

The Infinite Square Well

Lecture 6

Physics 342
Quantum Mechanics I

Friday, February 8th, 2008

With the equation in hand, we move to simple solutions. For a particle confined to a box, we find that the boundary conditions impose energy quantization (specific allowed energies), a new phenomenon with respect to classical mechanics in a box. This solution comes to us in a familiar way via separation of variables (think of separable solutions to Laplace's equation representing the electrostatic potential inside a box with grounded walls).

6.1 Separability of Schrödinger's Equation

For a time-independent potential, $V(x)$, Schrödinger's equation is separable in time, i.e.

$$i \hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x) \Psi \quad (6.1)$$

with the ansatz: $\Psi(x, t) = \psi(x) \phi(t)$ separates (notice that for $V(x, t)$ this may or may not be true)

$$i \hbar \frac{\dot{\phi}}{\phi} = -\frac{\hbar^2}{2m} \frac{\psi''}{\psi} + V(x) \quad (6.2)$$

where we define $\dot{\phi}(t) \equiv \frac{d\phi(t)}{dt}$ and $\psi'(x) \equiv \frac{d\psi(x)}{dx}$. Then the right-hand-side depends only on x , the left-hand side depends only on t , so they must separately be equal to a constant, call it E . The time-dependence of the wave function is then completely fixed:

$$i \hbar \dot{\phi} = E \phi \longrightarrow \phi = A e^{-i \frac{E}{\hbar} t}. \quad (6.3)$$

We then have the so-called time-independent Schrödinger equation, which is just the spatial portion:

$$-\frac{\hbar^2}{2m} \frac{\psi''}{\psi} + V(x) = E. \quad (6.4)$$

Notice that our full solution, whatever the solution to (6.4) is, has time-independent density:

$$|\Psi(x, t)|^2 = \Psi(x, t)^* \Psi(x, t) = \psi^*(x) \psi(x), \quad (6.5)$$

and the probabilistic normalization $\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 1$ becomes an issue for the spatial part alone.

As we saw at the end of last time, the spatial component of Schrödinger's equation can be viewed as the operator constructed from a Hamiltonian – that is, $H(x, p) = \frac{p^2}{2m} + V(x)$ becomes

$$\boxed{\hat{H} \left(x, \frac{\hbar}{i} \frac{\partial}{\partial x} \right) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)} \quad (6.6)$$

and we can write the separated form as:

$$\hat{H} \psi(x) = E \psi(x). \quad (6.7)$$

This looks an awful lot like an eigenvector equation for the operator \hat{H} with eigenfunction $\psi(x)$ and eigenvalue E (that's what it is).

We can calculate the expectation value of \hat{H} from the above, assuming the wavefunction has been normalized:

$$\langle \hat{H} \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{H} \psi(x) dx = E \int_{-\infty}^{\infty} \psi^*(x) \psi(x) dx = E, \quad (6.8)$$

so we say that the state represented by $\psi(x)$ has energy E . This is clearly a constant in time – what's more surprising, the variance of the energy is zero – i.e. the particle in state $\psi(x)$ has exactly energy E :

$$\sigma^2 = \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2 = E^2 - E^2 = 0. \quad (6.9)$$

Currently, E is continuous, we have no restriction on what its value can be – but in many cases, the energy itself is quantized (we will see this in a moment), so that there are a variety of states $\psi_E(x)$ with definite energy, and any linear combination of these is also a solution to the time-independent Schrödinger equation.

6.2 Infinite Square Well

Consider a particle confined to a box in one dimension. In this case, the confining potential takes the form:

$$V(x) = \begin{cases} 0 & 0 \leq x \leq a \\ \infty & x < 0 \text{ or } x > a \end{cases} \quad (6.10)$$

In the region $0 \leq x \leq a$, our eigenfunction equation: $\hat{H}\psi = E\psi$ reads:

$$\frac{-\hbar^2}{2m} \psi''(x) = E\psi(x) \longrightarrow \psi(x) = A e^{i \frac{\sqrt{2mE}}{\hbar} x} + B e^{-i \frac{\sqrt{2mE}}{\hbar} x}. \quad (6.11)$$

We have boundary conditions – we cannot have any ψ to the left of $x = 0$ or to the right of $x = a$. This first condition gives:

$$\psi(x = 0) = A + B = 0 \longrightarrow A = -B, \quad (6.12)$$

at which point we can write the solution in the form:

$$\psi(x) = \tilde{A} \sin\left(\frac{\sqrt{2mE}}{\hbar} x\right), \quad (6.13)$$

for some new (but still arbitrary) constant \tilde{A} ($= 2iA$). Then the boundary condition at $x = a$ gives

$$\psi(x = a) = 0 = \tilde{A} \sin\left(\frac{\sqrt{2mE}}{\hbar} a\right) \quad (6.14)$$

with trivial solution $\tilde{A} = 0$, which gives $\psi(x) = 0$ and is not normalizable. The more interesting (viable) case is:

$$\frac{\sqrt{2mE}}{\hbar} a = n\pi \quad \text{for } n \in \mathbb{Z}. \quad (6.15)$$

The energy of the particle, then, can take only particular values, in integer multiples:

$$\boxed{E_n = \frac{\hbar^2 n^2 \pi^2}{2m a^2}}. \quad (6.16)$$

So define the infinite set of solutions:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), \quad (6.17)$$

where the normalization factor is for later convenience.

We see that the energy for the state $\psi_n(x)$ is directly related to its wavelength. Since we have a finite domain, that wavelength defines the number of cycles that can fit in our interval, and the energy is a measure of the number of full cycles as shown in Figure 6.1.

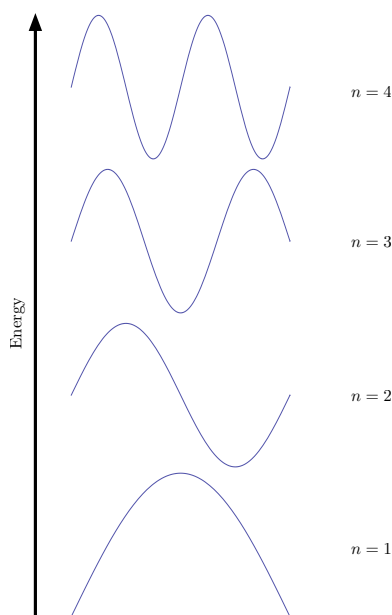


Figure 6.1: The first four infinite square well energy eigenfunctions. The number of extrema is related to the energy ($\sim n^2$)

The most general spatial solution is a sum:

$$\psi(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right). \quad (6.18)$$

Now, as we discussed in the linear algebra section, we can view $\psi_n(x)$ as a basis for functions that are periodic – the inner product that is relevant is:

$$\psi_n \cdot \psi_m = \int_0^a \psi_n(x) \psi_m(x) dx = \frac{a}{2} \left(\frac{2}{a}\right) \delta_{mn} = \delta_{mn} \quad (6.19)$$

(that naked δ_{mn} is the motivation for the funny factor of $\sqrt{\frac{2}{a}}$ in (6.17)). If we were given an initial wavefunction $\psi_0(x)$, we could define the coefficients

c_n in the obvious way:

$$c_n = \int_0^a \psi_0(x) \psi_n(x) dx \quad \text{for } n = 1 \longrightarrow \infty. \quad (6.20)$$

In addition, we know that such an initial waveform must be normalized: $\int_0^a \psi_0(x)^2 dx = 1$. Suppose we had the coefficients c_n , then:

$$\int_0^a \left(\sum_{n=1}^{\infty} c_n \psi_n(x) \right)^2 dx = \sum_{n=1}^{\infty} c_n^2 = 1 \quad (6.21)$$

is the requirement.

The full wave-function is built up out of the infinite spatial expansion with appropriate temporal evolution term:

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n e^{-i \frac{E_n t}{\hbar}} \psi_n(x) = \sum_{n=1}^{\infty} c_n e^{-i \frac{\hbar n^2 \pi^2 t}{2m a^2}} \sqrt{\frac{2}{a}} \sin\left(\frac{n \pi x}{a}\right), \quad (6.22)$$

6.2.1 Examples

The Schrödinger equation is first order in time, hence the need to specify an initial waveform at $t = 0$. That gives us the spatial decomposition discussed above, and familiar from almost all treatments of separation of variables (where the solutions form a “complete” basis). Suppose we start with a pure $n = 1$ solution, that is, we require that $\Psi(x, 0) = A \sin\left(\frac{\pi x}{a}\right)$ – here we don’t need any fancy integration, the solution is obvious:

$$\Psi(x, t) = A e^{-i \frac{\hbar \pi^2 t}{2m a^2}} \sin\left(\frac{\pi x}{a}\right). \quad (6.23)$$

Now, we require that $\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 1$, and that can be used to set the constant A :

$$\int_{-\infty}^{\infty} \Psi^* \Psi dx = \int_0^a A^2 \sin^2\left(\frac{\pi x}{a}\right) dx = A^2 \frac{a}{2} = 1 \longrightarrow A = \sqrt{\frac{2}{a}}, \quad (6.24)$$

and we have the appropriately normalized final form

$$\Psi(x, t) = \sqrt{\frac{2}{a}} e^{-i \frac{\hbar \pi^2 t}{2m a^2}} \sin\left(\frac{\pi x}{a}\right). \quad (6.25)$$

From here, we can calculate the expectation value of three of our operators of interest: x , p and H , giving us the average position, momentum and energy of the particle:

$$\begin{aligned}\langle x \rangle &= \int_{-\infty}^{\infty} \Psi^*(x, t) x \Psi(x, t) dx = \frac{a}{2} \\ \langle p \rangle &= \int_{-\infty}^{\infty} \Psi^*(x, t) \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi(x, t) dx = 0 \\ \langle H \rangle &= \int_{-\infty}^{\infty} \Psi^*(x, t) \left(-\frac{\hbar^2}{2m} \right) \Psi''(x, t) dx = \frac{\hbar^2 \pi^2}{2 m a^2}.\end{aligned}\tag{6.26}$$

The expectation value of position is at half the width of the confinement, which is sensible. The energy expectation value is also precisely what we expect.

If we think of the “classical” version of this problem, a particle moving back and forth with constant momentum, the expectation value of the momentum would be zero, in the sense that the particle spends equal time moving to the left and the right. To find the (classical) expectation value of position, we must know the time-independent position density (the analogue of $|\Psi(x, t)|^2$). The particle moves back and forth, so technically, at a given time, its position is known and the density is a delta function about the actual location of the particle: $\rho(x, t) = \delta(x - x(t))$. In this case, we want the pure spatial density, so we average over “one full cycle” in time. Consider the trip from $x = 0$ to $x = a$ at constant velocity. For this segment of the motion, we go from $t = 0 \rightarrow T \equiv a/v$ with $x(t) = vt$. As we go from $x = a \rightarrow 0$, we have $t = T \rightarrow 2T$ with $x(t) = -a + v(t - T)$. Then if we average over a round trip:

$$\rho(x) = \frac{1}{2T} \left[\int_0^T \rho(x, t) dt + \int_T^{2T} \rho(x, t) dt \right].\tag{6.27}$$

We just need to input and evaluate the delta functions for the two different trajectories, then

$$\begin{aligned}\rho(x) &= \frac{1}{2T} \left[\int_0^T \delta(x - vt) dt + \int_T^{2T} \delta(x - a + v(t - T)) dt \right] \\ &= \frac{1}{2T} \left[\int_x^{x-a} \delta(y) \left(-\frac{1}{v} \right) dy + \int_{x-a}^x \delta(y) \left(\frac{1}{v} \right) dy \right] \\ &= \frac{1}{T} \frac{1}{v}\end{aligned}\tag{6.28}$$

where the second equality follows from a change of variables in each integration. Using the definition of the travel time: $vT = a$, we learn that $\rho(x) = \frac{1}{a}$, i.e. the probability that the particle is in an interval dx is proportional to dx ($\rho dx = dx/a$) – that makes sense, the larger the interval, the more likely the particle is in it. In addition, the normalization has come out correctly: $\int_0^a \rho(x) dx = \int_0^a \frac{1}{a} dx = 1$, so we are bound to find the particle somewhere between the walls.

From this classical density, it is clear that the expectation value of position is $\langle x \rangle = \frac{a}{2}$, identical to the quantum prediction¹. So the only real difference between the expected values associated with a stationary solution $\psi_n(x)$ of Schrödinger's equation and the classical expectation values is the restriction to a finite set of energies – this does not hold on the classical side.

There are other differences – suppose we look at the variance for the position, momentum and energy operators for $n = 1$. For the quantum mechanical density, these are (remember that the variance of an operator Q is $\sigma_Q^2 = \langle Q^2 \rangle - \langle Q \rangle^2$)

$$\begin{aligned}\sigma_x^2 &= \frac{a^2}{12\pi^2} (\pi^2 - 6) \\ \sigma_p^2 &= \frac{\hbar^2 \pi^2}{a^2} \\ \sigma_E^2 &= 0.\end{aligned}\tag{6.29}$$

The last relation tells us that we are in a state of definite energy (no width to the energy expectation value) – an energy eigenstate.

For the classical quantities, we have constant energy, so the variance will be zero. The classical position variance can be found using the classical density, it ends up being $\sigma_x^2 = \frac{a^2}{12}$, the first term of the quantum form. If we were to calculate the variances using a generic eigenstate, labelled by n , we would find:

$$\begin{aligned}\sigma_x^2 &= \frac{a^2}{12} - \frac{a^2}{2n^2\pi^2} \\ \sigma_p^2 &= \frac{n^2 \hbar^2 \pi^2}{a^2} \\ \sigma_E^2 &= 0.\end{aligned}\tag{6.30}$$

These energy eigenstates all have *definite* energy, and from the variance for position, we can see that in the limit $n \rightarrow \infty$, we recover the classical

¹We calculated this quantum $\langle x \rangle = \frac{1}{2}a$ for $n = 1$, but this is the position expectation value for all n .

distribution.

6.2.2 Mixed States

The above discussion is highly specialized to eigenstates of the Hamiltonian – as we have seen, these have time-independent expectation values and well-defined energies (although only a “small” set are allowed). Suppose we prepare (in some manner) a system that is an equal admixture of the n and ℓ states:

$$\Psi(x, t) = \left(c_n e^{-i \frac{E_n t}{\hbar}} \psi_n(x) + c_\ell e^{-i \frac{E_\ell t}{\hbar}} \psi_\ell(x) \right). \quad (6.31)$$

We must first choose c_n and c_ℓ to normalize the wavefunction:

$$\begin{aligned} \Psi(x, t) \cdot \Psi(x, t) &= \int_0^a \left(c_n^* e^{i \frac{E_n t}{\hbar}} \psi_n(x)^* + c_\ell^* e^{i \frac{E_\ell t}{\hbar}} \psi_\ell(x)^* \right) \\ &\quad \times \left(c_n e^{-i \frac{E_n t}{\hbar}} \psi_n(x) + c_\ell e^{-i \frac{E_\ell t}{\hbar}} \psi_\ell(x) \right) dx \\ &= \left[c_n^* c_n \psi_n(x) \cdot \psi_n(x) + c_n^* c_\ell e^{i \frac{(E_n - E_\ell) t}{\hbar}} \psi_n(x) \cdot \psi_\ell(x) \right. \\ &\quad \left. + c_\ell^* e^{i \frac{(E_\ell - E_n) t}{\hbar}} \psi_\ell^*(x) \cdot \psi_n(x) + c_\ell^* c_\ell \psi_\ell(x) \cdot \psi_\ell(x) \right], \end{aligned} \quad (6.32)$$

and keeping in mind that $\psi_n(x) \cdot \psi_\ell(x) = \delta_{n\ell}$, we can simplify:

$$\Psi(x, t) \cdot \Psi(x, t) = c_n^* c_n + c_\ell^* c_\ell. \quad (6.33)$$

Since we have already decided to make our state an *equal* admixture, we must have $c_n = c_\ell = \frac{1}{\sqrt{2}}$. Our final form is

$$\Psi(x, t) = \frac{1}{\sqrt{2}} \left(e^{-i \frac{E_n t}{\hbar}} \psi_n(x) + e^{-i \frac{E_\ell t}{\hbar}} \psi_\ell(x) \right). \quad (6.34)$$

To calculate the expectation value for energy, we have

$$\begin{aligned} \langle H \rangle &= \frac{1}{2} \int_0^a \Psi^*(x, t) \hat{H} \Psi(x, t) dx \\ &= \frac{1}{a} \int_0^a \Psi^*(x, t) \left(E_n e^{-i \frac{E_n t}{\hbar}} \psi_n(x) + E_\ell e^{-i \frac{E_\ell t}{\hbar}} \psi_\ell(x) \right) dx. \end{aligned} \quad (6.35)$$

We have used Schrödinger’s equation to simplify the action of the operator H on $\Psi(x, t)$ – since the wave function is already decomposed in terms of

eigenstates. In dot-product notation, the above is

$$\begin{aligned} \langle H \rangle &= \frac{1}{2} \left[E_n \psi_n(x) \cdot \psi_n(x) + \left(E_\ell e^{i \frac{(E_n - E_\ell)}{\hbar}} + E_n e^{-i \frac{(E_n - E_\ell)}{\hbar}} \right) \psi_n(x) \cdot \psi_\ell(x) \right. \\ &\quad \left. + E_\ell \psi_\ell(x) \cdot \psi_\ell(x) \right] \\ &= \frac{1}{2} (E_n + E_\ell). \end{aligned} \tag{6.36}$$

It is possible to pick an eigenstate with the same expectation value for the energy, and it is interesting to ask how one might distinguish between such a state and the above. For example, if we set $n = 7$, $\ell = 1$, then the expectation value for E is:

$$\frac{\hbar^2 \pi^2}{2 m a^2} \frac{50}{2}, \tag{6.37}$$

and this is identical to $\langle H \rangle$ for $n = 5$.

It is the variance that makes the difference – for a pure $n = 5$ state, the variance of the energy is zero, it is an eigenstate of the Hamiltonian. In the mixed state setting, we have:

$$\sigma_H^2 = \frac{1}{2} (E_\ell^2 + E_n^2) - \frac{1}{4} (E_\ell + E_n)^2 = \frac{\hbar^4 \pi^4 (\ell^2 - n^2)^2}{16 a^4 m^4}, \tag{6.38}$$

and we see that these states do not have definite energy – there is a spread, depending on the eigenstates making up $\Psi(x, t)$.

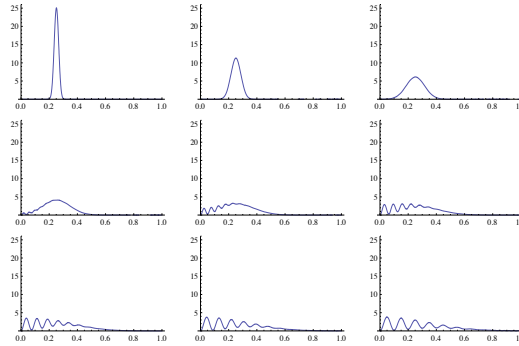
Example

To see how the mixed states lead to time-evolution, we can pick an arbitrary (but normalized) initial state, decompose it into the sine basis that are the eigenvectors of the Hamiltonian operator for the infinite square well, and form $\Psi(x, t)$ explicitly. Start with

$$\Psi(x, 0) = A e^{\beta (x-d)^2} x (x - a), \tag{6.39}$$

so that the initial wavefunction satisfies the boundary conditions, and we can use A to ensure that $\int_0^d \Psi(x, 0)^* \Psi(x, 0) dx = 1$. This initial distribution represents a Gaussian peaked about the value d , and vanishing at $x = 0, a$, the walls of our box.

We calculate the coefficients in the expansion of the wavefunction in the usual way from (6.20). Then all we have to do is input these coefficients in (6.22). We can plot the resulting $\rho(x, t) = \Psi^*(x, t) \Psi(x, t)$ as a function of time, and a few snapshots are shown below:



6.3 Measurement

The final input into our quantum mechanical picture is a statement of what a measurement *does*. What a measurement *is* is another question – if you think about it, though, most measurements involve interaction. Those interactions can be carried out using other particles (so we have multiple particles) or turning on and off various detection equipment that measures properties of a particle (effectively introducing time-dependent potential interactions). These considerations take us away from our static $V(x)$ potentials acting on single particles, and so are difficult to analyze at this stage.

What a measurement does is defined with reproducibility in mind. For an operator like \hat{H} , corresponding to the observable “energy”, we say that a measurement of energy puts the system into an energy eigenstate and returns one of the energy eigenvalues. Therein lies part of the “magic” of quantum mechanics. Never mind *how* this happens. Think about the dull implications for our particle in a box. When we measure the energy of a generic state like (6.22), we get a measured value that *must be* one of the eigenvalues:

$$E = \frac{n^2 \pi^2 \hbar^2}{2 m a^2} \quad (6.40)$$

and we subsequently know that the particle is in the n^{th} eigenstate of \hat{H} . Of course, once the particle is an eigenstate of \hat{H} , its energy does not change. So an immediately repeated measurement will return the same energy value and leave the particle in the same state.

Given a general solution like (6.22), we can compute the expectation value of energy in terms of the decomposition coefficients (exploiting the inner product relation for the $\psi_m(x)$ from (6.19)):

$$\begin{aligned} \langle H \rangle &= \int_{-\infty}^{\infty} \left(\sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) e^{-i\frac{E_n t}{\hbar}} \right)^* \\ &\quad \times \left(\sum_{m=1}^{\infty} E_m c_m \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi x}{a}\right) e^{-i\frac{E_m t}{\hbar}} \right) \\ &= \sum_{m=1}^{\infty} E_m |c_m|^2. \end{aligned} \quad (6.41)$$

This is reminiscent of the discrete probability expectation values we discussed, in which we had averages like: $\langle f(j) \rangle = \sum_{j=0}^{\infty} f(j) P(j)$, and suggests that we might interpret the coefficients $|c_m|^2$ as probabilities. This idea is supported by the normalization of the wavefunction – from (6.21), we must have:

$$\sum_{m=1}^{\infty} |c_m|^2 = 1, \quad (6.42)$$

which is also required if we want to understand $|c_m|^2$ as $P(m)$. For a generic state like this, we say that a measurement of energy will return the value E_n with probability $|c_n|^2$ and upon measurement, the wavefunction is in the stationary state $\Psi_n(x, t)$. This interpretation is also reasonable from a linear algebra point of view – the decomposition coefficients c_m tell us how much $\Psi_m(x, t)$ is in $\Psi(x, t)$, and so it is easy to predict the state selected by measurement.

The story is only mildly different for other operators – if we make a position measurement, we will recover one of the eigenvalues of the position operator², these do evolve in time (as it turns out), but an immediately repeated measurement of position must return the same location.

²Position, as an operator, has a continuous spectrum, and its eigenvectors are Dirac delta functions, as we shall see later on.

Homework

Reading: Griffiths, pp. 24–38.

Problem 6.1

Knock 'em dead.