the eigenvalue *a*

more explicit notation $\hat{A}f_n(x) = a_n f_n(x)$

Operator	An Eigenfunction	Its eigenvalue
$\hat{A} = \frac{d}{dx}$	e^{ax}	a
$\hat{B} = \frac{d^2}{dx^2}$	$\sin bx + \cos bx$	$-b^2$
$\hat{C} = x\frac{d}{dx}$	ax^n	n

3. Important Operators in Quantum Mechanics (part of McQuarrie's postulate #2)

For every *physical quantity* there is a *linear operator*

coordinate $\hat{x} = x$

momentum $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$ (at first glance, this seems surprising. Why?)

kinetic energy $\hat{T} = \widehat{p^2}/2m = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$

potential energy $\hat{V}(x) = V(x)$

energy $\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$ (the "Hamiltonian")

Note that these choices for $\hat{x}$ and $\hat{p}$ are dimensionally correct, but their "truthiness" is based on whether they give the expected results.

4. There is a very important fundamental property that lies behind the uncertainty principle: non-commutation of two operators. $\hat{x}\hat{p} \neq \hat{p}\hat{x}$

To find out what this difference between $\hat{x}\hat{p}$ and $\hat{p}\hat{x}$ is, apply the commutator, $[\hat{x}, \hat{p}] \equiv \hat{x}\hat{p} - \hat{p}\hat{x}$, to an arbitrary function.

$$\hat{x}\hat{p}f(x) = x(-i\hbar)\frac{df}{dx} = -i\hbar x\frac{df}{dx}$$

$$\hat{p}\hat{x}f(x) = (-i\hbar)\frac{d}{dx}(xf) = (-i\hbar)\left[f + x\frac{df}{dx}\right]$$

$$\left[\hat{x},\hat{p}\right] \equiv \hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar \qquad \text{a non-zero “commutator”.}$$

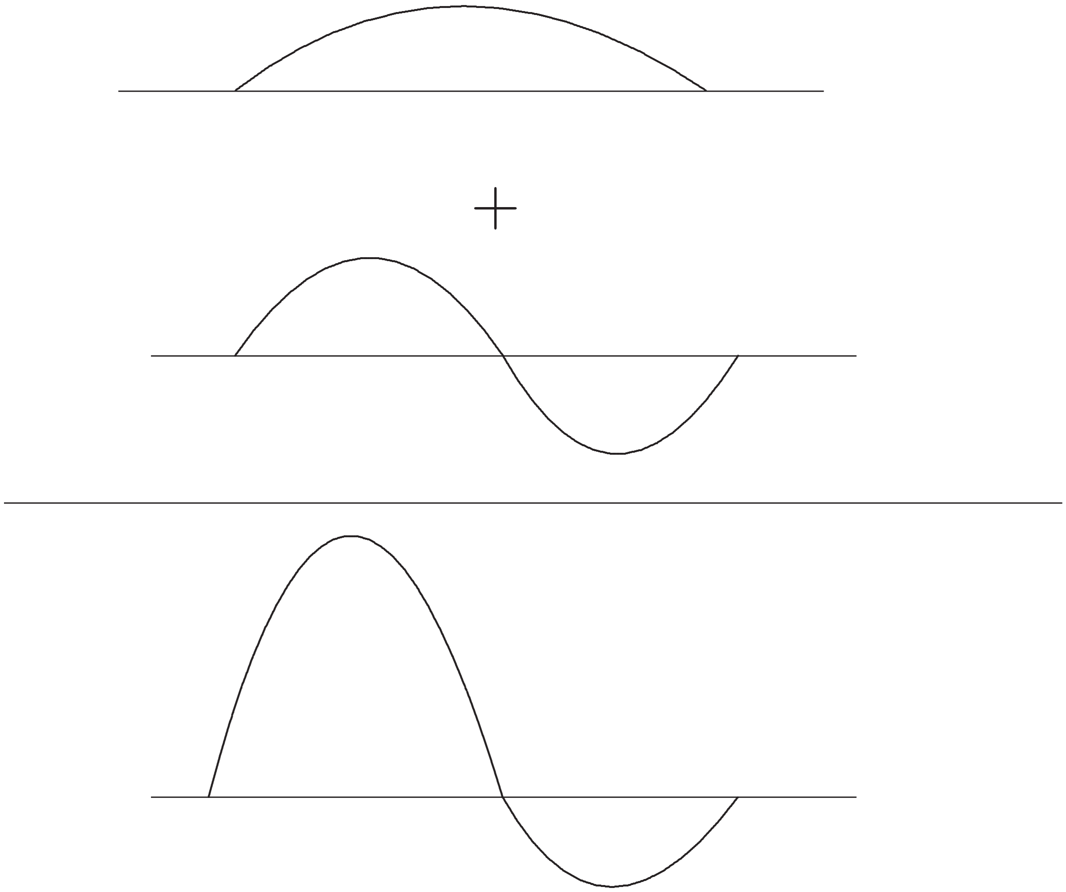
We will eventually see that this non-commutation is the reason we cannot sharply specify *both* x and p_x.

5. Wavefunctions (McQuarrie’s postulate #1)

$\psi(x)$: state of the system – contains *everything that can be known*. Strangely, $\psi(x)$ itself can never be directly observed. *The central quantity of quantum mechanics is not observable*. This should bother you!

* $\psi(x)$ is a “probability amplitude” – similar to the amplitude of a wave (can be positive or negative)

* $\psi(x)$ can exhibit interference



* probability of finding particle between x, $x + dx$ is $\psi^*(x)\psi(x)dx$ (ψ^* is the complex conjugate of ψ)

6. Average value of observable $\hat{A}$ in state ψ? Expectation value. (part of McQuarrie's postulate #4)

$$\langle A \rangle = \frac{\int \psi^* \hat{A} \psi dx}{\int \psi^* \psi dx}$$

Note that the denominator is needed when the wavefunction is not normalized to one.

7. Schrödinger Equation

$\hat{H}\psi_n = E_n\psi_n$ ψ_n is an eigenfunction of $\hat{H}$ that belongs to the specific energy eigenvalue, E_n. (part of McQuarrie's postulate #5)

Let's look at two of the *simplest* quantum mechanical problems. They are also very important because they appear repeatedly.

1. Free particle: $V(x) = V_0$ (constant potential)

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_0$$

$$\hat{H}\psi = E\psi, \text{ move } V_0 \text{ to RHS}$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = (E - V_0)\psi$$

$$\frac{d^2}{dx^2}\psi = \frac{-2m(E - V_0)}{\hbar^2}\psi.$$

Note that if $E > V_0$, then on the RHS we need ψ multiplied by a negative number. Therefore ψ must contain complex exponentials. This is the physically reasonable situation.

But if $E < V_0$ (how is such a thing possible?), then on the RHS we need ψ multiplied by a positive number. ψ must contain real exponentials.

$$\left.\begin{array}{l} e^{+kx} \text{ diverges to } \infty \text{ as } x \to +\infty \\ e^{-kx} \text{ diverges to } \infty \text{ as } x \to -\infty \end{array}\right\} \text{unphysical [but useful for } |x| \text{ finite (tunneling)]}$$

So, when $E > V_0$, we find $\psi(x)$ by trying $\psi = ae^{+ikx} + be^{-ikx}$ (two linearly independent terms)

$$\frac{d^2\psi}{dx^2} = -k^2 \underbrace{\left(ae^{ikx} + be^{-ikx}\right)}_{\psi}$$

$$-\frac{2m(E-V_0)}{\hbar^2} = -k^2$$

Solve for E,

$$E_k = \frac{(\hbar k)^2}{2m} + V_0 .$$

You show that $\begin{cases} * \ \psi = ae^{ikx} \text{ is eigenfunction of } \hat{p} \\ * \text{ with eigenvalue } \hbar k \\ * \text{ and } \langle p \rangle = \hbar k. \end{cases}$

No quantization of E because k can have *any* real value.

NON-LECTURE

What is the average value of momentum for $\psi = ae^{ikx} + be^{-ikx}$?

$$\langle p \rangle = \frac{\int_{-\infty}^{\infty} dx \psi^* \hat{p} \psi}{\int_{-\infty}^{\infty} dx \psi^* \psi} \qquad \text{normalization integral}$$

$$= \frac{\int_{-\infty}^{\infty} dx \left(a^* e^{-ikx} + b^* e^{ikx}\right)(-i\hbar)\frac{d}{dx}\left(ae^{ikx} + be^{-ikx}\right)}{\int_{-\infty}^{\infty} dx \left(a^* e^{-ikx} + b^* e^{ikx}\right)\left(ae^{ikx} + be^{-ikx}\right)}$$

$$= \frac{-i\hbar \int_{-\infty}^{\infty} dx \left(a^* e^{-ikx} + b^* e^{ikx}\right)(ik)\left(ae^{ikx} - be^{-ikx}\right)}{\int_{-\infty}^{\infty} dx \left(|a|^2 + |b|^2 + a^* b e^{-2ikx} + ab^* e^{2ikx}\right)}$$

$$= \frac{\hbar k \int_{-\infty}^{\infty} dx \left(|a|^2 - |b|^2 + ab^* e^{2ikx} - a^* b e^{-2ikx}\right)}{\int_{-\infty}^{\infty} dx \left(|a|^2 + |b|^2 + ab^* e^{2ikx} + a^* b e^{-2ikx}\right)}$$

Integrals from $-\infty$ to $+\infty$ over oscillatory functions like $e^{\pm i2kx}$ are always equal to zero. Why?

$$\langle p \rangle = \hbar k \frac{|a|^2 - |b|^2}{|a|^2 + |b|^2}$$

$$\text{if } a = 0 \qquad \langle p \rangle = -\hbar k$$

$$\text{if } b = 0 \qquad \langle p \rangle = +\hbar k$$

$\frac{|a|^2}{|a|^2+|b|^2}$ is fraction of the observations of the system in ψ which have $p > 0$

$\frac{|b|^2}{|a|^2+|b|^2}$ is fraction of the observations of the system in ψ which have $p < 0$

END OF NON-LECTURE

Free particle: it is possible to specify momentum sharply, but if we do that we will find that the particle must be delocalized over all space.

For a free particle, $\psi^*(x)\psi(x)dx$ is delocalized over all space. If we have chosen only one value of $|k|$, $\psi^*\psi$ can be oscillatory, but it must be positive everywhere. Oscillations occur when e^{ikx} is added to e^{-ikx}.

NON-LECTURE

$$\psi = ae^{ikx} + be^{-ikx}$$

$$\psi^*\psi = |a|^2 + |b|^2 + 2\text{Re}[ab^*e^{2ikx}]\text{, but if } a,b \text{ are real}$$

$$\psi^*\psi = \underbrace{a^2+b^2}_{\text{constant}} + \underbrace{2ab\cos 2kx}_{\text{oscillatory}}$$

Note that $\psi^*\psi \geq 0$ everywhere. For x where cos $2bx$ has its maximum negative value, cos $2kx = -1$, then $\psi^*\psi = (a-b)^2$. Thus $\psi^*\psi \geq 0$ for all x because $(a-b)^2 \geq 0$ if a,b are real.

Sometimes it is difficult to understand the quantum mechanical free particle wavefunction (because it is not normalized to 1 over a finite region of space). The **particle in a box** is the problem that we can most easily understand completely. This is where we begin to become comfortable with some of the mysteries of Quantum Mechanics.

* insight into electronic absorption spectra of conjugated molecules.
* derivation of the ideal gas law in 5.62!
* very easy integrals

Particle in a box, of length a, with infinitely high walls.

"infinite box"

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

$$\left.\begin{array}{ll} V(x) = 0 & 0 \leq x \leq a \\ V(x) = \infty & x < 0, x > a \end{array}\right] \quad \text{very convenient because } \int_{-\infty}^{\infty} dx\psi^* V(x)\psi = 0.$$

(convince yourself of this!)

$\psi(x)$ must be continuous everywhere.

$\psi(x) = 0$ everywhere outside of box $\left(\text{otherwise } \int_{-\infty}^{\infty} \psi * V\psi = \infty\right)$.

$\psi(0) = \psi(a) = 0$ at edges of box.

Inside box, this looks like the free particle, which we have already solved.

$$\hat{H}\psi = E\psi \qquad \text{Schrödinger Equation}$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi \qquad (V(x) = 0 \text{ inside the box})$$

$$\frac{d^2}{dx^2}\psi = -\frac{2m}{\hbar^2}E\psi = -k^2\psi$$

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

$$\psi(x) = A\sin kx + B\cos kx \qquad \text{satisfies Schrödinger Equation (it is the general solution)}$$

Apply boundary conditions:

$\psi(0) = \mathrm{B} = 0$ therefore $\mathrm{B} = 0$

$\psi(a) = \mathrm{A} \sin ka = 0$ therefore $\mathrm{A} \sin ka = 0$ (quantization!)

$ka = n\pi$ $\quad k = \frac{n\pi}{a}$ $\quad n$ is an integer

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

$$\int_0^a dx\psi * \psi = 1 \qquad \text{normalize}$$

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

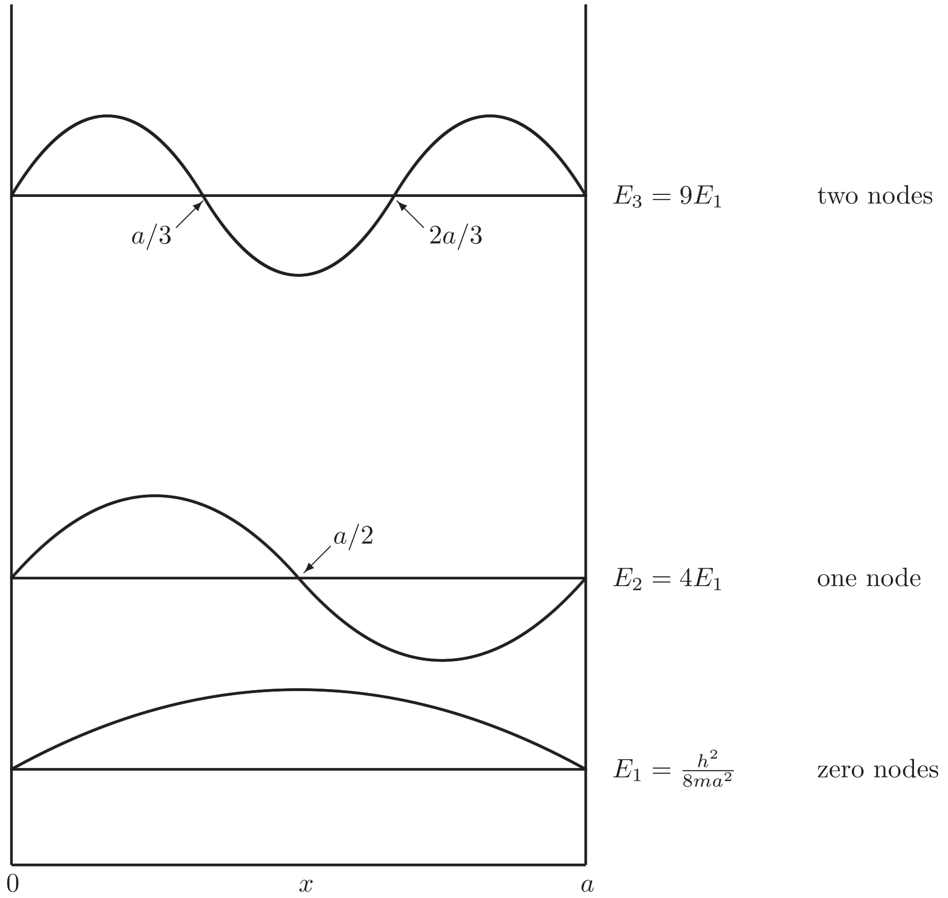
$$A = \left(\frac{2}{a}\right)^{1/2}$$

$\boxed{\psi_n = \left(\frac{2}{a}\right)^{1/2} \sin\frac{n\pi}{a}x}$ is the *complete* set of eigenfunctions for a particle in a box. Now find the energies for each value of n.

$$
\begin{aligned}
\hat{H}\psi_n &= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\left(\frac{2}{a}\right)^{1/2}\sin\frac{n\pi}{a}x \\
&= +\frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2\psi_n \\
&= \frac{h^2n^2}{8ma^2}\psi_n.
\end{aligned}
$$

$$E_n = n^2\underbrace{\frac{h^2}{8ma^2}}_{E_1} = n^2E_1 \qquad n = 1,2,3\ldots \qquad \text{(never forget this!)}$$

$n = 0$ means the box is empty
what would a negative value of n mean?



n–1 nodes, nodes are equally spaced. All lobes between nodes have the same shape.

Summary:

Some fundamental mathematical aspects of Quantum Mechanics.
Initial solutions of two-simplest Quantum Mechanical problems.

- Free Particle
- Particle in an infinite 1-D box

Next Lecture:

1. * more about the particle in 1-D box
   * Zero-point energy (this is unexpected)
   * $\Delta x \Delta p$ vs. n ($n = 1$ gives minimum uncertainty)

2. particle in 3-D box
   * separation of variables
   * degeneracy

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