ROBERT FIELD: So today we're going to go from the classical mechanical treatment of the harmonic oscillator to a quantum mechanical treatment. And I warn you that I intentionally am going to make this look bad, because the semi-classical approach at the end of this lecture will make it all really simple. And then on Monday I'll introduce creation and annihilation operators, which makes the harmonic oscillator simpler than the particle in a box. You can't believe that, but all right.

So last time we treated the harmonic oscillator classically and so we derive the equation of motion from forces equal to mass times acceleration, and we solved it. And we saw that we have this quantity omega, which initially I just introduced as a constant, which was a way of combining the force constant and the mass. And then I showed that the period of oscillation is 1 over the frequency, which is 2 pi over omega.

Now one of the things that people have trouble remembering under exam pressure is turning points. And this comes when the energy is equal to the potential at a turning point. And since the potential is 1/2 kx squared we get the equation for the turning point at a given energy, which is equal to plus or minus the square root of 2e/k.

Now when you're drawing pictures there are certain things that anchor the pictures, like turning points. And now at the end of the previous lecture I calculated the classical mechanical average, and we use we use this kind of notation in classical mechanics. Sometimes we use this notation, too, but this is what we mean by the average value in quantum mechanics. And we found that this was the total energy divided by 2. And the average momentum is the energy divided by 2.

And that's the basis for some insight, because as a harmonic oscillator moves it throws energy back and forth between kinetic energy and potential energy. And then one of my favorite things, and one of my favorite tortures on short answers, is the average values of-- And does anybody want to remind the class the easy way, or the two easy ways to know what this is? And the person who answered the question last time is disqualified. Yes.

AUDIENCE: There is the symmetry method.

ROBERT FIELD: What?

AUDIENCE: There's symmetry. So if the system's symmetrical that the average value will actually be that symmetry point.

ROBERT FIELD: Yes. So and the other is that the harmonic oscillator isn't moving, and so there is no way that the coordinate-- that the average value of either the coordinate or the momentum could be different from 0. However you do it you want to be doing it in seconds, not minutes. And certainly not by calculating integral.

And now x squared and p squared, they're easy too. Especially if you know t and v. And so we then use those to calculate the variance. And that's defined as the average value of the square minus the square of the average square root.

And what we find is that the variance of x times the variance of p is equal to e over omega. So as you go up in energy this joint uncertainty increases. And we'll find that that also is true for quantum mechanics.

So this is sort of the kind of questions you want to be asking in quantum mechanics. And you want to be able to be guided by what you know from classical mechanics, and you want to be able to do it fast. Today's menu is what I would call-- This lecture is gratuitous complexity. Does everybody know what gratuitous means?

This is one of my favorite Bobisms. And you'll hear other Bobisms during the course of this course. What I want you to be able to do for a lot of mechanical problems is to know the answer, or know what things look like without doing a calculation. In particular, not solving a differential equation or evaluating in the integrals. You want to be able to draw these pictures instantly.

Now in the modern age everyone has a cell phone, and one could have a program in there to calculate what anything you wanted for harmonic oscillator. But chances are you won't be prepared for that. And if you want to have insights into how do various things you want to know about harmonic oscillators come about? You need the pictures, as opposed to the computer program. Now the pictures involve an advance investment of energy. You want to understand every detail of these little pictures.

I'm going to write this runner equation, I'm going to clean it up to get rid of units which makes it universal. So it becomes a dimensionless equation. And the unit removal, or the thing that takes you from a specific problem where there's a particular force constant and a particular reduced mass, and makes it into a general problem. There is one or two constants that combine those things. And you've taken them out at the end of a calculation.

If you need to have real units you can put those back in. And that's a very wonderful thing, and that enables us to draw pictures without thinking about, what is the problem? And then the solution of this differential equation-- which is actually quite an awful differential equation at least for people who are not mathematicians-- and the solution can be expressed as the product of a Gaussian function which goes to 0 at plus and minus infinity, so it makes the function well behaved. Times something that produces nodes, a polynomial.

Does anyone want to give me a definition of a polynomial? Silence. OK, your turn.

AUDIENCE: It's the linear combination of some numbers taken to different power

ROBERT FIELD: Right. A sum of integer powers of a variable. And when we take a derivative of a polynomial we reduce the order of the polynomial. A little bit of thought, if you have a first order polynomial there'll be one node. If there is a second order there'll be two nodes. And nodes are very important.

And so when we're going to be dealing with cartoons of the wave function, and then using semi-classical ideas to actually semi-calculate things that you'd want to know, the nodes are really important. And what's going to happen Monday is we'll throw away all this garbage and we will replace everything by these creation and annihilation operators. Which do have really simple properties, which you can use to do astonishingly complicated things without breaking a sweat.

And the final exam is in this room on the first day of exam period, at least it's on a Monday, and it's in the afternoon. In the non-lecture part of the notes I replaced the mass for one mass on a spring by the reduced mass, which is m1 m2 over m1 plus m2 for two masses connected by a spring. And I go back and forth between using mu and m, and that's OK.

All right so in the notes the differential equations in the first few pages are expressed as partial differential equations. They're total differential equations. That'll get changed. The Hamiltonian is t plus v, and in the usual form t is p squared over 2 mu. And so we get minus h-bar squared

over 2 mu par-- not partial, I'm so used to writing partials that I can't stop. Second derivative with respect to x, plus 1/2 kx squared. So that's the Hamiltonian.

Now that looks kind of innocent, but it isn't. And so the first thing we want to do is get rid of the dimensionality, the units. So this is xi and it's defined as square root of alpha times x. Where alpha is defined as k mu square root over h-bar.

Now it would be a perfectly reasonable exam question for you to prove that if I take this combination of physical quantities this will have dimension of 1 over length. That makes xi a dimensionless quantity. I'm not even going to bother going through the derivation. The Hamiltonian becomes h-bar of omega times 2, minus second derivative with respect to xi plus xi squared.

So this is now dimensionless. This has units. We divide by h-bar omega to make now everything dimensionless. And we get a differential equation that has the form minus the second derivative with respect xi plus xi squared, minus 2e over h-bar omega, times the wave function, expressive function of xi, not x.

This is the differential equation we want to solve, and we don't do that in 5.61. You're never going to be asked to solve a differential equation like this. But you're certainly going to be asked to understand what the solution looks like, and perhaps that it is in fact a solution. But that's still pretty high value stuff, though you wouldn't really have to do that. This is the simplest way of writing the differential equation and it's dimensionless.

The standard way of dealing with many differential equations is to say, OK, we have some function and it's going to be written as an exponential, a Gaussian, times some new function. And for quantum mechanics this is perfectly reasonable because we have a function in a well and the wave functions have to go to 0 at plus minus infinity. And this thing goes to zero at plus and minus infinity pretty strongly.

So it's a good way of building in some of the expected behavior of the solution. And that's perfectly legal, and it just then defines what is the difference equation remaining for this? And it turns out, well we're going to get the Hermite equation. And this will be a Hermite polynomial, the solutions.

Now one way of dealing with this is to simply say, well, we know the solution of this differential equation if this term weren't there. Because this is now the equation for a Gaussian. So

building in a Gaussian as a factor in the solution, it's a perfectly reasonable thing. And then we have to say, what happens now when we put this term back in?

And when we do we get this thing. Second derivative with respect to this polynomial-- I mean of this polynomial is equal to minus 2 xi times the hn d xi plus 2n hn. This is a famous differential equation, the Hermite equation, which is of no interest to us. And it generates the Hermite polynomials. These things are the Hermite polynomials.

And they are treated in some kind of sacred manner in most of the textbooks, and I think that's really an offense because, well, we're not interested in mathematical functions. We're interested in insight and this is just putting up another barrier. Now with this equation, you can derive two things called recursion relations, and one of them is the derivative of this polynomial with respect to xi is equal to 2n times hn minus 1 of xi.

Now that's not a surprise, because this is a polynomial. If you take a derivative of the variable you're going to reduce the power of each term by 1. Now it just happens to be lucky that when we reduce it to 1 you don't get a sum of many different lower order polynomials, you just get 1. And there is another one, another recursive relation, where it tells you if you want to increase the order you can do this, you can multiply hn by xi.

And that's obviously-- it is going to increase the order, but it might not do it cleanly. And it doesn't. And so we get-- We have a relationship between these three different polynomials. Now it turns out that these two equations are going to reappear, or at least their progeny will reappear, on Monday in terms of raising and lowering operators.

And what you intuit about what happens if you multiply polynomial by the variable? Or what happens if you take its derivative? And it is very simple and beautiful, but I don't think this is very beautiful for our purposes as chemists. And one of the things that these recursive relationships do, which also hints at what's to come on Monday, is that we can calculate integrals like this.

That's not what I want. This is a quantum number, it's an integer. It's v, not nu, and multiply it by x to the n, p to the m, psi that should be complex conjugated, v plus l, dx. It turns out for almost everything we want to do with harmonic oscillators we're going to want to know a lot of integrals like this.

And one of the things we like is when an integral is promised to be 0 so we don't ever have to

look at it. And so there are selection rules. And the selection rules for this kind of integral is l is equal to m plus n, m plus n minus 2, down to minus m plus n. So the only possible non-zero integrals of this form are for the change in quantum number by this l, which goes from m plus n down to minus m plus n in steps of two.

The two shouldn't be too surprising, because there is symmetry and we have odd functions for odd quantum numbers and even functions for even quantum numbers. And so something like this is going to have a definite symmetry and it's going to change things within a symmetry, and so it's going to change the selection rule in steps two. Now you don't know what selection rules are for, or why you should get excited about these sorts of things, but it's really nice to know that almost all the integrals you are ever going to face for a particular problem are zero. And you can focus on a small number of non-zero ones, and it just turns out that the non-zero ones have really simple value.

There also exists what's called a generating function, which is the Rodriguez formula. And that is the hn of xi is equal to minus 1 to the n, e to the psi squared, the derivative with respect to xi, e to minus xi squared. We have one that has a positive exponent, and one has a negative exponent, and we have this.

So we could calculate any Hermite polynomial using this formula, which you will never do. But it's treated with great fanfare in textbooks. Now the solution to the harmonic oscillator wave function in real units, as opposed to dimensionless quantities, is-- and I'm just writing this down because I never would ever think about it this way, but I have to at least provide you with guidance-- so we have a factor 2 to the v, again this is v.

Now the reason I'm emphasizing this is that in all texts v quantum numbers are italicized. And if you've thought about it for a minute, an italic v-- for mortals-- looks like a nu. It isn't quite. I don't know what the difference is, but if you have them side by side they are different. And so a large number of people who should know better refer to the vibrational quantum number as nu, which marks that person as, well, I won't say but it's not complimentary!

We have this factor to the square root, and that's a normalization-- oh we got another part of it. Alpha over pi to the 1/4 power. So that's normalization. Then we have the Hermite polynomial. And you notice I've got xi back in here, which is really a shame. And we have--

So this is the general solution, we have the exponentially damped function, we have polynomials. These are all the actors that we're going to have to deal with. And I promise you,

you will never use this unless you want to program a computer to calculate the wave function for God knows what reason.

The quantum numbers we are 0, 1, 2. And for a harmonic oscillator, which goes to infinity, v goes to infinity, too. There's an infinite number of eigenfunctions of the quantum mechanical Hamiltonian-- of quantum mechanical harmonic oscillator. We have-- and the functions are normalized, we have psi plus and minus infinity goes to 0, we have psi v of 0. So this for all the-- I put a v there.

Psi v is 0 for odd v, derivative of psi with respect to x, at x equals 0 is 0 per even v. So we have symmetric functions. And we have the energy levels is equal to h-bar omega, v plus 1/2. Now this is h over 2 pi, and this is nu times 2 pi, the frequency times 2 pi. So it could also be h nu.

I have trouble remembering when there is a 2 pi involved. And we have this wonderful thing. It's as if v prime is equal to v this integral is 1, it's normalized. And a v prime is not equal to v, it's zero. And that stems from a theorem I mentioned before, is if you have two eigenvalues of the same Hamiltonian, eigenfunctions of the same Hamiltonian, and they belong to different eigenvalues their overlap integral is 0.

We like zeros. We like normalization because the integral is just 1, it goes away. Or the integral is 0, the whole thing goes away. So that's really good. So we call this set of v's is orthonormal. Orthogonal and normalized. And the orthonormal terminology is used a lot. And in almost all quantum mechanical problems we like using an orthonormal set of functions to solve everything.

Sometimes we have to do a little work to establish that, and I'll show much later in the course how when you have functions that are not orthogonal, and not normalized, you can create a set of functions which are. And this is something that a computer will do without breaking a sweat. Now we're back to my favorite topic, semi-classical. Because it's really easy to understand. Not just to understand the harmonic oscillator, but to use it in many problems.

So in classic mechanics the kinetic energy is e minus v of x, or p squared over 2 mu. And so we can derive an equation for p of x classical mechanically, which is 2 mu e minus v of x square root. This is an extremely useful function. It's not an operator. It's a thing that we're going to use to make sense of everything, but it's not an operator.

And so this is classic mechanics, and then in quantum mechanics, we know that Mr. de Broglie

told us that the wavelength is equal to h over p. And we can generalize and say, well, maybe the wavelength is a function of x for potential, which is not constant. And even though this is not an operator in quantum mechanics this is true. That you can say the distance between consecutive nodes is lambda over 2. We can use this node relationship to great advantage.

For the pair of nodes closest to x we can use this to calculate the distance between them. Very valuable. Because I also want to mention something. If you have an integrand which is rapidly oscillating, or if you have two rapidly oscillating functions and you're multiplying them together, that integral will accumulate to its final value at the position where the two oscillating functions are oscillating at the same frequency. That's the stationary phase point.

And this is also a wonderful thing, because if you can figure out where the things you're multiplying together are oscillating at the same frequency, your integral becomes a number. No work ever. And that's a useful thing. OK, so the stationary phase method enables you to use this in a really fantastic way. And it's a little bit like Feynman's path integral idea, that you can calculate a complicated thing by evaluating an integral over a convenient path as opposed to integrating overall space, because everything that you care about comes from a stationary phase.

Quantum mechanics is full of oscillations, classical mechanics doesn't have oscillations, and the two meet at the stationary phase point. Now we're going to use these ideas to calculate useful stuff for quantum mechanical vibrational wave functions. The shapes of psi of x gets exponentially damped, but it extends into the classically forbidden e less than v of x regions.

The wave function, if we have potential and we have a wave function, that wave function is going to not go to 0 at the edge but it's going to have a tail. And that tail goes to 0 at infinity. And so there is some amplitude where the particle isn't allowed to be, classically. And that's where tunneling comes in.

But the important thing, the important insight is that there are no nodes in the classically forbidden region. There is only exponential decay towards 0, and if you've chosen the wrong value of the energy, in other words a place where there is no eigenfunction, the wave function in the classically forbidden region will usually go to infinity. Either over here or over here, and says, well, it's clearly not a good function.

But there are no 0 crossings. It's oscillating in e greater than v of x, the classically allowed

region. The number of nodes is v. So we can have a v equals 0 function that just goes up and goes down, no internal nodes. v equals one, it crosses zero right in the middle. And we have the even oddness. Even v, even function. Odd v, odd function. For an even function you have a relative maximum at x equals 0, and for an odd function you have a 0. And the opposite further derivatives.

The outer lobes, the ones on the ends just before the particle encounters the classical wall, you get the maximum amplitude. And so you can draw cartoons which look sort of like that. Most of the valuable stuff is at the other turning point. And there's oscillations in between, but often you really care about these two outer lobes.

That's a pretty good simplification. Now there's a nice picture in McQuarrie on page 226 which shows, especially for psi squared, that the nodes are pretty big. But they're not as big for relatively low quantum numbers as I've implied. But at really high quantum numbers we have a thing called the correspondence principle.

And the corresponding principle says that quantum mechanics will do what classical mechanics does in the limit of high quantum numbers. And in the limit of high quantum numbers essentially all the amplitude is at the turning points. And in classic mechanics the particle is moving fast in the middle, and stops and turns around, and essentially all of the amplitude is at the turning point. So this is nice.

Now we're getting into Bobism territory, because I'm really going to show you how to calculate whatever you need using these semi-classical ideas. We have the probability envelope. Psi star of x psi of x, and we're going to have both of these having the same quantum number, dx. So this is the probability of finding the particle near x in a region with dx.

And this is the same thing as dx over v classical. It's not the same thing, there is a constant here, sorry. This probability density that you want is basically 1 over the classical velocity. And I demonstrated that when I walked across the room, when I walked fast in the middle and slow the outside. And you get the probability, you get this constant, by saying, OK, how long did it take for me to go from one end to the other? And comparing that, how long it took for me to go in some differential position. You get this constant in a simple way.

v classical is equal to p classical over the mass, over the mu. But we know the function for p classical. We have 1 over mu times 2 mu e, minus v of x. So we know the velocity everywhere, and there's nothing terribly hard about figuring that out. And now we want to know what this

proportionality constant is.

And so for that we say the time to go from x to x plus dx, over the time to go from x minus to x plus. Because what's happening, the particle is going back and forth inside this well and so this is the time it takes to go one pass, and this is the time it takes to go through the region of interest. And so this ratio is the probability.

And so we have the probability moving from left turning point the right turning point, and we want to know the probability in that interval. And so that's just dx over v classical at x, over tau, over 2. Because tau is the period, and we have half of the period, and so it's all together. I'm going to skip a little step, because it's taking too long.

Psi star psi dx is equal to k over 2 pi squared, e minus v of x square of dx. Now so if we know the potential, and we know the energy, and we know the force constant we can say, well, this is the probability and-- but this is the probability of the semi-classical representation of psi star psi dx at x.

Now this is oscillating, and this is not. So what we really want to know-- here's the-- if we have psi star whoops, slow down. This is oscillating and what we've calculated before is something that looks sort of like that. And if we multiply by 2 we have a curve that goes to the maximum of all these oscillations.

The envelope psi star psi has the form. We've multiplied by 2, and so we end up getting 2k over pi squared, e minus v of x square root. Now you might say, well these are complicated functions, why should I bother with them? But if you wanted anything starting from the correct solution to the harmonic oscillator, using the Hermite polynomials, there's a whole lot more overhead.

Notice also this is a function of x, not xi. This is the overlap function, it's the curve that touches the maximum of all these things and it's very useful if you want to know the probability of finding the system anywhere. And we get the node spacing from the equation h over p of x. And now here comes something really nice.

It's called the semi-classical quantization interval. If we have any one dimensional potential, and we're at some energy, we'd like to be able to know how many levels are at that energy, or below. Or where are the energy levels? And we get that from this really incredible thing.

We want to know that-- this is the difference between nodes. Right? And now if we would like to know x minus to x plus and some energy, we can replace lambda of x by h over p of x. And so we get p of x at that energy over h dx. pdx, that's called an action integral.

Now I have to tell a little story. When I was a senior at Amherst College we had a oral exam for whether my thesis was going to be accepted or not. And one of my examiners asked me, what is the unit of h? Well, it's energy times time. And he wouldn't stop. He said no, I want something else. It's called action. Momentum times position.

This is an action integral. And so anyway that's just a story. I spent a half an hour, and I was damn stubborn. I was not-- you know, it was energy times time. But that is much more insight here and that's maybe why I got so excited about this sort of an integral. If we want to know if we have an eigenvalue this integral has to be equal to h over 2 times the number of nodes.

Well it's pretty simple. So we can adjust e to satisfy this. Or if we wanted to know how many energy levels are at an energy below the energy we've chosen we evaluate this integral, and we get a number like 13.5. Well, it means there are 13 energy levels below that. Now often you want to know the density of states, the number of energy levels per unit energy, because that turns out to be the critical quantity in calculating many things you want to know. And you can get that from the semi-classical quantization.

We're close to the end, I just want to say where we're going. We have classical pictures and I really, really want you to think about these classical pictures and use them rather than thinking, well, I'm going to have my cell phone program to evaluate all the necessary stuff. And there are certain things you want to remember about this semi-classical picture.

And now we have the ability to calculate an infinite number of integrals involving harmonic oscillator functions in certain operators. Well, la-di-da. Why do we want them? Well one of the things we want is to be able to calculate the probability of a vibrational transition. That's called a transition element, and that's an easy thing to calculate.

Another thing we want to do is to say, well, nature screwed up. This oscillator isn't harmonic, there's anharmonic term, and I would like to know what is the contribution of a constant times x cubed in the potential to the energy levels. And that's called perturbation theory. Or I want to have many harmonic oscillators in a polyatomic molecule, they talk to each other, and I want to calculate the interactions between these harmonic oscillators affect the energy level.

Remember, when we have a separable Hamiltonian we can just write the energy levels as the sum of the individual Hamilton. And then there's coupling terms, and we deal with those but perturbation theory. There's all sorts of wonderful things we do.

But we're going to consider these magical operators, a creation and annihilation operator, where a star-- a dagger operating on psi v gives the square root of v plus one, times psi v plus 1. And a dagger operating on v gives the square root of v-- let's write it-- I mean a non-dagger gives v square root times psi, v minus 1. And that x is equal to a plus a dagger times a constant.

And so all of a sudden we can evaluate all integrals involving x, or powers of x, or momenta, or powers of momenta without thinking. Without ever looking at a function. And I guarantee you that this is embodied in the incredible amount of work done wherever we pretend almost every problem is a harmonic oscillator in disguise. Because these a's and a daggers enable you to generate everything without ever converting from x to xi, without ever looking at an integral.

It's all just a manipulation of algebra. And it's not just convenient, but there's insight and so this is what I want to convey. That you will get tremendous insight. Maybe, maybe I sold you on semi-classical, and I don't apologize for that because that's very useful. But the next lecture, when you get the a's and a daggers, it'll just knock your socks off. OK, that's it.