Phys 342 Lecture 31

Welcome back to more reading lecture notes online ☺. This week, we are going to step back from the exact solutions of the Schrödinger equation (i.e., diagonalization of the Hamiltonian) and introduce methods for approximation. We have nearly exhausted those problems for which there exists a known, exact, analytic solution to the Schrödinger equation, and much of modern research on quantum mechanics or its generalizations focuses around approaches to approximating the eigenvalues of the Hamiltonian. We will just barely scratch the surface of techniques for approximation this week, focusing on three different methods; one for each lecture.

For today, we will study the following problem: given an arbitrary potential $V(x)$, what are the eigenvalues/states of the Hamiltonian $\hat{H}$:

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

(We'll just work in one-dimension this week; these methods can be extended to higher dimensions, but one dimension is interesting enough.) We've identified all sorts of fun tricks for doing this in special examples, but the general problem has no closed-form solution. So, we need an efficient way to estimate the eigenstates/values. Further, it's not just enough to estimate it; we want to have a framework for estimation that is systematically improvable which means that we have an algorithm for improving the accuracy of the estimate. It just involves calculating more and more terms or something that we can do and is only limited by our time and calculational ability. Our first technique we will employ is

the systematic method for estimating nearly everything in physics: the Taylor expansion. Recall that the taylor expansion is used to estimate an unknown functional value, say $f(x_0+\Delta x)$, from a known functional value, say $f(x_0)$, for some function $f(x)$.

So, with this in mind, the problem we want to solve is:

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

for some eigenvalue E and eigenstate $\psi(x)$. Now, $V(x)$ is arbitrary, and to use the Taylor expansion we need some toehold, some familiar place to start from which we can then work to estimate the unknown E and $\psi(x)$.

The trick for this method is the following: if $V(x)$ is similar or close to a potential whose eigenvalues <u>are</u> known, then we can make progress. So, let's assume we can write

$V(x) = V_0(x) + \varepsilon V'(x)$, where $V_0(x)$ is a simple potential (1D well, harmonic oscillator, or the like), $V'(x)$ is the "difference potential", and ε is a value that controls the effect of the perturbation away from $V_0(x)$. So, the eigenstate problem we want to solve is:

$\hat{H}|\psi\rangle = E|\psi\rangle = \left(\frac{\hat{p}^2}{2m} + V_0 + \varepsilon V'\right)|\psi\rangle$, where we have

written everything in a basis independent way for now. The quantity ε is our Taylor expansion parameter, just like Δx in the Taylor expansion of $f(x_0+\Delta x)$. So, we can in general express the unknown quantities $|\psi\rangle$ and E as Taylor expansions

in ε as: $E = \sum_{n=0}^{\infty} \varepsilon^n E_n$, $|\psi\rangle = \sum_{n=0}^{\infty} \varepsilon^n |\psi_n\rangle$,

and now E_n and $|\psi_n\rangle$ are just terms in the expansion. To make progress, we just insert these ansätze for E and $|\psi\rangle$ into our Schrödinger equation and expand order-by-order in ε. Each order in ε will correspond to a new equation we can solve for those corresponding terms in the expansion.

Concretely, plugging these expansions in, we find:

$$\left(\frac{\hat{p}^2}{2m} + V_0 + \varepsilon V'\right) \sum_{n=0}^{\infty} \varepsilon^n |\psi_n\rangle = \sum_{n=0}^{\infty} \varepsilon^n E_n \sum_{m=0}^{\infty} \varepsilon^m |\psi_m\rangle$$

The ε^0 equation is: $\left(\frac{\hat{p}^2}{2m} + V_0\right)|\psi_0\rangle = E_0|\psi_0\rangle$. By construction, we assumed we could solve this equation for E_0 and $|\psi_0\rangle$. Further, for simplicity we will denote this "unperturbed" Hamiltonian as:

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + V_0.$$

Next, the ε^1 terms in the expansion are:

$$\varepsilon \hat{H}_0|\psi_1\rangle + \varepsilon V'|\psi_0\rangle = \varepsilon E_0|\psi_1\rangle + \varepsilon E_1|\psi_0\rangle.$$

We'll first isolate the first-order energy term, E_1. To do this, let's hit everything with a bra $\langle\psi_0|$:

$$\langle\psi_0|\hat{H}_0|\psi_1\rangle + \langle\psi_0|V'|\psi_0\rangle = \langle\psi_0|E_0|\psi_1\rangle + \langle\psi_0|E_1|\psi_0\rangle.$$

I've canceled out the & overall ε for cleanliness. Now, note that

$\langle\psi_0|\hat{H}_0|\psi_1\rangle = E_0\langle\psi_0|\psi_1\rangle$, as $|\psi_0\rangle$ is an eigenstate of the unperturbed Hamiltonian, $\hat{H}_0$. Then, this term cancels

from both sides of the equation. Further, $|\psi_0\rangle$ is normalized, $\langle\psi_0|\psi_0\rangle = 1$, so we find:

$$E_1 = \langle\psi_0|V'|\psi_0\rangle.$$

That is, the first correction to the energy is the expectation value of the perturbation potential V' in the unperturbed state, $|\psi_0\rangle$.

Now, the first correction to the wavefunction is a bit trickier. Let's rearrange the first order equation to read:

$$(\hat{H}_0 - E_0)|\psi_1\rangle = (E_1 - V')|\psi_0\rangle. \qquad (*)$$

Now, remember we want to solve for the ket $|\psi_1\rangle$, which is some vector in a Hilbert space. Also, the right side of this equality is another, known, vector on this Hilbert space. $\hat{H}_0 - E_0$ is some operator/matrix that acts on the states of the Hilbert space, so this equation is nothing more than the familiar equation for a system of linear equations:

$\mathbb{A}\vec{x} = \vec{b}$, where $\mathbb{A}$ is a matrix, $\vec{b}$ is a known vector, and we want to find $\vec{x}$. Of course, we know how to solve for $\vec{x}$: we just invert $\mathbb{A}$:

$$\vec{x} = \mathbb{A}^{-1}\vec{b}.$$

This is only possible if, in fact, $\mathbb{A}$ is invertible/non-singular/ has non-zero determinant. By our analogy, $\mathbb{A} = \hat{H}_0 - E_0$ in our problem, so we want to invert this:

$$\mathbb{A}^{-1} = \frac{1}{\hat{H}_0 - E_0}.$$ Does this actually exist?

Recall that E_0 is an eigenvalue of $\hat{H}_0$ and $\mathbb{A} = \hat{H}_0 - E_0\mathbb{1}$ is just the operator that we we would consider to determine the eigenvalue:

$$(\hat{H}_0 - E_0\mathbb{1})|\psi_0\rangle = 0.$$

That is, the operator/matrix $\hat{H}_0 - E_0$ has an eigenvector with 0 eigenvalue, thus its determinant vanishes:

$\det(\hat{H}_0 - E_0) = 0$. Hence, we would (naïvely) say that

$\hat{H}_0 - E_0$ is not invertible, so it would seem that we can't solve for $|\psi_1\rangle$. Or can we?

Let's write our equation (*) in a more illuminating way, using the completeness of the eigenstates of $\hat{H}_0$. We will denote an eigenstate as

$\hat{H}_0 |\psi_0^n\rangle = E_0^n |\psi_0^n\rangle$, where "n" denotes the n^{th} energy eigenstate/value.

Now, assuming that the eigenvectors of $\hat{H}_0$ form an orthonormal and complete basis, we can rewrite our equation for $|\psi_1\rangle$ in another useful manner. We have:

$(\hat{H}_0 - E_0^m)|\psi_1\rangle = (E_1 - V')|\psi_0^m\rangle$, where we have denoted the eigenstate/value of $\hat{H}_0$ by an integer m. Also,

$E_1 = \langle\psi_0^m|V'|\psi_0^m\rangle$. Now, by completeness, we can write

$\mathbb{1} = \sum_{n=0}^{\infty} |\psi_0^n\rangle\langle\psi_0^n|$, and as the states $|\psi_0^n\rangle$ are eigenstates of $\hat{H}_0$, we can write it as the outer product:

$\hat{H}_0 = \sum_{n=0}^{\infty} E_0^n |\psi_0^n\rangle\langle\psi_0^n|$.

Then, we can express our equation as:

$$(\hat{H}_0 - E_0^m)|\psi_1\rangle = \sum_{n=0}^{\infty} (E_0^n - E_0^m)|\psi_0^n\rangle\langle\psi_0^n|\psi_1\rangle$$

$$= E_1|\psi_0^m\rangle - \sum_{n=0}^{\infty} |\psi_0^n\rangle\langle\psi_0^n|V'|\psi_0^m\rangle$$

Now, in this form, we recognize the solution to our problem of inverting the operator $\hat{H}_0 - E_0^m$. The only issue is that $|\psi_0^m\rangle$ is an eigenvector of $\hat{H}_0 - E_0^m$ with 0 eigenvalue. So, in our new equation above, we can focus on individual terms and identify their consequence. First, if $n=m$, then we have the problematic term, but note that the left side vanishes, and the right is:

$E_1|\psi_0^m\rangle = \langle\psi_0^m|V'|\psi_0^m\rangle|\psi_0^m\rangle$, is exactly what we found earlier for E_1. Note that we are allowed to look at individual terms in the expression above because the $|\psi_0^n\rangle$ states are orthogonal, so $|\psi_0^n\rangle$ and $|\psi_0^m\rangle$ for $n \neq m$ have no components in common.

Now, we have shown that the $n=m$ term cancels, so for $n \neq m$, we find:

$$\langle\psi_0^n|\psi_1\rangle = \frac{\langle\psi_0^n|V'|\psi_0^m\rangle}{E_0^m - E_0^n}, \quad n \neq m$$

which is the coefficient of $|\psi_1\rangle$ in the expansion of energy eigenstates of $\hat{H}_0$. That is, our first correction to the wavefunction is:

$$|\psi_1\rangle = \sum_{\substack{n=0 \\ n\neq m}} \frac{\langle\psi_0^n|V'|\psi_0^m\rangle}{E_0^m - E_0^n}|\psi_0^n\rangle.$$

As long as all energy eigenvalues of $\hat{H}_0$ are distinct ("non-degenerate"), all coefficients in the expansion are non-zero and finite, in general.

So, to summarize, for our Schrödinger equation written as:

$$\left(\hat{H}_0 + \varepsilon V'\right)|\psi\rangle = E|\psi\rangle,$$

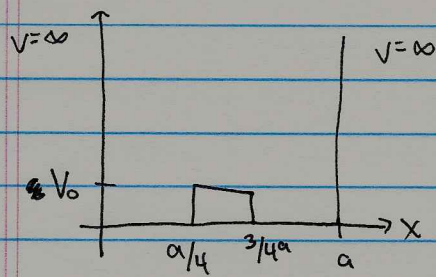
we can write the energy eigenvalue as

$$E = E_0^m + \varepsilon \langle \psi_0^m | V' | \psi_0^m \rangle + \mathcal{O}(\varepsilon^2)$$

$$|\psi\rangle = |\psi_0^m\rangle + \varepsilon \sum_{\substack{n=0 \\ n\neq m}} \frac{\langle \psi_0^n | V' | \psi_0^m \rangle}{E_0^m - E_0^n} |\psi_0^n\rangle + \mathcal{O}(\varepsilon^2).$$

The "big O notation" $\mathcal{O}(\varepsilon^2)$ means that our expression is correct, up to terms in the Taylor expansion in ε at and beyond ε^2 that we have ignored. One can work to calculate these terms, but we'll leave that for another time.

Finally for today, let's see what this formalism for an explicit example. Let's consider a potential that is the infinite square well that has a little bump in the center:



That is, $V(x) = \begin{cases} 0, & 0 < x < a/4,\ 3/4 < x < a \\ V_0, & a/4 < x < 3a/4 \\ \infty, & \text{else} \end{cases}$

So, our Schrödinger equation is:

$$\left(\frac{\hat{p}^2}{2m} + V_0 \,\textcircled{u}(x - a/4)\,\textcircled{u}(3a/4 - x)\right)\psi(x) = E\,\psi(x),$$

where $\textcircled{u}(x)$ is called the Heaviside theta function and is defined to be:

$$\textcircled{u}(x) = \begin{cases} 0, & x < 0 \\ 1, & x > 0. \end{cases}$$

So, we identify the little bump as our perturbation potential:

$$V' = V_0 \Theta\left(x - a/4\right) \Theta\left(3a/4 - x\right)$$

and let's see how the ground state of the well is affected by the bump. Recall that the energies of the ∞-$\square$ well are:

$E_0^n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$, for $n = 1, 2, 3, \ldots$, so the ground state is:

$E_0^0 = \frac{\pi^2 \hbar^2}{2ma^2}$. Now, the first correction to the ground state energy is:

$$E_1^0 = \langle \psi_0^0 | V' | \psi_0^0 \rangle = \int_{a/4}^{3a/4} dx \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) V_0 \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$$

$$= \frac{2+\pi}{2\pi} V_0,$$ where I have used that the ground state wavefunction of the good ole' ∞-$\square$ well is:

$\psi_0^0(x) = \sqrt{\frac{2}{a}} \sin\frac{\pi x}{a}$. Then, to linear order in V_0, the small perturbation potential, the new ground state of the ∞-$\square$ well with a bump is:

$$E_a^0 = \frac{\pi^2 \hbar^2}{2ma^2} + \frac{2+\pi}{2\pi} V_0 + \mathcal{O}(V_0^2).$$

We could also find the correction to the ground state wavefunction to this order, but you'll play with more in homework, as well as a first look at the $\mathcal{O}(V_0^2)$ corrections to the energies.

On to new techniques next time...