

The following content is provided under a Creative Commons license. Your support will help MIT OpenCourseWare continue to offer high-quality educational resources for free. To make a donation or to view additional materials from hundreds of MIT courses, visit MIT OpenCourseWare at ocw.mit.edu.

ROBERT FIELD: Well, we're now well underway into quantum mechanics. So a lot of the important stuff goes by very fast. So we represent a quantum mechanical operator with a little hat, and it means do something to the thing on its right. And it has to be a linear operator, and you want to be sure you know what a linear operator does and what is not a linear operator.

This is an eigenvalue equation. So we have some function which, when the operator operates on it, gives back a constant times that function. The constant is the eigenvalue, and the function is an eigenfunction of the operator that belongs to this eigenvalue, and all of quantum mechanics can be expressed in terms of eigenvalue equations. It's very important, and you sort of take it for granted.

Now, one of the important things about quantum mechanics is that we have to find a linear operator that corresponds to the classically observable quantities. And for x the linear operator is x , and for the momentum the linear operator is minus \hbar partial with respect to x . That should bother you two ways. One is the i , and the other is the partial derivative. But when you apply this operator to functions, you discover that out pops something that has the expected behavior of momentum, and so this is in fact the operator that we're going to use for momentum.

And then there is a commutation rule. This commutation rule, xp minus px , is equal to this. This is really the foundation of quantum mechanics, and as I've said before, many people derive everything from a few commutation rules. It's really scary, but you should be able to work out this commutation rule by applying xp minus px to some arbitrary function. And going through the symbolics should take you about 30 seconds, or maybe it shouldn't. Maybe you can go faster.

OK. We have an operator, and we often want to know what is the expectation value of the particular function, which we could symbolize here, but it's never done that way. So we have some function, and we want to calculate its expectation value of operator A , and this is it. And so this is a normalization integral, and this normalization integral is usually taken for granted,

because we almost always work with sets of functions which are normalized. And so if you convince yourself that it is, in fact, they are normalized, fine, and then this is the thing that you normally would calculate.

Then, we went to our first problem in quantum mechanics which is the free particle, and the free particle has some idiosyncrasies. The wave function for the free particle has the form e^{ikx} plus e^{-ikx} , and the Hamiltonian is $-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_0$. So there's no V_0 here, and we have two different exponentials and so is this really going to be an eigenfunction of the Hamiltonian? This is really p^2 , and so this is going to be an eigenfunction of p^2 too.

All right, so let's show a little picture here. Here is energy, and this is V_0 , and let's say this is the 0 of energy. What are the eigenvalues of this? What does the Hamiltonian do to this function?

Well, in order to do that, you have to calculate something like where you have to calculate the second derivative of each of these terms, and the second derivative of this term brings down a minus k^2 . Now, the second derivative of this term brings down a minus k^2 , and so the energy eigenvalues are going to be given by $\frac{\hbar^2 k^2}{2m} + V_0$. So these are the eigenvalues, eigenfunctions, the energies of a free particle, and they're not quantized. Now this V_0 is something that will often trip you up, because it's hidden here. It's not in here.

OK. I'm going to torture you with something. So why are these two k 's the same? What would happen if the k for the positive term were different from the k for the negative term? Simple answer. Yeah?

AUDIENCE: There'd be two eigenvalues?

ROBERT FIELD: That's right. It wouldn't be an eigenvalue. It wouldn't be an eigenfunction of the Hamiltonian. It's a mixture of two eigenvalues, and so that's simple. But often we might be dealing with a potential that's not simple like this but has got complexity. So suppose we had a potential that did this. The potential is constant piecewise, and so what do we do? Yes?

AUDIENCE: Break down the function into pieces for each in certain boundaries?

ROBERT FIELD: Yes, and that's exactly right. You do want to break it up, but one of the things I'm stressing

here is that you want to be able to draw cartoons. And so we know that if we choose an energy here, there is a certain momentum, or a certain kinetic energy here, and a different kinetic energy here, and so somehow, what you write for the wave function will reflect that. But now qualitatively, pictorially, if we have a wave function in this region which is oscillating like this, and it'll be oscillating at the same spatial frequency over here, well what's going to be happening here? Is it going to be oscillating faster or slower?

AUDIENCE: Faster. Faster.

ROBERT FIELD: Absolutely, and is it going to have amplitude smaller or larger than here? You're going to answer, yes? Well, let me do a thought experiment. So I'm going to walk from one side of the blackboard to the other, and I'm going to walk at a constant velocity. Then, I'm going to walk faster and then back to this original velocity. So what's the probability of seeing me in the middle region relative to the edge regions? Yes?

AUDIENCE: It's less.

ROBERT FIELD: That's right. The probability, local probability, is proportional to 1 over the velocity, and the wave function is proportional to 1 over the square root of the velocity. And the velocity is related to the momentum, and so we have everything. So we know that the wave here will be oscillating faster and with lower amplitude.

This is what I want you to know, and you'll be able to use that cartoon to solve problems. If you understand what's going on here, these pictures will be equivalent to global understanding, and these pictures are also part of semi-classical quantum mechanics. I believe you all know classical mechanics at least a little, enough to be useful. And what we want to be able to do in order to draw pictures and to understand stuff is to insert just enough quantum mechanics into classical mechanics so that it's correct. Then, all of a sudden, it starts to make a lot more sense. OK.

So the particle in a box, well, we have this sort of situation, and we have 0 and a . So the length of the box is a , and the bottom of the box V_0 is 0 for this picture. Now, one of the things that I want you to think about is, OK, I understand. I've solved this problem. I know how to solve this problem. I know how to get the eigenvalues, and I know how to get the eigenfunctions, and I know how to normalize them. Well, suppose I move the box to the side. So I move it from say b to $a + b$. So it's the same width, but it's just in a different place. Well, did anything change? The only thing that changes is the wave function, because you have to shift the

coordinates. What happens if I raise the box or lower the box? Will anything change?

AUDIENCE: [INAUDIBLE]

ROBERT FIELD: You're hot.

AUDIENCE: [INAUDIBLE]

ROBERT FIELD: I'm sorry?

AUDIENCE: [INAUDIBLE]

ROBERT FIELD: Yeah. If I move the box so that v_0 is not 0, but v_0 is 10.

AUDIENCE: Then, the weight function will oscillate slower.

ROBERT FIELD: No.

AUDIENCE: [INAUDIBLE]

ROBERT FIELD: So if you move the box up in energy, the wave function is going to look exactly the same, but the energies are going to be different by the amount you move the box up or down, and this is really important. It may seem trivial to some of you and really obscure to others, but you really want to be able to take these things apart. Because that will enable you to understand them in a permanent way, and the cartoons are really important. So if you have the solution to the particle in a box, then it doesn't matter where the box is. You know the solution to any particle in a box.

OK. There is something that I meant to talk about briefly, but when we write these solutions-- where did the other blackboard go? All right, well, I've hidden it-- so when we have solutions like e to the ikx and e to the minus ikx , so we have say a here and b here. When we go to normalize a function like this-- let's put the plus in here-- then we write $\psi^* \psi dx$. So ψ^* would make this go to a^* and this go to e to the minus ikx , and this go to $b^* e$ to the plus ikx .

So now, we multiply things together. We get an a , a^* which is the square modulus of a , and we get e to the ikx and e to the minus ikx . It's 1. This is why we use this form. The integrals for things involving e to the ikx are either 1 or 0.

So if you took e to the ikx , this term, and multiplied it by this term, you'd get an $a, b \star e$ to the $2 ikx$ integrated over a finite region. That's 0. So we really like this exponential notation, even if you've been brought up on sines and cosines, and you use the sines and cosines to impose the boundary conditions.

OK, another challenge. So this is v_0 , and the only problem is this v_0 -- well, it looks like this. So this is v_1 . OK, so we have now a particle in this straight. It's a hybrid between the free particle and a particle in a box.

So suppose we're at an energy like this. What's going to happen? Well, everything that's outside-- everything that's in the classically-allowed region, we understand. We know how to deal with it, but in here, well, that's OK too. But inside this classically-forbidden region, the wave function is going to behave differently.

Now, I'm going to assert something. It doesn't have nodes. It doesn't oscillate. It's either exponentially decreasing or exponentially increasing, and it will never cross 0, never.

OK. So now, if we're solving a problem involving any kind of 1D potential, number of nodes. So for 2D-bound problems, the number of nodes starts with 0, and it corresponds to the lowest energy state. The next state up has 1 node, and the next state has 2 nodes. So by counting the nodes, you would know what the energy order is of these eigenvalues which is also an extremely useful thing. If you're thinking about it or telling your computer to find the 33rd eigenvalue of something, because you just run a calculation that solves for an approximate wave function, and the 33rd, it needs 32 nodes. And so the computer says, oh, thank you, master, and here is your wave function, but you have to find the right thing.

OK. Now, here is the picture that you use to remember everything about a particle in a box. And the wave function looks like this, and the next wave function looks like that, and the next wave function looks like this. And so no nodes, 1 node, 2 nodes, the nodes are symmetrically arranged in the space available. And the lobes on one side of the node and the other side have the same amplitude, different sine, and they're all normalized. And so the maximum value for each of these guys is 2 over a square root, where this is 0 to a .

So that's a fantastic simplification, and it also reminds you of Mr. DeBroglie. He said, you have to have an integer number of half wavelengths-- well, for the hydrogen-- an integer number of wavelengths around a path. And for here, you need an integer number of wavelengths for that

round trip which is the same thing or an integer number of half wavelengths. That's DeBroglie's idea, and it enables you to say, oh well, let's see if we can use this concept of wavelength to approach general problems.

OK. Well, if you do something to the potential by putting a little thing in it, well, the wave function will oscillate more slowly in that region, and that causes it to be at a higher or lower energy? If it's oscillating more slowly here, it has to make it to an integer number of half wavelengths, and so that means it pushes it up. And if you do this, it'll push it down, and you can do terrible things. You can put a delta function there, and now you know everything qualitatively that can happen in a 1D box.

OK. One of the things that bothers people a lot is, OK, so we have some wave function, it's got lots of nodes, and the particle starts out over here. How did it get across the node? How does it move across the node? Well, the answer is it's not moving. It's here. It's here. It's here.

It's everywhere, and this is just the probability amplitude. There is no motion through a node, no motion at all. We are going to do time-dependent quantum mechanics before too long, and then there will be motion, but that motion is encoded in a different way.

OK. Another thing, suppose you have a particle in a box, and it's in some state, and I'm going to draw something like this again. OK, first of all, one, two, three, four, five, which state is that? I got-- the hands are right, six, it's the sixth eigenstate.

OK. Now, suppose-- nothing is moving. Right? This is a stationary state. How would you experimentally, in principle, determine that the particle is in this n equals 6 state? Now, this can be a completely fanciful experiment, which you would never do, but you could still describe how you would do it and what it would tell you. And so, yes.

AUDIENCE: Try to find the n equals 6 to n equals 7 transition by irradiating it or something?

ROBERT FIELD: OK. That's the quantum mechanical-- I agree, spectroscopy wins always. But if you want to observe the wave function or something related to the wave function, like the number of nodes, what would you do? And the reason I'm being very apologetic about this is because it's a crazy idea, But this is a one-dimensional system. Right? It's in the blackboard, and so you could stand out here and shoot particles at it from the perpendicular direction and collect the number of times you have a hit. And so you would discover that you would measure a probability distribution which had the form-- well, I can't draw this properly.

It's going to have one, two, three, four, five, six, six regions separated by a gap, and what it's measuring is ψ^2 . Well, you can't measure, you cannot observe a wave function, but you can observe a probability distribution wave function squared. You can also do a spectroscopic experiment and find out what is the nature of the Hamiltonian. And if you know the nature of the Hamiltonian, you can calculate the wave function, but you can't observe it.

OK. Another thing, this harmonic oscillator-- this particle in a box has a minimum energy which is not at the bottom of the box. Well, we have something called the uncertainty principle. Now, I'm just pulling this out of my pocket, but I know that x, p is equal to $i \hbar$ not 0, and one can derive some uncertainty principle by doing a little bit more mathematics. But basically that uncertainty principle is where σ_x is expectation value of x^2 minus expectation value of x squared square root.

So if we can calculate this and calculate that, we can calculate the variance in x , and you can calculate the variance in p . That's exact, and that's what you can derive from the computation rule, but for our purposes, we can be really crude. And so if I'm in this state, what is Δx ? What is the range of possibilities for x ?

AUDIENCE: The box link?

ROBERT FIELD: Yeah, a. OK, and what is the possibility-- what is the uncertainty in p sub x ? In an eigenstate, we've got equal amplitudes going this way and going that way. So we could just say p sub x positive minus p sub x negative which is $2p$. That's the uncertainty.

And if we know what quantum number we're in we know what the expectation value for p of the momentum is, and what we derive is that $\Delta x \Delta P$ is equal to $\hbar n$. You can do that, and maybe I should ask you to really be sure you can do that. In seconds, because you really know what the possible values of momentum or momentum squared are for a product of a box.

OK. So why is there zero-point energy, because if you said, I had a level at the bottom of the box, we would have the momentum 0. The uncertainty and the momentum is 0, and the product of the uncertainty of the moment times the product of the uncertainty in the position has to be some finite number, and you can't do that here. And so this is a simple illustration of the uncertainty principle that you have to have a non-zero zero-point energy. That's true for all one-dimensional problems. OK. We've got lots of time.

One of the beautiful things about quantum mechanics is that if you solved one problem, you could solve a whole bunch of problems, and so to illustrate that, let's consider the 3D particle in a box. So for the 3D particle in a box, the Hamiltonian can be written as a little Hamiltonian for the x degree of freedom y and z. OK. So we have three independent motions of the particle.

They're not coupled. They could be, and we're interested in letting them be coupled. But that's where we start asking questions about reality, and that's where we bring in perturbation theory. But for this, oh, that's fantastic, because I know the eigenvalues of this operator and of this operator, eigenfunctions, and of this operator. So the problem is basically solved once you solve the 1D box.

Now, one proviso, what you can do this separation completely formally as long as H_x , H_y commute, and basically we say the x, y, and z directions don't interact with each other. The particle is free inside the box. It's just encountering walls. There are no springs or anything expressing the number of degrees of freedom. OK.

So we have now a wave function, which is a function of x, y, and z, but we can always write it as $\psi_x(x)$, $\psi_y(y)$, $\psi_z(z)$. So it's a product of three wave functions that we know, and the energy is going to be expressed as a function of three quantum numbers, where the box is edge lengths a, b, and c. You didn't see me looking at my notes. I'm just taking the solution to 1D box, and I'm multiplying it. And so now we have the particle in a 3D box, and this is where the ideal gas law comes from, but not in this course. So anyway, this is a simple thing, and the wave functions are simple as well, and you can do all these fantastic things.

So there are many problems like a polyatomic molecule. In a polyatomic molecule, if you have n atoms, you have $3n - 6$ vibrational modes. You might ask, what is a vibrational mode? Well, are they're independent motions of the atoms that satisfy the harmonic oscillator Hamiltonian, which we'll come to next time. And so we have $3n - 6$ exactly solved problems all cohabiting in one Hamiltonian.

And then we can say, oh yeah, we got these oscillators, and if I stretch a particular bond, it might affect the force constant for the bending. So we can introduce couplings between the oscillators, and in fact, that's what we do with perturbation theory. That's the whole purpose. And with that, we can describe both the spectrum and how the spectrum encodes the couplings between the modes.

And also, we can describe what's called intramolecular vibrational redistribution, which happens when you have a very high density of vibrational state. Energy moves around, because all the modes are coupled, and so even if you've plucked one, the excitation would go to others. And we can understand that all using the same formalism that we're about to develop.

All right. I'm not using my notes this time, because I think there's just so much insight, so I have to keep checking to see what I've skipped. All right. So what I've been saying is whenever the Hamiltonian can be expressed as a sum of individual Hamiltonians, whenever we can write the Hamiltonian this way, we can write the wave function as a product of wave functions for coordinates, $\psi = \prod_{i=1}^N \psi_i$. And the energies will be the sum $E = \sum_{i=1}^N E_i$. I equals 1 to N.

So this is really easy. If we have simply a Hamiltonian, which is a sum of individual particle Hamiltonians, we don't even have to stop to think. We know the wave functions and the eigenvalues.

OK. Now, suppose the Hamiltonian is this plus that. So here, we have a Hamiltonian, and this is this simply the uncoupled Hamiltonian. This is what we'd like nature to be, but nature isn't so kind, and there are some coupling terms. And so we know the eigenfunctions and eigenvalues for this Hamiltonian. We call them the basis functions and the zero-order energies, and then there is this thing that couples them and leads to complications, and that's perturbation theory. We're going to do that.

OK. So now, let me just say, on page nine of your notes, there's the words next time, and those are going to be replaced by you should. There's a whole bunch of things that I want you to consider, and I was planning on talking about them, but they're all pretty trivial. And so there are a whole bunch of things you should study, because I will ask you questions about them. And of greatest importance is the ability to calculate things like that.

OK. Now, I'm going to give you a whole bunch of facts which I may not have derived. But you're going to live with them, and you can ask me questions. Some of these things are theorems that we can prove, but the proof of the theorem is really boring. Understanding what it is is really wonderful.

So all eigenfunctions that belong to different eigenvalues-- of whatever operator we want, the

Hamiltonian, some other operator-- are orthogonal. That's a fantastic simplification. So if you have two eigenfunctions of the Hamiltonian, of the position operator, anything, those eigenfunctions are orthogonal. Their integral is 0, very, very useful.

Then, one of the initial postulates about quantum mechanics is this idea that the wave functions are well-behaved. Well, if I were to state it at the beginning, you wouldn't know what's well-behaved and ill-behaved, but now I can tell you. One of the things is that the wave function is continuous, no matter what the potential does. The derivative is continuous, except at an infinite barrier.

So you come along, and you hit an infinite barrier, and you've already seen that with the particle in a box. The wave function is continuous at the edge of the box, but the derivative is discontinuous, and it's because it's an infinite wall. That's a pretty violent thing to make the first derivative be discontinuous. The second derivative is continuous, except at any sudden change in the potential.

So when you're solving 1D problems, and you've got a solution that works in the various regions, and you want to connect them together, these provide some rules about the boundary conditions. So now, most real systems don't have infinite walls or infinitely sharp steps. So for calculation of physically reasonable things, wave function for the first derivative, second derivative, they are continuous. But for solving a problem, we like these steps, because then we know how to impose boundary conditions, and that gets us a much easier thing to calculate.

OK. Now-- oh, that's where it went, OK-- semi classical quantum mechanics. We know that the energy classically is p^2 over $2m$. Right? It's $\frac{1}{2}mv^2$, but that's the same thing as p^2 over $2m$. In quantum mechanics, when we talk about Hamiltonians, the variables are x and p not x and v . So that seems like a picky thing, but it turns out to be very important.

And so we can say, well, the momentum can be a function of x , classically. So I just solved this problem, and if the potential is not constant, then the momentum, classical momentum, is not constant. But we know what it is everywhere, and we also know that the wavelength is equal to h over p . So we could make a step into the unknown saying, well, the wavelength for a non-constant potential is a function of coordinate, and it's going to be equal to h over p of x . That's semi-classical quantum mechanics, everything you would possibly want.

Now, for one-dimensional problems, you can solve in terms of this coordinate dependent

wavelength which is related to the local momentum. And so it doesn't matter how complicated the problem is, you know that you can calculate the spatial modulation frequency, you could calculate the amplitude, is it big or small, based on these ideas of the classical momentum function. So this demonstration of my walking across the room slow, fast, slow tells you about probability. So if you use this formula, you know the node spacings, and you know the amplitudes.

Now, what you don't know is where are the nodes? You know how far they are apart, but I have to be humble about this. In order to calculate where the nodes are, I have to do a little bit more in order to pin them down. But mostly, when you're trying to understand how something works, you want to know the amplitude of the envelope, and that's a probability, and so it's related to 1 over the square root of the momentum. I'm sorry, the amplitude is 1 over the square root of the momentum, and the nodes spacings, those are the things you want to do, and you want to know them immediately.

And a couple other facts that I told you earlier, but I think I want to emphasize them-- the energy order, number of nodes, number of internal nodes. For 1D problems, you never skip a number of-- so you can't say, there is no wave function with 13 nodes, even if you don't like being unlucky. And it's there, and so if you want the 13th energy level, you want something with 12 nodes, and that also focuses things. So these are amazingly wonderful things, because you can get them from what you know about classical mechanics, and it's easy to embed them into a kind of half quantum mechanics.

And since, I told you, this course is for use and insight, not admiration of philosophy or historical development, and this is what you want to do. You look at the problem and sketch how is the wave function going to behave and perhaps how a particular thing at some place in the potential is going to affect the energy levels or any other observable property. And so the cartoons are really your guide to getting things right, but you really have to invest in developing the sense of how to build these cartoons.

OK. I'm finished early again. Does anybody have any questions? OK. We start the harmonic oscillator next time. OK, so I can say a couple of things. The wave functions, the solution to the 1D box and the free particle, they're really simple.

The solution to the harmonic oscillator involves a complicated differential equation which the mathematicians have solved and worked out all the properties. But there is a really important

simplification that enables us to proceed with even greater velocity in the harmonic oscillator than we would in a particle in a box. And they are these things called a and a^\dagger , creation and annihilation operators, where when we operate on ψ with this creation operator, it converts it to $\sqrt{v+1} \psi_{v+1}$. These things, we don't ever have to do an integral.

Once you're in harmonic oscillator land, everything you need comes from these wonderful operators. And so even though the differential equation is a little bit scary for chemists, these things make everything trivial. And so we use the harmonic oscillator, and the particle in a box to illustrate time-dependent quantum mechanics. They each have their own special advantages for simplifications, but it's wonderful, because we can use something we barely understand for the first time. And actually reach that level of, yeah, I can understand macroscopic behaviors too and how they relate to quantum mechanical behavior of simple systems. OK, so that's where we're going. We're going to have two or three lectures on harmonic oscillator.