PROFESSOR: The outline for today is a little bit more review of feeling the power of the creation and annihilation operators. They enable you to do anything with harmonic oscillators, really fast. And so you don't spend time thinking about how to do the math. You think about the meaning of the problem and understanding how to manipulate, or how to understand harmonic oscillators.

And then the exciting thing. The real Schrodinger equation is not the one we've been playing with. It's the time dependent Schrodinger equation. And I like to introduce the time independent one first, because it enables you to sort of develop some insight and assemble some of the tools before we hit the really serious stuff.

And so I will talk about this and use the time dependent Schrodinger equation to show what it takes to get a motion of this product of the psi star psi.

What does it take? It takes a superposition state consisting of at least two different energies. Then this normalization integral-- well, you'd expect normalization, or something like this to be preserved. And in fact, the normalization is time independent.

Then, if we calculate-- now, this is a vector rather than just a simple coordinate. If we calculate the expectation value of the position, and the expectation value of the momentum, Ehrenfest's theorem tells you that this is going to describe the motion of the center of the wave packet.

And the motion of the center of the wave packet is following Newton's laws. No surprise. And so we're seeing how classical mechanics is given back to you once we start making particle-like states. We can see how these particle-like states evolve.

But there is a lot more than just particle-like behavior. You would, perhaps, challenge any outfielder for the Red Sox to go beyond calculating the center of the wave packet. That's what they know to do. But they don't know some other things like survival probability, how fast does the wave packet move away from its birthplace, or the wave packet does stuff and wanders around and comes back and rephases sometimes.

And sometimes it just dephases. And these are words that you're going to want to put into your vocabulary. So there's a lot of really beautiful stuff when we start looking at the time dependent Schrodinger equation. And we are going to mostly consider the time dependent Schrodinger equation when the Hamiltonian is independent of time, because we can get our arms around that really easily. But when the Hamiltonian is dependent on time, then it opens up a world of complexity that is really best left to a more advanced course.

But how do molecules get excited from one state to another? A time dependent Hamiltonian. So we are going to have to at least briefly talk about a time dependent Hamiltonian and what it does. And you'll see that eventually.

I'm first going to do a little bit of review of the a's and a daggers. So the most important thing is, we're going to have some problem where we have this x operator to some integer power. And so we need to be able to relate that to the a's and a daggers.

I'll drop the hats, because we know they're there. And one of the nice things is, if we have this operator to the nth power, we have this co-factor to the nth power. So we don't ever have to deal with it until the end of the problem when we say, oh, wow, we had x to the n. Well, we have then n h bar. I'm sorry. We have h bar over 2 mu n n over 2 power.

So it really saves a lot of writing. And it means you solve one problem for a harmonic oscillator. And you've solved it for all harmonic oscillators. And this is just details about what is the mass and what is the force constant, which you need to know. And there is a similar thing for p.

So that opens the door. It says, OK, we have some problem involving the coordinate and the momentum, some function of the coordinate and momentum, and we want to know things about the coordinate and momentum. And so we use this operator algebra.

And so a operating on psi v gives v square root v minus 1. And a dagger, we know that. So that's hardwired.

But suppose we wanted a to the 5th, operating on psi v. Well, what do we do? Well, we start, and we start operating on...

You know, if this were a complicated operator, we would take the rightmost piece of that operator and operate on the wave function. And that will give us v and then v minus 1 and then v minus 2, v minus 3. I've got five of them. 1, 2, 3, 4, 5. v minus 4. Square root psi v minus 5.

OK. It's mechanical. You don't remember this. You generate this one step at a time. And it's automatic. And so it doesn't stress your brain. You can be thinking about the next thing while you're writing that garbage.

We have this number operator, which is a friend, because it enables you to just get rid of a bunch of terms. The number operator is a dagger a, and the number operator operating on psi v gives v psi v.

If we want any harmonic oscillator function, we can operate on psi 0 with a dagger to the v power. And then we have to correct, because you know that this operating v times on this will give psi v. But it will also give a bunch of garbage, right? And you want to cancel that garbage. And so you write v factorial minus 1/2.

And so that gives you the normalized function. So these are really, really simple things. And most of them, once you've thought about it a little bit, you can figure out yourself.

OK. Now, many problems involve x, x cubed, x to the 4th. And we know that x is this. And x squared is this squared. And x cubed is this cubed. And so we have to do a little algebra to simplify.

And what we want to do is simplify to sum of terms according to delta v selection rule. So there is some algebra that we do, when we have, say, a dagger, a dagger, a, a, a dagger. But we know that three a daggers and two a's means delta v of plus 1.

And that came from x to the 5th power. But you get a lot of terms from x to the 5th power. And you have to simplify them. And in order to do that, you use this commutation rule-- a, a dagger is equal to 1. And that rearranges terms.

So all of the work you do when you're faced with a problem involving integrals of integer powers of x and p for a harmonic oscillator is playing around with moving the a's and a daggers around, so that you have all the terms that have the same selection rule compressed into one term.

That's the work. It's not much. And once you've done it for x squared, x cubed and x 4th, you've done it as much as you'll ever need to do. And that's it. That's the end. OK.

Now here's an example of a problem that's a little bit tricky. And it's sort of right at the borderline of what I might use on the exam.

So we have this, we have a dagger to the m power. A to the n power. Psi.

OK. Now, here. What v is going to give a non-zero integral? We have a dagger to the m. And we have a to the n. And so that's going to be v minus n plus m, right?

Because we lose n quanta, because of this. And we gain m quanta because of that.

And now, well, that's good. You've used the selection rule. Now, how do we write out this interval? And there is a little bit of art there too. Because we have a whole bunch of terms. We have n plus m terms in the square root. And how do you generate them without getting lost?

Yes?

AUDIENCE: I think you have it backwards. Shouldn't it be plus n minus n? It means you're going to lower it n times.

PROFESSOR: Yes. Yes. I wonder what I had in my notes. This is wrong.

OK. So this has to withstand this and this. And so, yes. OK. However you remember it, you've got to do it right.

And now we have the actual matrix element. And so the first term is going to be what does a n do to that?

So you start on the right. And you start building up this way. And so the first term is going to be, what does a do to this? Well, it's going to leave it alone. But it's going to lower v.

So we have v plus n minus m. And then we have v plus n minus m minus 1, et cetera, until we have n terms.

And then we start going back up, because we're now dealing with this. And so I'm not going to write the rest of this. Maybe this is going to be a problem I start the exam with.

So you don't want to get lost. And the main thing is, you have these operators. And you start operating on the right, and one step at a time. And this is a little tricky because you're changing the quantum number, and you're changing the wave function. And you have to keep both in mind, but you're only writing down this. OK?

I want to save enough time so that we can actually do the time dependent Schrodinger equation. The time dependent Schrodinger equation.

H psi. It still looks pretty simple. Instead of e psi here, we have this thing. This is the time dependent Schrodinger equation. This is it. This is quantum mechanics. Everything that comes from quantum mechanics starts with this.

When we don't care about time, we can use the time independent Schrodinger equation. But when we do care about time, we have to be a little bit careful. So this is the real Schrodinger equation.

And notice that I'm using a capital psi, rather than a lower case, or less decorated psi. And so this is usually used to indicate the time dependent Schrodinger equation. It's time dependent wave function. This is used to indicate the time independent equation.

Now, if the Hamiltonian-- and this is wonderful-- if the Hamiltonian is independent of time, then if we know the solutions psi n en. If we know all of these solutions, then there's nothing new. We just are repackaging the stuff that we know from the time independent Schrodinger equation.

So the first thing I want to do is to show you that if the Hamiltonian is independent, we can always write a solution to the time dependent Schrodinger equation-- e to the minus i e n t over h bar psi n x.

So this, for a time independent Hamiltonian, is always the solution of the time dependent Schrodinger equation.

So we're just using this stuff that we know, or at least we barely know, because we just started playing the game. But we can manipulate to see all sorts of useful stuff.

OK. So let's show if this form satisfies the Schrodinger equation. So we have ih bar partial PSI with respect to t. So we get an ih bar. And then we take the partial with respect to t. This is independent of time. This has time [INAUDIBLE] And so we get a minus i e n over h bar. And then we get e to the minus i e n t over h bar psi n of x.

Well. So, let's put this together. We have an i times i times minus 1. So that's plus 1. We have an h bar in the numerator and h bar in the denominator. That's 1. And so what we end up getting is e n e to the minus i e n t over h bar psi n.

Well, this is psi. This function here is the solution to the time dependent Schrodinger equation. How do we know that?

Well, we have this factor, h psi. Well, h doesn't operate on either the i e n t.

So what we have is that we get E n e to the i omega t. Sorry. I'm jumping ahead. i e n t over h bar psi.

All right. So, if we apply the Hamiltonian to this function, we get just e n times the function.

And that's what we got when we did i h bar times a partial with respect to t. So what that shows is that this form always satisfies the time dependent Schrodinger equation, provided that the Hamiltonian is independent of time.

Now, that's a large range of problems, things that we need to understand. But it's not the whole potato, because the Hamiltonian is often dependent on time. But it enables us to build up insight, and then treat the time dependence as a perturbation. And we're going to do perturbation theory in the time independent world. And then we're going to do perturbation theory a little bit in the time dependent world.

OK. So what we always do here is we solve a familiar problem, and then we say, OK, well, there's something more to this familiar problem. And so we treat that as something extra. And we work out the formalism for dealing with that extra thing. But before we do the extra thing, we have to really kill the problem that is within our grasp. OK.

So now, our job is to just explore what we've really got here. So the first problem is motion. So we have psi star x and t psi x and t.

So we have this thing, which we're not going to integrate yet. Well, when is this thing going to move? Well, the only way this probability density is going to evolve in time is going to be if we have a wave function, psi, which is of x and t is equal to c1 psi 1, e to the minus i e 1, e over h bar, plus c2, psi 2, e to the minus i e 2, t over h bar, where e1 is not equal to e2.

So this is the first, most elementary step. And remember, we have this notation e to the i something. And e to the minus i something. And when we take a plus 1 and a minus and put them together, we get 1. So this notation, this exponential notation, is really valuable.

OK. So now let's just look at this quantity, psi star psi.

OK. Psi star psi. Well, it's going to be c1 squared, psi 1 squared-- square modulus-- and we get c2 square modulus, psi 2 square modulus.

Are we done? No. So, what we did is, I put in c1, psi 1 plus c2, psi 2. And I looked at the easy terms, the terms where the exponential factor goes away.

And then there's two cross terms. Those two cross terms are c1 star-- whoops-- c2 e to the minus i e 2 minus e1 t over h bar psi 1 star, psi 2. And we have c1, c2 star e to the plus i e2 minus e1 t over h bar, psi 1 star. psi 1, psi 2 star.

Now, this is just the automatic writing. OK. So we have two terms that are time independent.

So, this is no big surprise. But then we have this stuff here. And if we say e2 minus e1 over h bar is omega 2, 1, everything becomes very transparent, because now we have something that looks like it looks like it's trying to be a cosine omega t.

We have to be a little bit careful. These are the two time dependent terms. And they are the complex conjugate of each other.

And so we know that if we have two complex numbers, c plus c star, we're going to get twice the real part of c.

So this enables us to take these two terms and combine them. And we know it had better be real, because we're talking about a probability here. This probability has got to be real. And it's got to be positive. It's got to be real and positive everywhere and forever. Because there's no such thing as a negative probability. There's no such thing as a negative probability in a little region of space, and we say, well, we integrate over all space, and so that goes away.

This psi star psi is going to be real everywhere for all time. And so that's a good thing, because we have a sum of a plus its complex conjugate. And so this is real. And we can simplify everything, and we can write it simply.

But suppose we choose a particular case-- c1 star is equal to c1, which is equal to 1 over square root of 2. And we can say psi 1 and psi 2 are real.

When we do that, then this complicated-looking thing, psi star psi, becomes 1/2 psi 1 squared, plus 1/2 psi 2 squared, plus cosine omega 1 2 t psi 1 psi 2.

OK. Well, these two guys aren't moving. And they're real. And positive. Yeah.

AUDIENCE: Wait, is c2 also 1 over square root of 2?

PROFESSOR: I had 1 over square root of 2, one over square root of 2. That's 1/2. But then when you add the two terms, you get twice the real part. So we get a 1/2 times 2. And so this is not a mistake. It comes out this way, OK?

AUDIENCE: I think you meant c2. You're only finding c1 star and c1 to be 2 over square root-- 1 over square root of 2. You didn't say anything about c2.

PROFESSOR: Oh. OK. I want c1 and c2. That's what I wanted. OK. Thank you. That shows you're listening. And it shows that I'm sufficiently here to understand your questions, which is another wonderful thing.

So this is now, we have something that's positive everywhere. It's time independent. And we have something that's oscillating. And so this term can be negative.

But you can show-- I don't choose to do that. You can show that this term is never larger than psi 1 squared plus psi 2 squared.

And so even though this term can be negative at some points, it never is a negative enough to make the evolving probability go negative.

Now, you may want to play with that just to convince yourself. And it's an easy proof. And I'm just not going to do it.

OK. So we have something that says, just like for the wave equation, what does it take to get motion? And to get motion you had to have a superposition of two waves of different energy or different wave vector.

And so here we have, if e1 is not equal to e2, we have a non-zero omega 1, 2. It doesn't matter whether it's omega 1, 2, or omega 2, 1, because it's cosine.

And so that's motion. So we get a standing wave sort of situation. And then we get this motion.

OK, now, the fun begins. Suppose we want to calculate the expectation value of x and p.

OK. And let's just take it as a 1D problem. And so x of t. No, there was no question. All right. We have--

OK. And again, we take this thing apart. And we say, all right, suppose we have the same superposition of psi is equal to c1. psi 1.

OK. Actually, these should be the time independent.

So what we get is, when we do this integral, we get c1 squared integral psi star x, psi 1 dx. And we get c2 squared integral psi 2 star x, psi 2 dx.

And then we get cross terms. c1 star, c2. e to the minus i omega 2, 1 t times the integral psi 1 star x psi 2 dx. And we have c1, c2 star, e to the plus i omega 2 1 t integral psi 2 star x psi 1 dx.

A lot of stuff here. Now, we're talking about the harmonic oscillator. This integral is 0. Because x is a plus a dagger. The selection rule is delta v of plus and minus 1. This one is 0.

For the particle in a box, one can also ask, what about this integral? And for the particle in a box, it's a little bit more complicated. Because we've chosen a mathematically simple way to solve the particle in a box, with the box having a zero left edge.

If we make the box symmetric, then we can make judgments and say, oh, yeah. This integral is also 0 for the particle in a box. And that's a little bit more complicated, the argument, than what I just did.

So these two terms are 0. And now we have motion of the expectation value, which is described by these two terms. And again, they're the complex conjugate of each other.

And so what we have is x of t is equal to twice the real part of c1 star, c2 e to the minus i omega 2, 1 t. Times x 1, 2.

OK. This x 1, 2 is an integral. So x 1, 2 if these are the vibrational quantum numbers, well, then this is non-zero. This is just the square root of 2, or square root of 1.

OK. So we have motion described by this. And so the only time we get motion is if v1 is equal to v2 plus or minus 1, for the harmonic oscillator. For the particle in a box, there's different rules. And often, for these simple problems, you want to go through in your head all of the simple cases.

Now, we already can see that-- I don't want to talk about the particle in a box. So now let's just take another step.

And we're going to have Ehrenfest's theorem, which you can prove, says that m times the derivative of vector p-- so this is a time dependent expectation value-- is equal to-- I'm sorry. This is not vector p. This is vector r-- is equal to--

So this is the vector p. So this is the derivative of the coordinate, with respect to time. That's velocity. Velocity times mass is momentum.

And so we have a relationship between the expectation value of the position and the expectation value of the momentum. And that's for Newton's first law.

And then there is another Newton's equation translated into quantum mechanics. So we have the expectation value of the momentum, dt, is equal to minus the expectation value of the potential.

While this is acceleration times mass, and this is force-- minus the gradient of a potential is the force-- these are Newton's two equations. And what they're saying is, if we know these things, we know something about the center of the wave packet, and how the center of the wave packet moves.

Now, the wave packet might be localized at one time. It might be mushed out at another time. But you can always calculate the center of the wave packet. It's just that there are only certain times that it looks like a particle.

But this thing, these quantities, which you define by an integral, they evolve classically. So I told you at the beginning, you had to give up classical mechanics. It's all coming back.

But it's coming back in a quantum mechanical framework, because we're talking now about wave functions, which have amplitudes and phases, and can do terrible things. But at certain limits, they're going to act like particles.

But if you were to ask a question, well-- suppose we do this experiment. And so here we have an electronic ground state potential surface. Now, I'm jumping way ahead.

But this is the wave function for that vibrational level. And you excite the molecule with a time dependent Hamiltonian, a time dependent radiation field light. And you vertically transport this wave function to the upper state, until you get something which is not an eigenstate.

It's a pluck. This pluck is a superposition of eigenstates. And we can ask, how does this evolve? And what it's going to do is, it's going to start out localized. And at some point, it'll do terrible things. And then at some other time it'll be localized again at the other turning point.

And it will come back and forth. And now, if it's not a harmonic oscillator, it won't quite relocalize. It'll mush out a little bit, and it'll come back and it'll mush out more.

And so again, we can use the evolution of the wave packet to sample the shape of the potential. We can measure the anharmonicity. And so let's now talk about that.

What are other quantities that we can calculate from the wave function of the time dependent Schrodinger equation? So let's talk about the survival probability.

So this is a capital P. Survival probability. It's going to be the wave function. The time dependent wave function is created at t equals 0. It has some shape. Now, we always like to have a simple shape at t equals 0.

And we'd like to know how fast that thing moves away from its birthplace. So we have this survival probability. It's a probability. So we're going to have integral psi star xt psi xt dx. And this integral is going to look like that.

Now, whoops. I knew I was going to screw up. If I put a t here, then it would just be the normalization interval. And we already know what that is.

But this is the birthplace. This is what was created at t equals 0. And this is time evolving thing.

And so we can calculate how that behaves. And I'm just going to write the solution. So the result is, if we have the same kind of two state c1 psi 1, e to the minus i e1 t for h bar plus c2 psi 2 e to the minus i e2 e over h bar, well then, what we get is c1 to the 4th power plus c2 to the 4th power plus c1 squared, c2 squared, times e to the i omega 2, 1 t plus e to the minus i omega 2, 1 t.

Now we're integrating. When we integrate, the wave functions go away. The wave functions become either 1 or 0. And so we're integrating. We're making the wave functions go away.

And we have some amplitudes of the wave functions. And we have a time independent part and a time dependent part. And this is 2 cosine omega 2, 1 t.

So what we see is this survival probability, the wave function, starts out at some place. And it goes away. And it comes back. And it goes away. And it comes back.

And it does that. It completely rephases, because there's only two terms. But if there were three terms that are not satisfying a certain requirement, then when it comes back, it can't completely reconstruct itself.

And this is the basis for doing experiments. One can observe the periodic rephasings of some initial pluck. And you can look at the decay of them, and that gives you something about the shape of the potential, the anharmonicity.

And you can do all sorts of fantastic things. You can create a wave packet, and you can wait until it reaches the other turning point. And at the other turning point, it's possible that you could excite it to a different higher excited state. Ahmed Zewail got the Nobel Prize for that.

So we're right at the frontier of what you can do, and what you can understand using this very simple problem of a time independent Hamiltonian and a 2 or a 3 term superposition.

OK. Recurrence.

This is a special property. When all of the wave functions, or all of the difference-- all of the energy levels, or differences in energy levels are integer multiples of a common factor, well then any coherent superposition state you make will rephase at a special time.

And so what we can do is say, OK, for a particle in a box, the energy levels are e1 times n squared. For our harmonic oscillator, the energy level difference is ev plus n minus ev our n h bar omega.

For a rigid rotor, which we haven't seen yet, the energy levels are a function of this quantum number j hcb. This is the rotational constant-- times j plus 1.

So all of the energy levels are related. I'm jumping ahead. Sorry.

So the energy levels are j times j plus 1. And the differences, ej plus 1 minus ej, are given by 2 hcb times j plus 1.

So for these three problems, we have this perfect situation where one can have these oscillating terms all have a common factor. And at certain times, the oscillating terms are all 1. Or some are 1 and some are minus 1. And we get a really wonderful simplification.

So at a time which we call, or I call, the grand recurrence time, where it's equal to h over e1 for this case of the particle in a box, or h over h bar omega, or h over 2 hcb, we get all of the phase factors becoming 1.

And sometimes, something special happens at the grand recurrence time divided by 2. And that's a little bit like this. We have a wave function here. And at half the recurrence time, it's over here.

And so you want to work your way through the algebra to convince yourself that that is in fact true. And in between, if you have enough terms in your superposition, which is usually the case, in between you get this. You get garbage looking.

It's still moving. It's still satisfying the Ehrenfest theorem, but it doesn't look like a particle. It just looks like garbage.

But you get these wonderful things happening. And now, if they're not perfectly satisfying this integer rule, then each time you get to a turning point, the amplitude has decreased and decreased and decreased. And at infinite time, it might recur.

But nobody waits around for infinite time, because other things happen and destroy the coherence that you built. So this is a glimpse.

Time independent quantum mechanics is complicated enough. Well, we can embed what we understand in the time dependent mechanics. And there are a lot of beautiful things that we can anticipate.

Now, we can use these beautiful things to do experiments which measure stuff that is related to, how does energy move in the molecule? What is going on in the molecule? What are the mechanisms for stuff happening? And in magnetic resonance, there are all sorts of pulse sequences that interrogate distances and correlated motions. And it is really a laboratory for time dependent quantum mechanics with a time dependent Hamiltonian. But a lot of stuff that we do with ordinary laser experiments are usually understandable in a time independent way.

Now, we want to get rid of things that are complicated. And so one of the things that we do is, we map a problem onto something which is time independent. And so one of the tricks that you will see is that if we go into what's called a rotating coordinate system, this rotating coordinate system is rotating at an energy level different divided by h bar. And that converts the problem into a time independent problem in the rotating coordinate system.

So that you're in a rotating coordinate system and, basically, you use the ordinary perturbation theory. And then you go back to the non-rotating coordinate system. So there's all sorts of tricks where we build on the stuff that we understood. And we can have a picture which is intuitive, because we want to strip away a lot of the mathematics and see the universal stuff.

And so I'm going to try to present as much of that as I can during this course. But a lot of the time independent stuff is heavy lifting, and I'm going to have to do a lot of that too.

OK. Have a nice long weekend. I'll see you on Monday.