ROBERT FIELD: Today is the first of two lectures on the rigid rotor. And the rigid rotor is really our first glimpse of central force problems. And so although the rigid rotor is an exactly solved problem, it's also a problem that we-- it involves something that is universal. If we have a spherical object, then the angular part of the Hamiltonian for that spherical object is solved by the rigid rotor.

And so if we understand the rigid rotor and know how to draw pictures, we're going to be able to understand the universal part of all central force problems. So it's not just a curiosity. It's a really major thing.

OK. And I'm going to do a lot of unconventional stuff in this lecture and the next lecture, as far as the rigid rotor is concerned. Because it's covered to death, but with lots of equations in all textbooks. And there is very little effort to give you independent insights. And so my discussion of the vector model is something that I consider really special.

And what I want you to be able to do is to draw cartoons that capture essentially all of the important points. And that you won't find anywhere except in my notes. But I think it's really important that you have your own point of view on these problems.

So let me just do a quick review, with the exam in mind, of the perturbation theory stuff. So we had a harmonic oscillator. And it's perturbed by some anharmonicity terms. So the potential is going to 1/2 kQ squared plus bQ cubed plus cQ to the fourth. And we could go on. But this is enough. Because it gives a glimpse of all of the important stuff that emerges qualitatively as well as quantitatively from perturbation theory.

So this is part of the H0 problem. And this is H1. And so you know now that doing second order perturbation theory is tedious and ugly. And it's easy to get overwhelmed by the equations. But what I want to do is to just review how you get the crucial structure of the problem.

So the Q cubed' term-- there are no diagonal elements of the Q cubed term. And so we're always going to be talking about the second order corrections to the energy. The selection rules are delta v equals plus and minus 3 and plus n minus 1.

And so what I told you is, if you're going to do the algebra, which you probably don't want to ever do, you're going to want to combine the delta v of plus 3 and minus 3 terms of the perturbation sum. Because the algebra simplifies. They have similar expressions. And you have a denominator, which is 3 Hc omega and minus 3 Hc omega. That factors out. And you just have a plus 3 and minus 3 in the denominator.

And similarly here, so when you do this, you lose the highest order term. What's the highest order term? It's v plus 1/2 to the third power. Because we have delta v of 3. We have Q cubed. And the matrix elements of Q cubed are a plus a-dagger cubed. And the selection rule for them-- or the matrix-- must go as the square root of the power of the a's.

And so all of the matrix elements have the leading term v plus 1/2 to the 3/2 power. But we're squaring. And we lose the highest order because of the subtraction. So this one gives rise to terms in v plus 1/2 squared. Q4 has selection rules delta v plus or minus 4, plus or minus 2, and 0. This is important. Because this one says, we have a contribution from the first order-- in the first order of energy.

And so in the first order of energy, we're going to have v plus 1/2 to the fourth power-- I'm sorry-- to the 4/2 power. Because we only have the matrix element, we don't square the matrix element. So this gives rise to a term in v plus 1/2 squared. But it's sensitive to the sign of the Q to the fourth term in the Hamiltonian. It's the only thing that's sensitive to the sine.

We also have terms that are v plus 1/2 to the 4/2 times 2. So we can have matrix elements to the four-- because it's a fourth power term, we get 4/2. And because it's squared, we multiply by 2. And then we lose the highest order. So we get, from this, v plus 1/2 to the third power.

So what we're hoping to get from the perturbation theory is the highest order terms in the energy expression. And so Q to the fourth gives a signed v plus 1/2 squared term. And it gives an unsigned always positive v plus 1/2 cubed term. And this one gives v plus 1/2 squared term.

OK. So this would tell you, when you're organizing your work, what to expect and how to organize it. And I'm really not expecting you to do very much with this level of complexity on an exam problem. But on homework, all bets are off. OK. So that's all I want to do as far as the review is concerned.

So the rigid rotor-- we have a molecule. So we have a bond of length r sub 0. And we have two masses. And if the masses aren't equal, the center of mass isn't in the middle. The center of mass-- you need to know how to calculate where the center of mass is. There are all sorts of simple algebra-- but what is happening is this guy is rotating without stretching about the center of mass.

Now, what we want to do is think about this problem as if it were-- here's our 0. And this is the reduced mass. This is a motion of a fictitious particle of mass mu. Mu is m1 m2 over m1 plus m2 on the surface of a sphere. They're all the same problem. But the question is, how do we interpret what we get from the solution to this problem?

So what we care about is a description of, where is the molecular axis? The molecule is rotating. And we're solving the Schrodinger equation. And we get things like the expectation value of J squared and Jz and maybe some other things where these are the angular momenta.

And how do the eigenfunctions for these states-- we have a state. And we have quantum numbers Jm and their probability amplitudes and theta and phi. That's a whole lot of stuff to digest. We want to go as quickly as we can to how this is related to the thing we really care about, which is, where is the bond axis?

So the molecule is rotating. And so the bond axis is moving in laboratory frame. And we want to be able to take, from that, the minimal amount of information that we memorize or remember-- I don't like "memorize." Because "memorize" doesn't involve understanding. But "remembering" does. We want to be able to, at a drop of a hat, be able to say, yes, if we pick these two quantum numbers, which are related to the eigenvalues of these two operators, we can describe the spatial distribution of the molecular axis.

There is an extra complication. So we live in the laboratory. And we have a coordinate system that we care about, the lab-fixed coordinates. And they're always going to be represented with capital letters. And there's also the body frame. And things are in the body frame. That's what the molecule cares about. And how do things in the body frame relate to the laboratory frame? It's not trivial.

And that's where the real effort at understanding comes. And it's kind of trivial for a diatomic molecule. But it's far from trivial when you have a nonlinear molecule, a molecule with many atoms and properties of each of the atoms that somehow combine to give things that you observe.

And so these two coordinate systems are very different. And actually, the solutions of the rigid rotor Hamiltonian gives you the relationship of the body coordinates to the laboratory coordinates. And that's kind of important. So we'll see how this develops as I go on.

And I feel quite passionate about this. Because one of the things that I do as an experimentalist is I observe fully resolved spectra. And the big-- the most information-rich feature of the spectrum is the rotational spectrum. And so it contains a lot of really good stuff.

OK. So first of all, the Hamiltonian is just the kinetic energy. Because it's a rigid rotor, it's free. There's no potential. But that's the last nice thing about it. Because we have to go from Cartesian to spherical polar coordinates. And there are a lot of unfamiliar things in this kinetic energy expression.

And when I write it down, you're not going to like it. Unless you're a mathematician, and you say, oh, yeah, I want to be able to solve these kinds of equations. Because the Schrodinger equation is, considering the simplicity of the problem, terrible. And except for mathematicians who just love it because they know-- oh, I know that equation. I know how to write down everything that I care about. But we care about different things.

So we want to know the energy levels of the rigid rotor. And we also want pictures. And remember, a picture is a reduced form of all the details that you have at your disposal. And you have to really sweat to make sure you understand every detail of the pictures and the stuff that you've averaged over, or you've concealed, because you don't need it, OK?

All right. So I'm going to be generating a lot of pictures. And one of the things we want to understand is-- so we have this vector, J. The J is the angular momentum of the molecule. And it's a vector as opposed to a scalar. That means it has three components. So for this part of the problem that I've just hidden over here, that's a one dimensional problem. We have a momentum and a conjugate coordinate and it's 1D. This is 3D. And there's all sorts of subtle stuff that goes on.

OK. So we would like to understand how this vector moves. Well, there is a question. I said moves. We're talking about the time independent Schrodinger equation. Nothing moves. We can use our concept of motion from classical mechanics to describe certain features of the average of some quantum mechanical system. And so there is kind of a motion. But we'll see what that is.

OK. We have some operators that we like. OK. Total angular momentum, projection of the angular momentum on a laboratory z-axis-- it's kind of hard to draw capital Z and small z if you haven't got anybody nearby. But anyway, this is a capital Z. And this is the thing that's analogous to the creation and annihilation operators. We need them. And it gives us a lot of insight. And that will be the subject of Monday's lecture.

And so we're going to have solutions, which are described by J and m quantum numbers. And we want to understand what these things look like. Where are the nodal surfaces? The nodal surfaces give us basically everything we want to know. There is the direct correlation to where the nodes are and how many of them there are with these quantum numbers. That's one of the important things you have to come away with.

OK. In my next lecture on angular momentum, I'm going to introduce a commutation rule, Ji Jj equals I H bar sum over K epsilon I Jk Jk. Isn't that a strange looking thing? Because I haven't told you what this epsilon is. There's lots of names for it. It won't help. Because I'm not going to talk about it here.

But this is actually the fundamental definition of an angular momentum. And from this commutator rule, we can generate all the matrix elements of angular momentum. And there's another family of commutation rules where we have a component of angular momentum and a component of what we call a spherical tensor.

Any operator can be classified according to spherical tensor rank. And that then determines all the matrix elements of that operator. And so you can imagine that this is a really powerful way of approaching stuff. And what I said before about the commutation rule of x and P sub x is that many people regard that as the foundation of quantum mechanics. And this is just an extension of that. So there is a way of getting all quantum mechanics from a few well-chosen commutation rules. And that's really neat.

OK. Let's get down to business. So I already drew this. But I'll draw it again. Because I'm going to drop a companion. OK. So we have here-- OK. So we have an angular momentum. And we have the bond axis. And this angular momentum is perpendicular to the bond axis.

So if we know something about how the angular momentum is distributed in space, we know something about how the bond axis is distributed in space. But it's not trivial. But once you've learned how to make those connections, it's fine. OK. So now, let's draw--

So we have a right-handed coordinate system. And we have, say, the vector J. Now, this is the laboratory frame. We have J. And we have a molecule, which is perpendicular to J. And we have the projection of J on the body axis, on the z-axis, and that's M.

OK. So when we talked about the quantum number J, which is the length of this vector, and m, which is the projection of that vector on this axis, that's beginning to be how we understand how this works. Because this is perpendicular to that.

Now, here we have one of the sins. So we begin by saying, well, this is a picture. And J precesses, or moves, on a cone around z. How do we have motion? This is a time independent Schrodinger equation. It's a way of saying, well, it doesn't matter where J is. It's more or less equally distributed in probability on this cone.

But not an amplitude. Remember, when we have something that's moving in the time independent Schrodinger equation, we get oscillations. But we need a complex function in order to have those oscillations. If we're going to take psi star psi, there is no complex part. And you do have uniform amplitude of J. And so it's sensible to say, well, it got that way because J precesses. Maybe.

There is something if you say, well, maybe if I created a system at t equal 0 where J was at a particular position, and then I let that thing evolve-- this is not an eigenstate. It would be a complicated superposition. That thing would precess. And you would observe what we call polarization quantum beats.

Now, that's getting way ahead of things. But it is helpful to think about J precessing on this cone. Because that gives you a sense that the length of J is conserved. And the orientation about the z-axis is not. And it's more or less uniform probability, but not uniform probability amplitude.

But you don't need that for a lot of the things. If you're looking at the wave function, yeah, there's going to be some oscillation. The real part and the imaginary part will oscillate in such a way that the probability is constant about that. I finally realized that this morning. So it's not as much of a lie as you think.

OK. So this is the picture. And this is what it looks like in the laboratory. And now, I'm going to prepare you for-- so suppose you had a molecule. And you have a little person standing on the molecule frame. And now, you have somebody out here observing as the molecule rotates.

Well, and here's J. All information that you're allowed to know from outside the molecule comes from the projection of whatever is in the molecule frame on J. And that's what the vector model does. It tells you how to take stuff you know about the individual atoms and project it on the thing that communicates with the outside world. There are a couple of other things that I'm going to say about this. But now, let's get down to the business of actually doing a little bit of the solution of the Schrodinger equation.

So for our free rotor, the potential is r equals r0 theta phi. And it's equal to 0 if r equals r0. And it's equal to infinity if it's not. So this is very much like a particle in an infinite box. In fact, you can do a really cheap solution if you say, well, let's consider a particle in an infinite circular box.

Well, you can solve this problem just using the de Broglie wavelength. And you get that the energy levels for this circular box problem go as the quantum number squared. And that's almost exactly like the solutions to the free rotor. The difference is the energies for this go as the quantum number squared. And the energies for this go as the quantum number times the quantum number plus 1. It's almost the same.

OK. So because the potential is constant as long as r is fixed, the Hamiltonian is just theta-- OK. And so we have to understand this kinetic energy. For 1D problems, the kinetic energy is P squared over 2 mu, the linear momentum. I should put a hat on this.

Well, we have motion in three dimensions, or two dimensions, theta and phi. And so we want to do something. We want to generate a kinetic energy Hamiltonian, which is analogous to this, some kind of momentum squared over some kind of a mass. And so we can go by analogy. Or we can go back to classical mechanics.

We know that the orbital angular momentum is r cross P. So these are two vectors. Cross product is a vector. We know all that stuff. We know how to write the cross product in terms of a matrix involving unit vectors and stuff like that. You've done that before.

OK. So now, we have an angular motion, omega. And we would like to know what the velocity of the mass points are on a sphere. Or if we think of this as just a particle of mass mu rotating, then we want to know its velocity. And to get from the angular velocity to the linear velocity, the linear velocity is r omega.

So we can say, all right, knowing-- well, for a vector cross product, if the two things-- the r and the P-- are always orthogonal, well, then we just do r times P. And in fact, for motion on this sphere, here's r. And the motion is always orthogonal to r. And so we can write that the angular momentum is m1 r1 squared omega plus m2 r2 squared times omega. Or it's just I omega.

OK. And so we can write the kinetic energy term just goes as L squared over 2I where I is the sum of the individual masses M sub r I squared. OK. So we have an angular momentum operator, which is the guts of the kinetic energy.

OK. Now, we're thinking Cartesian. And this is a spherical problem. And so we want to go from Cartesian coordinates to spherical polar coordinates. And that's a non-trivial problem. And it's also an extremely boring problem. And what you get is also something that's not terribly rewarding, except it's the differential equation you have solve.

So T, when you go to spherical polar coordinates, is minus h squared over 2I 1 over sine theta partial with respect to theta times sine theta partial with respect to theta plus 1 over sine squared theta second partial with respect to phi. So that's the kinetic energy operator.

So first of all, you say, what am I going to do? And the first thing you say is, separate the variables. So you do that. And you do the standard trick for separating variables. And you get two differential equations-- the theta equation and the phi equation. I'm sorry?

AUDIENCE: H bar!

ROBERT FIELD: When I wrote it, I said, why is that not H bar? OK. All right, so when you separate variables, we have this result-- 1 over phi of phi. This is the phi part of the equation. Whoops, yeah, that's right. m squared is the separation constant.

So we arrange to have a differential equation that depends only on phi and another that depends only on theta. And they're equal to each other. And so we call the thing that they're equal to a constant. And we call it m squared. We like that because m can be positive or negative. And the sign of m determines whether you have an oscillating function or an exponential function. You're all familiar with that.

And so this is the phi equation. And this one, you can solve easily. You know the solution to this. You could, with a little bit of thought, write down the solution and have normalized functions. So I'll just do that. So the phi part of the solution is-- it's not the order in which I wrote my notes-- 1 over the square root of 2 pi times e to the i m phi. And m is equal to 0 plus and minus 1 plus and minus 2 et cetera.

Quantization comes from imposition of what we call periodic boundary conditions. The wave function has to be the same for phi and phi plus 2 pi and phi plus 4 pi. And so that gives quantization. So this is the phi part. That's simple. That's simple. It's wonderful. We understand that perfectly. And one of the nice things about the vector model is mostly that's what you're focused on.

So immediately, we can draw some pictures. And we can look at the nodes in the xy plane. So m equals 0, there are no nodes. m equals 1, first of all, let's draw where phi is 0. So this is phi. And so there can be a nodal plane like that. And there could be a nodal plane like that.

And already, you know this looks like an S orbital. And this looks like a Px orbital and a Py orbital. And then we could also have-- yeah, m equals 2, we could have this, and this, and that-- no node, one node, two nodes. I'm sorry, yeah. What am I doing here? This is one node.

I have to be a little bit more careful here. So what I wrote down is not true here. There are going to be two nodes. So they're probably like this and like that. But it's clear that what I have in my handwritten notes-- I'm not sure what the printed notes say. But there are going to be two nodes.

And so immediately, you know something about-- if you draw a reduced picture and you show the nodal structure in the xy plane, you can tell what the projection of the angular momentum quantum number is, which is really important.

There's the other differential equation. And that's the theta differential equation. And that is complicated. It is an exactly solved differential equation. But one of the things it gives you, which is easily memorized-- remembered, I'm sorry-- is that the energy levels have-- where this is the overlying momentum. So you can solve this. And you can get the eigenenergies. And the eigenenergies do not depend on m. They only depend on the L quantum number.

And they have this nice form.

OK. Now, in my notes and in all the textbooks, there are these horrendously beautiful detailed expressions of the solution, the mathematical form to the solution of the theta equation. And it's the Legendre equation. And there's Legendre polynomials. And remember, with the harmonic oscillator, I told you, you don't ever want to look at these things. The computer will look at them. And if you have integrals, the computer will know how to do those integrals. Because you told it how. And you don't have to keep that in your head. You've got better things to do with your limited attention.

So there is a solution. And it has a form, which I have decided that I won't talk about. Because you get much more insight into real problems from the vector model. Now, the vector model is really only marginally useful for a diatomic molecule in an electronic state, which you don't know about yet, which is called sigma sigma plus, where there is no angular momentum associated with the electron and when there is no angular momentum associated with the nuclei.

So this is just practice for real life when you have to understand other things about what is living in the molecular frame. But this is hard enough to understand completely that it's a worthwhile investment. And you will be doing most of the understanding of more complicated problems on your own if you ever do anything with diatomic molecules or polyatomic molecules. And so, OK.

So what is the vector model? Well, the things we want to know about the vector model is, how long is J? So if we have a state with J and m quantum numbers, how long is the vector associated with J? And what is the angle-- what is the projection of J on the laboratory z-axis? So we want to know the length of J. And we want to know the projection of J on z.

OK. And we want to know the angle between the z-axis and J. That's the beginning of a picture. And again, we stick with this idea that J-- so here's the z-axis. And J precesses about z. And here is an angle we want to know. This theta is a different theta from the theta in-- in fact, I should call it alpha.

OK. So some things we know-- we know that the eigenvalues of the rigid rotor equation are this. And we know that Jz operator operating on y Lm gives H bar m y Lm. And J squared operating on y Lm gives H bar squared J J plus 1.

So what do we do with these two things? Well, one is to say, all right, the length of J is going to be the square root-- times y Lm. So the length of J is going to be the square root of H bar squared J J plus 1. So that becomes H bar and approximately J plus 1/2.

Because the square root of J J plus 1 is almost exactly J plus 1/2. When you get really high J, it's exactly. At low J, It's a little bit less than exact. So we know the length of J is this. And we know the length of m is H bar m. The length of J z is H bar m.

So now, we know that this is H bar m. And this is H bar times J plus 1/2. And so this is alpha. So we know how to calculate the cosine of alpha. So the cosine of alpha is equal to H bar m over H bar J plus 1/2, or m over J-- oh, right, plus 1/2, really small.

So the angle, the cosine of the angle that j makes with the z-axis is m over J. And all of a sudden, now, we have lengths of things and angles of things. And we can do all sorts of stuff. Remember, what we care about is, if this is J, the body axis is like that. So we now know where the body axis is relative to the laboratory. So we have the body axis is perpendicular to J. And so we can then calculate where everything is.

All right, so special cases-- if m is equal to plus or minus J, then what does that mean for this picture? Well, we have the z-axis. And we have J. And J is almost exactly along the z-axis. It would be exactly along if there wasn't this plus 1/2. And so what that means is the bond axis is almost exactly rotating in the xy plane. So if we choose m equals plus or minus J, the molecule is rotating in the xy plane. That's kind of nice to know.

The other easy case is m equals 0. If m equals 0, J is perpendicular to the z-axis. And so the body axis is in the yz plane. Or if we're coming around here, it's in the xz plane. So we have xz yz. And together, what it says is the body axis is more along z than along anything else. That's a lot of insight.

And so we can go to our friendly extreme cases, special cases. And we could say, where's the body axis? In the laboratory, which is where we're making the observations. That should make you happy. Because there's no equations here. There's just a lot of pictures that you can understand and develop your intuition.

Now, I want a blackboard. OK. Suppose you have a laboratory in which you can make a molecular beam. And that's easy enough to do. You squirt molecules out of a pinhole. And you have some kind of an aperture. And so you have a directed flow of molecules in one direction.

And you could also say, all right, I'm going to do something with my laser. And I'm going to make the molecules, which are like a helicopter, in other words, the molecular axis is rotating in a circle about the propagation axis of the beam, so a helicopter.

And we can also do this. And so these are two ways that you can prepare molecules in this beam. And you could say, oh, I've got a whole bunch of molecules that are not in the beam. And these molecules are going to collide with the molecules outside the beam and get scattered.

Well, which one is going to be scattered more? The one that sweeps out a big volume or the one that sweeps out something only essentially one dimension? That's insight. There's lots of other things, too.

Now, let's do something which is actually slightly exam relevant. Suppose we have a diatomic molecule which is positive on one end and negative on the other, OK? And we're going to apply an electric field. And if the electric field is in this direction and the molecule is doing this, the molecule doesn't care.

But if the electric field is in that direction and the molecule is doing this, the energy levels-- the energy goes up and down as the molecule rotates. Well, how is that? The molecule was free to precess. And we knew the amplitude along this axis. But if there's some angle dependence, what we're doing is we're mixing in a different J.

And so that's telling you that, if you apply an electric field, there will be a Stark effect. And it will affect the m equals 0 levels differently from the m equals J levels. Now, I'm not going to tell you which one is more affected. But it's clear that one is hardly affected. And the other is profoundly affected. And that gives rise to a splitting of the energy levels in an electric field, which depends on J at m in a way that you would recognize.

Time to quit. I did what I was hoping I could do. Now, there is some stuff at the end of the notes which is standard textbook material about polar plots of the wave functions. These polar plots are useful. But most of the time, when you first encounter them, you have no idea what they mean, except that they express where the nodes are.

Now, you want to go back and you want to actually think about what these polar plots mean and whether you can use them as an auxiliary to this vector picture. OK. So I will then lecture, and it's exam relevant, on commutation rules on Monday. And then have a good weekend.