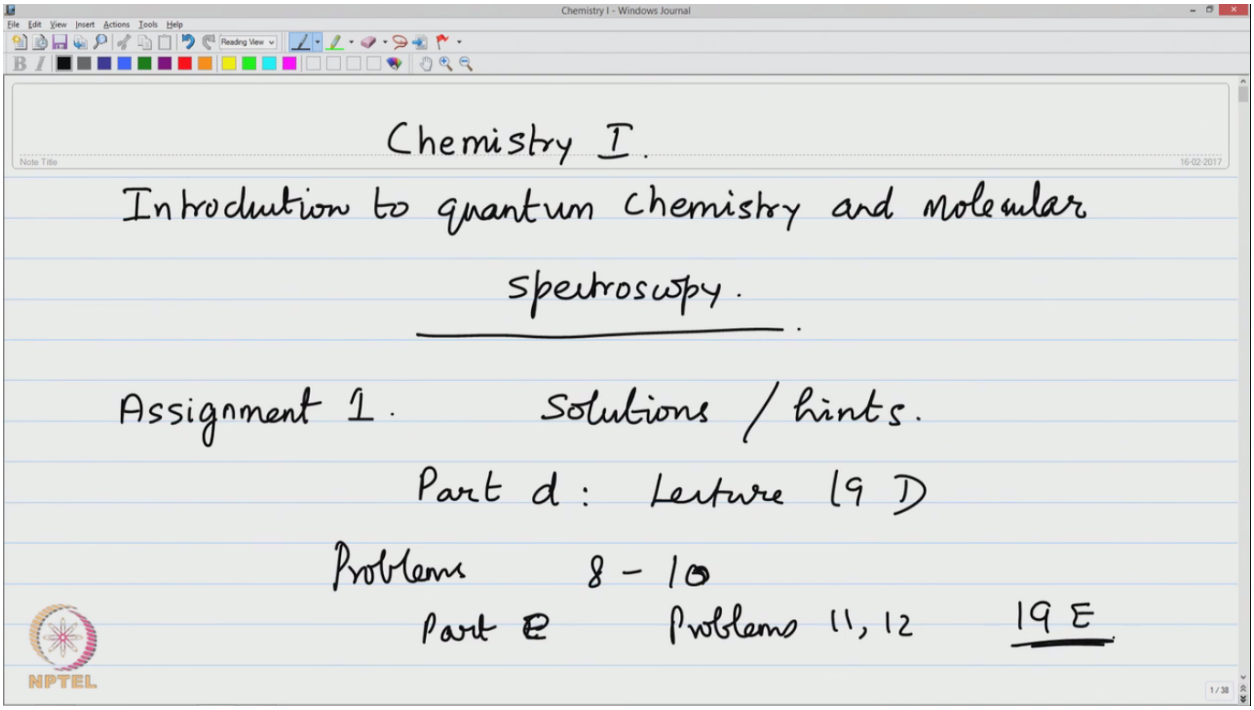
Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy

Lecture 19E
Assignment 1
Solution/Hints

Prof. Mangala Sunder Krishnan,
Department of Chemistry,
Indian Institute of Technology Madras

Welcome back to the lectures in quantum chemistry and molecular spectroscopy. We shall complete assignment 1 with the last part, part E of problems 11 and 12, 19E, lecture 19E. Let's go to the – let's go to problem 11.

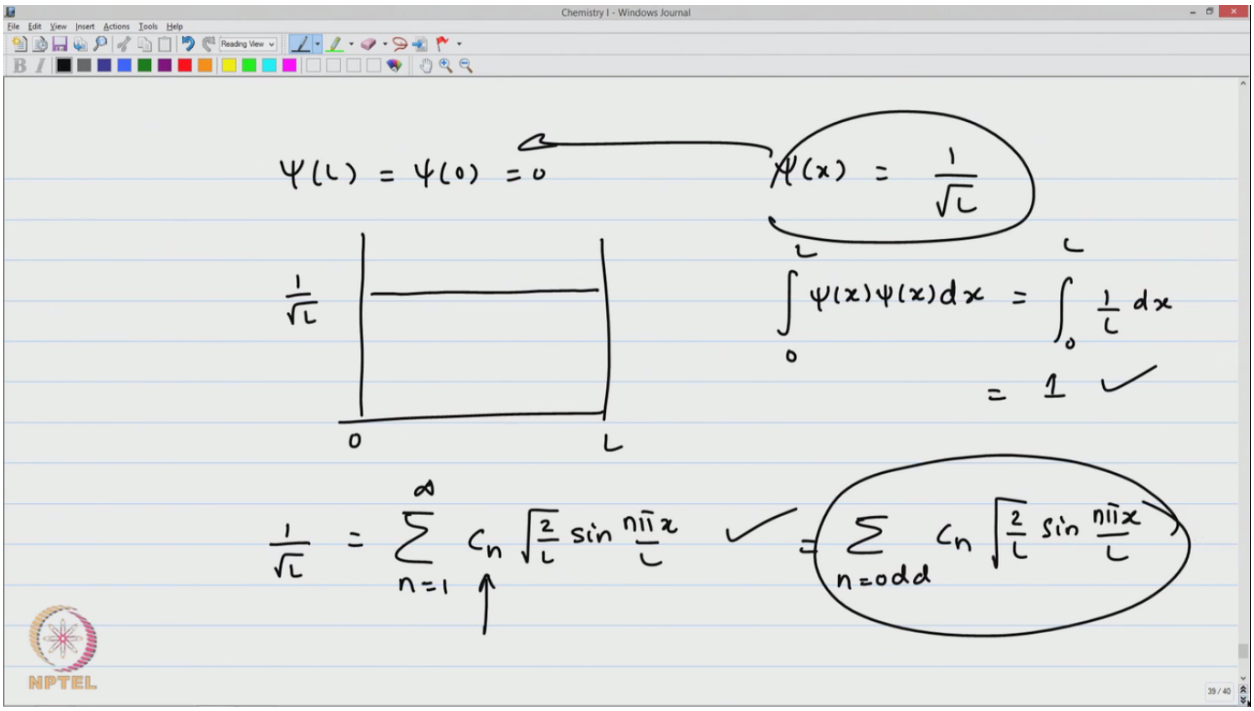


Problem 11 is to consider the rectangular wave function phi x is square root of 1 by l between 0 less than x less than 1 and if the function is 0 otherwise it's given that way and you are asked to express the wave function as a linear combination of the eigen functions of the Hamiltonian and also obtain an expression for Cn and Cn square. Is this an acceptable wave function?

Given the fact that this wave function satisfies the boundary condition namely phi of l and phi of 0 is 0 phi of x is 1 by square root of l. So what this function looks like is that and this value is 1 by root l is as close to the edge as possible and at the edge of the potential is infinite it goes to 0. So this is what the function given. Acceptable of course it is because the integral is phi of x phi of x if you do that the probability integral you do that 0 to l then you get is 0 to l 1 by l dx and that you know is 1 so it's normalized. It has two discontinuities at the two boundaries. Other than that the function is well-behaved. It's normalizable and it's a general function satisfying the boundary condition therefore we can always write 1 by square root of L as a linear combination of n Cn root 2 by L sin n pi x by l n equal to 1 to infinity.

Now from the previous problem that was that had this particular in the box wave function arbitrary wave function. We know exactly immediately how to calculate Cm because that is essentially taking the integral on the left hand side with any arbitrary eigen function sin m pi x by l square root of 2 by l this is the wave function 0 to l into 1 by root l this is the wave function Phi of x. This you remember is the phi n the eigenfunctions and this is the phi of x dx will immediately give you Cm on the right hand side because this will pick only the Cm all the others will go to 0. Therefore this integral is root 2 by L, l by m pi with the minus sign cos m pi x by l

between the limits 0 to l and cos m pi x by l between 0 to l if m is 1, 3, 5 etc. this is non-zero because cos0 and cos odd l this will be cosine of odd pi minus cosine zero if m is less. This is minus 1. This is minus 1 so it's minus 2. But if m is even etc. this will be cosine of even pi minus cosine 0 both of which are 1 and therefore this goes to 0. Therefore, the summation this one contains only n odd Cn root 2 by l sin n pi x by l. This function is the same. It's a constant and it's the same about the middle l by 2 and L by 2 you can see that this is even with respect to the middle part the sin function is if it is odd number.



Please remember the odd number of sin functions pictorially look like this. The odd number of sine function look like this. This is one, n equal to 1. If it is n equal to 3 between the same interval this will be odd number of m the same function will look like that about the middle it's symmetric. If it is 5 you will have 1, 2, 3, 4, 1, 2, 3, 4, 5, so it's again symmetric therefore all the odd sin functions which are symmetric about l by 2 between 0 to l they contribute to the overall wave function which is also symmetric about to the middle. So that is you have to see the nature of the solutions and you should be able to explain them why they are what they are.

Now the rest of the question is if I understand is this an acceptable wave function. I said yes it is acceptable and we calculate Cn square. Of course you know the sum over Cm square will give you obviously 1 because this is a normalized eigen function. This is also a normalized eigen function therefore the product will give you 1 similar to what I have done in the last problem.

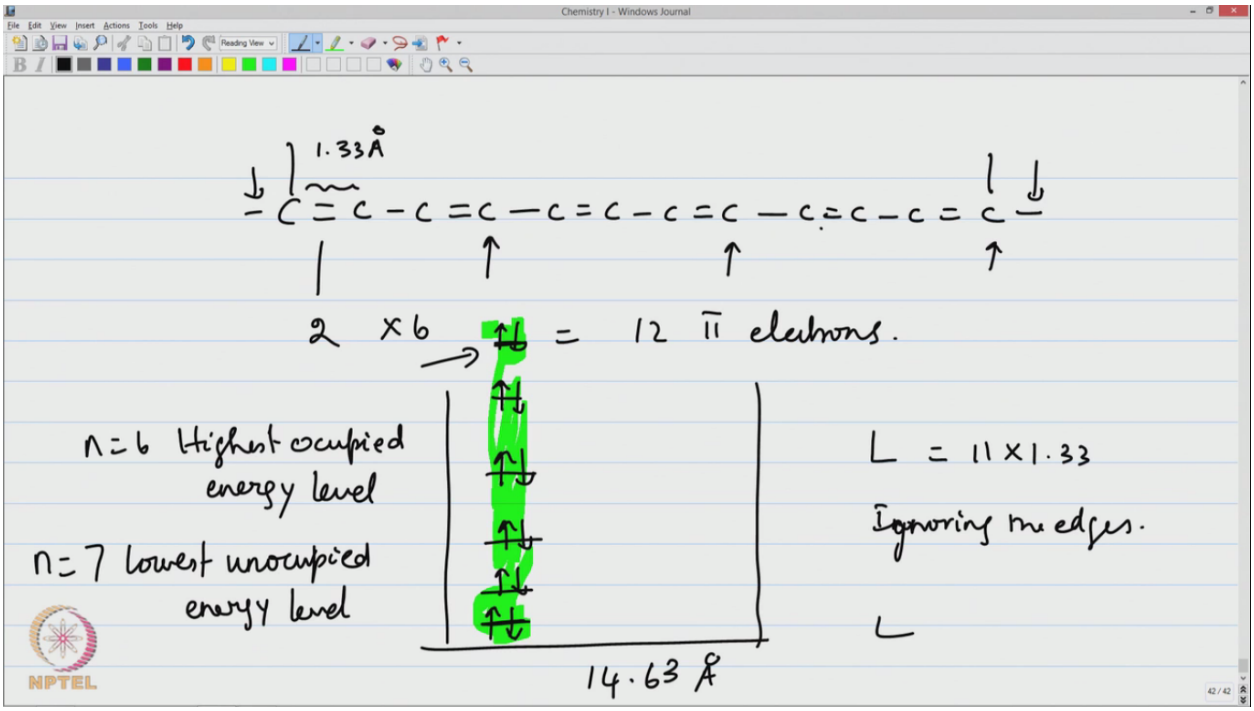
Now problem 12 is something that a chemist should be seriously interested in because this a simple model for understanding one dimensional systems, polymeric systems and the example the problem given here is a linear one-dimensional chain of conjugated polyene it contains in this

case of course 12 carbon carbon links. C double bond single bond, C single double bond C repeated two more times. So you have one, two, three, four, and you have another eight carbons. So the entire sequence is C double bond C single bond C double bond C then you have C double bond C single bond C double bond C and once more. So you have four units, another four units, and another eight units and this is edge the two hydrogen and I have not given you the hydrogen's in between for the problem the hydrogen's are not relevant. What is the problem? Given this and the average bond distance being 1.33 angstrom. We want to use the particle the one-dimensional model to understand the properties of the electrons. So first of all approximation. Ignore the end effect and assume that the PI electrons are free to move along the bonds. End effect is the end effect being the carbon, the two carbon for the terminal positions and the hydrogens. Therefore we assume that the wall, the box wall is at those two carbons. One way to look at it and then you study the energy levels of how many electrons which do not interact with each other. How many pi electrons are there? Each double bond contains two electrons pi electrons. So it's one, two, three, four, five, six. So there are 12 pi electrons. Electrons of course strongly correlate they interact with each other but for this problem let's assume that the electrons are not interacting. They're free particles. The problem ask you to determine the energy difference between occupied energy level and the lowest unoccupied energy level with the assumption that at most two electrons can occupy each energy level.

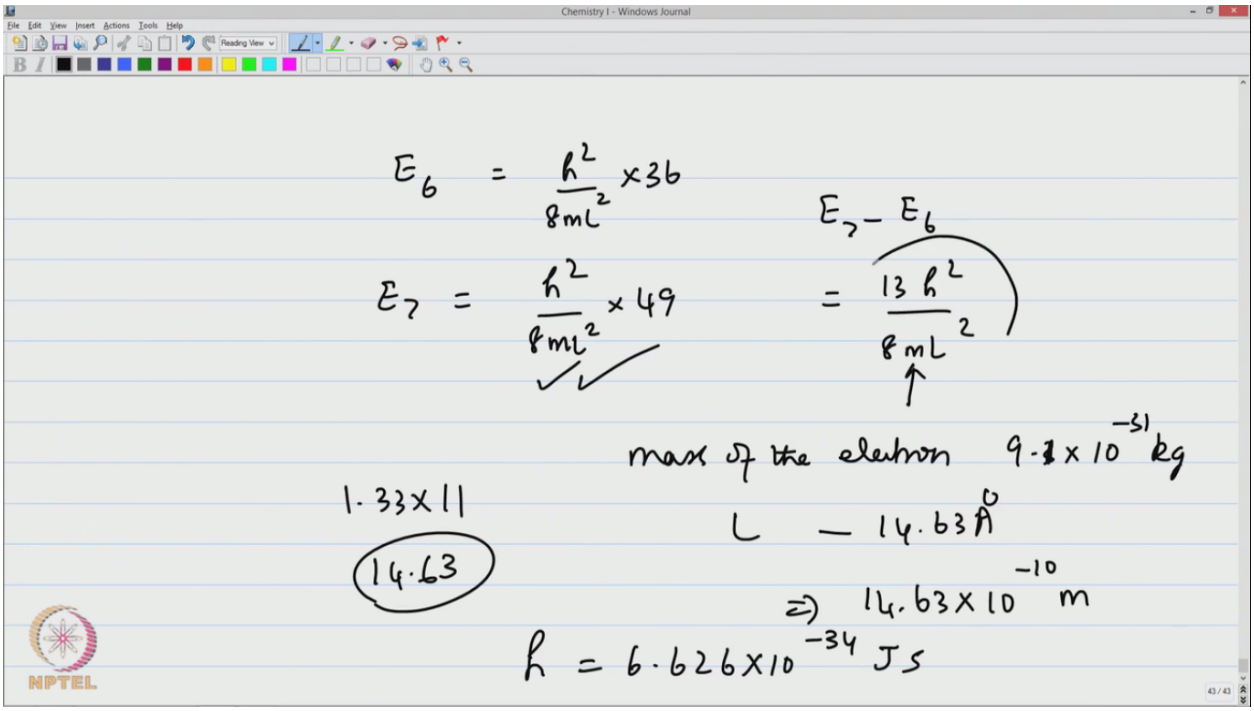
So the physical picture is we have a box whose width is given by this distance and you are given the average distance C double bond C this one, the average distance C is single bond C all of this is 1.33 angstroms. So there is one, two, three, four, five, six, seven, eight, nine, ten, eleven, bond lengths are there. Therefore the length of the box is 11 x 1.33 ignoring the edges. Ignoring these. Ignoring the edges. So l is 14.63 angstroms. This is the length of the box. You have 12 particles they don't interact with each other. Therefore, we can consider each particle as a particle in the box and each particle occupies one of the energy levels n equal to 1, n equal to 2, n equal to 3, equals 4, 5, 6, and so on.

Now the problem tells you that that utmost you can put two electrons in one of these orbitals, one of these energy levels. I mean it's a simple assumption of the Pauli exclusion principle that no two electrons can have the quantum numbers the same. Here of course there's only one quantum number namely the quantum number for the energy of the orbit. It's a one-dimensional system. In a three dimensional system you will have three quantum numbers and the fourth quantum number is the spin of the electron. So here we have only one dimension therefore utmost you can put only two electrons therefore these 12 electrons can be accommodated in these six of the lowest orbitals orbits are the energies that you have six of these. So these are the six energy levels that we have. And the 12 electrons are in these.

So this is the highest occupied energy level this one n equal to 6 highest occupied energy level. Therefore, the lowest unoccupied energy level is 7th energy lowest unoccupied. The question is to find out the energy difference between these two levels.



So you have a particular in the box model in which the length of the box is approximately model as the 11 times the distance of the carbons that the electrons have freedom to move around and the model is that the electrons don't hit each other, don't see each other, they don't interact with each other. Of course it's a it's a primitive it's a course model but the point is it's still a model and so you have 11 times that distance of the length of the box and there are 12 electrons and utmost two electrons can occupy one of the chairs and there are six chairs that you have, the six energy levels that you have and the seventh one is the first unoccupied. Therefore what's the energy gap between the 6th and the 7th, it's very simple because you know the energy level expression for the particle e6 is h square by 8 m l square into 36 and E7 which is unoccupied is h square by 8 m l square into 49 therefore the difference between E7 and E6 is 13 h square by 8 m l square. M is the mass of the electron. So you can write that as 9.3 times or 9.1 times 10 raise to minus 31 kilograms and l i have already given 14 point something 63 or how much is it, yeah 14.63 it is 1.33 into 11 I'm very poor in doing the math using in English so I will do it in my own language [Indiscernible] [00:14:23] this is what I know you know you have to do your maths in your language. 14.63 angstrom and so what you have is 14.63 into 10 raise to minus 8 centimeters or 10 raise to minus 10 meters so l is known m is know, h is known 6.626 into 10 raise to minus 34 joule second therefore you can calculate this number.



I leave it to you as an exercise and this completes the assignment one. I took the time to explain the assignment one clearly elaborately with all the details simply because there are many ideas involved in elementary quantum mechanics in that long assignment and I hope you enjoyed the solutions and the presentation and I hope it makes sense to you. We will continue with similar exercises maybe a week or two later with the second assignment and probably some more assignments for which I will give written solutions instead of video recording. Until then thank you very much.