Quantum Chemistry of Atoms and Molecules
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Lecture-13
Harmonic Oscillator: Part 2

All right we are back and we are about to embark on a rather interesting journey remember in the next module last module we had talked about ladder operators for simple harmonic oscillator quantum harmonic oscillator we are going to in this module learn what ladder operators are and we will end the module at a point where we just see why ladder operators are so interesting.

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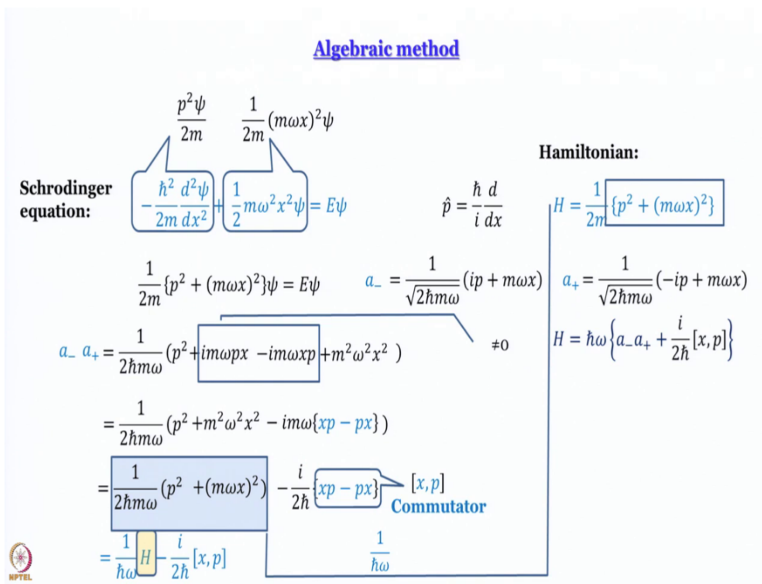

But let us quickly recap what we have done in the last module for a simple harmonic well for a quantum harmonic oscillator we have written Schrodinger equation minus h cross square by 2 m d 2 Psi dx 2 + 1/2 m Omega square x square Psi equal to E Psi. Then we have rewritten the first term on the left hand side in terms of the momentum operator linear momentum for motion along x operator h cross i by d dx and that has become p Square Psi by 2m.

And then for further simplification we have rewritten the second term as 1 by 2 m into square of m Omega x operating on Psi that is equal to E Psi so this is the modified Schrodinger equation we got 1 by 2 m p Square + m Omega x whole square whole thing operating on Psi gives us E Psi and then we said that the Hamiltonian is 1 by 2 m p square + square of m Omega x what we are really trying to do now is that we are trying to write the Hamiltonian in terms of some new operators we are trying to construct some new operators which will make evaluation of the Hamiltonian very, very simple and these are the ladder operators that is where we are headed.

And we have already defined the ladder operators a minus is 1 by root over 2 h cross m Omega multiplied by ip + m Omega x this whole thing is a minus operator remember we are not writing hat explicitly but please do not get confused about which one is an operator and which one is just a number or something a minus is this a plus is 1 by root over 2 h cross am omega x – ip + m Omega x this a minus and a plus as we will see are really the ladder operators.

And why this is minus why this is plus we will see later what we are trying to do now is that we got it we were we started working with this because in the Hamiltonian if these were numbers this is an e square + u square + v square kind of quantity that could have been just a simply product of this u + v + - u + v well iu + v + - iu + v kind of quantities okay if then if these were numbers p and m Omega x then just by multiplying them together I would have got it, I would have got the Hamiltonian.

But obviously we would not because these are not numbers it involves position and momentum operators. So, let us see what we get so essentially what we will do is we are going to express the Hamiltonian in terms of these operators a minus and a plus ladder operators and we will see why they are called ladder operators of all things. Okay as we said when we close the last module we are going to work out a minus a plus.

And I would like you to work out a plus a minus after this module here go. So, if you want to work out a minus a plus what do we get? First of all the easiest thing to work out with to work with is this coefficient so let us take that out one by square root of 2 h cross m Omega multiplied by itself gives us 1 by 2 h cross m Omega the square root sign just goes. And inside the bracket first term is ip dot - ip so i into i is minus 1 and there is a minus 1 already so that becomes plus 1 p dot p is written as p Square.

And the sake of boring you let me repeat once again p is an operator and not a number p Square is an operator and not a number great I think we have said it enough number of times now let us go ahead. The first one is p Square next what do we get we can work with this i ip and this m Omega x will get i m Omega p x this ordering is important ok in the next one we will see but let us get done with this m Omega x dot m Omega x thing first.

What do we get there, m square Omega square x square again remember x is really an operator what is left? What is left is m Omega x dot minus ip in that what we get is minus i m Omega x p okay so inside the bracket what we have got is p Square + im Omega px - im Omega x p + m square Omega square x square that is your a minus a plus. Now if p and x were numbers then this im Omega p x - im Omega x p would have been 0 but well I am breaking a promise now I have said it again these are not numbers these are operators as we have said time and again.

So this is not really equal to 0 as well see ok so what is it, we will see. But first let us tidy up a little bit that a Psi a minus a plus as 1 by 2 h cross m Omega multiplied by p Square + m square Omega square x square do you see a pattern emerging here do you see something is this looking like something that is already there on the slide well keep looking we will come back to it but let us write this - im Omega is common of course you could have taken +im Omega common as well.

But this is our Griffith has done it so I want to stick to it - im Omega is common and you are left with xp – px. Now xp - px for operators is called a commutator. We will come back to that before that let me just say this the first term that we get 1 by 2 h cross m Omega p Square + square of m Omega x square of m Omega x I hope you have already spotted elsewhere on this slide if not just wait a little bit. Second term will be -i divided by 2 h cross m Omega in the numerator m Omega in the denominator just cancel and you are left with - i by 2 h cross x p - p x.

Now see what is the first term is not it something that is closely related with the Hamiltonian yeah let us multiply this Hamiltonian 1 by 2 m p Square + square of m Omega x by 1 by h cross Omega and you get what you have on the left hand side already so a minus a plus is equal to the first term is going to be 1 by h cross Omega h remember what we are trying to do is we are trying to express a Hamiltonian in terms of ladder operators, we are already; we have already made some progress in that ok.

Now the second xp - px as I told you is called the commutator and in the language of quantum mechanics it is written as x, p with in third brackets ok I mean you can do it for any pair of operators say operator a operator b a, b in third brackets basically means ab - ba and here again please do not forget that the sequence is important commutator of a and b has the opposite sign of commutator of b and a okay sequence is important.

If you write x, p in third bracket that will have negative sign compared to that of p, x in third bracket okay so this is a commutator we are going to write it as this x, p in third bracket and we are going to now on just read it as the commutator of x and p so this is your Schrodinger equation 1 by h cross well not Schrodinger equation sorry this is your product a minus a plus 1 by h cross Omega h - i by 2 h cross multiplied by commutator of x and p the advantage of this is that the value of commutator of x and p is actually worked out already and we are going to work it out anyway in the next part of the discussion.

So once you have that you get a convenient notation a convenient way of writing the Hamiltonian. So, Hamiltonian h then becomes just rearrange this h cross Omega multiplied by a minus a plus I am just rearranging this equation making the Hamiltonian h the subject of formula h cross Omega multiplied by a - a + i by 2 h cross multiplied by commutator of x and p.

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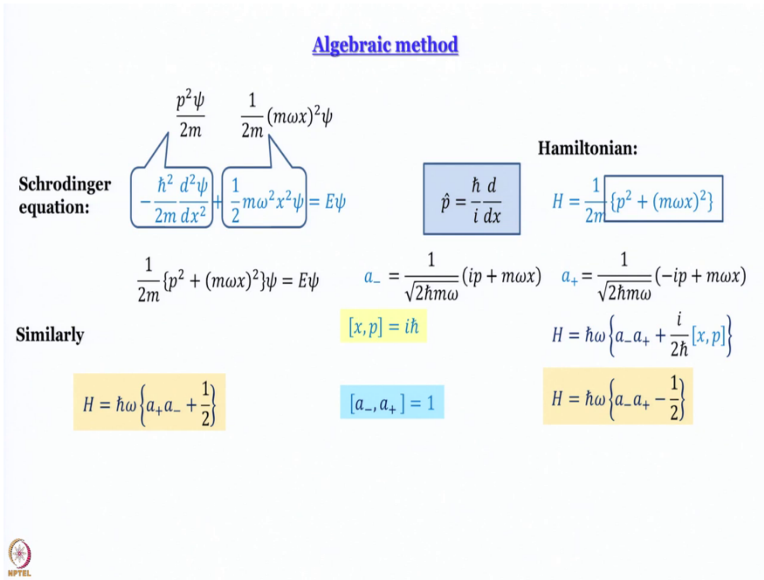

So, what would be the next step? The next step would be to work out the value of the commutator of position and momentum operator's right. There is to that, now let us not forget that these are operators and to work with operators they must operate on some function right I mean there was this joke that somebody was asked to work out sine x by x and the cancel x and x and were left with sine so in of course that makes no sense right sine has to operate on something. Here also the commutator of x and p itself is a function and must be able to operate on some function.

Let us take a generic general function fx and let us see what happens when the commutator operates on fx while doing that let us not forget that the momentum operator is h cross by i d dx we are going to use it let us do it. So, what will it be first we have x dot p operating on Psi p operating on fx so it is x dot h cross by i df x dx so in this term what I have done is p has operated on fx p operator h cross i h cross by i d dx and then it is left multiplied by x operation of x is just multiplication by the position file.

That gives us a first term what happens in the second term its opposite right it is minus px so will be something like this minus h cross by i d dx operating on now the product of x and f, f of x okay I hope this is clear to everybody. Commutator of x and p operating on fx gives us x dot h cross by I d fx dx minus h cross by i d dx of the product of x and f of x. Of course you know very well what you do when you have to differentiate a product yeah d dx of uv is equal to u dv dx plus v du dx let us do that first time remains same.

Second term first I can take x out and I can write minus h cross by i x multiplied by d dx of f of x second one will be f of x will come out so I get minus h cross by I f of x d dx of x right. Now see things have become simpler why because these two terms cancel each other the first one is h cross x of i df of x dx minus h cross x by i d f of x dx so this is 0 and also in the second term I will in the third term actually d dx of x what is d dx of x and that is the easiest question one could ask me dx of x is obviously 1.

So these first two terms give you 0 in the second term this factor becomes 1 so you are left with minus h cross by i f of x right. So, the commutator of x and p operating on fx gives us minus h cross by I fx eigen value equation. So, what is the value of the commutator of xn p the value is minus h cross by i or I have written it in another form ih cross this is a very fundamental relationship that comes handy in many applications of quantum mechanics here we are just worked it out.

And we will see how this makes the subsequent treatment extremely simple and useful. So, commutator of x and p equal to ih cross what will do it what will do is that we are going to take this and we are going to plug it into the expression for Hamiltonian that we have worked out earlier Hamiltonian is h cross Omega x remember a minus a plus plus i by 2 h cross multiplied by the commutator.

Now instead of this commutator I am going to write ih cross ok let us do it so we get h Hamiltonian is equal to h cross Omega multiplied by a minus a plus minus 1/2, the minus half okay let us check in so this will write ih cross i into i is minus 1 h cross in the numerator and h cross in the denominator cancel each other left with 2 in the denominator so -1 by 2 it is so simple the Hamiltonian simply becomes h cross Omega a minus a plus minus 1/2 right.

So we have been able to write the Hamiltonian in terms of ladder operators and it has taken a rather simple form. Now remember your homework is you have to work out a plus a minus please do it and please work out the relationship between Hamiltonian and a plus a minus you see that you get a very similar expression instead of minus 1 you get plus 1 here. Hamiltonian can also be written as h cross Omega multiplied by a plus a minus plus 1/2 ok.

So this is something that I would like you to work out by yourself another point that I will just give you the result and you should be able to work out now that we have discussed the commutation of x and p is the commutation of a minus and a plus. See here you can take the Hamiltonians yeah and you can make the Hamiltonian operator on some function. Whatever you get there should be equal to each other.

Now instead of the Hamiltonian take these expressions and from there you will get a relationship between a plus and a minus a plus a minus and a minus a plus that will give you the commutator of a minus and a plus. It will; you will see that the commutator of a minus and a plus turns out to be 1, once again I will not work it out because it is going to become repetitive but I request you to do it there is any doubt please post on the forum we will work it out for you whenever we have the live session if required.

But it is important that you do things by yourselves okay otherwise I go on saying something and you go on listening it will not sync in you understand it only when you write things. So, I of course are not and it plunge you into water but what I will do throughout the courses I will solve part of it and whenever there is something that is repetitive I will request you to do it yourself okay that is how it will work great.

So we have some interesting relationships in hand we have expressions of Hamiltonian in terms of the ladder operators and we have this commutation relation of ladder operator also that the commutator of a minus and a plus equal to 1. What we are not convinced to you so far yet is why is it that these are called ladder operators of all things let us see if we can come to that shortly. So, for now what we can also do is we can write the Hamiltonian is the same thing right.

We can write it in the general form h cross Omega a plus minus a minus plus a plus minus 1 by 2 which means if you take the top ones you get h cross Omega a plus a minus plus half if you take the bottom ones you get a minus a plus minus half okay just written that these two together. So this is what we have got so far.

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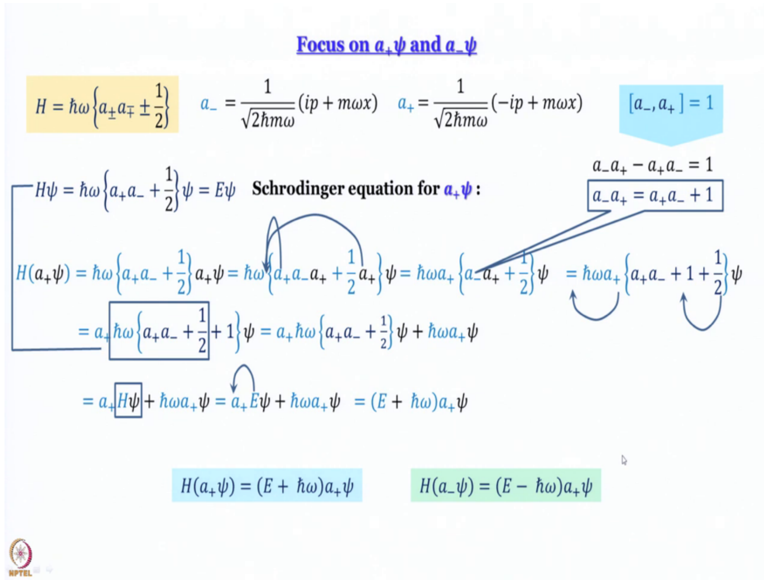

Now let us try to see what happens when a plus operates on Psi and I will ask you to work out what happens when a minus operates on Psi okay and when we do that then we will finally understand why these are called ladder operators here of course. We know each Psi let us take one I mean we can take either of the 2 I just take this it is i equal to h cross Omega multiplied by a plus a minus plus half operating on Psi that will give us E Psi what is E? E is the energy corresponding to the wave functions Psi.

Now what we want to do is we want to write a similar Schrodinger equation not for Psi but for a plus Psi see a plus is an operator right so in this operator operates on Psi a function it will give us some other function okay whether it is an eigen function whether it is not an eigen function will see that it will give a function right. So, we want to write Schrodinger equation for this function a plus Psi and it will unfold in front of our eyes whether a plus Psi is also an eigen function of Hamiltonian or not, let us proceed.

So what we will do is in this Schrodinger equation which instead of Psi we just write a plus Psi left hand Psi so here h cross Omega a plus a minus plus half instead of Psi I have written a plus Psi. What will the right hand side be it will not be E Psi it will be something like E dash multiplied by a + Psi if it is an eigen value equation some other energy will be there corresponding to the a plus sign wave function is it there does it still remain eigen value equation we will see, let us proceed.

So what we can do is we can just take this a plus inside the bracket yeah the associativity is still there is not it so we can just take it so it becomes h cross omega then inside bracket a plus a minus a plus plus half a plus this whole thing operates on Psi then what do you get what we are doing now is simple mathematical manipulation when you do a lot of it then the logic sort of comes to you naturally, for now just bear with me.

So what we do is that we like to things common and we will take this a plus outside the bracket remember I cannot take this a plus I have to take the one that is on the left. In the second term that question does not arise there is only one Operator in the first time however you have to be careful because you have a plus a minus a plus I am taking this first a plus on the left outside when I do that I get h cross Omega a plus operates on a minus a plus plus half operating on Psi right.

Now I do not like a minus a plus at the moment why, because you see look at this a minus a plus plus half and look at the Hamiltonian, what we have inside the Hamiltonian is a plus well a plus a minus plus Psi if I want to take a minus a plus then it would better be minus okay. So, what I try to do is I try to somehow find a way of replacing this a minus a plus by a plus a minus if I can. And to do that we will use this commutation relation.

The commutator of a minus and a plus is one this is something that I have asked you to work out yourself. Okay so let us expand this a little bit what it means is a minus a plus minus a plus a minus is equal to 1 or a minus a plus is a plus a minus plus 1. Next step should be very obvious I will take this and I plug it in there why am I doing this in order to get an expression like that of the Hamiltonian. So, I get h cross Omega a plus and inside the bracket I get a plus a minus plus one plus 1/2 Psi.

So I move the 1/2 first so that I have a plus a minus plus half very much like what is there in the Hamiltonian and then we will see what to do with this one. And we can take this a plus in front as well because h cross Omega will be a number anyway so write like this a plus operating on h cross Omega a plus a minus plus half plus one Psi. Why did I take a plus in front because h cross Omega into a plus a minus plus half is Hamiltonian here right that is the Hamiltonian.

So we write like this which is a break into two terms first one is a plus h cross Omega multiplied by a plus a minus plus half operating on Psi so this is a Hamiltonian plus h cross Omega a plus Psi we are nearing our answer. Now see I think you will agree with me if I write a plus h Psi because as we said many times h cross Omega multiplied by a plus a minus plus half is simply the Hamiltonian h second term is h cross Omega a plus Psi.

What is h Psi from Schrodinger equation h Psi is equal to E Psi yeah so instead of this h Psi I am going to write E Psi so I will get a plus operating on E Psi, E remember is a number is the eigen value of the Hamiltonian E Psi plus h cross Omega a plus Psi we are almost there. Now let me move E to the front with this rewrite because it is a number whether you write inside the operator if you write outside does not matter you are working with linear operators here.

So we get E and here also h cross Omega multiplied by a plus Psi when he goes out what do I get E multiplied by a plus Psi second term is h cross Omega multiplied by a plus Psi. So, I can take this in bracket and right E + h cross Omega multiplied by a plus Psi okay. So, what is the final equation left hand Psi was h operating on a plus Psi right hand Psi has become e + h cross Omega multiplied by a plus Psi remember a plus Psi is a function okay.

Let us call it Psi dash so we got we get is h operating on Psi dash gives us the same Psi dash a plus I back multiplied by this time E plus h cross Omega this is a beautiful result yeah eigen value equation and the eigen value is the energy of the earlier wave function Psi + h cross Omega remember what h cross Omega is we said it in the previous module h cross Omega is a quantum of vibrational energy okay.

So what has happened through all this mathematical manipulation is this when we make a plus operator operate on Psi I generate another wave function whose energy is more than the wave function of the original Psi by one quantum of vibrational wave function that is why it is called a step up ladder operator. Similarly now I ask you to work this out yourself please convince yourself that when h E minus Psi is also equal to E minus h cross Omega a plus Psi.

So when a minus of sorry sorry this is a printing mistake h operates on a minus Psi to give us E minus h cross Omega a minus Psi okay is a peril of copy and paste is copy pasted and forgot to change plus to minus please correct it yourself.

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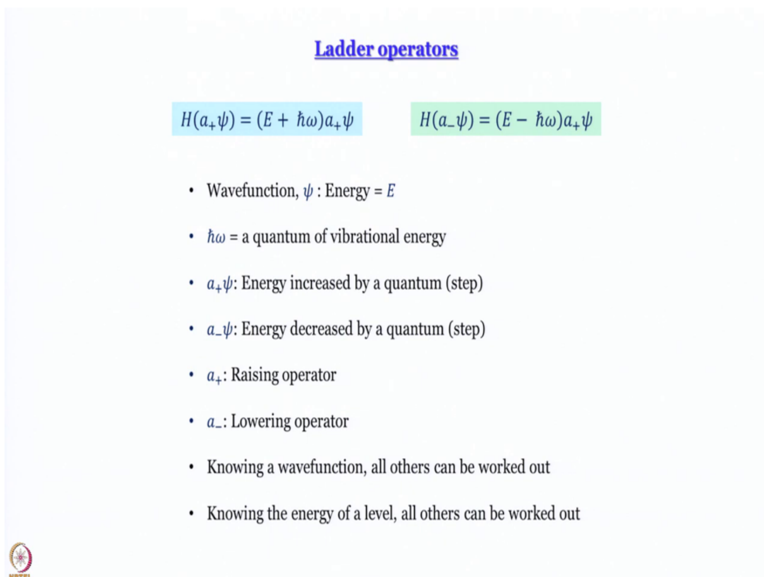

But let us go ahead and now conclude this discussion on ladder operators. Using the ladder operators a minus and a plus we have got these 2 Schrodinger equations. So, we start with a wave function Psi of energy E and remembering that h cross Omega is a quantum of vibrational energy when a plus operates on Psi energy well you produces a new wave function whose energy is more than the energy of the original wave function by a quantum or a step.

When a minus operates on Psi it produces a wave function that is lower in energy by a step by a quantum okay so a plus is like climbing the energy ladder it is called the raising operator a minus is like going down the energy ladder is called the lowering operator. What does this ladder look like remember equispaced energies energy levels equispaced rungs. So, this a plus and a minus can take you up or take you down this energy ladder of the simple harmonic oscillator that is why they are called ladder operators.

And the great thing about ladder operators is this suppose you know one wave function using this ladder operator you can generate the next one in higher or lower order of energy. Similarly if you know one energy you can work out the energies of the higher and lower end you can keep going until you have worked out as many energies as you can as you want. So, this is why ladder operators are great and they are used in many other applications not just your harmonic oscillator.

But this is where we get introduced to this fantastic tool of quantum mechanics. So, we stop here today but please remember in the last two modules we have really embarked upon something very new and very profound. It is extremely important that we are up-to-date with these concepts so that next day in the next module when we come back and when we actually work try to work out the wave functions and the energies and we try to answer that question that we asked why is it that there is a nonzero minimum allowed value of energy what is the value we already answered why you will see that we can do all that using ladder operators, until then.