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Contributor Okay, let's get going. So, on Friday we used the commutation relations that we had deduced for the angular momentum operators to find what the spectrum of j^2 , and any one of the j s, for example j_z , could be. And now we can use this information to understand ... to interpret the spectra, the infrared, the near infrared and terahertz spectra of diatomic molecules, which are very common. They're in the room here, O_2 and N_2 ; much of the mass of the barriers of the universe is contained in H_2 and, from a practical point of view, a very important molecule, for reasons I'll explain, turns out to be carbon monoxide, CO .

So a molecule like this consists, for our purposes, of two masses, being the nuclei, for example, of the oxygen and the carbon, on a light spring. So we have two massive nuclei and a light spring formed by the electrons, and this is capable of being a simple harmonic oscillator in that it does this, but also, at lower energies, it's capable just of rotating, end over end as a dumb bell and having rotational kinetic energy.

So, if you go to classical mechanics and ask yourself what is the energy of this thing? The energy of this thing is given by the classical angular momentum around the x-axis squared over twice the moment of inertia around the x-axis plus the classical angular momentum squared around the y-axis over twice the moment of inertia, around the y minus axis plus the classical angular momentum squared over two iz . So this is reminiscent of, this is a piece of classical physics that the kinetic energy of a moving particle is P^2 over two m so this is classical mechanics.

Classical mechanics. And those who did short option seven, will, I hope, recognise this formula. So we have angular momentum, x component here, instead of x component of linear momentum, divided by moment of inertia around the x minus axis, instead of divided by mass. So this is what the classical expression for the energy of a thing like this is.

So what we say now, we conjecture, that quantum mechanically, we put j_x , the classical thing, goes to \hbar times j_x , the operator. So we define these operators ... many people define them to have dimensions of \hbar , but we would define them so they were dimensionless. This thing has the dimensions of \hbar so we make this transformation, we take this classical expression and we turn it into \hbar times the quantum mechanical operator etc., and then we infer that the Hamiltonian should be \hbar^2 over two, j_x the operator squared over ix , I've taken that out, plus j_y squared the operator over iy plus j_z squared over iz . So these are operators now.

So you should think of this as a guess. It will be confirmed by experiments to be shown soon. Now we say if, for this diatomic molecule, we take the z-axis to be the symmetry axis of the molecule, that's the axis that runs through both nuclei. And then the moment of inertia around

that axis, around that now z-axis, is negligible because all the mass in this molecule is almost entirely contained in these nuclei which are very close to being point particles. And if you rotate it around this axis, those nuclei provide very little moment of inertia.

The electrons could provide a certain amount of moment of inertia, so it's possible for the electrons to have some angular momentum around this axis and in some molecules they do, but in most molecules they don't. So, the moment of inertia is, in any case, very small so this implies that I_z is very much less than I_y , than I_x , which is the moment of inertia about an axis and it sticks out here whether ... if you spin it around there, the two nuclei go around in a decent circle of radius half the length of that bond, say. And, for a diatomic molecule `[[asymmetry 0:06:00]]`, I_x is going to equal I_y .

So given that I_x equals I_y , it's natural to re-write this Hamiltonian as h equals \hbar^2 squared over two, brackets, J^2 , which is J_x^2 plus J_y^2 plus J_z^2 divided by I_x , which equals I_y . So these first two I've combined together into here. I've now, in here, also got a J_z^2 over I_x , which I don't really want, so I simply get rid of this J_z^2 , (one over I_z , minus one over I_x). So this is just a repackaging of that expression to group together the terms which have a common factor one over I_x .

And now, the beauty of this is that we know what the eigenvalues of this operator are and what the eigenvalues of this operator are, so we can immediately say what the eigenvalues of this operator are. So this says, immediately, what the spectrum of h is: E_{jm} , which is going to be \hbar^2 squared over two, brackets, J , J plus one, because remember we showed the eigenvalues of this were J , J plus one, where J is allowed to be an integer or a half integer divided by I_x plus m squared one over I_z , minus one over I_x .

So because the Hamiltonian for this rotating system is simply a function of the angular momentum operators, and because we have already found out what the spectrum of the angular momentum operators is, we can immediately say what the spectrum of the Hamiltonian is, i.e. we now know what the allowed energy levels are of these rotating molecules. Almost no further investment of effort.

Now, we know that m lies in the range minus J , less than or equal to m , less than or equal to J , that was one of the things we showed on Friday, so this number is generically of the same order as this number, but this one over I_z , I've explained, is a very much bigger number; I_z is a very much smaller number than I_x , so this number is very much bigger than this number, which is the same as one over this number here. So the coefficient of m squared is huge. That means that if n were anything other than zero, the energy would be enormous.

So if you're dealing with the molecules in the room or in inter stellar space or somewhere where they only have moderate amounts of energy, we can argue that this thing is going to be zero. So this number here is very large, I mean it really is huge because I_z is so very small for a diatomic molecule, which means that this is always zero. That's just saying that these molecules have their own momentum around an axis which is perpendicular to their symmetry axis. So that means that, effectively, the energy levels are simply E_J , \hbar^2 squared, over two I_x times J , J plus one.

So those are the energy levels, now that's all been totally generic for diatomic molecules. Let's now talk about carbon monoxide.

Carbon monoxide has a much more interesting spectrum, a much more easily observed electromagnetic spectrum because the carbon is slightly positive and the oxygen is slightly negative ... I've lost this. Right, oxygen has a great affinity for electrons, so it borrows some of carbon's electrons and ends up being a little bit negative. This is a little bit positive, so a carbon monoxide molecule, which is spinning end over end, is a rotating dipole, an electric dipole. So CO, this is plus, this is minus, will be a rotating electric dipole.

The same will not be true of a hydrogen molecule because obviously the two hydrogen atoms will have equal affinity for electrons and so neither will be charged. Or an oxygen molecule, or

a nitrogen molecule, all of these molecules are not dipoles so they can rotate without emitting electromagnetic radiation. But if a carbon monoxide molecule is rotating, it will emit, or potentially absorb, electromagnetic radiation at some frequency which we would imagine would be the frequency at which it rotated end over end, right, classically, that would make sense.

A rotating dipole should emit or absorb radiation at the frequency that it rolls over. Let's see whether that's true, according to quantum mechanics.

So, it will emit or absorb E-M radiation and the angular frequency, let's have the frequency, so the frequency is going to satisfy ν equals E_j minus E_{j-1} . Sorry, another point: photons carry one unit of angular momentum it turns out, right, not more, not less. So a photon can move a molecule which has a total angular momentum j , which has a state which has a total angular momentum j minus one or j plus one, but it can't move it to j plus two or j plus three, it can only move it by one unit in j , because it's only got one unit of angular momentum and by conservation of the angular momentum of the photon plus the molecule, right, so you can or destroy the photon or create the photon so you can add the angular momentum of the photon into the molecule or you can dump into a photon one unit of angular momentum and hence make one step like this.

But only adjacent j s can be moved to, and this is the key point, by interaction with electromagnetic radiation. So we're going to have, with ν , the energy of the photon equals the difference in the energies of the molecule between the excited state it started and the state it finished and what's that going to be according to this formula here? That's going to be \hbar^2 squared over two I , brackets, $j, j+1$, minus this same expression with j put equals minus one, so it becomes j minus one times j and I think you can see that this cleans up very nicely to two j , so we end up with \hbar^2 times j over I . *[Mobile phone rings]* I think somebody must have a call.

What does that tell us about ν ? It tells us that ν maybe should go to subscript j to indicate that it's the frequency which will be emitted as it goes from a state j to $j-1$. We can cancel one of the \hbar s, well, this is an h , not an \hbar , so this becomes equal to \hbar times j over two πI . So, according to quantum mechanics, that's the frequency of emitted light.

Can we reconcile this with our classical picture? So, how fast was the molecule going around? So classically we can say that the angular momentum j equals I times ω ; this is the angular frequency of the tumbling, of the rotation. So this is a piece of classical mechanics again; the relationship between angular momentum and frequency ... this is like the relationship between momentum ... so this mirrors the classical statement that p equals m times \dot{x} ; ω is $\dot{\theta}$. rate of change of angle, I mean is the analogue of \dot{x} ; this is the rate of change of position, that's the rate of change of angle, I've already said that moment of inertia plays a role a bit like mass and this momentum plays the role of ... right, so that's where this thing comes from. It's just a piece of classical physics.

So when you are in a state ... so what do we think that ω should be? ω should be on the order of; well it should be equal to j over I , that's classical. Doing it quantum mechanically, this is going to be \hbar times the square root of $j+1$, so this is a heuristic sort of thing. Supposing its angular momentum is along the x -axis, right, then j^2 is going to be on the order of \hbar^2 times $j+1$; j^2 is going to be on the order of j^2 which will be this, divide through by I .

And we want to relate this to the frequency we had up there, a factor of two π ... what have I done wrong? Oh, it's because this is the angular frequency, that's the actual frequency, right? So this is equal to two π frequency of ... this was angular frequency, this will be frequency of rotation. So we have the frequency of rotation we expect to be \hbar over two πI times the square root of $j+1$.

So this is going to be, so what can we say? This is slightly bigger, this is greater than ... just a bit, if j is a larger number it's only a smidgeon bigger than \hbar times j over two πI . So, in its upper state when it had total angular momentum, $j, j+1$, \hbar^2 squared, the rate at which it was

tumbling was a bit larger ... this is the frequency of emitted light, sorry, this is ν_j from above. So in its upper state, its rate of tumbling, on this classical picture, will be slightly larger than the frequency with which it emits the light and you can check that in its lower state we would have a minus sign here, a minus one, so just a bit below the frequency which emits the light.

So the light is, in fact, emitted at just the average of the expected rotational or tumbling rates at the upper and lower levels which makes, I think, perfectly good physical sense.

So in lower state, that's when j , well, j minus one, tumbling rate, is just a bit lower. Oh no, this thing, it's gone to sleep again. It's not my computer that's gone to sleep; it's the wretched lecture room that's gone to sleep. It's too irritating. We must get it to stop doing this. I really do want to show you something today. Is it coming back? Okay, right.

So this is the actual experimental spectrum of carbon monoxide so this is in gigahertz, so this is two terahertz, three terahertz along there, and you have a line here, there's a line being drawn of the frequency measured associated with the transitions from j equals one, to j equals nothing.

So you get photons out with this frequency which is almost but not quite twice the previous frequency according to this mathematics we've done so far, the next frequency up should be exactly twice ... this frequency here should be exactly twice that frequency there and you can't tell the difference, actually, on this plot, and so on and so forth. So you get each line, here, is telling you the measured frequency of a spectral line from these carbon monoxide molecules and you can see that they do form a regular grid, just like this says. So this is the transitions from one to nothing, this is the transitions from two to one, this is three to two and so on and so forth. And if we go up here this is ... I don't know, can't count, ten to nine or something, right?

There are a couple of missing lines in here where somebody hasn't published a measurement or something. The other interesting thing to note ... so that even spacing is confirming this frequency, ν_j is proportional to j business. And that's the interpretation. There's another interesting to notice here, which is that as you go along here, the black lines get slightly to the left of the dotted lines and the dotted lines are exactly at multiples of the frequency of this lowest transition – j equals one to nothing.

So what's happening is that the measured frequencies almost conform to this rule up here, but not quite. They turn out to be slightly smaller than the number ν_j given up there and the physical interpretation of that is interesting, it's that ν_{measured} , minus ν_j is slightly negative, if you like. And that's because ν_{measured} is equal to, well this is what you would think classically, is equal to \hbar over two π j over I , which itself is a function of j .

So if you're firing in circularly polarised photons and making this molecule spin faster and faster end over end, obviously the centrifugal force will stretch that spring out a bit – the spring is stiff but not infinitely stiff so if you're swinging it faster and faster, the centrifugal force pulls the spring longer, increases the distance between the nuclei and in that way increases the moment of inertia. So this moment of inertia that's appearing on the bottom of this formula should really be itself a function of j which increases. So some of this increase here is cancelled by a slight increase in the bottom and that's the interpretation anyway, of these spectral lines falling behind the measured numbers, which are the black lines, falling behind the perfectly evenly spaced grid of dotted lines.

So one of the problems on the problem set is to use this phenomenon to estimate how stiff this spring is because you can calculate using classical physics, you can calculate what this force is, the centrifugal force. You know how fast the molecule is going around so you can calculate what v^2 over r is, which is the force pulling the spring. From the change in the spectral line frequency, you can estimate the change in moment of inertia – so you have a given force, a given displacement so you can work out the spring constant.

Then you can check, you can make a prediction of what the frequency is at which the carbon and the oxygen would oscillate in and towards each other using the spring, all right, which occurs at a different part of the spectrum and so that's what that problem is about.

So I think that's all ... there are other nice things you can do with carbon monoxide molecules, but I think we'll leave it at that because we have an important additional item to put on the agenda which is orbital angular momentum. Maybe we should put it over here.

Classically, we know what angular momentum is for a particle ... well, let's be careful. So the world, the earth, has angular momentum about the centre of the sun for two reasons. One is that it's moving around the sun once every year and that motion contains a great deal of angular momentum and the other is it's spinning on its own axis, which accounts for a slightly smaller amount of angular momentum, and orbital dynamics are very much involved with the interchange of angular momentum between orbital motion and spin motion and so on. It's the same quantity.

It's exactly the same on atomic scales or whatever and, as I've said, electrons and protons and neutrons are all gyros that, like the earth, they spin on their own axis, but of course they also move around and in moving around, they have angular momentum. So we, at the end of last term, we introduced these angular momentum operators, by very general considerations to do with what happened when we generated the operators that were generating n states which gave us system just like our old system except rotated through some angle.

That, apparently, has nothing to do with angular momentum as classically conceived so in classical physics we have a thing, orbital angular momentum which is going to be given by \mathbf{l} is equal to \mathbf{r} cross \mathbf{p} , so this is classical physics. This is classical orbital ... so this describes the angular momentum of the earth about the centre of the sun, by virtue of the motion of the earth around the centre of the sun, where \mathbf{p} is the momentum of the sun in a frame of reference in which the sun is stationary.

Right, so we can define an operator. So, in quantum mechanics, by analogy with this, it's natural to define an operator, \hat{l} , which is equal to one over \hbar , $\hat{\mathbf{r}}$ cross $\hat{\mathbf{p}}$. Let's write that out in components to make sure we know what we're doing. That's one over \hbar , the sum $\epsilon_{ijk} \hat{x}_i \hat{p}_j$... which way round do I want to do this? It doesn't actually matter which way round I do it, but for consistency I should try to keep it the same as we have here. Yes, so that's consistent with what was down in the book. So this is summed over j and k .

So, things to notice. One is, we put a one over \hbar in here to make this thing dimensionless. It's a close call whether you should make it dimensionless or not, most people probably don't have it dimensionless. I think, on balance, you're better off having it dimensionless and we introduced the angular momentum operators in such a way that they were dimensionless; they didn't have an \hbar which made our formulae simpler. So for consistency we need to make these dimensionless, right? So this has dimensions of this and therefore this ratio is dimensionless.

Does this make sense? Do we have to worry about the order in which we write down \mathbf{r} and \mathbf{p} ? In classical physics, we clear don't. In quantum mechanics you would think you would have to worry about the order; does it matter whether this is xp or px ? Well, it doesn't matter because in this sum, the only terms which occur are when the subscript on the \mathbf{r} is different from the subscript on the \mathbf{p} because this epsilon symbol, remember, vanishes if any two of its subscripts are the same.

So for example, we have an \hat{l}_x is equal to one over \hbar , the sum over j and k of $\epsilon_{xjk} \hat{x}_j \hat{p}_k$. So j 's sums goes over x, y and z , but when it's x you get nothing here, so there are only two places to consider when it's y and when it's z and when it's y we don't need to consider the possibilities that k arrive at x or y because this will vanish if k is either x or y , so this is one over \hbar of x , sorry, xy which is $y \hat{p}_z$ minus $z \hat{p}_y$. So that's how it will work out. These two operators commute and these two operators commute so it doesn't matter about the order. So order's not important.

\hat{L}_x is also going to be a Hermitian operator because if we take the dagger of this, right, the dagger of this equation, we will have the dagger of, well, let's do it. \hat{L}_x dagger is going to be one over \hbar – the rule is, when you take the Hermitian joint you have to reverse the order of the operators, so it's going to be $\hat{p}_y \hat{z} - \hat{p}_z \hat{y}$, these things are all operators.

But each of these things is its own dagger because the momentor and coordinates are Hermitian operators and the order in which you write them down, we've already agreed is unimportant, so this is in fact equal to l_x . So it's a Hermitian operator.

So we expect it to be associated with an observable and the observable is obviously going to be orbital angular momentum. That done ... one more thing, we introduce, by analogy with angular momentum, we introduce a new operator, l squared, which by definition is l_x squared plus l_y squared, plus l_z squared. Again, it will be Hermitian because l_x is Hermitian so l_x squared is Hermitian, right, so this is another Hermitian operator.

The next thing to do is to work out some commutation relations now that we've defined these operators, defined what commutation relations we have. Let's do $l_i x_l$, well mind if I leave off these hats now, we're thoroughly stuck into quantum mechanical operators. So what's this commutator? Well, we should write in what this is. This is $\epsilon_{ijk} x_j p_k$, this will be summed over j and k , so this is this, commutator on x_l .

So this is the commutator of an operator with a product, so in principle there are two terms. There's this thing stands idly by while that commutes with that and then there's this thing stands idly by in the back while this commutes with this, but obviously the x s all commute so forget that. So we only have to consider this commutator, so this is equal to the sum ϵ_{ijk} of x_j standing idly by while we do the commutator $p_k x_l$. But this is minus $i \hbar \delta_{kl}$.

So we have minus i ... sorry, I'm missing here one on \hbar , am I not? Because one up on \hbar of this product. So we have one on \hbar here. Then, this generates a minus $i \hbar$ – the \hbar s cancel, the minus i sticks around and is a pain, times $\epsilon_{ijk} x_j \delta_{kl}$. This is still summed over j and k . When we sum over k , this becomes an i , so this becomes minus i summed over j of $\epsilon_{ijl} x_j$ and we can get rid of this unattractive minus sign by swapping the order of these two, right? So we can write this as plus i , the sum over j of $\epsilon_{ilj} x_j$. So let me just write in the left side again, so we can appreciate the pattern that we're getting.

The commutator of l_i with x_l is i times ϵ_{ilj} , these two letters being those two letters, sorry ... this was summed over j . So between here and here I've merely reversed the order of the subscripts on the epsilon dealing with the minus side. Now this is exactly the same as a result we already had, so we need to recall at this point that $j_i x_l$ is equal to i sum over j $\epsilon_{ilj} x_j$. So the commutator of this orbital angular momentum operator with this position operator is the same as the commutator of this total angular momentum operator with the position operator.

Similarly, just the same calculation, a precisely analogous calculation implies that $l_i p_l$, if we just sit down and calculate this in exactly this way, we will find it is i sum over j of $\epsilon_{ilj} p_j$ which mirrors and there's an analogous relationship between j and p .

The next thing to calculate is: so what's l_j ? We've introduced a family of three operators, we should investigate what the commutation relations are between any two of them. So we know what the answers are in the case of the angular momentum operators $j_i j_j$, is $i \epsilon_{ijk} j_k$. So this is setting us up for expecting what the answer is here.

Okay. In order not to ... so it's an exercise that I would encourage you to do just to work it out as it stands, but I'm now going to do a simpler calculation, just one component. There's a question mark associated with this, it's a good exercise to do that but it's slightly complicated to do it in the general case. So let's do something that's slightly similar, let's work out what $l_x l_y$ is.

So what do we do? What we do is replace one of these, shall we say this one, by its expansion in terms of x and p . So this is going to be one over \hbar of $l_x l_y$. So what is l_y ? Well, l_y must be, I think, $z p_x$ minus $x p_z$. All right, so this product divided by \hbar is that if I've not got my signs wrong. And we know now how l_x commutes with this and how l_x commutes with that so we can work it all out. So this is going to be one on \hbar , open a big bracket, of l_x commuted with z , with p_x standing idly by, plus z standing idly by, l_x commuting with p_x minus l_x commuting with x and p_z standing idly by minus x standing idly by, while l_x works on p_z .

The easy terms here are this and this, because they're what? Zero, right. Because this would be $\epsilon_{ijk} x_k$, that vanishes. Similarly here. So these two are nice and equal to zero and these two we have to work out using horrible cyclical everything, so this is going to be minus... so $\mathbf{L} \times$ commuted with a component of \mathbf{x} is going to produce i times the third component which will be y and I think we'll probably get a minus sign. So I think this will be one over \hbar , brackets, and there'll be an i , sorry, an i , and I think we'll have a minus i times y from here, times p_x and this was zero, this was zero.

This is the other interesting one, it will be the same thing – this commuted with this will be minus p_y . So we have two minuses, so we'll have a plus $i \hbar p_y$, so this is equal to $i \hbar$ of $x p_y$ minus $y p_x$, which, this \hbar and this stuff together make \hbar so it's $i \hbar$.

So, in summary, this again mirrors the result we saw with the total angular momentum operators, this is one component of... I'm going to now write down the answer for that calculation up there without proving it. But you can see that it's going to happen: L_i , L_j is i summed over k of $\epsilon_{ijk} L_k$. So, let me repeat a result we've already got: $L_i x_j$ is equal to $i \epsilon_{ijk} x_k$. So, \mathbf{L} commuted with any component of a vector produces i times the third component of the vector and that rule even works for \mathbf{L} itself which is itself a vector, all right? So we regard this as analogous to this relationship here because we also had that $L_i p_j$ is equal to $i \epsilon_{ijk} p_k$.

The point is that what goes in here for \mathbf{L} to work on can be any vector, a component of any vector, and then you always get out i times the other component of the vector that you put in here. So here also we get out i times the other component of the vector that we put in here, which in this case was \mathbf{L} itself. This is mirroring precisely, so these results exactly the same. If you replace all of those L s with J s, everything remains true.

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