

V25.0109: General Chemistry I (Honors)

Notes for Lecture 6

I. PREDICTING ENERGY LEVELS AND PROBABILITIES: THE SCHRÖDINGER EQUATION

In the last lecture, we saw that the Bohr model is able to predict the allowed energies of any single-electron atom or cation. However, the Bohr model is, by no means, a general approach and, in any case, it relies heavily on classical ideas, clumsily grafting quantization onto an essentially classical picture, and therefore, provides no real insights into the true quantum nature of the atom.

Any rule that might be capable of predicting the allowed energies of a quantum system must also account for the particle-wave duality and include a wave-like description for particles. In 1926, the Austrian physicist Erwin Schrödinger posited an equation that predicts both the allowed energies of a system as well as the probability of finding a particle in a given region of space. The equation, known as the Schrödinger wave equation, does not yield the probability directly, in fact, but rather the probability amplitude alluded to in the previous lecture. This amplitude function is, in general, a *complex* function denoted $\psi(x)$ (for a single particle in one spatial dimension) and is referred to as the *wave function*. It is related to the probability as follows:

The probability that a single quantum particle moving in one spatial dimension will be found in a region $x \in [a, b]$ if a measurement of its location is performed is

$$P(x \in [a, b]) = \int_a^b |\psi(x)|^2 dx$$

The square of the wave function $|\psi(x)|^2$ is known as the probability density $p(x)$. In general, the probability that a quantum particle will be found in a very small region dx about the point x is

$$p(x)dx = |\psi(x)|^2 dx$$

Since particles can exhibit wave-like behavior, the amplitude or wave function $\psi(x)$ should have a wave-like form.

The Schrödinger equation cannot be derived from any more fundamental principle. However, in order to motivate it, let us use the assumption that $\psi(x)$ should have a wave-like form. Thus, consider a free particle of mass m and momentum p . Recall the de Broglie hypothesis stating that the particle has a wavelength λ given by

$$\lambda = \frac{h}{p}$$

or

$$p = \frac{h}{\lambda}$$

If the particle is a free particle, its potential energy $V(x) = 0$, so that its energy is purely kinetic

$$E = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}$$

If the amplitude $\psi(x)$ describes a wave, then it should take the mathematical form

$$\psi(x) = A \cos\left(\frac{2\pi x}{\lambda}\right) \quad \text{or} \quad B \sin\left(\frac{2\pi x}{\lambda}\right)$$

(we are considering a wave that is not changing in time here). Consider the cosine form (the same will hold for a sine for as well) and consider the first two derivatives of $\psi(x)$:

$$\frac{d\psi}{dx} = -\frac{2\pi}{\lambda} A \sin\left(\frac{2\pi x}{\lambda}\right)$$

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} A \cos\left(\frac{2\pi x}{\lambda}\right)$$

We see, therefore, that $\psi(x)$ and $d^2\psi(x)/dx^2$ are related by

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \psi(x)$$

or

$$-\frac{h^2}{8\pi^2 m} \frac{d^2\psi}{dx^2} = \frac{h^2}{2m\lambda^2} \psi(x)$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi(x)$$

The last line of the above expression is, in fact, the Schrödinger equation for a free particle moving along the x -axis.

We can always set up the Schrödinger equation via the following simple prescription. Start with an expression for the classical energy. In this case, for a free particle

$$\frac{p^2}{2m} = E$$

Now multiply by the wave function $\psi(x)$:

$$\frac{p^2}{2m} \psi(x) = E\psi(x)$$

Finally replace the momentum p by the following derivative:

$$p \longrightarrow -i\hbar \frac{d}{dx}$$

which is equivalent to replacing p^2 by a second derivative:

$$p^2 \longrightarrow -\hbar^2 \frac{d^2}{dx^2}$$

When this is done, we arrive at:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi(x)$$

If the particle has a potential energy $V(x)$ affecting it, then the same prescription can be used. Start with the classical energy expression:

$$\frac{p^2}{2m} + V(x) = E$$

Multiply by $\psi(x)$:

$$\left[\frac{p^2}{2m} + V(x) \right] \psi(x) = E\psi(x)$$

Replace $p \longrightarrow -i\hbar(d/dx)$, and we arrive at the Schrödinger equation for the general case of a single quantum particle in one spatial dimension:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x)$$

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) = E\psi(x)$$

The object on the left that acts on $\psi(x)$

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

is an example of an *operator*. In effect, what it says to do is “take the second derivative of $\psi(x)$, multiply the result by $-(\hbar^2/2m)$ and then add $V(x)\psi(x)$ to the result of that.” Quantum mechanics involves many different types of operators. This one, however, plays a special role because it appears on the left side of the Schrödinger equation. It is given a special name, therefore – it is called the *Hamiltonian operator* and is denoted as

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

Therefore, the Schrödinger equation is generally written as

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

Note that \hat{H} is derived from the classical energy $p^2/2m + V(x)$ simply by replacing $p \rightarrow -i\hbar(d/dx)$.

Since $|\psi(x)|^2 dx$ is a probability, we require that the probability of finding the particle *somewhere* in space be exactly 1. That is, we require that the probability that $x \in (-\infty, \infty)$ be 1, which means

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$$

This is known as the *normalization condition* on $\psi(x)$. Note that if we are working on a subset of the real line, then the integral in the normalization condition must be restricted to the part of the line to which we are restricted.

Finally, we need to specify how $\psi(x)$ behaves at the physical boundaries of the space we are working in. These conditions are known as *boundary conditions*.

Once we specify the Schrödinger equation, the boundary conditions on $\psi(x)$ and the normalization condition, we have all the information we need to calculate both the allowed energies and the wave function $\psi(x)$. We will see shortly how this prescription is applied to a few simple examples.

Before we embark on this, however, let us pause to comment on the validity of quantum mechanics. Despite its weirdness, its abstractness, and its strange view of the universe as a place of randomness and unpredictability, quantum theory has been subject to intense experimental scrutiny. It has been found to agree with experiments to better than $10^{-10}\%$ for all cases studied so far. When the Schrödinger equation is combined with a quantum description of the electromagnetic field, a theory known as *quantum electrodynamics*, the result is one of the most accurate theories of matter that has ever been put forth. Keeping this in mind, let us forge ahead in our discussion of the quantum universe and how to apply quantum theory to both model and real situations.

II. A SIMPLE MODEL OF A CHEMICAL BOND: A PARTICLE IN A ONE-DIMENSIONAL BOX

In this section, we will consider a very simple model that describes an electron in a chemical bond. This is the so-called *particle in a box* model. We imagine a particle strictly confined between two “walls” by a potential energy $V(x)$ that is shown in the figure below. $V(x)$ confines the particle to the region $x \in [0, L]$. Such a model, although simple, is physically reasonable. For example, imagine an electron in a CC single bond. Since carbon atoms are roughly 24000 times more massive than an electron, thinking classically for a moment, this would be like a ball-bearing between two wrecking balls, which would certainly seem like two infinitely high walls. The box length L for a CC single bond would be roughly 1.5 Å.

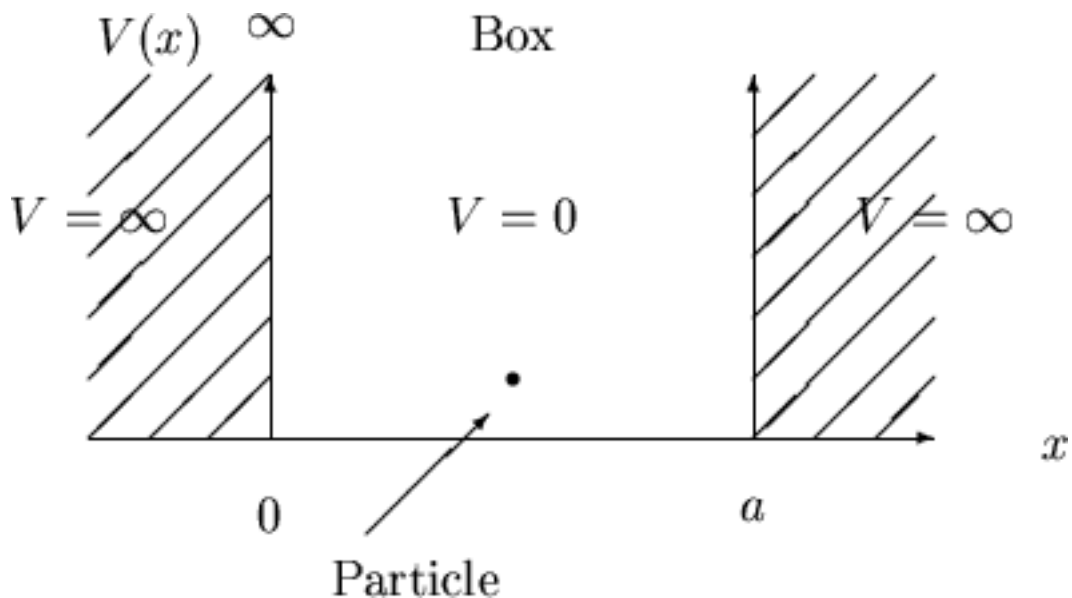


FIG. 1. Illustration of a particle in a box

Mathematically, the potential energy is expressed as

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

If the potential is infinite outside the box, then there is zero probability that the particle will be found there. Thus, we require $\psi(x) = 0$ outside the box, and this can only happen if at the boundaries $x = 0$ and $x = L$, $\psi(0) = \psi(L) = 0$. These, then, are the boundary conditions on $\psi(x)$. We will also require that the wavefunction be normalized to 1. Since $\psi(x) = 0$ outside the box, we only need to integrate between 0 and L , so that

$$\int_0^L |\psi(x)|^2 dx = 1$$

Since we already know that $\psi(x) = 0$ outside the box, we only need to solve the Schrödinger inside the box where $V(x) = 0$. In this case, the Schrödinger looks like the free-particle equation we already wrote down

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi(x)$$

Rearranging gives

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x)$$

We have already seen that the solutions are sin or cos functions. In fact, we can easily show that the solution of this differential equation must be either

$$\psi(x) = A \sin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) \quad \text{or} \quad \psi(x) = B \cos\left(\sqrt{\frac{2mE}{\hbar^2}}x\right)$$

where A and B are arbitrary constants. But since we need $\psi(0) = 0$, the only solution that is consistent with the boundary condition is the sin solution. Thus, we take

$$\psi(x) = A \sin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right)$$

It's a simple matter to verify that this function satisfies the differential equation:

$$\begin{aligned}\frac{d\psi}{dx} &= A\sqrt{\frac{2mE}{\hbar^2}} \cos\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) \\ \frac{d^2\psi}{dx^2} &= -A\left(\frac{2mE}{\hbar^2}\right) \cos\left(\sqrt{\frac{2mE}{\hbar^2}}x\right) \\ &= -\left(\frac{2mE}{\hbar^2}\right)\psi(x)\end{aligned}$$

At this point, all we have is a general solution to the equation, but we still do not know the allowed values of E . But, there is also still one boundary condition we have not yet enforced. We need $\psi(L) = 0$. This requires

$$A \sin\left(\sqrt{\frac{2mE}{\hbar^2}}L\right) = 0$$

In order to satisfy this, we can take any point where the sin function vanishes. We know that $\sin(n\pi) = 0$ for any value of n . Thus, our boundary condition is equivalent to

$$\sqrt{\frac{2mE}{\hbar^2}}L = n\pi$$

Solving this equation for E gives us the allowed energies:

$$E = \frac{\hbar^2 \pi^2}{2mL^2} n^2 \equiv E_n$$

Note, first, that there are many allowable values of E , so we denote these by E_n according to the value of n that we choose. For each allowable energy, there is also a wavefunction $\psi_n(x)$ obtained by substituting E_n into the expression for $\psi(x)$. This yields

$$\psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right)$$

We still need to determine the constant A , but before we do this, a comment is in order. Specifically, we are going to place a restriction on n . We will restrict n to be the natural numbers $n = 1, 2, 3, \dots$. The value $n = 0$ gives a wavefunction $\psi_0(x)$ that is everywhere 0, and since the particle must be somewhere, this solution is not allowed. In addition, although the negative numbers $n = -1, -2, \dots$ also satisfy the boundary condition, since $\psi_{-n}(x) = -\psi_n(x)$, because $\sin(-y) = -\sin(y)$, we do not need to keep the negative values of n because an overall minus sign on $\psi(x)$ does not change the probability of finding the particle in a region of the box because $p(x) = |\psi(x)|^2$. Thus, those wavefunctions that give unique probability densities are those for which $n = 1, 2, 3, \dots$.

Let us now determine the constant A . There is still one piece of information we have not used and that is the normalization of $\psi_n(x)$. For each n , this function must be normalized to 1. This requires

$$\begin{aligned}\int_0^L |\psi_n(x)|^2 dx &= 1 \\ A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx &= 1 \\ A^2 \int_0^L \left[\frac{1}{2} - \frac{1}{2} \cos\left(\frac{2n\pi x}{L}\right)\right] dx &= 1 \\ A^2 \left[\frac{x}{2}\Big|_0^L - \frac{L}{4n\pi} \cos\left(\frac{2n\pi x}{L}\right)\Big|_0^L\right] &= 1\end{aligned}$$

$$A^2 \frac{L}{2} = 1$$

$$A = \sqrt{\frac{2}{L}}$$

Thus, each wavefunction takes the form

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

The figure below shows the energy level diagram together with some of the wavefunctions and their associated probability densities $p_n(x) = \psi_n^2(x)$:

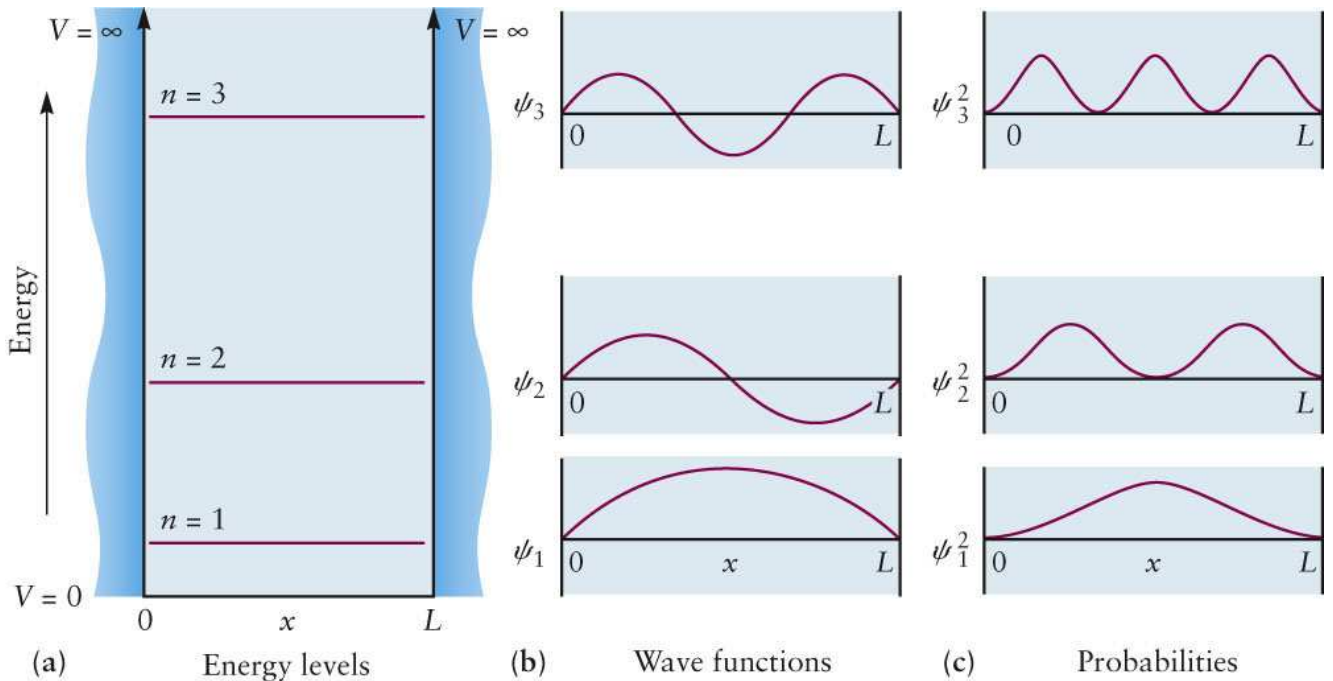


FIG. 2. Energy level diagram, lowest order wavefunctions and lowest order probability densities for the particle in a box.

That the $\psi_n(x)$ satisfy the Schrödinger equation can be expressed compactly as

$$\hat{H}\psi_n(x) = E_n\psi_n(x)$$

Let us now make a few important points that help us with a physical interpretation of the functions $\psi_n(x)$ and energies E_n .

1. First what do we really mean when we refer to the E_n as the “allowed” energies? “Allowed” here means that if we perform an experiment to measure the energy of the system, the only possible outcome of such a measurement is one of the E_n . That is, the E_n are the only possible values we can obtain in a measurement of the energy. Thus, we often refer to the E_n as the *eigenvalues* of \hat{H} , *eigen* being the German word for “own” or “characteristic”.
2. What do we mean by the “allowed” wave functions $\psi_n(x)$? In general, the wave function of a particle is *not* restricted to be one of the $\psi_n(x)$. We can prepare the particle in a state or with a wave function $\Psi(x)$ that is different from $\psi_n(x)$, however, $\Psi(x)$ must be a combination of the allowed $\psi_n(x)$, and it must satisfy $\Psi(0) = 0$, $\Psi(L) = 0$, and it must be normalized:

$$\int_0^L |\Psi(x)|^2 dx = 1$$

3. If we do prepare the system such that $\Psi(x) = \psi_n(x)$ for some value of n , then a measurement of the energy will yield the value E_n with probability 1. For example, if $\Psi(x) = \psi_2(x)$, we would then obtain E_2 with probability 1 if we were to measure the energy. If $\Psi(x)$ were a combination of more than one of the $\psi_n(x)$, then identical energy measurements will have different outcomes that cannot be predicted. For example, if $\Psi(x) = (1/\sqrt{2})(\psi_1(x) + \psi_2(x))$, then a measurement of energy would yield E_1 with probability 1/2 and E_2 with probability 1/2.

Several other things are worth noting before we proceed with this example. First, as n increases, the number of *nodes* in the wave function increases. A *node* is a point at which the wavefunction cross the x -axis. For $n = 1$, $\psi_1(x)$ has zero nodes, for $n = 2$, $\psi_2(x)$ has one node, for $n = 3$, $\psi_3(x)$ has two nodes, and in general, $\psi_n(x)$ has $n - 1$ nodes. Also note that $\psi_n^2(x) \geq 0$ for all x , even though $\psi_n(x)$ can be either positive or negative. This distinction will become particularly important when we consider the quantum theory of chemical bonding.

Another important property of the allowed wave functions is known as the *orthogonality property*. It is straightforward to show that

$$\int_0^L \psi_n(x)\psi_m(x)dx = 0 \quad \text{if } m \neq n$$

Obviously, the integral must be 1 if $m = n$. To prove the orthogonality property, one only needs to substitute the form of $\psi_n(x)$ and $\psi_m(x)$ and do the integral. Again, we will make use of this property when we consider chemical bonding.

Finally, note that the lowest energy a particle can have is not 0! The lowest energy corresponds to $n = 1$

$$E_1 = \frac{\hbar^2 \pi^2}{2mL^2} > 0$$

This is true for any bound system in quantum mechanics. This lowest energy is called the *zero-point* energy of the system. This zero-point energy is consistent with the uncertainty principle. Since there is always energy in the system, it will never be possible to obtain $\Delta x = 0$ and $\Delta p = 0$ under any circumstances.

Let us now proceed to work through an example that illustrates what the wavefunctions mean.

Example: A particle in a one-dimensional box of length L has an energy

$$E = \frac{2\hbar^2 \pi^2}{mL^2}$$

What is the probability that a measurement of the location of the particle will find it between $x = 0$ and $x = L/2$?

From the given energy, the particle must be in the $n = 2$ state so that its wavefunction is

$$\psi_2(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right)$$

The probability that the particle will be found in the region $x \in [0, L/2]$ when its position is measured is then

$$\begin{aligned} P(x \in [0, L/2]) &= \int_0^{L/2} \psi_2^2(x)dx \\ &= \frac{2}{L} \int_0^{L/2} \sin^2\left(\frac{2\pi x}{L}\right) dx \\ &= \frac{2}{L} \int_0^{L/2} \left[\frac{1}{2} - \frac{1}{2} \cos\left(\frac{4\pi x}{L}\right)\right] dx \\ &= \frac{2}{L} \left[\frac{x}{2} \Big|_0^{L/2} - \frac{L}{8\pi} \sin\left(\frac{4\pi x}{L}\right) \Big|_0^{L/2} \right] \\ &= \frac{2}{L} \cdot \frac{L}{4} = \frac{1}{2} \end{aligned}$$

Therefore, the probability is exactly 1/2 that the particle will be found in the left half of the box.

It is important to note that if the particle is prepared with one of the allowable wavefunctions $\psi_n(x)$, then a measurement of its energy will *always* yield the same value E_n . Thus, since the energy has a well-defined value, this value will be obtained in all independent measurements in which the system is prepared the same way. This is to be contrasted with a measurement of position, which can yield any value between $x = 0$ and $x = L$ with varying probability. Moreover, preparing the system in the same energy state and repeating the measurement of position will yield different values in different repetitions of the experiment. All we can determine from the theory is the probability that the particle will be found in a certain region.

Example: A particle of mass m in a box of length L is prepared in a quantum state such that its wave function is

$$\Psi(x) = \frac{1}{\sqrt{2}} [\psi_1(x) + \psi_2(x)]$$

- Show that this state is correctly normalized.
 - What is the probability that a measurement of the particle's position will yield a value between $x = 0$ and $x = L/4$?
 - What is the probability that a measurement of the particle's energy yields a value $\hbar^2\pi^2/(2mL^2)$?
- a. The normalization condition requires that

$$\int_0^L |\Psi(x)|^2 dx = 1$$

Taking the square of the given wave function and integrating, we have

$$\begin{aligned} \int_0^L \frac{1}{2} [\psi_1(x) + \psi_2(x)]^2 dx &= \frac{1}{2} \left[\int_0^L \psi_1^2(x) dx + 2 \int_0^L \psi_1(x)\psi_2(x) dx + \int_0^L \psi_2^2(x) dx \right] dx \\ &= \frac{1}{2} [1 + 0 + 1] \\ &= 1 \end{aligned}$$

- b. The probability is given by

$$P(x \in [0, L/4]) = \int_0^{L/4} |\Psi(x)|^2 dx$$

Substituting in gives

$$P(x \in [0, L/4]) = \frac{1}{2} \frac{2}{L} \int_0^{L/4} \left[\sin^2\left(\frac{\pi x}{L}\right) + 2 \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{2\pi x}{L}\right) + \sin^2\left(\frac{2\pi x}{L}\right) \right] dx$$

In order to calculate this, the following trig identities are useful:

$$\begin{aligned} \sin^2(ax) &= \frac{1}{2} - \frac{1}{2} \cos(2ax) \\ \sin(ax) \sin(bx) &= \frac{1}{2} [\cos(a-b)x - \cos(a+b)x] \end{aligned}$$

Using these, the probability becomes

$$\begin{aligned}
P(x \in [0, L/4]) &= \frac{1}{L} \int_0^{L/4} \left[\frac{1}{2} - \frac{1}{2} \cos\left(\frac{2\pi x}{L}\right) + \cos\left(\frac{\pi x}{L}\right) - \cos\left(\frac{3\pi x}{L}\right) + \frac{1}{2} - \frac{1}{2} \cos\left(\frac{4\pi x}{L}\right) \right] dx \\
&= \frac{1}{L} \left[\frac{L}{4} - \frac{L}{4\pi} \sin \frac{\pi}{2} + \frac{L}{\pi} \sin \frac{\pi}{4} - \frac{L}{3\pi} \sin \frac{3\pi}{4} - \frac{L}{8\pi} \sin \pi \right] \Big|_0^{L/4} \\
&= \frac{1}{4} - \frac{1}{4\pi} + \frac{\sqrt{2}}{3\pi} \approx 0.32 = 32\%
\end{aligned}$$

- c. Just as we cannot predict the outcome of a measurement of the particle's position, we cannot predict the outcome of a measurement of a particle's energy. We can, however, predict the probability for obtaining any of the allowed energy values. Since these are the only allowed values, such a measurement must yield one of these values *cannot* yield any other value. This is what is actually meant by the term "allowed" for an arbitrary quantum state.

The formula that we need for predicting the probabilities of energy measurements is the following: If $\Psi(x)$ is the quantum state of a system, the probability that a measurement of energy yields the allowed value E_n is calculated using the corresponding wave function $\psi_n(x)$ from

$$P(E = E_n) = \left| \int_0^L \psi_n^*(x) \Psi(x) dx \right|^2$$

This is a general formula. For any other problem, the only possible change is that the integration region $x \in [0, L]$ would be replaced by whatever the spatial domain of the problem is. Despite how it looks, this formula is actually much easier to use than the one for predicting the probabilities of position measurements, thanks to the orthogonality property.

In order to answer the specific question, note that the energy $\hbar^2\pi^2/(2mL^2)$ is actually the energy E_1 , so the question is really asking what is the probability that a measurement of energy yields the value E_1 . According to the formula, this requires that we use the wave function $\psi_1(x)$. Substituting this and $\Psi(x)$ into the formula yields

$$P(E = E_1) = \left| \int_0^L \psi_1(x) \frac{1}{\sqrt{2}} [\psi_1(x) + \psi_2(x)] dx \right|^2$$

Now, the integral itself can be solved without integrating anything. Note that because of orthogonality, the integral is just

$$\begin{aligned}
\int_0^L \psi_1(x) \frac{1}{\sqrt{2}} [\psi_1(x) + \psi_2(x)] dx &= \frac{1}{\sqrt{2}} \int_0^L \psi_1^2(x) dx + \frac{1}{\sqrt{2}} \int_0^L \psi_1(x) \psi_2(x) dx \\
&= \frac{1}{\sqrt{2}} \cdot 1 + \frac{1}{\sqrt{2}} \cdot 0 \\
&= \frac{1}{\sqrt{2}}
\end{aligned}$$

Hence, squaring this result give the probability of 1/2 to find obtain the result $E = E_1$. Note that this is just the square of the coefficient of $\psi_1(x)$ in $\Psi(x)$. From this result, it can be seen that the probability of obtaining the result $E = E_2$ is also 1/2.

As a question for thought, what would be the probability that a measurement of energy would yield the value $\hbar^2\pi^2/(\sqrt{2}mL^2)$?

III. A WORD ABOUT TIME DEPENDENCE IN QUANTUM MECHANICS

Recall that the Schrödinger equation

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

yields the allowed energies and corresponding amplitude (wave) functions. But it does not tell us how the system evolves in time. It would seem that something is missing, since, after all, classical mechanics tells us how the positions and velocities of a classical system evolve in time. The time dependence is given by solving Newton's second law

$$m\frac{d^2x}{dt^2} = F(x)$$

But where is t in quantum mechanics?

First of all, what is it that must evolve in time? The answer is that the wavefunction (and associated probability density) must evolve. Suppose, therefore, that we prepare a system at $t = 0$ according to a particular probability density $p(x, 0)$ related to an amplitude $\Psi(x, 0)$ by

$$p(x, 0) = |\Psi(x, 0)|^2$$

How will this initial amplitude $\Psi(x, 0)$ look at time t later? Note, by the way, that $\Psi(x, 0)$ does *not* necessarily need to be one of the energy states $\psi_n(x)$.

In fact, there is a second version of the Schrödinger equation, called the time-dependent Schrödinger equation, that tells us how $\Psi(x, t)$ will evolve starting from the initial condition $\Psi(x, 0)$. This equation is

$$\hat{H}\Psi(x, t) = i\hbar\frac{d}{dt}\Psi(x, t)$$

For much of what we are going to do in this course, we will not need the time-dependent Schrödinger equation, but it is important to know that it exists. It is also important to know how it works physically and when it is sufficient to work with the time-independent version of the Schrödinger equation $\hat{H}\psi(x) = E\psi(x)$.

Suppose that we are lucky enough to choose

$$\Psi(x, 0) = \psi_n(x), \quad p(x, 0) = |\psi_n(x)|^2$$

We will show that

$$\Psi(x, t) = \psi_n(x)e^{-iE_n t/\hbar}$$

From the time-dependent Schrödinger equation

$$\frac{d\Psi}{dt} = \psi_n(x) \left(\frac{-iE_n}{\hbar} \right) e^{-iE_n t/\hbar}$$

$$i\hbar\frac{d\Psi}{dt} = E_n\psi_n(x)e^{-iE_n t/\hbar}$$

Similarly

$$\hat{H}\Psi(x, t) = e^{-iE_n t/\hbar}\hat{H}\psi_n(x) = e^{-iE_n t/\hbar}E_n\psi_n(x)$$

Hence $\psi_n(x)\exp(-iE_n t/\hbar)$ satisfies the equation.

Next, consider the probability density $p(x, t) = |\Psi(x, t)|^2$:

$$\begin{aligned} p(x, t) &= \left[\psi_n(x)e^{iE_n t/\hbar} \right] \left[\psi_n(x)e^{-iE_n t/\hbar} \right] \\ &= \psi_n^2(x)e^{iE_n t/\hbar}e^{-iE_n t/\hbar} \\ &= |\psi_n(x)|^2 = p(x, 0) \end{aligned}$$

We see, therefore, that the probability does not change in time! For this reason, we call $\psi_n(x)$ a *stationary state*. In such a state, the energy remains fixed at the well-defined value E_n .

Suppose, however, that we had chosen $\Psi(x, 0)$ to be some arbitrary combination of the two lowest energy states:

$$\Psi(x, 0) = a\psi_1(x) + b\psi_2(x)$$

for example

$$\Psi(x, 0) = \frac{1}{\sqrt{2}} [\psi_1(x) + \psi_2(x)]$$

as in the previous example. Then, the probability density at time t

$$p(x, t) = |\Psi(x, t)|^2 \neq p(x, 0)$$

However, in order for such a mixture to be possible, there must be sufficient energy in the system that there is some probability of measuring the particle to be in its excited state. For most molecules that we will examine, the first electronic excited state is at a very high energy above the ground state, and at normal temperatures, most molecules are in their electronic ground states. This being the case, the probability density will not vary in time, and it is sufficient for us to consider only the time-independent Schrödinger equation and its solution for the lowest allowable energy.

Finally, suppose we start with a state $\Psi(x, 0) = (1/\sqrt{2})[\psi_1(x) + \psi_2(x)]$, and we let this state evolve in time. At any point in time, the state $\Psi(x, t)$ will be some mixture of $\psi_1(x)$ and $\psi_2(x)$, and this mixture changes with time. Now, at some specific instance in time t , we measure the energy and obtain a value E_1 . What is the state of the system *just after* the measurement is made? Once we make the measurement, then we know with 100% certainty that the energy is E_1 . From the above discussion, there is only one possibility for the state of the system, and that has to be the wave function $\psi_1(x)$, since in this state we know with 100% certainty that the energy is E_1 . Hence, just after the measurement, the state *must be* $\psi_1(x)$, which means that because of the measurement, any further dependence on $\psi_2(x)$ drops out, and for all time thereafter, there is *no* dependence on $\psi_2(x)$. Consequently, any subsequent measurement of the energy would yield the value E_1 with 100% certainty. This discontinuous change in the quantum state of the system as a result of the measurement is known as the *collapse of the wave function*. The idea that the evolution of a system can change as a result of a measurement is one of the topics that is currently debated among quantum theorists.

The fact that measuring a quantum system changes its time evolution means that the experimenter is now completely coupled to the quantum system. In classical mechanics, this coupling does not exist. A classical system will evolve according to Newton's laws of motion independent of whether or not we observe it. This is not true for quantum systems. The very act of observing the system changes how it evolves in time. Put another way, by simply observing a system, we change it!