Physics 342 Lecture 13

It's good to be back! Hope you had a good time in my absence. As it has been a bit since I've lectured, I need to remind myself where we have been.

Over the last week, we have introduced the Schrödinger equation, the fundamental equation that governs time evolution in quantum mechanics:

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

where $\hat{H}$ is the Hamiltonian and $|\psi\rangle$ is an arbitrary quantum state that lives in some Hilbert space. We can expand the state in a basis of eigenstates of the Hamiltonian as:

$$|\psi\rangle = \sum_i \beta_i e^{\frac{-iE_i t}{\hbar}}|\psi_i\rangle,$$ where β_i are complex coefficients, E_i and $|\psi_i\rangle$ are energy eigenvalues and eigenstates of a time-independent Hamiltonian:

$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle.$$

In the last couple of lectures, we had also introduced <u>commutation relations</u> between Hermitian operators defined on the Hilbert space. The most profound consequence of the <u>canonical commutation relation</u> of position and momentum:

$$[\hat{x},\hat{p}] = i\hbar$$

is the <u>Heisenberg uncertainty relation</u> which quantifies the limit to which a state $|\psi\rangle$ can be an eigenstate of position and momentum simultaneously. We have:

$$\sigma_x \sigma_p \geq \frac{\hbar}{2},$$ where σ_x, σ_p are the standard deviations of the ~~xxxx~~ $\hat{x}$ and $\hat{p}$ matrix elements on state $|\psi\rangle$:

$$\sigma_x^2 = \langle\psi|\hat{x}^2|\psi\rangle - \langle\psi|\hat{x}|\psi\rangle^2,$$ and similar for $\hat{p}$.

Today, and throughout the next few weeks, we will take all of this abstractness and make it concrete in actual examples. Our goal for these examples will be to solve the time-independent eigenvalue problem:

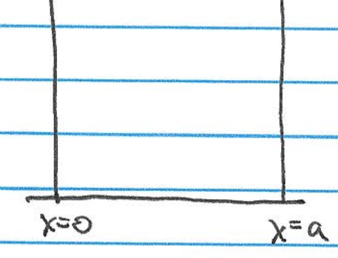
$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle,$$

as once we know E_i and $|\psi_i\rangle$, we then know the time evolution of an arbitrary quantum state $|\psi\rangle$.

The problem we will study this week is the <u>infinite-square well</u>, a very canonical problem in quantum mechanics. The system is defined by the potential:

$$V(x) = \begin{cases} \infty, & x<0 \\ 0, & 0 \leq x \leq a \\ \infty, & x > a \end{cases}$$

So, the picture of the infinite square wells' potential is:



the width of the well is a, and because of the infinitely high walls at $x=0,a$, any object placed in the well stays in the well. That is, to leave the well would require infinite kinetic energy, which is not possible. Therefore, as the wavefunction $\psi(x,t)$ represents the probability amplitude for a particle to be at position x at time t, if the particle cannot leave the well, then

$$\psi(x,t)=0 \quad \text{for } x<0,\ x>a \text{ for } \underline{\text{all}}\ t.$$

So, an eigenstate of the Hamiltonian:

$$\hat{H}|\psi_i\rangle = \frac{\hat{p}^2}{2m}|\psi_i\rangle = E_i|\psi_i\rangle,$$

only has support in the region where $0<x<a$.

To determine the energy eigenvalues E_i and eigenstates $|\psi_i\rangle$, there are numerous ways forward. Griffiths and Schroeter take the eigenvalue equation as a differential equation:

$$\frac{\hat{p}^2}{2m}\psi_i(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_i(x) = E_i\psi_i(x),$$

and solve it with the specified boundary conditions. One can do that, but that treats the Schrödinger equation as just another differential equation. We've developed a powerful language of linear operators so let's see how far that can get us.

First, the form of the Schrödinger equation for the infinite square well is intriguing:

$$\frac{\hat{p}^2}{2m}|\psi_i\rangle = E_i|\psi_i\rangle.$$

First, as the eigenvalues of momentum $\hat{p}$ are real, the energy E_i of an eigenstate is necessarily non-negative. This means that we can meaningfully take the square-root of both sides to find:

$$|\hat{p}|\,|\psi_i\rangle = \sqrt{2mE_i}\,|\psi_i\rangle$$

The absolute value of momentum $|\hat{p}|$ means that we just take ~~its~~ the absolute value of its eigenvalues. Therefore, the energy eigenstates $|\psi_i\rangle$ of energy E_i correspond to <u>fixed</u> magnitude of momentum, where

$$|p_i| = \sqrt{2mE_i}\,, \quad \text{where now } p_i \text{ is an eigenvalue of } \hat{p}.$$

We've mentioned before that we can <u>always</u> expand any wavefunction in a sum/integral over momentum eigenstates. Recall that, for momentum p, the eigenstate of the momentum operator is:

$$\hat{p}|v_p\rangle = p|v_p\rangle \Rightarrow |v_p(x)\rangle = e^{+i\frac{px}{\hbar}}.$$

So, if an energy eigenstate of the infinite square well corresponds to a ~~fix~~ fixed magnitude of momentum, we just sum together the two momentum eigenstates with equal magnitude but opposite sign of momentum:

$$\psi_i(x) = \alpha e^{\frac{ip_ix}{\hbar}} + \beta e^{-\frac{ip_ix}{\hbar}}, \quad \text{where } p_i = \sqrt{2mE_i},$$

and α, β are some complex numbers, that we will will work to determine.

There are a few constraints to consider. First, because the particle is confined to $0 < x < a$, it has 0 probability to be at $x=0$ or $x=a$. So, we must demand that the wavefunction vanishes at thesepoints. That is:

$$\psi_i(x=0) = 0 = \alpha + \beta, \quad \psi_i(x=a) = \alpha e^{\frac{ip_i a}{\hbar}} + \beta e^{-\frac{ip_i a}{\hbar}} = 0$$

The first constraint requires that $\beta = -\alpha$, and the second constraint becomes

$$\psi_i(x=a) = \alpha\left(e^{\frac{ip_i a}{\hbar}} - e^{-\frac{ip_i a}{\hbar}}\right) = 2i\alpha \sin\left(\frac{p_i a}{\hbar}\right) = 0.$$

The trivial solution is to just set $\alpha = 0$; but then $\psi_i = 0$, which says that there is 0 probability for the particle to be anywhere. So, instead, we demand that the sinusoidal factor vanishes. sine is 0 if its argument is an integer multiple of π, $n\pi$, so we must enforce:

$$\frac{p_i a}{\hbar} = n\pi = \frac{\sqrt{2mE_n}\, a}{\hbar} \quad \text{or that} \quad E_n = \frac{n^2\pi^2\hbar^2}{2ma^2},$$

which is thus the spectrum of eigenvalues of the Hamiltonian $\hat{H}$, for integer n. Actually, we can restrict to non-negative integers because $n^2 = (-n)^2$, and further to strictly positive integers, i.e., natural numbers. If $n=0$, $\sin 0 = 0$ over all $0 < x < a$, which again is trivially non-interesting. So, we require $n \in \mathbb{N}$.

With these identifications, we can express the energy eigenstate as

$$\psi_i(x) = \alpha\left(e^{\frac{ip_ix}{\hbar}} - e^{-\frac{ip_ix}{\hbar}}\right) = \alpha\left(e^{\frac{in\pi x}{a}} - e^{-\frac{in\pi x}{a}}\right)$$
$$= 2i\alpha \sin\left(\frac{n\pi x}{a}\right).$$

If this eigenstate is an element of the Hilbert space, then it must be L^2-normalized:

$$\langle\psi_i|\psi_i\rangle = 1 = \int_0^a dx\, |\alpha|^2 \left(e^{\frac{in\pi x}{a}} - e^{-\frac{in\pi x}{a}}\right)\left(e^{-\frac{in\pi x}{a}} - e^{\frac{in\pi x}{a}}\right)$$
$$= \int_0^a dx\, 4|\alpha|^2 \sin^2 \frac{n\pi x}{a}$$
$$= |\alpha|^2 \int_0^a dx \left(1 + 1 - e^{\frac{2in\pi x}{a}} - e^{-\frac{2in\pi x}{a}}\right)$$
$$= |\alpha|^2 \int_0^a dx \left(2 - 2\cos\frac{2n\pi x}{a}\right)$$

For the cosine term, note that its wave length is:

$$kx = \frac{2\pi}{\lambda}x = \frac{2\pi n x}{a} \Rightarrow \lambda = \frac{a}{n}.$$

So, the cosine term fits n full wavelengths in the well. The integral over cosine over a full wavelength is 0, so the normalization condition enforces that

$2a|\alpha|^2 = 1$, or that $|\alpha| = \frac{1}{\sqrt{2a}}$. We can choose α to be a real number so that $\alpha = \frac{1}{2a}$ or that the eigenstate is:

$$\psi_i(x) = \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}.$$

This point might have gone by a bit fast: why can we just set α to be a real number? The overall complex phase of a wavefunction ψ is unphysical. To understand this, not that if $|\psi\rangle$ is normalized, $\langle\psi|\psi\rangle = 1$, we can always multiply $|\psi\rangle$ by a unit-norm, complex number:

$$|\psi'\rangle = e^{i\phi}|\psi\rangle, \text{ for some real number } \phi.$$

This phase ~~f~~factor leaves the normalization unaffected:

$$\langle\psi'|\psi'\rangle = \langle\psi|e^{-i\phi}\, e^{i\phi}|\psi\rangle = \langle\psi|\psi\rangle = 1.$$

Further, given this state, any quantity that we measure on the state is defined by a corresponding Hermitian operator; call it T. Expectation values or other matrix elements of T with the state ψ are unaffected by the phase:

$$\langle\psi'|T|\psi'\rangle = \langle\psi|e^{-i\phi}\, T\, e^{i\phi}|\psi\rangle = \langle\psi|T|\psi\rangle, \text{ etc.}$$

Thus, if the phase cannot affect any measurement that we might imagine performing, it has no physical consequence. Thus, we can, with impunity, set normalization constants however convenient, as we do here.

Actually, this point places other constraints on the Hilbert space. All states on the Hilbert space are L^2-normalized, but further two states ψ and ψ' are ~~idea~~ physically identified if they only differ by an overall complex phase.

That is, our Hilbert space is actually:

$$\mathcal{H} = \{\psi(x,t) \in \mathbb{C} \mid \int dx\, \psi^* \psi = 1;\ \psi' \simeq e^{i\phi}\psi,\ \phi \in \mathbb{R}\},$$

where the symbol "$\simeq$" means "equivalent" (not equal). For those familiar with the math, this defines a conjugacy class of states related by a phase. We only need one representative in the Hilbert space, and all others are mapped onto it.

We'll dive more deeply into the ∞-□ well and other weirdness of quantum mechanics next time.