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**ROBERT FIELD:** OK, let's get started. So last time we talked about the one-dimensional wave equation, which is a second-order partial differential equation. This is not a math course. If you have a second-order differential equation, there will be two linearly independent solutions to it. And that's important to remember.

Now, there are three steps that we use in approaching a problem like this. Does anybody want to tell me what those three steps are? Yes?

**AUDIENCE:** [INAUDIBLE] it has separate functions that take only one variable.

**ROBERT FIELD:** OK, that's most of it. You want to solve the general equation, and one way to solve the general equation is to try to separate variables. Always you want to separate variables. Even if it's not quite legal, you want to find a way to do that because that breaks the problem down in a very useful way. So the first step is the general solution, and it involves trying something like this where we say  $u$  of  $x$  and  $t$  is going to be treated in the separable form. If it doesn't work, you're going to get 0. You're going to get the solution. The only solution with separated variables is nothing happening. And so that's unfortunate if you do work and you get nothing for it, but life is complicated.

So then after you do the general solution, what's next? Yes?

**AUDIENCE:** You need to set boundary conditions?

**ROBERT FIELD:** Yes. Now if it's a second-order differential equation, you're going to need two boundary conditions. And when you impose two boundary conditions, the second one gives some sort of quantization. It makes the solutions discrete or that there is a discrete set rather than a continuous set. The general solution is more or less continuous, or continuous possibility.

So we have now the boundary conditions, and that gives us something that we can start to visualize. So what are the important things that, if you're going to be drawing pictures rather than actually plotting some complicated mathematical function, what are the first questions you

ask? Yes?

**AUDIENCE:** Is it symmetric or asymmetric?

**ROBERT FIELD:** Yes, if the problem has symmetry, the solutions will have symmetry. But there's more. I want another, my favorite.

**AUDIENCE:** Where's it start?

**ROBERT FIELD:** I'm sorry?

**AUDIENCE:** Where does it start? So  $t$  equals 0 or  $x$  equals 0.

**ROBERT FIELD:** The initial condition is really the next thing I'm going to ask you about, and that's called the pluck. You're right on target. But now if you're going to draw a picture, the best thing you want to do to draw a picture is have it not move. So you want to look at the thing in position, and what are the things about the position function that you can immediately figure out and use in drawing a cartoon?

**AUDIENCE:** Nodes.

**ROBERT FIELD:** Yep. So how many nodes and where are they? Are they equally spaced? And that's the most important thing in drawing a picture, the number of zero crossings that a wave function has, and how are they distributed? Their spacing of nodes is half the wavelength, and the wavelength is related to momentum. And so I'm jumping into quantum mechanics, but it's still valid for understanding the wave equation.

So we want the number of nodes for each specific solution satisfying the boundary conditions and the spacing and the loops between nodes. Are they all identical? Is there some systematic variation in the magnitude of each of the loops between nodes? Because if you have just a qualitative sense for how this works, you can draw the wave function, and you can begin to make conclusions about it.

But it all starts with nodes. Nodes are really important. And quantum mechanics, the wave functions have nodes. You can't do better than focus on the nodes.

And then I like to call it pluck, but it's a superposition of eigenstates. And those superpositions for this problem can move. And so-- you're missing a great-- anyway. And so you want to know, what is the kind of motion that this thing can have?

And so one of the things-- this is really the three steps you go through in order to make a picture in which you hang up your insights. And so if there's one state or two states, one state is just going to be standing waves. Two states is all the complexity you're ever going to need. And if two states have different frequencies, there will be motion, and the motion can be side-to-side motion or sort of breathing motion where amplitude moves in from the turning-point region to the middle and back out again. And so you can be able to classify what you can understand and to imagine doing experiments based on this simplified version of the flux.

In my opinion, the most important thing you can do as a professional quantum machinist and in preparation for exams is to be able to draw these cartoons quickly, really quickly. That means you have to think about them in advance.

And so this recipe is how you're going to understand quantum mechanical problems too. And this differential equation is actually a little more complicated than the first few that we're going to encounter because the first few problems we're going to face are not time dependent. There may still be a separation of variables situation and imposing boundary conditions and so on, but there is no motion. But eventually we'll get motion because our real world has motion, and quantum mechanics has to reproduce everything that our real world does.

So, we're going to begin quantum mechanics, and first of all I will describe some of the rules we have to obey in building a quantum-mechanical picture. And then I'll approach two of the easiest problems, the free particle and the particle in an infinite box.

So we have the one-dimensional Schrodinger equation, and the one-dimensional Schrodinger equation looks like the wave equation. And why? Because waves interfere with each other. We can have constructive and destructive interference. Almost everything that is wonderful about quantum mechanics is the solutions to this Schrodinger equation also exhibit constructive and destructive interference. And that's essential to our understanding of how quantum mechanics describes the world.

The next thing I want to do is talk a little bit about postulates. Now I'm going to be introducing the quantum-mechanic postulates as we need them as opposed to just a dry lecture of these strange and wonderful things before we're ready for them.

But a postulate is something that can't be proven right. It can be proven wrong. And we build a system of logic based on these postulates.

Now one of the great experiences in my life was one time when I visited the Exploratorium in San Francisco where there are rather crude, or at least when I visited almost 50 years ago, there were rather crude interactive experiments where people can turn knobs and push buttons and make things happen. And the most wonderful thing was really young kids trying to break these exhibits. And what they did is by trying to break them they discovered patterns, some of them, and that's what we're going to do. We're going to try to break or think about breaking postulates and then see what we learn.

So, let's begin. We have operators in quantum mechanics. And we denote them either with a hat or as a boldface object. We start using this kind of notation when we do matrix mechanics, which we will do, but this is just a general symbol for an operator. And an operator operates on a function and gives a different function. It operates to the right, or at least we like to think about it as operating to the right. If we let it operate to the left, we have to figure out what the rules are, and I'm not ready to tell you about that.

So this operator has to be linear. And so if we have an operator operating on a function,  $A f + b g$ , it has to do this. Now you'd think, well, that's pretty simple. Anything should do that. So taking the derivative does that. Doing an integral does that, but taking the square root doesn't. So taking the square root-- an operator says take the square root, well, that's not a linear operator. Now the only operators in quantum mechanics are linear operators.

We have eigenvalue equations. So we have an operator operating in some function. It gives a number and the function back again. And this is called the eigenvalues, and this is the eigenfunction.

**AUDIENCE:** Dr. Field?

**ROBERT FIELD:** Yes?

**AUDIENCE:** In the [INAUDIBLE] that should be  $b$  times  $A$  hat [INAUDIBLE].

**ROBERT FIELD:** What did I do? Well, it should just be-- sorry about that. I'm going to make mistakes like this. The TAs are going to catch me on it, and you're going to do it too.

All right, so now here we have an operator operating on some function. And this function is special because when the operator operates on it, it returns the function times a number, the eigenvalue and the eigenfunction. We like these. Almost all quantum mechanics is expressed

in terms of eigenvalue equations.

Operators in quantum mechanics-- so for every physical quantity in non-quantum-mechanical life there corresponds an operator in quantum mechanics. So for the coordinate, the operator is just the coordinate. For the momentum, the operator is minus  $\hbar$  partial with respect to  $x$  or derivative with respect to  $x$ . Now this is not too surprising, but this is really puzzling because why is there an imaginary number? This is the square root of minus 1, which we call  $i$ . Why is that there and why is the operator a derivative rather than just some simple thing?

Another operator is the kinetic energy, and the kinetic energy is  $p$  squared over  $2m$ . And so that comes out to be minus  $\hbar$  squared over  $2m$  second partial with respect to  $x$ .

Well, it's nice that I don't have to memorize this because I can just square this and this pops out, but you have to be aware of how to operate with complex and imaginary numbers. And there are so many exercises on the problem set, so you should be up to date on that.

And now the potential is just the potential. And now the most important operator, at least when we start out, is the Hamiltonian, which is the operator that corresponds to energy, and that is kinetic energy plus potential energy. And this is called the Hamiltonian, and we're going to be focusing a lot on that. So these are the operators you're going to care about.

The next thing we talk about is commutation rules or commutators. And one really important commutator is the commutator of the coordinate with the conjugate momentum, conjugate meaning in the same direction. And that is defined as  $xp$  minus  $px$ . And the obvious thing is that this commutator would be 0. Why does it matter which order you write things? But it does matter. And, in fact, one approach to quantum mechanics is to start not with the postulates that you normally deal with but a set of commutation rules, and everything can be derived from the commutation rules. It's a much more abstract approach, but it's a very powerful approach.

So this commutator is not zero. And how do you find out what a commutator is? Well, you do  $xp$  minus  $px$ , operate on some function, and you find out. And you could do that. I could do that. But the commutator is going to be equal to  $\hbar$ .

Now there is a little bit of trickiness because the commutator  $xp$  is  $\hbar$  and  $px$  is minus  $\hbar$ . And so I don't recommend memorizing it. I recommend being able to do this operation at the speed of light so you know whether it's plus  $\hbar$  or minus  $\hbar$  because you get into a whole lot of trouble if you get it wrong. So this is really where it all begins, and this is why you

can't make simultaneously precise measurements of position and momentum, and lots of other good things.

And then we have wave functions. So wave function for when the time independent Hamiltonian is a function of one variable, and it contains everything we could possibly know about the system.

But this strange and wonderful thing, which leads to all sorts of philosophical debates, is that this guy, which contains everything that we can know, can never be directly measured. You can only measure what happens when you act on something with a given wave function. You cannot observe the wave function. And for a subject area where the central thing is unobservable is rather spooky.

And a lot of people don't like that approach because it says we've got this thing that we're relying on, but we can't observe it. We can only observe what we do when we act on it. And usually the action is destructive. It's destructive of the state of the system. It causes the state of the system to give you a set of possible answers, and not the same thing each time. So it's really weird.

So we have wave functions. And we can use the wave function to find the probability of the system at  $x$  with a range of  $x$ ,  $x$  to  $x$  plus  $dx$ . And that's  $\psi^* \psi dx$ .

So you notice we have two wave functions, the product of two, and this star means takes a complex conjugate. So if you have a complex number  $z$  is equal to  $x$  plus  $iy$ -- real part, imaginary part-- and if we take  $z^*$ , that's  $x$  minus  $iy$ .

So these wave functions are complex functions of a real variable. And so we do things like take the complex conjugate, and you have to become familiar with that.

Now we have what we call the expectation value or the average value, and we denote this as  $A$ . So for the state function  $\psi$ , we want the average value of the operator  $A$ . Now in most life, that symbol is not included just because people assume you know what you're doing. And this is  $\psi^* A \psi dx$  over  $\psi^* \psi dx$ . And this is integral from minus infinity to infinity.

So this down here is a normalization integral. Now we normally deal with state functions which are normalized to 1, meaning the particle is somewhere. But if the particle can go anywhere, then normalization to 1 means it's approximately nowhere. And so we have to think a little bit about what do we mean by normalization, but this is how we define the average value or the

expectation value of the quantity  $A$  for the state  $\psi$ . So this is just a little bit of a warning that, yeah, you would think this is all you need, but you also need to at least think about this.

That's great. I'm at the top of the board and we're now at the beginning.

So the Schrodinger equation is the last thing, and that's the Hamiltonian operating on the function and gives an energy times that function. And if it's an eigenvalue, then we have this eigenvalue equation. We have these symbols here. So that's the energy associated with the  $\psi_n$  function.

So now we're ready to start playing games with this strange new world. And so let's start out with the free particle. Now because the free particle has a complicated feature about how do we normalize it, it really shouldn't be the first thing we talk about. But it seems like the simplest problem, so we will.

So what's the Hamiltonian? The Hamiltonian is the kinetic energy, minus  $\hbar^2$ , or  $2m$  second derivative with respect to  $x$  plus the potential energy,  $V_0$ . Free particle, the potential is constant. We normally think of it as the potential is zero, but there is no absolute scale of a zero of energy, so we just need to specify this.

And so we want to write the Schrodinger equation, and we want to arrange it in a form that is easy to solve. There is two steps to the rearrangement, and I'll just write the final thing. So the second derivative of  $\psi$  is equal to minus  $2m$  over  $\hbar^2$  times  $E - V_0$   $\psi$ . So this is the differential equation that we have to solve. So there was a little bit of rearrangement here, but you can do that.

So the second derivative of some function is equal to some constant times that function. We've seen that problem before. It makes a lot of difference whether that constant is positive or negative, and it better, because if we have a potential  $V_0$  and we have an energy up here, well, that's perfectly reasonable. The particle can be there, classically.

But suppose the energy is down here. If the zero of energy is here, you can't go below it. That's a classically forbidden situation. And so for the classically allowed situation, the quantity, this constant, is negative.

For the classically forbidden situation, this constant is positive. You've already seen the big difference in the way a second derivative, this kind of equation, works when the constant is

positive or negative. When this constant is negative, you get oscillation. When this constant is positive, you'll get exponential.

Now we're interested in a free particle, so free particle can be anywhere. And we insist that the solution to our quantum-mechanical problem, the wave function is what we say well behaved. So well behaved has many meanings, but one of them is it never goes to infinity.

Another is that when you go to infinity, the wave function should go to zero. But there's also things about continuity and continuity of first derivatives and continuity of second derivatives. We'll get into those, but you know immediately that if this constant is positive, you get an exponential behavior, and you get the  $e$  to the  $ikx$  and  $e$  to the-- not  $ik$ --  $e$  to the  $kx$  and  $e$  to the minus  $kx$ . And one of those blows up at either positive infinity or negative infinity.

So it's telling you that in agreement with what you expect for the classical world, an energy below the constant potential is illegal. It's illegal when this situation persists to infinity. But we'll discover that it is legal if the range of coordinate for which the energy is less than the potential is finite. And that's called tunneling, and tunneling is a quantum-mechanical phenomenon. We will encounter that.

So we know from our experience with this kind of differential equation that the solutions will have the form sine  $kx$  and cosine  $kx$ . But we choose to use instead  $e$  to the  $ikx$  and  $e$  to the minus  $ikx$  because this cosine  $kx$  is  $1/2 e$  to the  $ikx$  plus  $e$  to the minus  $ikx$ . And so we can use these functions because they're more convenient, more memorable. All the integrals and derivatives are trivial. And so we do that.

So the differential equation-- and we saw before that we already have what  $k$  is. So minus  $k$  squared is minus  $2m$  over  $\hbar$  squared-- minus  $2m$  over  $\hbar$  squared  $E$  minus  $V_0$ .

We take the derivative of this function. This is the function, and this is the eigenvalue. We take the second derivative with respect to  $x$ . We get an  $ik$  from this term and then another  $ik$ , which makes minus  $k$  squared. And we get a minus  $ik$  and another minus  $ik$ , and that gives a minus  $k$  squared. And so, in fact, this is an eigenvalue equation. We have the form where this equation is an eigenfunction. With this, we have everything.

So the energies for the free particle,  $\hbar k$  over  $\hbar k$  squared over  $2m$  plus  $V_0$ , so this is an eigenfunction, and this is the eigenvalue associated with that function. We're done. That was an easy problem. I skipped some steps because it's an easy problem and I want you to



go over it and make sure that you understand the logic and can come to the same solution.

Let's take a little side issue. Suppose we have  $\psi$  of  $x$  is  $e$  to the  $ikx$ . Well, we're going to find that this is an eigenfunction of  $p$ , and the eigenvalue or the expectation value of  $p$  is  $\hbar k$ . And if we had  $e$  to the  $-ikx$ , then what we'd get is  $-\hbar k$ .

So we have this relationship between  $p$ , expectation value, and  $\hbar k$ . So this corresponds to the particle going in the positive  $x$  direction, and this corresponds to the particle going in the negative  $x$  direction. Everything is perfectly reasonable. We have solutions to the Schrodinger equation for the free particle. The solutions to the free particle are also solutions to the eigenvalue equation for momentum. And the two possible eigenvalues for a given  $k$  are  $+\hbar k$  and  $-\hbar k$ .

Now that's fine. So everything works out. We're getting things, although we have the definition of the momentum having a minus 1, an  $i$  factor, and a derivative factor. Everything works. Everything is as you would expect. And the general solution to the Schrodinger equation can have two different values, the superposition of these two.

Right now, this wave function is localized overall space. Now if we want to normalize it, we'd like to calculate  $\int_{-\infty}^{\infty} \psi^* \psi dx$ .

This is why we like this notation because suppose we have a function like this,  $\psi^*$ -- well, actually like this.  $\psi^*$  is equal to  $a e^{-ikx} + b e^{ikx}$ , and  $\psi$  is  $a e^{ikx}$ . This would be  $e$  to the  $-ikx$ .

And so when we write this integral, what we get is  $\int_{-\infty}^{\infty} \psi^* \psi dx$  is equal to a squared integral  $\int_{-\infty}^{\infty} (a^2 + b^2) dx$ . So we have two constants which are real numbers because they're square modulus. They're additive. And we're integrating this constant from  $-\infty$  to  $\infty$ . We'll get  $\infty$ . We can't make this equal to 1.

So we have to put this in our head and say, well, there's a problem when you have a wave function that extends over all space. It can't be normalized to 1, but it can be normalized so that for a given distance in real space, it's got a probability of 1 in that distance. So we have a different form of normalization. But when we actually calculate expectation values, we can still use this naive idea of the normalization interval and we get the right answer, even though because both the numerator and denominator go to  $\infty$  and those infinities cancel and

everything works out.

This is why we don't do this first usually because there's all of these things that you have to convince yourself are OK. And they are and you should.

But now let's go to the famous particle in a box. It's so famous that we always use this notation. This is particle in an infinite box, and that means the particle is in a box like this where the walls go to infinity. And so we normally locate this box at a place where this is the  $x$  coordinate and this is the potential energy, and the width of the box is  $a$ . And we normally put the left edge of the box at zero because that problem is a little easier to solve than the more logical thing where you say, OK, this box is centered about zero.

And that should bother you because anytime you're interested in asking about the symmetry of things you'll want to choose a coordinate system which reflects that. Don't worry. I am going to ask you about symmetry, and it's a simple thing to take the solution for this problem and move it to the left by  $a/2$ .

So we have basically a problem where the potential is equal to 0 for  $0 \leq x \leq a$ , and it's equal to infinity when  $x < 0$  or  $x > a$ . So inside the box it looks like a free particle, but it can't be a free particle because there's got to be nodes at the walls.

We know that outside the box, the wave function has to be 0 everywhere because it's classically forbidden, strongly forbidden. We know that the wave function  $\psi$  is continuous. So if it's at 0 outside, it's going to be 0 at the wall. And so the wave functions have boundary conditions where, at the wall, the wave function goes to 0.

So now we go and we solve this problem. And so the Schrodinger equation for the particle in the box where  $V$  of  $x$  is 0. Well, we don't need it. We just have the kinetic-energy term,  $\hbar^2 \psi'' / 2m$  is equal to  $E \psi$ .

Again, we rearrange it. And so we put the derivative outside, and we have  $-\hbar^2 \psi'' / 2m = E \psi$ . And this is a number. And so we just call it  $-k^2 \psi$ . We know what that  $k$  is as long as we know what the energy is, and  $k^2$  is equal to  $2mE / \hbar^2$ .

Now we have this thing which is equal to a negative number times a wave function, and we already know we have exponential behavior. But in this case, we use sines and cosines

because it's more convenient.

So  $\psi$  of  $x$  is going to be written as  $A \sin kx$  plus  $B \cos kx$ . This is the general solution for this differential equation where we have a negative constant times the function. So the boundary condition,  $\psi$  of 0-- well,  $\psi$  of 0, this is 0, but this part is 1. So that means that  $\psi$  of 0 has to be 0, so  $B$  has to be equal to 0. And here, the other boundary condition, that also has to be equal to 0, and that has to be  $A \sin ka$ . And  $ka$  has to be equal to  $n$  times  $\pi$  in order to satisfy this equation. Sine is 0 at 0,  $\pi$ ,  $2\pi$ ,  $3\pi$ , et cetera.

So  $k$  is equal to  $n\pi$  over  $a$ . And so we have the solutions.  $\psi$  of  $x$  is equal to  $A \sin n\pi a$  over  $x$ .

And so we could put a little  $n$  here. And this is starting to make you feel really good because for all positive integers there is a solution. There's an infinite number of solutions. And their scaling with quantum number is trivial. And it's really great when you solve an equation and you are given an infinite number of solutions.

Well, there's one thing more you have to do. You have to find out what the normalization constant is, so you do the normalization integral. And when you do that, you discover that this is equal to  $2$  over  $a$  square root sine  $n\pi$  over  $a$ . So these are all the solutions for the particle in an infinite box, all of them.

And the energies you can write as  $n^2$  times  $h^2$  over  $8m a^2$  or  $n^2$  times  $E_1$ .

There's another thing.  $n$  equals 0. If  $n$  is equal to 0, the wave function corresponding to  $n$  equals 0 is 0 everywhere. The particle isn't in the box. So  $n$  equals 0 is not a solution. So the solutions we have--  $n$  equals 1, 2, et cetera up to infinity, and the energies are integer square multiples of a common factor.

This is wonderful because basically we have a problem. Maybe it's not that interesting now because why do we have infinite boxes and stuff like that? But if you ask, what about the ideal gas law? We have particles that don't interact with each other inside a container which has infinite walls. And I can tell you that in 5.62, there's a three-line derivation of the ideal gas law based on solutions to the particle in a box.

Also, we often have situations where you have molecules where there's conjugation so that

the molecule looks like a not quite flat bottom box with walls. And this equation enables you to learn something about the electronic energy levels for linear conjugated molecules. And this leads to a lot of qualitative insight into problems in photochemistry.

Now the most important thing, in my opinion, is being able to draw cartoons, and these cartoons for the solutions the particle in a box look like this. So what you frequently do is draw the potential, and then you draw the energy levels and wave functions. I have to cheat a little bit.

So number of nodes-- number of nodes, internal nodes. We don't count zeros at the walls. The number of nodes is  $n - 1$ .

The maximum of the wave function is always  $2/a$ . So here  $2/a$ , here  $2/a$ , here  $-\sqrt{2/a}$ . This slope is identical to this slope. This slope is identical to this slope which is identical to that slope. So there's a tremendous amount that you can get by understanding how the wave function looks and drawing these cartoons.

And so now if instead we were looking at problems where, instead of a particle in a box like this, we have a little dimple in the bottom of the box or we have something at the bottom or the bottom of the box is slanted. You should be able to intuit what these things do to the energy levels, at least have the beginning of an intuition.

So, we have an infinite number of oscillating solutions. That means that we could solve the problem for any kind of a box as long as it has vertical walls, and that's called a Fourier series. So for a finite range, we can describe the solution to any quantum-mechanical infinite box with a terrible bottom, in principle, by a superposition of our basis functions. That's what we call them.

Now, there are several methods for doing the solution of a problem like this efficiently. And you're going to see perturbation theory. And at the end of the course, you're going to see something that will really knock your socks off which is called the discrete variable representation. And that enables you to say, yeah, well, potential does terrible things. I solved the problem by not doing any calculation at all because it's already been done.

So these things are fantastic that we have an infinite number of solutions to a simple problem. We're always looking for a way to describe a simple problem or maybe not so simple problem with an infinite number of solutions where the energies for the solutions and the wave

functions behave in a simple  $n$ -scaled, quantum-number-scaled way.

And this provides us with a way of looking at what these things do in real life. You do an experiment on an eigenfunction of a box like this, and it will have certain characteristics. And it tells you, oh, if I measured the energy levels of a pathological box, the quantum-number dependence of the energy levels has a certain form, and each of the constants in that special form sample a particular feature of the pathological potential.

And that's what we do as spectroscopists. We find an efficient way to fit the observables in order to characterize what's going on inside something we can't see. And that's the game in quantum mechanics. We can't see the wave function ever. We know there are eigenstates. We can observe energy levels and transition probabilities, and between those two things, we can determine quantitatively all of the internal structure of objects that we can't see.

And this is what I do as a spectroscopist. And I'm really a little bit crazy about it because most people instead of saying let's try to understand based on something simple, they will just solve the Schrodinger equations numerically and get a bunch of small results and no intuition, no cartoons, and no ability to do dynamics except another picture where you have to work things out in a complicated way. But I'm giving you the standard problems from which you can solve almost anything. And this should sound like fun, I hope.

OK, so have a great weekend.