ROBERT FIELD: Last time, I talked a lot about the semiclassical method, where we generalize on this wonderful relationship to say, well, if the potential is not constant, then we can say, well, the wavelength changes with position. And we can say that the momentum changes with position.

But we're using this as the guide. And so the basis is really just saying, OK, we're going to take this kind of a relationship seriously. Because v is not constant. We have V of x. And we also know that the kinetic energy, which is an operator, is p squared over 2m. And the energy minus the potential is the kinetic energy.

And so we can use this to get a classical, mechanical function that this p of x is going to be 2m E minus V of x. So why are we doing all this when we can just solve the differential equations? And the answer is we want insight. And we want to build our insight on what we know.

And so we have this momentum function, which gives us a wavelength function, which tells us how far apart the waves are. But we also have another thing, which was demonstrated by my running across the room, and that the momentum is related to the velocity, which is related to the probability of finding the system at a particular place.

And so we have, if we commit the travesty of saying, OK, we have a classical function-- it's not the momentum-- but it's going to somehow encode the classical behavior, we can determine without solving any differential equation what the spacing between nodes in the exact wave function is, and the amplitude in that region. And that's a lot because then we can use our knowledge of classical mechanics to say, oh, this is what we expect in quantum mechanics. And that's very powerful.

And I keep stressing that you want to draw cartoons. And this is the way you get into those cartoons. OK, now, for the free particle, we have these kinds of wave functions, e to the ikx. And they're really great because often, we want to evaluate things like the integral of e to the ikx times e to the minus ikx dx. Well, that's one.

And so instead of remembering that we have to evaluate trigonometric integrals, sine, sine

theta, cosine, we can do this. And it really simplifies life. Now, using that insight, I'm asking you, OK, the expectation value for the momentum could be-- OK, if this is the expectation value for the momentum, what is psi of x?

I promised I would ask you this question. I don't know if anybody really thought about it. But first of all, we're talking about the free particle. And this is some sort of eigenfunction of the Hamiltonian for the free particle. So what can we say about k? We have two parts to the wave function. We have an e to the ikx. And we have a e to the minus ikx. And the k is the same for both of them. So with all those hints, what is this?

We have e to the ikx times something. And we have plus e to the minus ikx. So what are the somethings that go here? Yes?

AUDIENCE: A and B?

ROBERT FIELD: Right. And that didn't involve very much mental gymnastics if you really have done a little bit of practicing of integrals involving these sorts of things. Now there's two things. One is when you have the same k in e to the ikx and e to the minus ikx. The product is one. If you have different k's and you're integrating over all space, or over some cleverly chosen region, that integral is zero. Because these are eigenfunctions of-- these are different eigenfunctions of an operator belonging to different eigenvalues. And you always can count on those things being zero.

Now, quantum mechanics is full of integrals. Basically, there's an infinite number of them. And most of them are zero. And you want to be able to look at an integral and say, oh, I don't need to evaluate that. And often, you want to look at an integral and say, I do know how to evaluate that. And I know an infinite number of those like that. And all of a sudden, it starts to be transparent again. Because the barrier between insight and quantum mechanics is usually a whole bunch of integrals. And they're all yours.

And so we like problems where the wave functions have simple forms. And this is true for free particle. It's true for the particle in a box. We're going to start talking about their harmonic oscillator. And it seems like those integrals are not simple, but they are. I have to teach you why they're not simple.

So today, we're starting on the classical mechanical treatment of the harmonic oscillator. Then we'll do the traditional quantum mechanical treatment. And then, we'll come back and use these creation and annililation operators, which are the magic decoders for essentially

evaluating all the integrals trivially. And then, with all that in hand, we're going to make our first step into time-dependent quantum mechanics.

And we're going to use time-dependent quantum mechanics. Well, we're going to use our facility with integrals to describe the properties of some particle-like state we can construct. And these constructions are really simple for the particle in a box or the harmonic oscillator, depending on which properties you want. So your ability to draw cartoons and to use classical insights for the particle in a box and the harmonic oscillator will be incredibly valuable once we take our first step into the reality of time-dependent quantum mechanics.

Now, one of the things that's going to happen is that we're going to describe real situations, real situations that are not one of the standard solved problems. The standard solved problems are the particle in a box, or a particle in the infinite box, the harmonic oscillator, the hydrogen atom, and the rigid rotor. And the particle in a box-- so the potential for each of these is different. It looks like this. It looks like this. It looks like this. And it looks like that. So there is no stretching in a rigid rotor.

And so all of the complexity is in the kinetic energy, not the potential. But each of these has a different potential energy. And the energy levels for the particle in a box are proportional to n squared. For the harmonic oscillator, they're proportional to n plus 1/2. For the hydrogen atom, they are proportional to 1 over n squared. And for the rigid rotor, they're proportional to n times n plus 1.

So one of the valuable things you get from looking at these exactly soluble problems is that the energy level patterns for each of them are slightly different. And you can tell what you've got from the energy level pattern. And so when you take a spectrum, so often you want to know what kind of spectrum is this? Sometimes you can tell just by what frequency region it is. But usually, in a spectrum, there's a pattern of energy levels. And that gets you focused on well, what kind of problem-- what is the nature of the building blocks that we're going to use?

So this is wonderful. Now, we're also going to find that when we solve these problems in quantum mechanics, we get an infinite number of eigenfunctions and eigenvalues. And often, we get presented to us a lot of integrals involving the operators between different wave functions. And one of the beautiful things is when the theory gives you an infinite number of those integrals. So now we would have a collection of all sorts of integrals that are evaluated for us in a simple dependence on quantum numbers.

So what do we do with them? Well, there's two main things we do with these infinite numbers of integrals. One is we say, well, this problem is not the standard problem. There are defects. Instead of having the potential for the harmonic oscillator that looked like this, it might look like that. There might be some anharmonicity. Or there can be all sorts of defects. And these defects can be expressed by integrals of some other operator. And that goes into perturbation theory.

Or if we're going to want to look at wavepackets, creating a particle-like state and asking how it propagates in time, those integrals are useful. So there's all sorts of fantastic stuff, once we kill the standard problems. It's not just some thing you have to study, and it's over with. You're going to use this. As long as you're involved in physical chemistry, you're going to be using perturbation theory to understand what's going on beyond the simple stuff.

OK, so let's get started. So why is the harmonic oscillator so special? If we look at any potential energy curve, any one dimensional problem, it's typically harmonic at the bottom, no matter what it does. I mean, this is a typical molecular diatomic molecule potential. We have a hard inner wall. And we have bond breaking at the outer wall. And so this is an anharmonic potential. But the bottom part is harmonic.

And so we can use everything we learn about the harmonic oscillator to begin to draw a picture of arbitrary potentials. So this is hard wall bond breaking. Now, we're mostly chemists. And breaking a bond is-- how much energy does it take to break a bond? Well, is that encoded in the spectrum? Yeah. So this is the sort of thing we would care about.

And now let me put some notation here. So this is the potential. And this is the potential of-- the internuclear resistance, which is traditionally called R. We're going to switch notations really quickly from R to x. But this, the minimum of the potential, is the equilibrium internuclear distance R sub e. So for R near R sub e the potential V of R looks simply like k over 2, a forced constant, R minus R sub e squared.

So this is harmonic oscillator. And now we're going to change notation a little bit. We're going to use lowercase x to be R minus Re. In other words, it's the distortion away from equilibrium. And we can take any potential and write it as a power series. Sorry. And so on.

So if we know these derivatives, we know what to do with them. OK. So one standard potential is called the Morse potential. Because it looks like this. It looks like what you need for a

diatomic molecule. And the Morse potential has an analytic form, where the potential v of x is equal to D sub e, the dissociation energy, 1 minus e to the minus ax. Well, that doesn't look like polynomial of x. But we power series expand this, and we get a polynomial x.

OK, now, what is this D sub e? So if x is equal to 0-- this is 1 0. And so we get the energy. The potential at x equals 0 is 0. And if x is equal to infinity, v of x equals D sub e, so basically, this is the energy between the bottom of the well and where it breaks. This is D sub e. OK? So this is well interpreted. All the rest of the action is in here.

AUDIENCE: [INAUDIBLE]

ROBERT FIELD: I'm sorry?

AUDIENCE: Do you just square the x?

ROBERT FIELD: Yep! Thank you. It's an innocent factor. But it turns out to be very important. OK, so let's square this. We have v of x is equal to De times 1 minus 2e to the minus ax plus e to the minus 2ax. OK, so we're going to do power series expansions of these. And you can do that.

And so we have plus some function of x plus some function of x squared, et cetera. Now, what is the function of x? We're taking our derivatives at the equilibrium, at x equals 0. And we have a potential, which has a minimum. So what's the derivative of the potential at equilibrium? Yes?

AUDIENCE: Zero.

ROBERT FIELD: Right. And so the x term goes away. And so we have a constant term, which we usually choose to be zero. And we have this quadratic term. Looks like a harmonic oscillator. And then there are other terms which express the personality of the potential. This is universal. And the rest becomes a special case.

So we have v of x is De a squared x squared plus other stuff. OK, we're going to call this 1/2k. why? Because we'd like it to look like a harmonic oscillator. I mean, we know that the potential for a harmonic oscillator is described in this way. So let's just draw a picture.

So we have a spring and a mass. And I should have drawn this up a little higher. OK, so at equilibrium there is no force. If the mass is down here, there is a force pulling it up. And if it's up here, there's a force pushing it down. Hooke's Law says that the force is equal to minus k x

minus x 0. OK, and now we're going to switch to just the lowercase x in a second.

But now, the force according to Newton is minus gradient of the potential. So the potential for this problem is v of little x is equal to 1/2k x squared. OK, so we have what we expect for a harmonic oscillator. And we're going to say the small displacement part of the Morse oscillator looks like 1/2k. x squared looks harmonic. And so what do we do now?

Well, one of Newton's laws, force is equal to the mass times the acceleration. And so we can say, oh, well, the acceleration is the second derivative of x with respect to t. And the force is a minus gradient of the potential. So it's minus 1/2kx squared. Minus kx.

OK, so this is the gradient of the potential. This is the mass-- well, I need the mass-- times the acceleration. And so this is the equation we have to solve. And so we want to find the solution x of t. And this is a second order differential equation because we have a second derivative. So there's going to be two terms. And they'll be-- we'll have some sine and some cosine function.

And we're going to want a derivative, a second derivative, that brings down a constant k. And so we know that these are going to be things that have the form a sine kx k or m square root x plus b cosine k m x. So this is the solution. And we have to find A and B.

Now, why do we have k over m? Well, you can look at this differential equation. And you can see that we have an m here. We have a k here. And that's what you need in order to solve it. So now our job is simply to find A and B.

AUDIENCE: Should these be functions of t and not x?

ROBERT FIELD: You know, sometimes I go onto automatic pilot because it's so familiar to me. I'm just writing what comes up in my subconscious. But yes, that's a good point. All right, so we want x of t. And it is this combination. OK, so now we put in some insights.

We want to know what the period of oscillation is. And so x t plus tau has to be equal to x of t. And so when we do that, we discover-- and I'm just going to skip a lot of steps-- that k over m square root times tau has to be equal to 2 pi in order to satisfy that. We call k over m square root omega, just to simplify the equations. But we also discover that this actually is an angular frequency.

So if we say omega tau is equal to 2 pi, then tau equals 2 pi over omega, which is equal to 1

over the frequency. Just exactly what we expect. So we have the beginning of a solution and omega, tau, and frequency make sense. Everything is what we sort of expect.

OK, so now the next step is to determine the values of the constants. So normally, when we have a differential equation, after we find the general form, we apply boundary conditions. And so we're going to apply some boundary conditions. So here we have the potential. And-- so this is the potential as a function of coordinate. And this is the turning point, this is the inner turning point at energy E. This is the outer turning point.

Well, what's true at the turning point? The turning point, the potential is equal to the energy at the two turning points. So 1/2k x plus or minus of E squared. So if we know E, we know where the turning points are. And so x of plus minus of E, we can solve this. And so we have 2E over k. Yeah. So this is the turning points. These are the turning points.

Now, this is a fairly frequent exercise in quantum mechanics. You're going to want to know where are the turning points. Because this is how you impose boundary conditions easily. And so knowing that a turning point corresponds to where the potential is equal to the total energy is enough to be able to solve for this.

OK, so suppose we start at x equals x plus. And so x of 0 is equal to x plus. And that determines one of the coefficients. So x of 0-- so we have at t equals 0 the sine term is 0 and the cosine term is 1. And so the first thing we get at t equals 0 is that B is equal to x plus. Right?

The next step is to find a. There are several ways to do this. But it's useful to draw a little picture. So x plus is here. And that occurs at t equals 0. And x minus occurs at tau over 2. And in the middle we have tau over 4. So let's ask for, what is the value of the wave function when x is equal to 0? So how do we make the x be 0 at tau over 4? And that determines the value of B. I mean, the value of A.

So we have everything we need. And now, before just rushing on, let me just say, well, this just gives A is equal to zero. OK, there's a different approach. When we have a sine plus a cosine term, we can always re-express it as x of t is equal to some other constant times sine omega t plus phi.

And so the same sort of analysis gives c is equal to E over k square root. And phi is equal to minus pi over 2. OK, I'm just writing this. You want to do that. OK, so now we're going to be

preparing to do quantum mechanics, the quantum mechanical solution of the harmonic oscillator.

And so there are going to be other things that we care about, and one is the kinetic energy and one is the potential energy. And in particular, we'd like to know the kinetic energy, which we call t. And we'd like to know the expectation value of t as a function of time, or just T bar of t. And similarly, we'd like to know the expectation value of the potential energy as a function of time. And that's going to be V bar of t. And so from classical mechanics, we should be able to determine what these average values of the kinetic and potential energy.

So what do we know? We know that the frequency is omega over 2 pi. We know the period is 1 over omega. OK, and so T of t is 1/2 mv squared of t, or p squared over 2m. But all right, v is the derivative of x with respect to t. And we have the solutions over here. And so we know that we can write x of t and v of t just by taking derivatives.

And so we have x of t is 2e over k square root sine omega t plus phi. And v of t is omega times 2e over k square root cosine omega t plus phi. So we want v squared to be able to calculate the kinetic energy. And so we do that. And so the kinetic energy T of t is 1/2m m omega squared 2e over k cosine squared omega t plus phi.

This here, omega is k over m, the square root of k over m. S this is m times k over m. So we just get k out there. And so now we would like to know the average value of the kinetic energy. OK, so we have m omega squared. And so that's k over k. And so we just get E integral from 0 to tau bt of cosine square omega t plus phi over tau.

We want the time average. And so we calculate this integral and we divide by tau. That's how we take an average. And what we discover is that this integral is the numerator is 1/2 tau times E. No, I'm sorry. 1/2 tau, we have E times 1/2 tau divided by tau. And this becomes E over 2, an important result. And we're going to discover that the average value of the momentum for a harmonic oscillator is E over 2 in quantum mechanics.

We do the same thing for the potential. And we discover that it is also E over 2. So we know that E is equal to T of t plus V of t. But it's also true that the average is equal-- so T bar is equal to V bar which is equal to E over 2. So now we have an important interpretation of the harmonic oscillator.

The harmonic oscillator is moving from turning point to the middle to the other turning point.

And what's happening is energy is being exchanged between all potential energy at a turning point to all kinetic energy in the middle. So energy is going back and forth between kinetic energy and potential energy. We can solve for the relationship between T of t and V of t. And we can find that V of t is equal to T minus pi over 4. tau over 4.

So this is telling us just what I said before, that energy is being exchanged between potential and kinetic energy. And that the potential energy is lagging by tau over 4 behind the momentum. This is all very fast. But it's all classical mechanics, which you know. And we're going to be rediscovering all of this in quantum mechanics.

And so we have to know what are we aiming for in quantum mechanics? So that we can completely say, yes, it's consistent with classical mechanics. And there's some really-- now, there's another really neat thing. So if we look at X of t, X of t is oscillating. And suppose we start out at a turning point, the outer turning point.

So we can tell from this, the derivative of x with respect to t at x equals x plus is going to be 0. So at a turning point, the particle is hardly moving, not moving. And so what about the momentum? Well, the momentum is going to look like this. Yeah, it's going to look like that. And so at the time that we are starting at a turning point, the time derivative of the momentum is at its maximum value.

So this is going to be really important when we start looking at properties of time-evolving wave functions. Because what we're going to discover is, suppose we start our system here, at a turning point. And that's actually something that we can do very easily in an experiment. Because when we excite from one electronic state to another, you automatically create a wave packet, which is localized at a particular internuclear distance.

And so you go typically, to a turning point. So then, well, what's going to happen? Well, there is a thing in quantum mechanics, which you will become familiar with, called the autocorrelation function. No, it's not. It's called the survival probability. And that's going to be the product of the time-dependent wave function at x and T, the time-dependent wave function at x and 0.

So this is expressing somehow how the wave function that is created at t equals 0 gets away from itself. It's a very important idea. Because you make something. And it evolves. And for a harmonic oscillator, if you make it at a turning point, this thing changes. Because the momentum changes. And the contribution of the coordinate to the decay of the survival probability is-- it's all due to the momentum, and not the coordinate change. That's actually, a

very important insight.

Because the momentum, the time rate of change of the momentum, is minus the gradient of the potential. So this is one way we learn about the potential simply by starting at a turning point and knowing that this thing, which we can measure, is measuring the thing we want to know. Now, we will get to this very soon. Because I haven't even told you about time-dependent quantum mechanics. But those are the things that we expect to encounter.

OK, now I want to give you-- I'm going to throw at you-- some useful stuff, which turns out to be really easy. Suppose we want to know the expectation values, or the average values, of x, x squared, p, and p squared. OK, so we have a harmonic oscillator. And do we know what this is? Do we know the expectation value of the coordinate?

AUDIENCE: 0.

ROBERT FIELD: We have 0. Why is it 0? There's two ways of answering that question. But these are easy questions, which on an exam, you don't want to evaluate an integral. You want to know why is it 0. And there's two answers. You said 0, right? Why did you say 0?

AUDIENCE: Because it's symmetric.

ROBERT FIELD: Yes. OK, so there is a symmetry argument. Another is well, is the potential moving? The particle is in a potential. It's going back and forth. The potential is stationary. So there's no way that x could move. X could be time dependent. So we know this is 0. What about p? Same thing, whether you use symmetry or just physical insight. But what about x squared? Well, x squared is equal to V of x over k over 2. So expectation value of x squared is equal to the expectation value of V over k over 2.

But we know the expectation value of V. It's E over 2. So we know without doing any integrals what the expectation value of x squared is, and similarly, for p squared. And that's just going to be m times E. OK, so why do I care about these things? Well, we have a little thing called the uncertainty principle. And we'd like to know the uncertainty in the coordinate and the momentum. And this is our classical view of it. But it's going to remind us of what we find quantum mechanically.

So the uncertainty in x can be defined as the average value of x squared minus the average value of x squared square root. That's just the variance. And well, this is 0. And we know what

this is. So we know that the uncertainty in x is E over k square root. And the uncertainty in p is going to be p squared average value minus p squared. This is still 0. And this one is then m times E square root.

So delta x delta p, it looks like the uncertainty principle. This is classic mechanics, is just E over omega. But what's E over omega?

AUDIENCE: h? h bar.

ROBERT FIELD: Right. So it's all going to come around. This is related to the uncertainty principle in quantum mechanics. There is a minimum joint uncertainty between x and p. And it's just related to this constant. Now, this doesn't say the uncertainty grows as you go to higher and higher energy, as it will in quantum mechanics. But this is really a neat thing to see. OK, I've got two minutes left.

So if we wanted to know the probability of finding x as a function of the coordinate, the turning points. So here are the turning points. And we can calculate what is going to be the probability of finding the particle at one turning point. Well, it comes down from infinity, goes back up to infinity. So here at the turning points, the particle is stopped. And so the probability of finding it at a turning point is infinite, times dx. So we don't have an infinite number.

In quantum mechanics, we're going to discover that quantum mechanics is smarter than that. And what quantum mechanics does, suppose we have this is the energy. What quantum mechanics does is that the probability at a turning point is not 0. And there's something-- what happens is there's tunneling tails that instead of going to infinity, it has a finite value. And it reaches out into the forbidden region in an exponentially decreasing way. And that's basically the difference between classical mechanics and quantum mechanics. And there's an awful lot of important stuff that happens there.

Now, I've been very fast through all of this because it's built on stuff that you're supposed to know. And it's built on stuff that we're going to work hard to understand from a quantum mechanical point of view. But this sets the stage for, what are the things we have to look for in quantum mechanics? So I do recommend that you look at the notes and make sure you can follow all the steps, which I went through incredibly rapidly. And it'll be really helpful. Because your job will be to draw cartoons. And these will guide you through it. OK, so I'll see you on Friday.