▬▬ (7) Energy Eigenstates ▬▬

1 Thus Far

- Configuration determined by wavefunction $\psi(x)$
- Can make state from superposition of eigenfunctions $\psi(x) = \sum_n \psi_{A,n}(x)$
- Observation results in wavefunction collapse to eigenstate
- Time evolution related to energy $\hat{E} = i\hbar\frac{\partial}{\partial t}$

2 This Time

- Energy eigenfunctions and the special role they play in QM
- The example system in QM: a particle in a box

3 Energy Eigenstates

The Schrödinger equation is a standard Partial Differential Equation, and there are many ways to solve it.

Solve SE with

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) + V(x)\psi(x,t) \quad (1)$$

- Brute force (many hours with Mathematica)
- Extreme cleverness (find the answer that someone else got by brute force)
- Numerically (fine for finding a particular answer to a particular question, but gives no intuition)
- Superposition!

How can we use superposition to solve the Schrödinger equation?

We start by noting that energy eigenstates have very simple time dependence.

Energy ES

$$\hat{E}\,\psi_E(x,t) = E\,\psi_E(x,t)$$

$$\text{use SE} \;\Rightarrow (i\hbar\partial_t)\,\psi_E(x,t) = E\,\psi_E(x,t)$$

$$\text{separate time} \qquad \psi_E(x,t) = \phi_E(x)e^{-i\omega t}$$

$$\Rightarrow (i\hbar\partial_t)\,\phi_E(x)e^{-i\omega t} = E\,\phi_E(x)e^{-i\omega t}$$

$$\hbar\omega\,\phi_E(x)e^{-i\omega t} = E\,\phi_E(x)e^{-i\omega t}$$

Note that the time dependence separates from the spatial dependence.

If use the energy operator (instead of the Schrödinger equation),

Energy ES in SE

$$\hat{E}\,\psi_E(x,t) = \left(\frac{\hat{p}^2}{2m} + V(x)\right)\psi_E(x,t)$$

$$E\,\phi_E(x)e^{-i\omega t} = \left(\frac{\hat{p}^2}{2m} + V(x)\right)\phi_E(x)e^{-i\omega t}$$

$$E\,\phi_E(x) = \frac{-\hbar^2}{2m}\partial_x^2\,\phi_E(x) + V(x)\,\phi_E(x)$$

$$\Rightarrow \phi_E(x)\ \text{solves} \qquad E = \frac{\hat{p}^2}{2m} + V(x)$$

Note that the energy operator, like all operators, operates on x, not t.

Before moving on to more interesting potential functions, let's look back at the plane-waves we saw last time. Plane-waves fit the form given above, and they will play a role in many of the potentials we consider in the coming weeks.

SE with $V(x) = 0$

> plane-waves $\quad \psi_E(x, t) = e^{i(kx - \omega t)} = \phi_E(x)e^{-i\omega t}$
>
> with eigenvalue $\quad E = \hbar\omega = \dfrac{\hbar^2 k^2}{2m}$

Note the degeneracy! $E(k) = E(-k)$

Energy eigenstates which have the same eigenvalue, called degenerate states, play an interesting role in QM in general, and in atomic physics in particular. The implication for wavefunction collapse, for instance, is that if you make a measurement which cannot distinguish between multiple states due to degeneracy, the wavefunction can collapse to a superposition of degenerate states.

Finally, note the time dependence of energy eigenstates.

Energy ESs

$$\mathbb{P}_E(x) = \left|\psi_E(x)\right|^2 = \left|\phi_E(x)e^{-i\omega t}\right|^2 = \left|\phi_E(x)\right|^2 \quad (2)$$

are *time independent*, and thus the name "stationary states".

But take care, because the sum of energy eigenstates is not, in general, an eigenstate and is therefore not stationary.
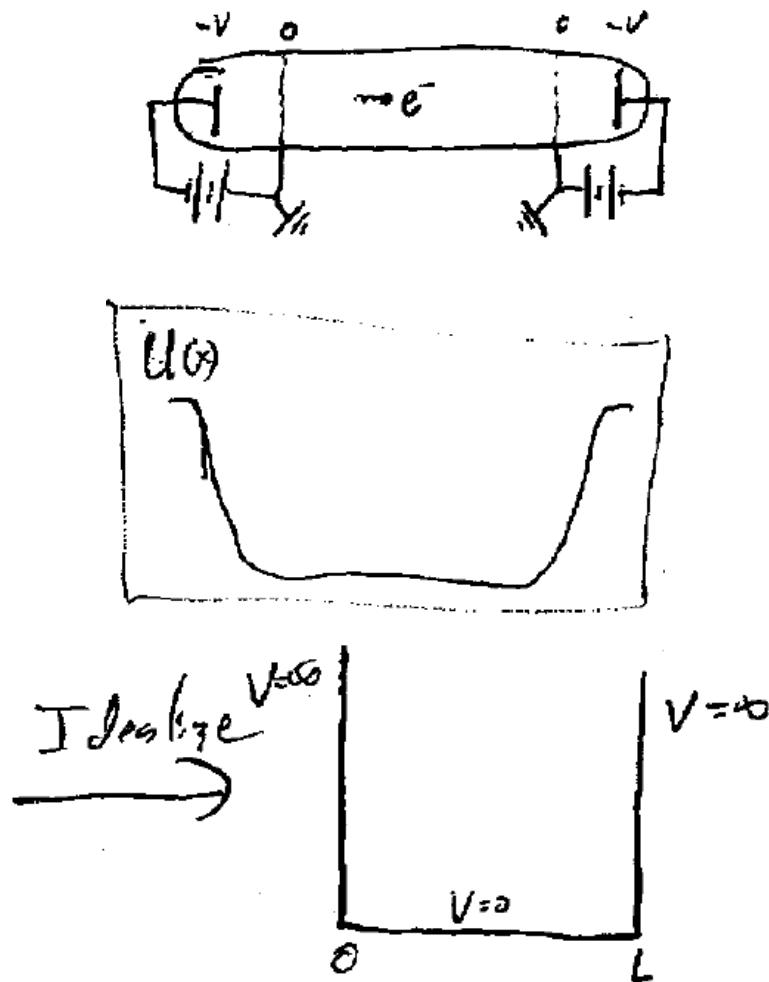
Superposition of Energy ESs

$$
\begin{aligned}
\mathbb{P}(x) &= \left|\phi_1(x)e^{-i\omega_1 t} + \phi_2(x)e^{-i\omega_2 t}\right|^2 \\
&= |\phi_1(x)|^2 + |\phi_2(x)|^2 + \phi_1^*(x)\phi_2(x)e^{-i\Delta\omega t} + \phi_1(x)\phi_2^*(x)e^{i\Delta\omega t} \\
&\quad \text{where } \Delta\omega = \omega_2 - \omega_1 \\
&\quad \text{take energy EFs to be real} \\
&= \mathbb{P}_1(x) + \mathbb{P}_2(x) + 2\phi_1(x)\phi_2(x)\cos(\Delta\omega t)
\end{aligned}
$$

are *NOT* time independent.

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4   Example: Particle in a Box

The particle in a box problem, also known as the "infinite square well" is the canonical toy problem involving the 1-D Schrödinger equation. You can think of this as a superball trapped between 2 brick walls, or, more realistically, an electron trapped in a steep potential well.

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{otherwise} \end{cases} \tag{3}$$

Solving this for an arbitrary wave function can be tricky.

But we can use superposition and energy eigenstates to make our lives easier. Recall that we can make any wavefunction from a superposition of eigenfunctions, and in this case we will use energy eigenfunctions to avoid the problem of time dependence.

Superposition!

$$\psi(x, t) = \sum_n c_n \phi_n(x)\, e^{-iE_n t/\hbar} \qquad (4)$$

where

$$c_n = \langle \phi_n | \psi \rangle = \int_{-\infty}^{\infty} \phi_n(x)^* \, \psi(x, t = 0)\, dx \qquad (5)$$

To do this we need to find $\phi_n(x)$ which solves the Schrödinger equation for this potential. Since our potential is piecewise flat, we already know the solution to the Schrödinger equation in the well. For $0 < x < L$, we can use $\phi(x) = e^{ikx}$, but we also need to satisfy the boundary conditions. We can do this by combining plane-waves with positive and negative k to get

5

Boundary Conditions

$$\psi(x, t) = 0 \text{ for } x \leq 0 \text{ and } x \geq L \tag{6}$$

in the well use

$$\phi_n(x) = A_n \frac{e^{ik_nx} - e^{-ik_nx}}{2i} = A_n \sin(k_nx) \tag{7}$$

with

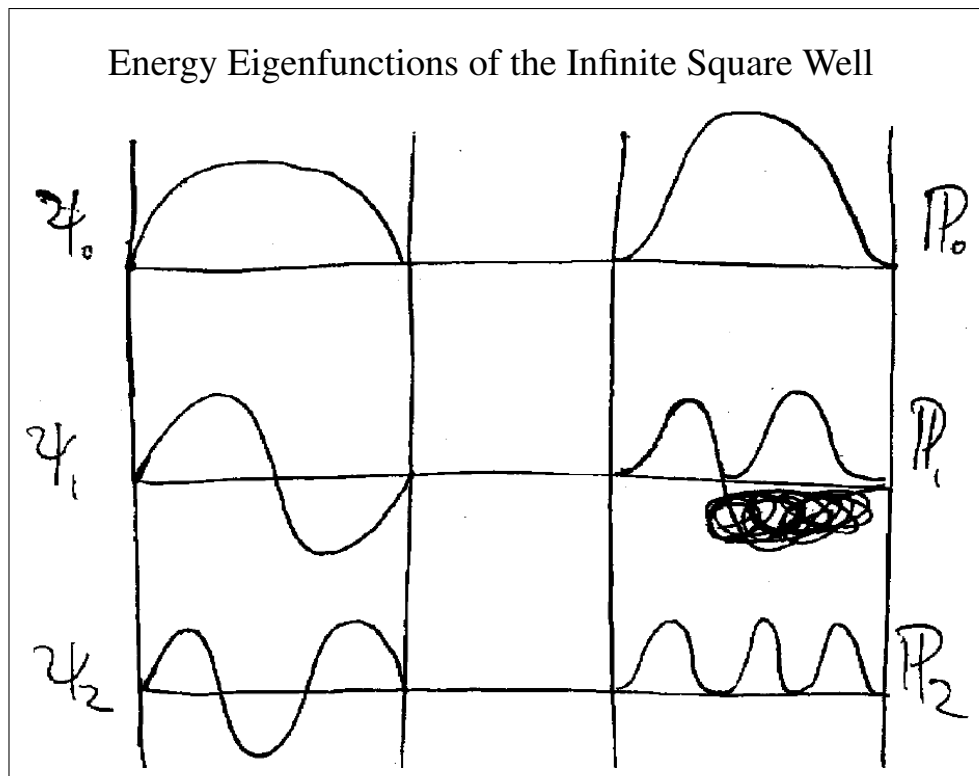$$k_n = \frac{(n+1)\pi}{L} \quad n \in \{0, 1, \ldots\} \tag{8}$$

gives

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 (n+1)^2 \pi^2}{2mL^2} \tag{9}$$

and

$$\begin{aligned}
\psi_n(x, t) &= A_n \sin(k_nx) \, e^{-iE_nt/\hbar} \\
\Rightarrow \mathbb{P}_n(x) &= |A_n|^2 \sin^2(k_nx)
\end{aligned}$$

There is something curious that just happened here. We just got our first set of discrete energy levels, reminiscent of the Bohr atom.

Note that $E_0 > 0$! Uncertainty does not allow a zero energy state!

Energy Eigenfunctions of the Infinite Square Well

I admit that these don't look much like our Gaussian wavepacket, but not to worry, we know how to build any wavefunction from these eigenstates, and that it will move because it is a *superposition* of stationary states.

Superpositions Move

$$\langle x \rangle = \int_{-\infty}^{\infty} \left(\sum_n c_n \phi_n(x)\, e^{-i\omega_n t} \right)^* x \left(\sum_m c_m \phi_m(x)\, e^{-i\omega_m t} \right) dx$$

$$= \sum_{n,m} c_n^* c_m e^{i(\omega_n - \omega_m)t} \underbrace{\int_{-\infty}^{\infty} \phi_n^*(x)\, x\, \phi_m(x)\, dx}_{\neq \delta_{n,m}}$$

The expectation value of the energy, however, does not change.

Energy is Conserved

$$\langle E \rangle = \int_{-\infty}^{\infty} \left(\sum_n c_n \phi_n(x)\, e^{-i\omega_n t} \right)^* \hat{E} \left(\sum_m c_m \phi_m(x)\, e^{-i\omega_m t} \right) dx$$

$$= \sum_{n,m} c_n^* c_m e^{i(\omega_n - \omega_m)t} E_m \underbrace{\int_{-\infty}^{\infty} \phi_n^*(x)\, \phi_m(x)\, dx}_{= \delta_{n,m}}$$

$$= \sum_n |c_n|^2 E_n$$

Energy conservation!

And the probability of measuring the particle to be in any particular energy eigenstate is constant

EES Probabilities

$$\mathbb{P}_n = |\langle \psi_{E,n} | \psi \rangle|^2$$

$$= \left| \int_{-\infty}^{\infty} \left(\phi_n(x)\, e^{-i\omega_n t} \right)^* \left(\sum_m c_m \phi_m(x)\, e^{-i\omega_m t} \right) dx \right|^2$$

$$= \left| \sum_m c_m e^{i(\omega_n - \omega_m)t} \langle \phi_n | \phi_m \rangle \right|^2$$

$$= |c_n|^2$$

This business of finding energy eigenstate of various potentials is the hallmark of QM and it will dominate the rest of this course!

5 Example: Measuring a Particle in a Box

Imagine we start with a particle in a superposition of the ground state and first excited state of our potential.

Start with state:

$$\psi(x,t) = \sqrt{\frac{1}{3}}\,\phi_0(x)e^{-i\omega_0 t} + \sqrt{\frac{2}{3}}\,\phi_1(x)e^{-i\omega_1 t} \qquad (10)$$

Draw this!

Next, let's measure the energy. What might we get? What are the probabilities of the possible results?

We can only measure $E = E_0$ or $E = E_1$.
The probabilities of these are:

$$\mathbb{P}_0 = |c_0|^2 = \frac{1}{3} \qquad\qquad \mathbb{P}_1 = |c_1|^2 = \frac{2}{3} \qquad (11)$$

Ok, now let's measure position.

Q: What are the possible results?   A: $0 < x < L$
Q: What is the most likely result?   A: $x \simeq L/4$ or $3L/4$
Q: What results are very unlikely?   A: $x \simeq 0,\ L/2,$ or L

Let's imagine that we find the $x = L/5$. What is the new state of the system?

Measure $x = L/5$.
New State: $\psi_{\text{newer}}(x) = \delta(x - L/5)$

But what is the time dependence of this state?

I'm venturing into some dangerous ground, because the time evolution of a delta function is not well defined, but formally we can write down the answer as superposition of energy eignenstates, for which we know the time evolution.

Write as superposition of energy eigenstates (EES):

$$
\begin{aligned}
\psi(x,t) &= \sum_n c_n \phi_n(x) e^{-i\omega_n t} \\
c_n &= \langle \phi_n | \delta(x - L/5) \rangle \\
&= \int_{-\infty}^{\infty} A_n \sin(k_n x) \delta(x - L/5)\, dx \\
&= A_n \sin(k_n L/5)
\end{aligned}
$$

Q: So, now what energies can we measure?
  A: Any! (Or at least any for which $\sin(k_n L/5) \neq 0$.)
Q: Where did these very high energies come from?
  A: The measurement!

As a physical example, imagine the electron in the voltage trap shown at the beginning of our discussion of this potential. To measure its position, you might shine some light on it and hope to see a photon scatter off (think Compton Scattering). The scattered photon will tell you something about the location of the electron, but it will also give energy to the electron. Higher energy photons will make better position measurements possible, and they will push the electron to higher energy states.

The normalization factor A_n is straight forward to compute.

EES Normalization

$$
\begin{aligned}
1 &= |\langle \phi_n | \phi_n \rangle|^2 \\
&= |A_n|^2 \int_0^L \sin^2(k_n x)\ dx \\
&= |A_n|^2 \frac{L}{2} \\
\Rightarrow A_n &= \sqrt{\frac{2}{L}} e^{i\theta} \quad \text{where we usually use } \theta = 0
\end{aligned}
$$

6 Next Time

Exam next week will cover all material up to now. Tuesday's lecture will be very interesting, but it will not be on this exam.

- Now that we know that EESs make things easy, let's learn how they work in any 1D potential