

Quantum Chemistry of Atoms and Molecules
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Lecture-17
Harmonic Oscillators: Conclusions

We are going through a little tedious but so far not very difficult treatment of trying to find an analytic solution for Schrodinger equation of a harmonic oscillator by using the power series method. This is where we have stopped in the last just module you just do a quick recap.

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Wavefunctions from Recursion formula

Recursion formula: $a_{j+2} = \frac{2j+1-K}{(j+1)(j+2)} a_j$

Generate even numbered coefficients from a_0 ,
 odd numbered coefficients from a_1

$$a_{j+2} = \frac{2(j-v)}{(j+1)(j+2)} a_j$$

$a_{j+2} = 0$ for $j = v$

$$K = \frac{2E}{\hbar\omega}$$

K is energy, in units of $\frac{\hbar\omega}{2}$

$$\xi = \sqrt{\frac{m\omega}{\hbar}} x$$

$\psi = h(\xi) e^{-\xi^2/2}$

$h(\xi) = a_0 + a_1\xi + a_2\xi^2 + \dots = \sum_{j=0}^{\infty} a_j \xi^j$

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega$$

$$K = 2v + 1$$

$v = 0, 1, 2, \dots$

- $j_{max} = v$: Essential for normalizability
- Since $j_{max} = v, a_{v+3} = 0 \Rightarrow a_{v+1} = 0 \Rightarrow a_{v-1} = 0 \dots$
- Depending on the vibrational quantum number, either odd or even numbered amplitudes are zero

Odd v : $h(\xi) = a_1\xi + a_3\xi^3 + \dots + a_v\xi^v$ Even v : $h(\xi) = a_0 + a_2\xi^2 + \dots + a_v\xi^v$

What are you doing is a proposing the solution of $h(\xi)$ please do not forget where is $h(\xi)$ come from or where ξ come from? ξ simply Root over $m\omega$ by \hbar cross multiplied by x . Wave function is h which is the function of Ω sorry function of ξ multiplied by e to the power ξ^2 by 2 now what we are trying to do is, we are trying to find out what this h of ξ is? If you remember for very large values of ξ is a constant.

But for all values of ξ what is the general expression? Know that we are expressed as a power series h of ξ is sum over j equal to 0 to infinity $a_j \xi^j$ to the power j . And then what we have done is, we have written this recursion formula a_{j+2} in terms of a_j then we have put in $j - v$ hence we have proved that j_{max} is equal to v , you cannot have a j value what is j value? j is the

number of terms in the summation of h of X_i . So in the most general form is an infinite sum what you are saying is actually it is a finite sum. You do not need to go beyond the v term which means suppose v equal to 0 then 0th term is enough does not means no term.

0th term means for j equal to 0 what will it be right X_i to the power j will be 0 X_i to power j will be 1 and you will be left with a 0. Suppose you have v equal to 5 that means you have to sum from j equal to 0 1 2 3 4 5 that is enough you do not have to go to j equal to 532097 that is what is the meaning of j max equal to v . Then we said that now the thing is, these recursion formulae connect alternate amplitudes.

So depending on whether j is even or odd all amplitudes for odd or even terms respectively are going to be 0 because you are not going be able to access that. That is what we say in this line. So, what we are been able to do is, we have been able to write instead of one, two separate series and this time terminated series for the function h of X_i . For odd values of v , h of X_i is equal to a 1 multiplied by X_i + a 3 multiplied by X_i cube + a 5 multiplied by i to the power 5 so on and so forth.

The last term is a v multiplied by X_i to the power v . For even values of v we have h of X_i equal to a 0 + a 2 multiplied by X_i square + a 4 multiplied by X_i to the power 4 so on and so forth last once again is a v multiplied by X_i to the power v . So we have 2 series, 2 kinds of functions. One for odd and one for even.

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Hermite polynomials

Recursion formula: $a_{j+2} = \frac{2j+1-K}{(j+1)(j+2)} a_j$

Odd v: $h(\xi) = a_1\xi + a_3\xi^3 + \dots + a_v\xi^v$
Even v: $h(\xi) = a_0 + a_2\xi^2 + \dots + a_v\xi^v$

$h(\xi) = a_0 + a_1\xi + a_2\xi^2 + \dots = \sum_{j=0}^{\infty} a_j\xi^j$

$E_v = \left(v + \frac{1}{2}\right) \hbar\omega \quad v = 0, 1, 2, \dots$

$K = \frac{2E}{\hbar\omega}$ K is energy, in units of $\frac{\hbar\omega}{2}$

$\xi = \sqrt{\frac{m\omega}{\hbar}} x$

$\psi = h(\xi) e^{-\xi^2/2}$

v	H_v
0	1
1	2ξ
2	$4\xi^2 - 2$
3	$8\xi^3 - 12\xi$
4	$16\xi^4 - 48\xi^2 + 12$
5	$32\xi^5 - 160\xi^3 + 120\xi$

Recursion relation:

$$2\xi \cdot H_v(\xi) = H_{v+1}(\xi) + 2v \cdot H_{v-1}(\xi)$$

Selection rules for spectroscopic transition

https://www.youtube.com/watch?v=g5EKQI_jMDY&list=PL0xYmoa65eCqECeSQJwmKX6D4zibX84&index=13

And now I said earlier even when the harmonic oscillator problem was being worked out using quantum mechanics for the first time the mathematics was already developed for this kind of differential equation that is how science progresses. You do things perhaps without even thinking that in application do it because there and applications often come out eventually. So, it was known that this kind of polynomial is actually are called Hermite polynomials.

So I will show you some examples of Hermite polynomials. These are the Hermite polynomial H_v for v equal to 0 1 2 3 4 and 5 see what you have for v equal to 0 the polynomial is just 1 these are normalized polynomial. For v equal to 1 it is 2ξ . For v equal to 2 note you have something in ξ to the power 0 and something ξ to the power 2. For V equal to 3 there is ξ to the power 0 term you have $- 12 \xi + 8 \xi$ cube. So that ξ square and ξ to the power cube are missing.

Similarly for v equal to 4 you have ξ to the power 4, ξ to the power 2, ξ to the power 0 and it goes off. So, these are the Hermite polynomials, how do you find a wave function by multiplying each Hermite polynomial by this common Gaussian function e to the power $-\xi$ square by 2. Using Hermite polynomial has advantages in fact at even if you cannot prove it, I will be sure what you can do is, you can at least verify what I am going to right now.

It was known already that Hermite polynomials I have this relationship to each other. We have already discussed one kind of recursion relation here we are something that is related. This is

what it is. I have written it a little different from that of the group that of the book. I have written $2 X_i$ multiplied by H_v of X_i is the sum of the Polynomial after $H_v + \text{half } X_i + \text{some constant}$ well, this should be $2v$ I am sorry. I should not be n should be v , $2v$ multiplied by $v - 1$ Hermite polynomial in X_i .

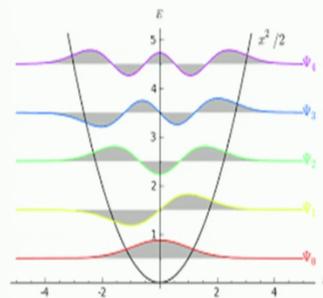
What does this mean? Let us take anything let us take X_i^3 multiply X_i^3 by X_i what do you get? You get term X_i to the power 4 and you get another term in X_i Square. Now look at the polynomial after you have something X_i to the power 4 something in X_i square and you have a constant. Look at the polynomial before; it is $4 X_i^2 - 2$. So what I am saying is that once you multiply any polynomial by X_i what you get is a linear combination of the polynomial before and polynomial after it becomes dimensionally consistent.

This is a very important recursion relation of Hermite polynomials which obviously also relate the vibration wave function. And this is a very handy in deriving the selection rule for Spectroscopy transition for harmonic oscillator. Well selection rule as many of us might know for harmonic oscillator is Δv equal to plus minus 1, you can only jump one step at a time. How that comes; we will not really into it further whoever is interested can see this recorded module and perhaps the module after this which is available on you tube.

This is from our NPTEL on molecular spectroscopy from last semester right. Now we can conclude a discussion on Quantum harmonic oscillator. We have not really done everything. There are certain things that are left but we are going to give some weight as tutorial problem to you, assignment problem to you. But let us summarize what we have learnt.

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Quantum harmonic oscillator: Conclusions



$$E_v = \left(v + \frac{1}{2} \right) \hbar \omega \quad v = 0, 1, 2, \dots$$

Zero point energy

$$\psi_v = N_v H_v(\xi) e^{-\xi^2/2}$$

Recursion relation



First thing we have learnt is that when to use quantum mechanics very naturally vibrational energy of a harmonic oscillator turns out to be quantized? The quantum numbers range from 0 to in principle infinity and the energy of the v th level turns out to $v + \text{half}$ multiplied by h cross Ω which the corollary that a harmonic oscillator and never be at rest its vibration energy can never be exactly equal to 0 because as we said several times already, but let me remind you once again.

Because if it comes to rest then it means that position is the mean position x equal to 0 plus minus 0 and momentum is also 0 plus minus 0. Uncertainty in position, uncertainty in momentum both are equal to 0 uncertainty principal is violated, uncertainty principle cannot be violated right. So, it make sense that Quantum harmonic oscillator can never be seen at rest even at 0 Kelvin the 0 point energy half h cross ω is there.

In fact once again perhaps I will give it you as a assignment, at room temperature for most molecular harmonic oscillators it is the v equal to 0 level that is only occupy, v equal to 1 level is usually not occupied at room temperature because the energy gap is too large. If you use the simple distribution then Boltzmann distribution you see that for energy gap of 1000 cm^{-1} only 8 molecules should reside in v equal to 1 level.

For 1000 molecules when v equal to 0 level so practically at room temperature even v equal to 1 is not occupied forget about v equal to 2 3 and 4 so on and so forth. So, 0 point energy is and fundamental important Concept for Quantum harmonic oscillator. Then we worked out the general expression for wave functions and it is beautiful. It is beautiful because it is a product of a constant Hermite polynomial and Gaussian function.

Gaussian factor ensure that no matter how far X_i you can go to the wave function falls of to 0 and too much beyond the potential energy surface. While can even go beyond the potential energy surface remember this is your homework problem you are to figure it out. And the Hermite polynomials if you remember are for v equal to 0 is just 1. For v equal to 1 it is a first order polynomial. So, first order polynomial means what? Is something like X_i .

So, for X_i equal to 0 where is X_i equal to 0 for x equal to 0 point then what will happen you will get a node wave function will change sign. If you go to v equal to 2 it is a second order polynomial X_i equate that to 0 you will get 2 roots and these are the 2 roots where the wave function will; not only become 0 but change sign, please remember a node is a point or later on a plane or surface of something where wave function changes sign.

It goes to 0 but it has to change sign, for example, if you were here at x equal to infinity or X_i is equal to infinity. There are also the wave function is equal to 0 but X_i equal to infinity or x equal to infinity is not a nodal point because a wave function becomes 0 asymptotically it does not change sign. So as you go higher up the energy ladder to get more and more and more nodes that leads to this rule of thumb that more the number of nodes higher is the energy associated with the wave function.

And the nodes here come from the Hermite polynomial being equated to 0. Whatever is the order of the polynomial will be equal to the number of nodes. That is why we get more and more nodes as we go higher order. Then we have learnt that the recursion relation is there among connecting this function, so just multiply wave function by X_i will be able to get a linear combination of the wave function before and wave function after.

So, that is all for simple harmonic oscillator. This as we said earlier has very a profound application in vibrational Spectroscopy. Next we move on to rigid rotor which also has a profound application in vibrational spectroscopy sorry rotational Spectroscopy. But also one more reason why we study is that the method that we develop there are going to come handy when we talk about the first molecule hydrogen sorry for the first atom hydrogen atom.

This course is quantum chemistry of atoms and molecules we have already learnt Quantum chemistry of vibrating molecules. Now we will learn Quantum chemistry of rotating molecules and that enable us to get into a hydrogen atom in which Schrodinger equation is exactly solvable that is what will take up in the next few modules.