Advanced Mathematical Methods for Chemistry
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Module - 06
Lecture – 05
Recap of Module 6, Practice Problems

So, this will be the last lecture of Module 6 and today I will start by recapping what you have learnt and then, we will do some practice problems. So, to recap in this module, we basically focused on maximization and minimization of functions and we looked at Lagrange's methods of undetermined multipliers which allows us to find maxima or minima of functions subject to certain constraints.

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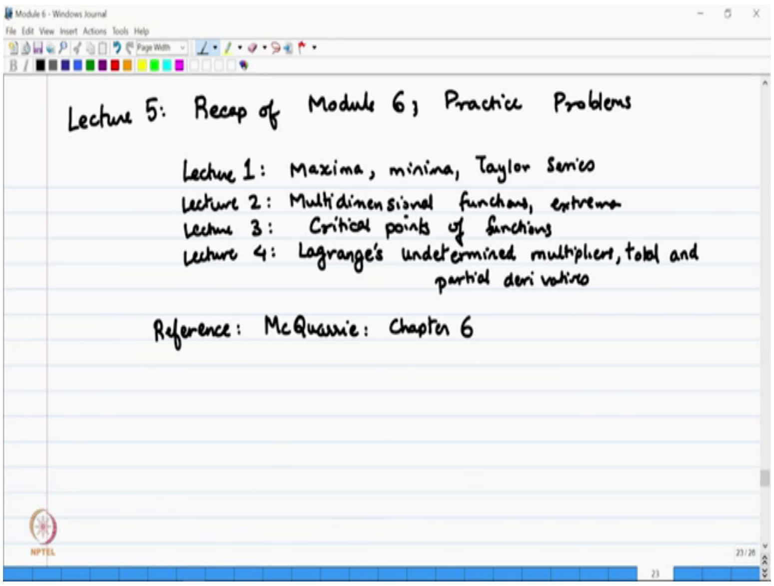

So, in the first lecture, we learnt about maxima minima and we also learnt about Taylor series. In the second lecture, we did maximization and minimization of multi-dimensional functions. We also looked at Taylor series for multi-dimensional functions and we looked at all the various extreme that you can have. In the third lecture, we classified all the critical points of functions into maxima minima saddle points etcetera, for multi functions of many variables and in the fourth lecture, I talked about Lagrange's undetermined multipliers to find maxima and minima subject to certain constraints. We also talked about total and partial derivatives, how these are related. Now, all of this is very nicely discussed in Mcquarrie chapter 6. Again chapter 6 has lot of other topics, but all these topics are fairly well covered here.

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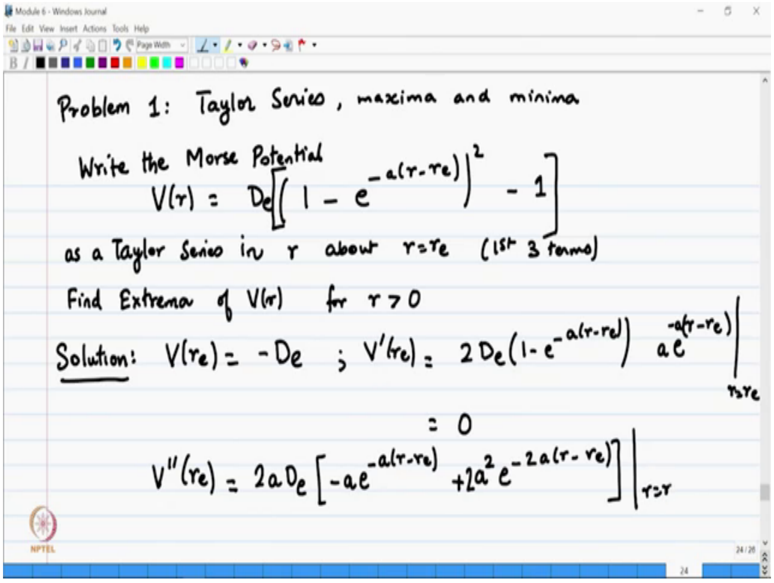

Now, let us look at some applications of these through some practice problems. So, the first problem that I am going to talk about has to do with Taylor series. Maxima and minima, the question is write the morse potential V is a function of r. V r is a scalar, V is a scalar. It is given by a constant demultiplied by this function. So, 1 minus e raise to minus a r minus re, this whole thing is squared and then, you have a minus 1. Write this as a Taylor series in r about r equal to re and I am asking you to write the first three terms and find the extrema of V of r for r greater than 0.

So, let us write a solution. So, suppose I take V of r e is equal to, if I put r equal to re, then this term. So, you have e raise to e2. So, this exponent goes to 0. So, exponent of 0 is 1. So, this first term goes to 0 and we are left with this minus De. So, this is the first term. So, this is equal to minus d, where d is a constant. I will come to it in a bit what these constants mean.

Now, what about V prime at r e. So, what you do is that they take a derivative of this. Now, clearly this minus 1 does not contribute at all. So, what will have is 2 De times, you will have exactly this term times e, e raised to r minus r e. So, this is ae raised to a minus a r minus re. So, this is derivative and this has to be evaluated at r equal to re and clearly this is equal to 0. So, when r equal to re, this goes to 1. So, 1 minus 1 is 0. So, the first derivative is 0. What about the second derivative?

So, if you want to do the second derivative, then what you get is, you have to take a derivative of this quantity. Now, I will just do this. So, you have 2 a D e times the derivative of this whole quantity. Now, what is the derivative of this quantity? So, the first term is just e to the minus a r minus re. So, the derivative of that is just minus a e to the minus a r minus re, ok.

Now, the second term has e to the minus a r minus re into e to the minus a r minus re. So, that is I can write it as e to the minus 2 a r minus re and if I take the derivative of that, so I already have an a. So, I have a plus a square e to the minus 2 and there will be a factor of 2 coming minus 2 a r minus re and this has to be evaluated at r equal to re.

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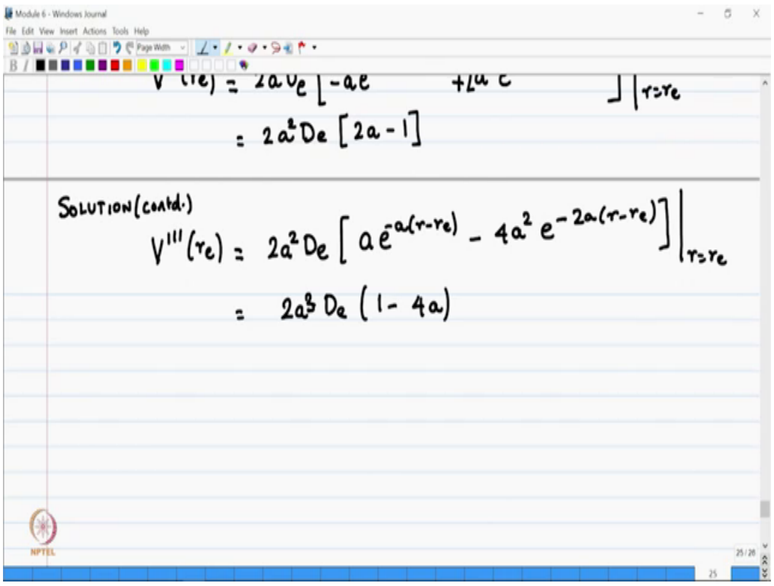

Now, when r equal to re, what you see is that this becomes minus a, this becomes 2a square. So, this becomes 2a square D e and you have 2a minus 1. This is some quantity. So, for completeness let me also do the third derivative V triple prime at re. So, this is given by, so I have to take a derivative of this whole thing. So, I have 2a square D e, I have minus e to the minus a. So, that becomes a e to a minus a r minus re and then, I have what I had is 2a. So, plus 2a is I have minus 4 a square e to the minus 2a r minus re and this whole thing has to be evaluated at r equal to re.

So, what you notice is that this works out to be to r equal to re. Again these two terms will go away. So, you will get 2a square D e a or 2a cube D e 1 minus 4a. So, now I can write my V of r. So, V of r 0 is minus De.

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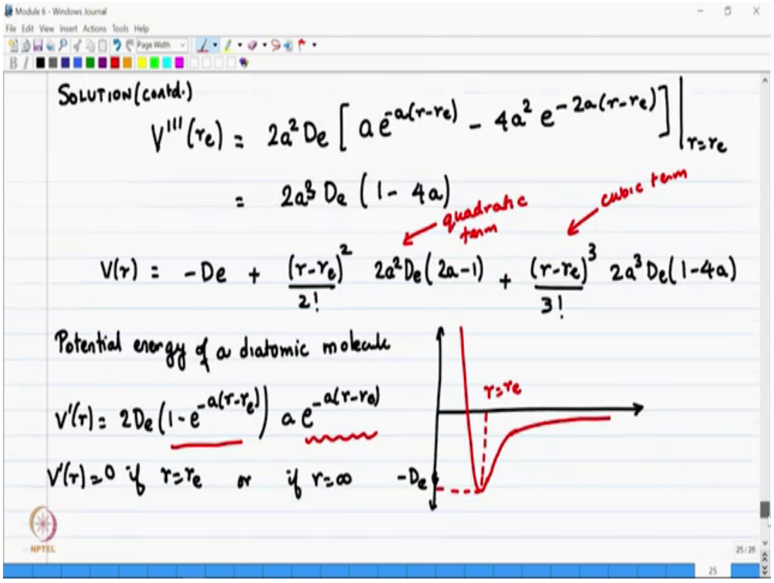

Now, the first derivative term is 0. So, the first non-zero term is a second derivative. So, the second derivative term will have a r minus re square divided by 2 factorial and you have some quantity which is 2a square De 2a minus 1 plus. Now you have r minus re whole cube divided by 3 factorial and what you have is 2a cube De 1 minus 4a. So, this is te final expression for V of r.

Now, a and d are constants. So, what this look like? So, this is actually a potential energy of a typical I will say diatomic molecule. So, this is used to model the potential energy of a diatomic molecule and what does it look like. So, if you look at the graph rs, we said r is greater than or equal to 0. Now, incidentally we see that at r equal to r e V prime of re equal to 0. So, re is clearly a minimum. So, V prime of r is equal to let us just write the expression again. So, 2De 1 minus e raise to minus a r minus re.

So, you have 2De 1 minus e raise to minus a r minus re into 2a 2a e to minus a r minus re. Sorry not 2, there should be a2 here. This is just a. So, what you notice is that this goes to 0 if r equal to r e. The middle term will go to 0 if r equal to re and if r equal to infinity, then you have e raised to minus infinity which goes to 0. So, this term will go to

0 if r equal to infinity. So, this e raise to minus a r minus re will go to 0 if r equal to infinity.

So, these are the two places where it goes to 0 and you can look at the second derivative. So, when r equal to r e, then this has this expression of 2a squared De times. You have a factor of 2a minus 1 and usually 2a minus a is chosen to be greater than half. So, this is usually taken as greater than 0. So, usually this is taken to be minimum at r equal to re, ok.

So, what this function looks like? So, at r equal to re, you have a minimum and what happens is that this function looks like and the value at r equal to re is minus De. So, this is minus De and this is the minimum value of the function and this function essentially looks something like this. So, this is r equal to re, it goes to 0 at infinity and also when r equal to 0, when r goes to 0, it actually becomes very large. So, when re at this e to the minus e to re, some is a fairly large number. So, this is the form of this function and then, this is well known Morse oscillator. So, what is interesting is that if you had only this term which is called the quadratic term and if you only had the quadratic term, then it would look like a harmonic oscillator. So, this is a cubic term. So, this allows you to go beyond the harmonic oscillator, ok.

Now, the next problem that I want to do is problem in statistical mechanics. This is the use of Lagrange's undetermined multipliers, ok.

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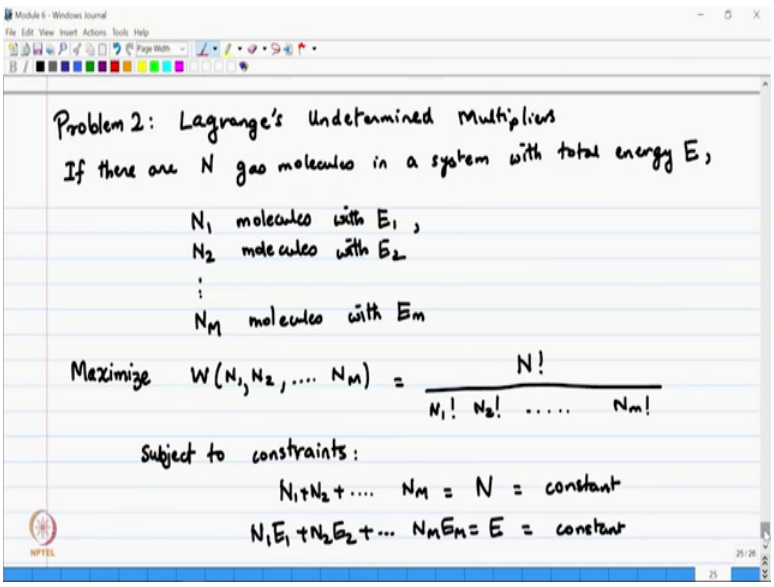

So, here you are told that if there are N gas molecules in a system with total energy E and out of these N 1 molecules have energy E 1 N 2 have molly molecules have E 2 and so on. N m have energy E m, then what you are asked to do is to maximize this w of N 1 up to N m. This is nothing, but a multinomial function. So, the total number of ways in which you can choose N 1 N 2 up to N m, such that they all add up to N and the other constraint is that the total energy should be E. So, N 1 times E 1 plus N 2 times E 2 plus up to N m times. C m should be some constant.

So, subject to these two constraints you maximize this function. So, let us go ahead, maximize it and then, once we maximize it, we will see some properties of this W. So, let us apply Lagrange's undetermined multipliers. Now, we see this factorial thing appearing.

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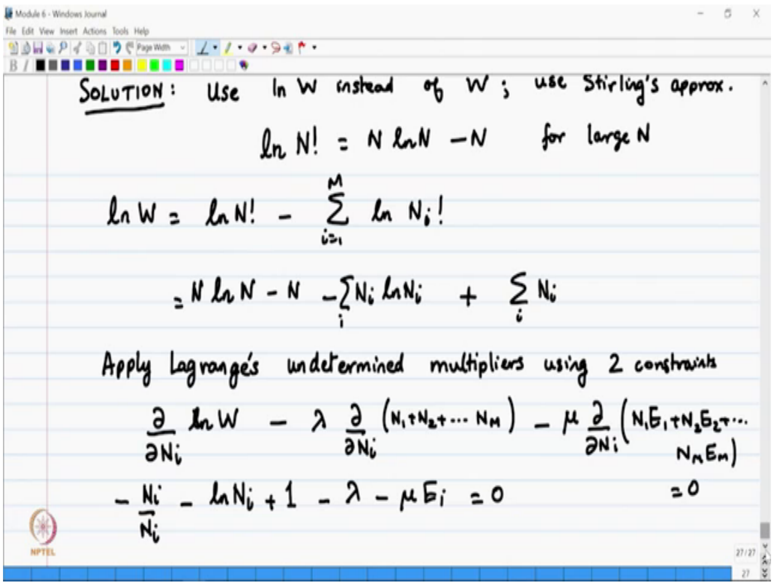

So, I will just emphasize a few things. So, the solution this is done and standard statistical mechanics books is used in of W. So, when W is maximum, natural log of W is also maximum and use stirlings approximation and that stirlings approximation is given by ln of N factorial equal to N ln N minus N for large N. So, we just use, these are the tips that you need before you attempt to solve this, ok.

So, what we will do is, ln of W now natural log of this is ln of N factorial minus I will just write sum over i equal to 1 to M ln of N i factorial and I can write this as natural log of. So, I can write this as N ln N minus N minus. Now, what I have is here, I have sum over i of N i ln N i minus sum over i of N i and what we are going to do is minimize this subject to two constraints. So, now here you have two constraints. So, what we are going to do is when you apply multipliers using two constraints, ok what will say is that dou by dou N i of natural log of W minus lambda times dou by dou N i of constraint 1. So, the first constraint is this N m, then minus mu times dou by dou N i of equal to 0 equal to 0 and you are going to apply this for all i.

So, when you do this, now let us take the derivative of ln of W with respect to N i. So, this term will go away, ok. Now, that should be a plus. So, we see that you have N and you have sum over N i. Now, these two should be equal. So, these two terms can just cancel off. So, then all you have is a derivative with respect to N i of this quantity. So, let us evaluate this explicitly. So, with respect to N i of this quantity will give me minus. Now, the term with only the Ni term will appear. So, I will have N i divided by N i that is due to derivative of the logarithm and then, minus ln N i and I have plus. Now, a derivative with respect to N i of this is just 1 because this is N 1 plus N 2. So, the derivative with respect to N i, there will be one term with just N i. So, the derivative is just 1. So, this minus lambda now dou by dou N i of this is just 1. So, then minus mu now dou by dou N i of this is just E i equal to 0, ok.

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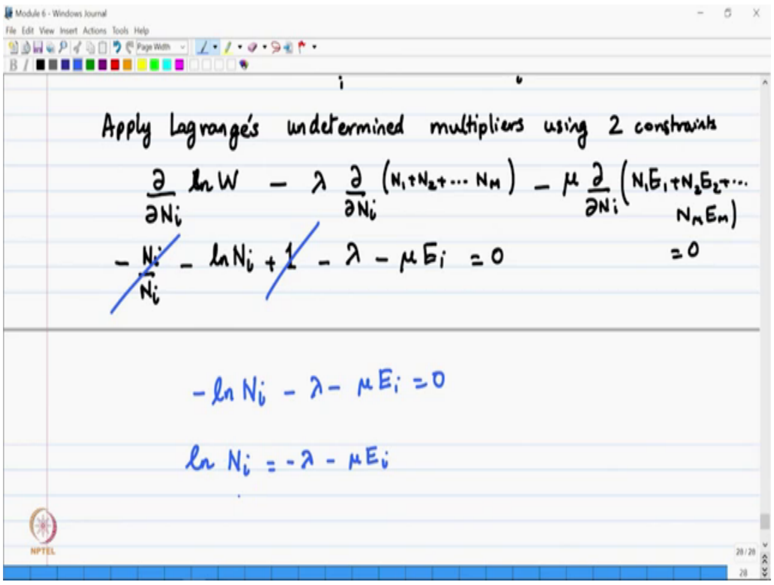

So, finally what you can see is that is that these two terms will cancel and what I have is my final expression. So, let me write this with 0 or I can write N i is equal to lambda E i.

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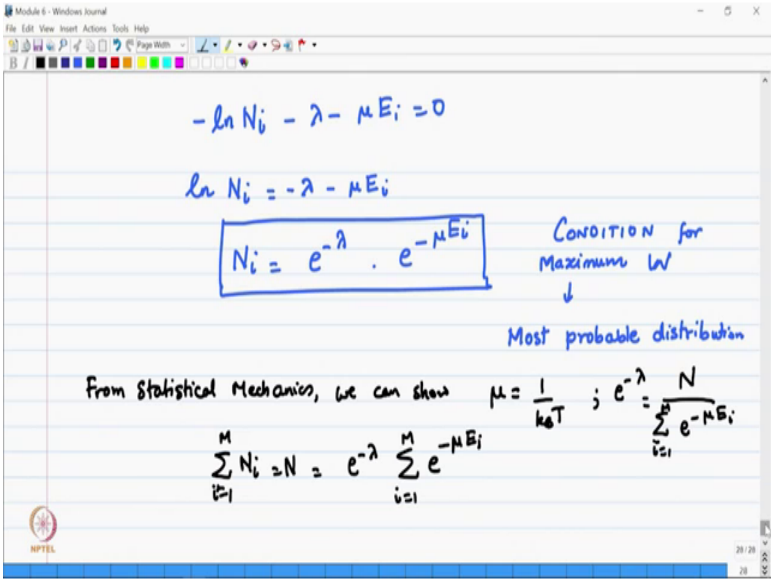

So, this is ln N i and you get a very useful relation. Now, if I write it in terms of exponential, I get N i is equal to E raise to minus lambda times E raise to minus mu E i. This is the solution, ok.

Now, this is what we are interested in. So, this is the condition for maximum W. So, it is also in statistical mechanics and this is called the most probable distribution. Now, lambda and mu are undetermined multipliers. So, again you know from statistical mechanics, we can show mu is equal to 1 by k b Tand E to the lambda is just, E to the minus lambda is equal to 1 over sum of i equal to 1 to M E to the minus mu E i because you can show this equal to N over.

So, you can show this by summing both sides. So, basically sum over i equal to 1 to MN i is equal to N is equal to e to the minus lambda sum over i equal to 1 to M e to the minus mu E i. So, you can get this at basically once you show these two, then you get a very well known expression.

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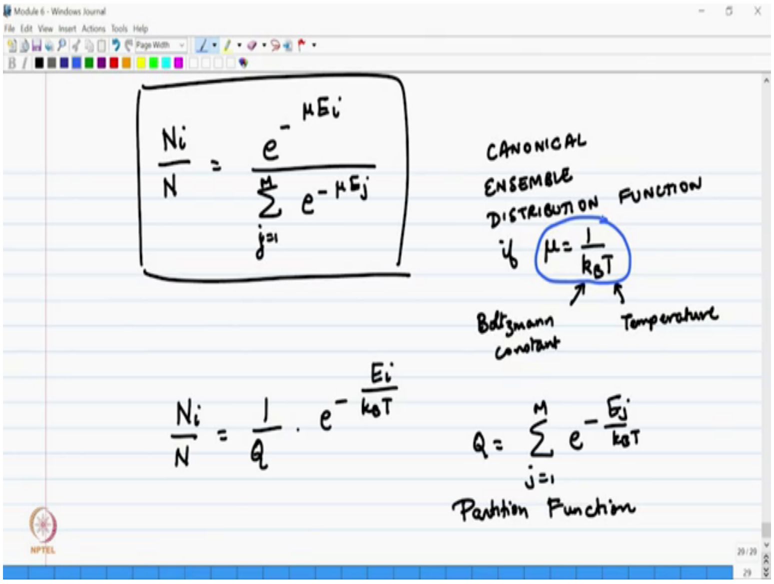

So, that is N i by N is equal to e to them are e to the minus mu E i divided by sum over i equal to 1 to M or let me call this j equal to 1 2 m just to distinguish it from i that we are using e to the minus mu E j. So, this is called the canonical ensemble distribution function and if you use mu i equal to I should emphasize. So, if mu is equal to 1 by k B T which is called Boltzmann constant and T is temperature, ok.

So, this is a very well known expression in statistical mechanics. So, sometimes this denominator is called the partition function Q and you have e to the minus E i by k B T, where Q is equal to sum over j equal to 1 to M e to the minus E J by k B T is sum over all states. So, this is called the partition function.

So, what we have seen is that the Lagrange's method of undetermined multipliers that we have used this method in order to calculate the distribution of a gas when at a given temperature. Now, I did not show one part. I did not show how you get mu equal to 1 by k B T. So, this is actually slightly more involved. I mean this you need to use some more thermodynamics. You cannot just do it by mathematics. So, the connection between mu and temperature is caught from thermodynamics, but essentially you get the basic form, you get this expression just from by using Lagrange's method of undetermined multipliers and maximizing this quantity W. So, we identified that W is the quantity that we have to maximize. So, this quantity W is what we have to maximize and we took logarithm of W and we use turnings approximation which is extremely valid. If you have a large ends which is what happens when you have a very large number of molecules. So, statistical mechanics whole when the number of molecules is of the order of avogadros number, ok.

So, this stirlings approximation is almost exact. So, with this I will conclude module 6 and in the next module, we will start looking at qualitative methods for non-linear differential equations.

Thank you.