Phys 342 Lecture 32

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Hello from afar and welcome back to quantum mechanics. This week, we are studying tools for approximation in diagonalizing the Hamiltonian or, correspondingly, solving the Schrödinger equation. Last lecture, we discussed quantum mechanics perturbation theory in which we identified a "small" perturbation from a known, exactly solvable Hamiltonian $\hat{H}_0$ of the form:

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

Hamiltonian and ε is a "small" (i.e., formally small, i.e., something we consider as small for the sake of expansion) parameter. Our trick for approximating the solutions of this eigenvalue problem was to expand the eigen value E and eigenstate $|\psi\rangle$ in powers of ε, like a Taylor expansion:

$$|\psi\rangle = |\psi_0\rangle + \varepsilon|\psi_1\rangle + \cdots, \quad E = E_0 + \varepsilon E_1 + \cdots,$$

and $|\psi_0\rangle$ and E_0 satisfy: $\hat{H}_0|\psi_0\rangle = E_0|\psi_0\rangle$ and are known. We identified the $\mathcal{O}(\varepsilon)$ or first corrections to be:

$$E_1 = \langle\psi_0|\hat{H}'|\psi_0\rangle, \quad |\psi_1\rangle = \sum_{\substack{n=0 \\ n\neq m}} \frac{\langle\psi_0^n|\hat{H}'|\psi_0^m\rangle}{E_0^m - E_0^n}|\psi_0^n\rangle,$$

where E_0^n is the n^{th} energy eigen~~state~~ value of $\hat{H}_0$ and $|\psi_0^n\rangle$ is its eigenstate. Here, m is the original eigenstate we are expanding about: $|\psi_0\rangle \equiv |\psi_0^m\rangle$, for instance.

These perturbative methods are great when you have a first guess for the eigenstate/value, or something to naturally expand about. What if no such state exists? Today and next lecture, we will introduce two methods which enable honest guessing of the eigenstates and we'll prove results which will allow us to bound eigenvalues in a robust way. The first technique we will study is the <u>variational method</u>.

The idea is extremely simple. Let's consider a system described by some Hamiltonian $\hat{H}$. The question we would like to ask is what the ground state energy of this Hamiltonian is. Solving this problem exactly might be challenging depending on what $\hat{H}$ is, but we can place an upper bound on the ground state energy quite easily. Everything that follows in this lecture comes from a very simple property, that we will prove. For <u>any</u> state $|\psi\rangle$ in a Hilbert space, the expectation value of the Hamiltonian on that state is bounded from below by the ground state energy of $\hat{H}$, E_0. That is, with a sufficiently good estimate for the state $|\psi\rangle$, we can get close to the value of the ground state energy, E_0. With a better estimate, we can get closer, and for many problems of interest getting the ground state energy is sufficient.

So, let's prove this. For a Hamiltonian $\hat{H}$, the expectation value of $\hat{H}$ on any state $|\psi\rangle$ in the Hilbert space is bounded from below by the ground state energy E_0 of the Hamiltonian:

$$\langle\psi|\hat{H}|\psi\rangle \geq E_0$$

<u>Proof</u>: Assuming orthonormality and completeness of the energy eigenstates of $\hat{H}$, we can expand $|\psi\rangle$ in the basis of energy eigenstates:

$$|\psi\rangle = \sum_{n=0}^{\infty} \beta_n |\psi_n\rangle,$$ where $|\psi_n\rangle$ is the n^{th} energy eigenstate and β_n is a complex coefficient.

Now, as $|\psi\rangle$ is in the Hilbert space $\mathcal{H}$, $\langle\psi|\psi\rangle = 1$ or that

$$\sum_{n=0}^{\infty} |\beta_n|^2 = 1.$$

Computing the expectation value of $\hat{H}$ on $|\psi\rangle$, we have:

$$\langle\psi|\hat{H}|\psi\rangle = \left(\sum_{n=0}^{\infty} \beta_m^* \langle\psi_m|\right) \hat{H} \left(\sum_{n=0}^{\infty} \beta_n |\psi_n\rangle\right)$$
$$= \sum_{n,m=0}^{\infty} \beta_m^* \beta_n E_n \langle\psi_m|\psi_n\rangle = \sum_{n=0}^{\infty} |\beta_n|^2 E_n,$$

as we assume that $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$ and $\langle\psi_m|\psi_n\rangle = \delta_{nm}$. Now, let's subtract E_0, the ground state, ~~from~~ energy, from this expectation value:

$$\langle\psi|\hat{H}|\psi\rangle - E_0 = \sum_{n=0}^{\infty} |\beta_n|^2 E_n - E_0 = \sum_{n=0}^{\infty} |\beta_n|^2 E_n - \sum_{n=0}^{\infty} |\beta_n|^2 E_0$$
$$= \sum_{n=0}^{\infty} |\beta_n|^2 (E_n - E_0) = \sum_{n=1}^{\infty} |\beta_n|^2 (E_n - E_0).$$

In this sequence of equalities, we have used that $\sum_{n=0}^{\infty} |\beta_n|^2 = 1$, and then removed the $n=0$ term (which was 0 anyway) in the final equality. As E_0 is the ground state energy, we have that $E_n > E_0$, for $n \geq 1$, and so the final expression is manifestly (i.e., "obviously") non-negative. This proves that therefore

$$\langle\psi|\hat{H}|\psi\rangle - E_0 \geq 0,$$ as we claimed.

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So, with a good enough guess, we can get close to the ground state energy. But how do we go about guessing? Just throwing out random states and testing the expectation value $\langle\psi|\hat{H}|\psi\rangle$ is incredibly inefficient and there is no guarantee that any individual guess will be close to the ground state energy at all (remember, $1000E_0 \geq E_0$:)). So, to use this result to its fullest potential, our plan will be to make a guess of a ground state $|\psi\rangle$ that contains parameters that we can minimize over. For quantum mechanical problems in one spatial dimension, we thus consider wavefunctions $\psi(x;\alpha_1,\alpha_2,\ldots,\alpha_n)$, where the α_i parameters specify the particular shape of the wavefunction, given a general functional form. Then, we can calculate the expectation value of the Hamiltonian as:

$$\langle\hat{H}\rangle = \int dx\, \psi^*(x;\alpha_1,\alpha_2,\ldots,\alpha_n)\,\hat{H}\,\psi(x;\alpha_1,\alpha_2,\ldots,\alpha_n).$$

By our theorem above, for any choice of the parameters $\{\alpha_1,\alpha_2,\ldots,\alpha_n\}$ this is guaranteed to be at least the value of the ground state energy. However, these parameters give us another handle to adjust the form of the wavefunction to minimize $\langle\hat{H}\rangle$ further. That is, with these parameters, we can minimize over them to get the least upper bound possible on the ground state energy, given the chosen (i.e. guessed) functional form of the wavefunction $\psi(x;\alpha_1,\alpha_2,\ldots,\alpha_n)$.

This is pretty abstract and possibly confusing. Seeing it work in an explicit example can demonstrate that it's actually very simple.

Let's test this idea out for the infinite square well, where we set $a=1$ for simplicity. That is, the potential we consider is:

$$V(x) = \begin{cases} 0, & 0<x<1 \\ \infty, & \text{else} \end{cases}.$$

We know what the ground state energy is in this case:

$$E_0 = \frac{\pi^2}{2}\frac{\hbar^2}{m} \cong 4.934802\,\frac{\hbar^2}{m},$$

where I've expanded the numerical value of $\pi^2/2$ to 7 significant figures. Now, onto a guess for the ground state wavefunction. We know that the wavefunction must vanish at both $x=0,1$, the boundaries of the well. Additionally, the well is symmetric about its central point, $x=1/2$, so we expect that the wavefunction would also be symmetric about $x=1/2$. A guess for a wavefunction that vanishes at the end points and is symmetric about $x=1/2$ is:

$$\psi(x;\alpha) = N\,x^\alpha(1-x)^\alpha,$$ where N is a normalization

constant and α is a parameter that we will vary to minimize the expectation value of the Hamiltonian on this state.

First, we will calculate the normalization N, for any α. We require that:

$$1 = \int_0^1 dx\,\psi^*(x;\alpha)\,\psi(x;\alpha) = N^2\int_0^1 dx\,x^{2\alpha}(1-x)^{2\alpha}.$$

Now, this integral can't be done with elementary functions for abitrary α, but can be expressed in terms of the Euler Beta function $B(a,b)$. The Euler Beta function is defined to be:

$$B(a,b) = \int_0^1 dx\,x^{a-1}(1-x)^{b-1} = \frac{\Gamma(a)\Gamma(b)}{\Gamma(a+b)},$$

where $\Gamma(x)$ is the Euler Gamma function, which we had seen earlier and is a continuous generalization of the factorial. Then, the integral we need, in terms of the Beta function, is

$$1 = N^2 \int_0^1 dx\, x^{2\alpha}(1-x)^{2\alpha} = N^2 B(2\alpha+1, 2\alpha+1) = N^2 \frac{\Gamma(2\alpha+1)^2}{\Gamma(4\alpha+2)}$$

Thus, it follows that the normalization factor N is:

$$N = \frac{\sqrt{\Gamma(4\alpha+2)}}{\Gamma(2\alpha+1)}.$$

With this result, we can then calculate the expectation value of the Hamiltonian, $\langle \hat{H} \rangle$. Recall that, for the infinite square well, the Hamiltonian is:

$$\hat{H} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}, \text{ in the position basis.}$$

Thus, the evaluation of the expectation value of $\hat{H}$ involves the second derivative of the wavefunction, where

$$\frac{\partial^2}{\partial x^2} N x^\alpha (1-x)^\alpha = \alpha N x^{\alpha-2}(1-x)^{\alpha-2}\left[\alpha - 1 + x(1-x)(2-4\alpha)\right].$$

Then, the expectation value of the Hamiltonian is:

$$\langle \hat{H} \rangle = -N^2 \frac{\hbar^2}{2m}\int_0^1 dx \left[x^\alpha (1-x)^\alpha \frac{\partial^2}{\partial x^2} x^\alpha (1-x)^\alpha\right]$$

$$= \frac{\hbar^2}{m}\frac{\alpha(1+4\alpha)}{2\alpha-1}, \text{ and } \alpha > 1/2.$$

Now, I don't expect you to just know how to evaluate this integral as I used extensive identities of the

Gamma Function to simplify it this far. Also note that this integral is actually only finite if $\alpha > 1/2$, which perhaps isn't so surprising. If $\alpha < 1/2$, then the second derivative of x^α has an exponent that is less than $-3/2$, and $x^{-3/2}$ is not integrable on $x \in [0,1]$.

At any rate, this final result is necessarily bounded from below by the ground state energy. To find the least upper bound given this form of the guess wavefunction we then minimize this result over α. To do the minimization, we just differentiate with respect to α and demand that it vanish:

$$\frac{d}{d\alpha}\frac{\alpha(1+4\alpha)}{2\alpha-1} = 0 = \frac{8\alpha^2-8\alpha-1}{(1-2\alpha)^2}$$

That is, $8\alpha^2-8\alpha-1=0$ or $\alpha = \frac{8\pm\sqrt{64+32}}{16} = \frac{1}{2}\pm\frac{\sqrt{6}}{4}$.

As $\alpha > 1/2$ established earlier, we take the "+" root, so the exponent that minimizes the expectation value is

$$\alpha_{min} = \frac{2+\sqrt{6}}{4} \cong 1.112372\ldots.$$

Now, at this point, we can evaluate the expectation value of the Hamiltonian:

$$\langle\hat{H}\rangle = \frac{\hbar^2}{m}\frac{\alpha_{min}(1+4\alpha_{min})}{2\alpha_{min}-1} = \frac{\hbar^2}{m}\left(\frac{5}{2}+\sqrt{6}\right) \cong (4.94948\ldots)\frac{\hbar^2}{m}$$

Note indeed that this is (very slightly!) larger than the true ground state value. The difference between this expectation value and the ground state is:

$$\langle \hat{H} \rangle - E_0 = \frac{\hbar^2}{m}\left(\frac{5}{2} + \sqrt{6} - \frac{\pi^2}{2}\right) \cong (0.01468\ldots)\frac{\hbar^2}{m},$$

or less than 1% the value of the true ground state. So this method gets us to an excellent estimate relatively easily! By the way, everything we did here was analytic in evaluating integrals, but it can be even easier if you just numerically evaluate them.

On to one more approximation technique on Friday...