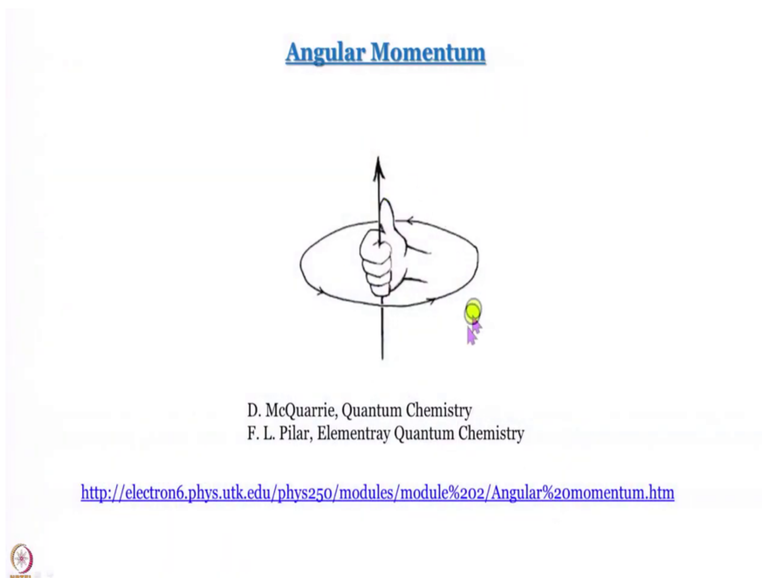
Quantum Chemistry of Atoms and Molecules
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture-22
Angular Momentum

We have discussed rigid rotor and very soon we are going to discuss hydrogen atom after that we will talk about multi-electron atoms where we will discuss something very strange enigmatic called spin. And in all these cases one quantity that keeps on coming at us is angular momentum. So, what we will do in the next one or two modules is that we are going to discuss a quantum mechanical description of this quantity angular momentum.

(Refer Slide Time: 00:58)



The quantity as such is not very new to us we are familiar with this kind of a diagram this is a cartoon that I have downloaded from this website. But in physics we have studied that whenever there is circular motion where the direction of motion is given by the direction of fingers of right. Angular momentum is a vector that arises perpendicular to the plane of rotation and is along the thumb of this right hand whose fingers are curled to tell us the direction of circular motion.

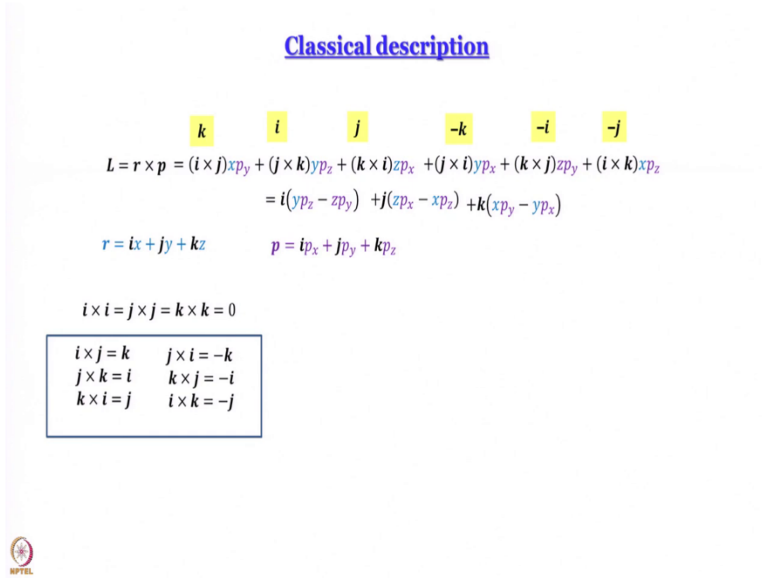
This is of utmost important because angular momentum is what defines rotational kinetic energy and when we talk about rigid rotor for example it is kinetic energy all the way. Remember we had reduced the problem to a one body problem so there is no question of potential energy the it is only kinetic energy that we talk about and that kinetic energy is given by you might remember L square by 2I. So, let us see; what is the quantum mechanical way of talking about angular momentum and also what we learn in this module and maybe the next is see we have been talking about this theta and Phi part of the wave functions.

Phi parts I think we understand very well because we actually solved that equation we did not solve the theta part of the equation. But we said we proved that Lz has this e to the power I M Phi, the Phi part of the wave function as an eigenfunction with an eigenvalue of M h cross, so we said that the z component of the angular momentum of rigid rotor is Mh cross. And then we said that the total angular momentum is h cross square multiplied by a j into j + 1 this is something we are going to use in hydrogen atom also.

What we have not really explained is why is it that there is an upper limit of the values of M why is it that there are 2J + 1 values of M. In this module or maybe the next we will get to learn that and initially I did not think that I will go that far but now I am tempted to also talk about ladder operators in angular momentum. Remember ladder operators in rigid rotor similarly we can talk about ladder operators here also.

And I am tempted to go a little further and talk a little more about energies and wave functions. Let us see whether we get there but at least by the end of this discussion we will get to know why there is an upper cap of the values of M. And also we will get to encounter a very, very important phenomenon in quantum mechanics which involves operators that commute with each other. What is the meaning of community I guess you know but in any case we are going to talk about it.

(Refer Slide Time: 03:55)



So, here course let us start at the very beginning and since I have got a feedback from many of our potential students that they would like to have things done from scratch as far as possible. We will start at the very beginning here we will talk about the classical description, the classical definition of angular momentum. As you know angular momentum is defined as the cross product of r and p, L is equal to r cross p what is the meaning of cross product?

Magnitude of a well first of all cross product is a vector product right magnitude is given by r well magnitude of the two vectors multiplied by each other multiplied by sine theta and what about direction that we have already talked about direction of the angular momentum vector. Here what we will do is we will work with the components. So, we can write like this that x the position we can write as I multiplied by x well our sorry r the position r is the position vector right.

So length of the position vector is given by i multiplied by x + j multiplied by y + k multiplied by z perhaps I do not have to explain to you what ijk are or I still will i is a unit vector along x axis j is unit vector along y axis k is unit vector along z axis and xyz are the magnitudes of the xyz coordinates of the point we are talking about in the first place. I hope that is clear similarly p is defined as I into px + j into py + k into pz.

Please remember these are vector sums ijk are vectors that is why I written them in bold and daleks and px py pz are the xyz components of momentum linear momentum xyz are xyz components of the position you can say. So, these are vector sums please do not forget. Now when I take a cross product between r and p what I really have to do is I have to take a cross product between this and this ix + jy + kz and i px + jp y + kp z while doing that how many times will I get well 3 into 3 9 terms.

Let us take them in groups first of all what you see here is the i cross I, j cross j, k cross k 3 terms the cross products of the same vectors same unit vectors. So, ix cross ipx gives you i cross i x px similarly j y cross jpy gives you j cross j ypy, kz cross kpz would give you k cross k jpz. So, what i cross I, j cross j are we will come to that shortly and I am hoping that most of you know anyway still in case you have forgotten or in case you have not come across this will do it.

What will the next term be? Next time what we can do is you can take an alphabetical order i cross j, j cross k, k cross I so I cross j term what will it be ix cross p y + jy well j cross k will be multiplied by yp said so sorry I will say that again ix cross jp y will be i cross j multiplied by x dot py remember x and py are just magnitudes. The direction is given by the direction of the unit

vectors i, j and k. So, then kz cross kpz would well sorry i cross j, j cross k and k cross i.

So kz cross i px would be k cross i multiplied by zp x this is what it is sorry for the overlap it was not like this but anyway I sorry about that i cross j multiplied by x py + j cross k multiplied by y pz + k cross i multiplied by zpx. So, we have got 6 terms out of the 9 that we promised would be there what would the last chance we can take the reverse order alphabetically. We have taken i cross j, now let us do j cross i.

We have taken k cross I now let us take k cross j and let us take i cross k, so this is what will get jy cross ipx that gives you j cross i, ypx then kz cross jpy gives you k cross j multiplied by zpy why am I saying j again and again kz cross jpy gives us k cross j zpy. And finally ix cross kpz gives us i cross k xz right these are our 9 terms fortunately not all 9 terms exist. I am sure most of you would know that cross product of same vector is actually 0, sine theta remember.

I said that magnitude contains sine theta and of course the angle between i and i is 0 so sine 0 is 0. So, i cross i is equal to j cross j is equal to k cross k is equal to 0. So, these first three terms in i cross I, j cross j and k cross k these are going to become 0 and therefore vanish. We are left with 6 terms i cross j xpy + j cross k ypz + k cross i is sorry about this plus j cross y ypx + k cross j zpy + i cross k xpz. Maybe I will just correct this for you otherwise it is too difficult to see that is much better.

So I have i cross j x py + j cross k yp z + k cross y zp x + j cross iI ypx + k cross j zpy + i cross k x pz 6 terms. Now we need to know what is i cross j what is j cross k so on and so forth and that is also very well known these are unit vectors remember. So, unit vector means magnitude is 1 and ijk are perpendicular to each other. So, when you take cross products of say i and j you get the third one i cross j is k j cross k is I, k cross i is j when you take them in the right correct cyclic order.

If you take them in reverse cyclic order instead of I crossly you write j cross i it just becomes minus k xyz it becomes minus said something like that k cross j is minus i and i cross k is minus j these are very standard things that one learns while studying the chapter on vector in high secondary mathematics. Good so let us start substituting the first term we have is i cross j instead of i cross j will write k second one is say cross k what is j cross k is a cross case obviously i is very simple I mean you just write the third one if it is incorrect cyclic order you write plus sign. If it is in reverse cyclic order you write minus sign.

So j cross k is going to be i, k cross i that it is a click order is going to be j, now j cross i is reverse cyclic order write in alphabet i comes before j so you are going to get minus k, k cross j similarly is minus i and i cross k is similarly minus j. So, now what we can do is we can collect the terms in i and j and k and we can get instead of 6 terms we can get 3 terms. So, if I collect the terms in I what do I get i multiplied by ypz minus zpy is not it, j multiplied by zpx minus xpz and k multiplied by x py minus ypx right.

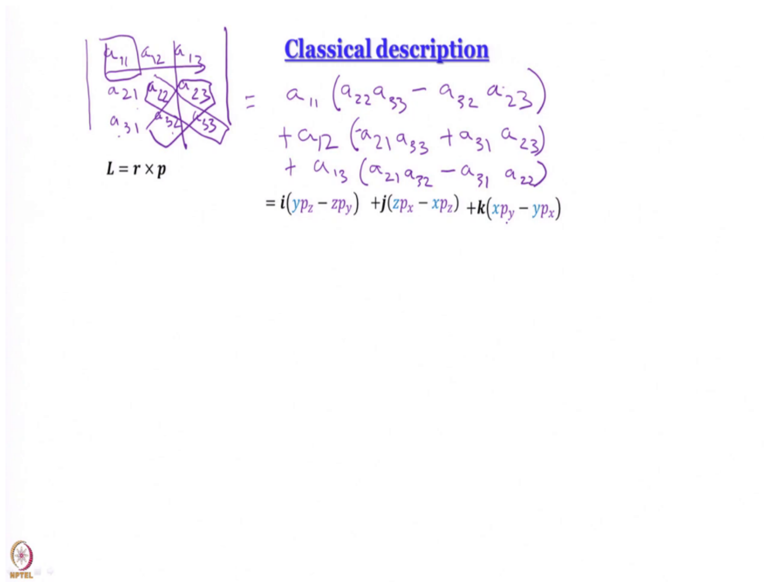
So i into ypz minus zpy j into zpx minus xpz and k into py minus ypx what I really need you to do is please make sure you have a pen and paper in your hand when you attend these modules you should keep writing that way you understand better. If you just look at the screen you may get it may not get it. Of course the advantages is that you can pause me and you can write do it no problem. But please write when you are hearing otherwise it is then it will register better the more senses we use while studying made a real prospect that is already well-known phenomena.

So remember this i multiplied by ypz minus zpy + j multiplied by zp x minus explicit plus k multiplied by x py minus ypx alright. So, now see what is this? That right hand side is an expression for angular momentum. So, obviously whatever is multiplying i is the x component of angular momentum whatever is multiplying j is y component of angular momentum whatever is multiplying k is z component of angular momentum.

So we can write Lx is equal to ypz minus zpy very nice right ypz minus zpy and what is that equal to Lx. So, you can think like this if think of three random variables I cannot use ijk and I cannot use xyz so maybe we will say pqr, this pqr so p is also there so we cannot use let me say 1 2 3 that is better. So, you can think like this when you talk about the components L1 is equal to i into 2p3 - 3p2 + j into 3p1 well sorry Ly so that is your x component right L1 is equal to well that holds for everything actually.

L1 equal to 2 multiplied by p3 - 3p2 this is a general way of writing your xy and z components of angular momentum ok.

(Refer Slide Time: 15:28)



So, let us write that this is what we have one way in which we can express very nicely and we are going to come across this tool in some other context also is determinants. I hope we all know what determinants are if not please brush up it is just ways of writing sounds like this. In a determinant what you have is if you have something like and just write once in case somebody needs to know how a determinant is written I will just write it once.

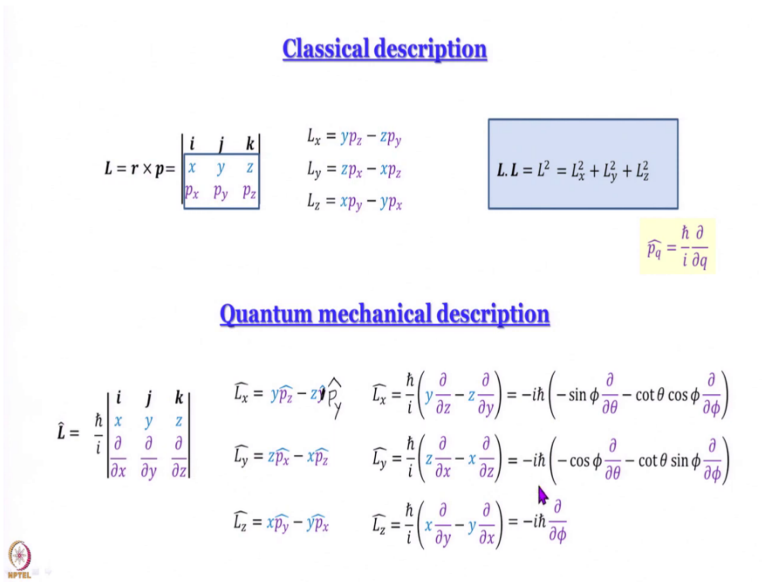
This is a determinant you write like this say a11 a12 a13 a21 a22 a23 a31 a32 a33 this can be anything we will just see an example of a determinant that is useful for us ok but this is what I determinant is and what it means essentially is you take a11 multiplied by this a22 into a33 - a32 into a23 a32 into a23 so this determinant will be a11 into a22 into a33 minus a32 into a23 then next term is in a12 but a12 the second term has a minus sign.

So you can write a minus a12 multiply it by again a21 a3 so what you do is you are leaving out this column and this row whatever is left in that block you take cross-product and subtract the other diagonal product. So, a12 is in is in the first row and second column say leave out those multiplied by you can write a21 multiplied by a33 - a31 a23 or if we want to write plus then all that happens is this it will become plus and this will become minus.

Then again + a13, a13 is first row and third column so leave those out it will be a21 into a32 - a31 into a22 a21 a32 - a31 a22 ok so this is our determinant is written and if you now compare this what I have written here by hand with what I have here you can correlate write a11 in this case is i a22 is y a33 is pz, a32 is z, a23 is py, a12 is j a21 is z px, a33 sorry a21 is z a33 is px sorry this is there is a minus sign here.

So this has to come here so a21 is actually x and so this way you can and just correlate with this and we will just write it in the determinant form before that let me erase this.

(Refer Slide Time: 19:28)



Now let us show you the determinant here this is what it is so ijk xyz pxp ypz very nice right. The way we have written it is that the first row is just the unit vectors along x y and z. The second row is the xyz coordinates right position third one third row is px py and pz the components of angular momentum along xy and z. So, very nice systematic way if you go from left to right you go from x direction to y direction to z direction.

If you go from top to bottom you go from the unit vector to position to momentum it is very nice systematic way of writing it and this is how it expands ypz minus zpy j into zpx minus xpz remember j had a minus sign so that has gone in plus k into xpy minus ypx this is what the determinant is. Now we know the x y and z components already these are the x y and z components. The other quantity that is very important is L square, square of angular momentum and you will appreciate it even more when we go into quantum mechanical description.

That is given by L x square + L y square + L z square I hope I will not work this out explicitly because I worked out the other one you can do it yourself. But remember when you try to do l dot L that is a dot product first of all so it will be a scalar product no direction but then you have to take i into L x + i is j into L y + k into L z take dot product of that with itself while doing that you have to remember that i dot i is equal to j dot j is equal to k dot k is equal to 1.

And i dot j is equal to j dot k is equal to k dot i is equal to the same thing written in the other direction is equal to 0 because dot product has cos theta in the expression. So, if angle between the 2 vectors is 90 degrees then of course you are going to get 0. So, that is how we get L x square + L y square + L z square it is important to understand that this is a scalar quantity not a vector quantity and L x, L y, L z are the components of angular momentum which itself is a vector quantity.

So this is the classical description of angular momentum. Now let us just build the quantum-mechanical description and then we will end this module we will go to the next module for the next part. So, the quantum-mechanical description is as you know we start from the classical definition and what we do is for every variable every observable that is there we replace it by the corresponding operator right.

So if you want to write this matrix what do we have to do we have to replace x by the position operator x which is just multiplying it by itself you have to replace px by the momentum operator px hat. So, these are the two rows in which this matrix is going to wear sorry this determinant is going to look different but mean the same when we try and build a quantum mechanical description.

While doing that x hat is very simple remember pq hat by q can be x or y or z is h cross by i del del q or you can write minus ih cross del del q in the later part we actually used that minus ih cross it means the same it is no big deal do not forget. The way I remember it is that where if i is in the denominator then it is positive if i is in the numerator then it is negative h cross always is in the numerator of course.

Now with that let us try to build try to write a similar determinant for the L hat operator the angular momentum operator. What will it be will be something like this first row remains the same ijk second row also remains the same. In the third row you are going to have h cross by i del del x h cross by i del del y h cross by i del del z so you might as well take the constant h cross by i outside the determinant because the determinant multiplied by a constant is what you get and then the x component very similar to what you have there instead of pz you write pz hat that is all.

Instead of I made a mistake here sorry about that this is not zy hat it is zpy hat of course it is obvious but it is a typo let us see if I have repeated the typo later I have not L y is equal to L y hat is equal to z we x hat minus xpz hat please do not forget that this is actually py hat is a typo here maybe I will just write it with my pen. So, this one I will cut and I will write py hat for now good L z hat is xpy hat minus ypx hat these are the operators for L x and L y and LZ components and these operators are extremely useful you keep on using them in many situations later on.

So L x you can write like this instead of pz hat you write this del del z and this is similar now what is what about L square operator? L square operator for that you have to simply substitute this by L x square L y square L z square and that will come from these L x operators so I am not working it out explicitly we will do it whenever required but please remember that we have to build an operator for L x square L xl square also in fact that is the most useful operator.

I am not doing it because we are not going to use the Cartesian form we are going to use the spherical polar coordinate form. Remember your rigid rotor problem or any problem where rotation is involved angular momentum means rotation some sort of rotation would be there, notionally yes. Even though for hydrogen atom we say that we cannot talk about rotation but still angular momentum is there same for spin.

But will cross those bridges when we come to them. But what I am saying is this L square operator is actually of most importance that is what we work with. And we always use this spherical polar coordinate form which we do not have to remember we will give it to you but since we are talking about spherical polar coordinates form it makes perfect sense to show you what these L x hat L y hat and L z hat operators are for in the spherical polar coordinates.

This minus ih cross multiplied by minus sine Phi del del theta minus cot theta cos Phi del del Phi this is L x hat operator sometimes I make mistakes in writing these expressions. So, please the cross-check with the book this part you can study from Pilar's book but I have followed Macquarie not Macquarie and Simon physical chemistry, Macquarie quantum chemistry book or Prasad or any book that you are comfortable with.

But please double check and make sure that whatever is there is correct it should not be that I make a mistake while typing here and then I do not notice it and you learn the wrong expression that should not be the case. This is L x hat next we have L y hat very similar instead of sine we have cos instead of cos we have sine. L z hat fortunately is very simple ih cross del del Phi. Why yz hat is so simple because remember what is Phi?

We have talked about this by talking about rigid rotor changing Phi essentially means circular motion in the xy plane. So, the associated angular momentum has to be in z direction. So, that is L z hat and it makes perfect sense it you can correlate it you can correlate say L z hat the angular momentum operator in z direction with the linear momentum operator also they are very similar is not it.

This is h cross by i or minus ih cross del del q you can even write this as h cross by i del del q if you write q equal to Phi very similar. What linear momentum is in a linear motion angular momentum is in circular motion it is very important to get this correlation right. And sometimes students ask this question how do I know how do I know which is x-axis which is y axis which is z axis? And the honest answer to that is that we do not we define one direction as said.

If we have an external perturbation like if we apply an external field electric field or magnetic field then of course we define that to be z axis, why, because then we have to deal with an easier operator ok. So, it is of course in our hands but you see that will always work with the z direction because it is easier to handle ok. Maybe we will stop this module here and continue from here in the next module.