NPTEL

NPTEL ONLINE COURSE

Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy

Lecture 19D
Assignment 1
Solution/Hints

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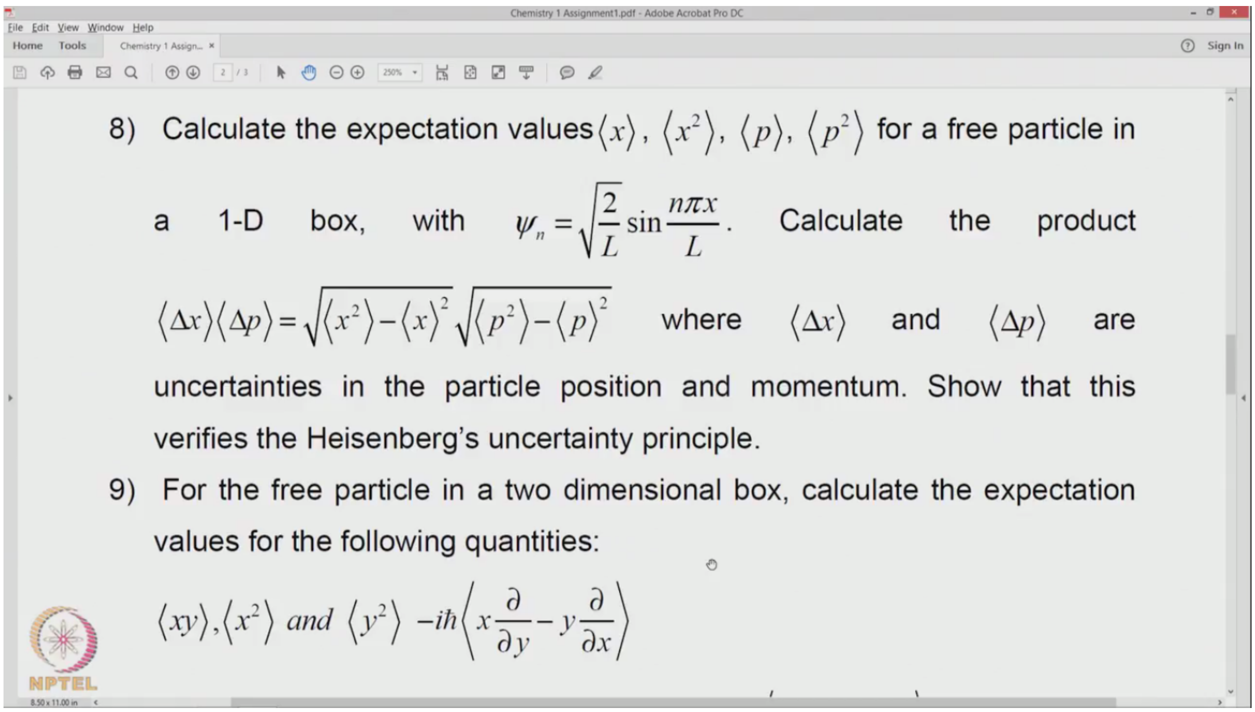
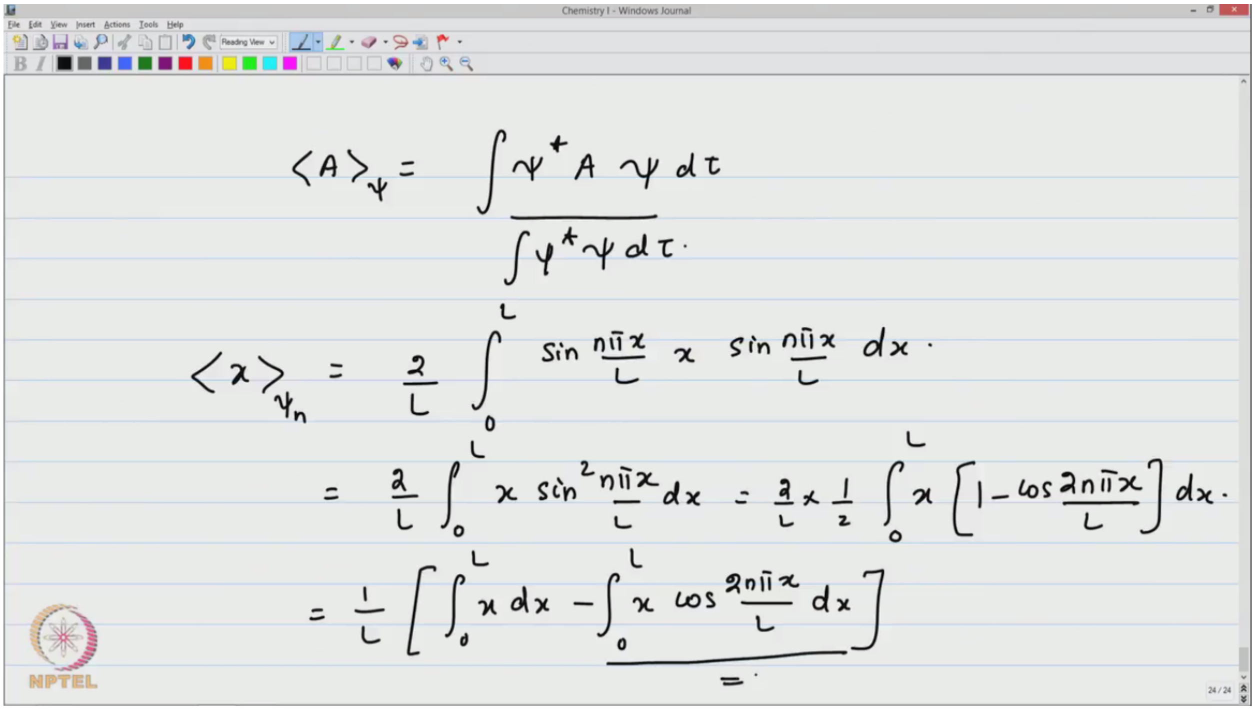
Welcome back to the lectures on quantum chemistry and molecular spectroscopy. We shall continue to resolve the assignment one. There are some more problems left. The problems 8 to 12 at least I will give you hints on how it should be solved. So let's go to problem 8.

The problem 8 ask you to calculate the expectation values or work on the average values of the operators for position x, x square which is the square of the position operator, p the momentum, and p square the square of the momentum for a particle, free particle in the 1-D box. And the eigenfunction is given to you as square root of 2 by L sine n π x by L. Also it asks you to calculate the uncertainty product known as the delta x delta p which is defined as given here and verify the Heisenberg's uncertainty principle.



Let's recall the definitions. The expectation value of any operator A in the base φ is φ * A φ d tau divided by φ * φ d tau. So in the case of a particle in the box the position operator the expectation value is there is a root 2 by L but the function, by function is multiplied by itself so you have 2 by L 0 to L sine n π x by L this is in the state π n x times sine n π x by L dx. The denominator is 1 because the wave function is normalized. Therefore what you have is 2 by L integral 0 to L x sin square n π x by L dx and that would be 2 by L times 1 by 2 0 to L you write the sine square in terms of the double angle formula 1 minus cos2 n π x by L dx. So that gives you 1 by L times 2 integrals namely 0 to L x dx minus 0 to L x into cosine 2n π x by L dx. It's straightforward to show that this integral is 0 because you can write this as x into d of sine 2npi x by L times L by 2 n π if you write this as a partial derivative between 0 to L and that's given as x times this is a UDV formula therefore UV x into sine 2n π x by L times L by 2 n π UV between the limits 0 to L minus BDU which is 0 to L sine 2n π x by L dx. This is 0. This is 0 because at x is equal to at 0 x 0 at L sine 2n π x is 0 so this is 0. Therefore that integral is 0. So if you go back you would see that there is only one integral namely 1 by L 0 to L x dx and that's given as L by 2.

So the average value of x is L by 2. The average value of x square is obviously L square by 4. So that's [Indiscernible] [00:04:26].



The calculation of the average value of the square of the X this is the average of the position squared. This is the square of the position and this is given by again 2 by L integral 0 to L sine square n π x by L x square dx. Again you can do this using the partial integration with the UDV type formula. So if you have to do the integral sine square n π x by L x square dx [Indiscernible] [00:05:09] is integral 0 to L x square d, sorry it's a – you again split this into two terms namely 1 by 2 1 minus cos2n π x by L like what you did dx and the first term gives you x square dx by 2 so it is x cube by 3 and there is a 2 by L in front of it. So if you put the 2 by L here you have 1 by L and then this is x square dx will give you x cube so it is L cube by 3 minus the integral 1 by L 0 to L x square cos2n π x by L dx. This has to be done in two steps like what I did in the first step. Therefore, I will give you the answer namely it is L square by 3 minus L square by 2 n square π square. This is the final answer for this.

This is the integral or the average value squared; that is the average value of the square of the deposition. The average value for the momentum for particle is 0. During the lectures we have mentioned this and we calculated it and the average value for the square of the momentum is if you recall it is 2m times the average value for the energy and the energy for this particle at this state is given by h square n square by 8m L square so you get h square n square by 4 L square. So that's the P squared [Indiscernible] [00:07:07].

$$\frac{2}{L}\int_0^L \sin^2\frac{n\pi x}{L}\, x^2\, dx = \frac{2}{L}\,\frac{1}{2}\int_0^L x^2\left[1-\cos\frac{2n\pi x}{L}\right]dx.$$

$$= \frac{1}{L}\times\frac{L^3}{3} - \frac{1}{L}\underbrace{\int_0^L x^2\cos\frac{2n\pi x}{L}\,dx}.$$

$$\langle x^2\rangle = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}.$$

$$\langle p\rangle = 0 \qquad \langle p^2\rangle = 2m\langle E\rangle$$

$$= 2m\,\frac{h^2n^2}{8mL^2} = h^2 n^2$$

For now let's get the Delta x Delta p. If you take the square of this that's equal to x squared average minus x average square multiplied by p squared average minus p average square. This will be L cube by 3 minus L square by 2 n square π square that we calculated and the x average square is minus L square by 4 so this is the Delta x square and the Delta p square is simply h square n square by 4 L square. So the L goes away from all of this and you remember it is 1 by 3 minus 1 by 2 n square π square. It's minus 1 by 4 so it is 1 by 12. 1 by 12 and then you have h square n square by 4.

Now you can see that this is greater than or equal to h by 4 π. Remember the difference is the largest here when the n is 1 the smallest state. For all other n's this is greater than the n equal to 1 value. Therefore this term keeps on increasing and this term also keeps on increasing. Therefore the smallest value is obtained when the n is one and when n is 1 you have 1 by 12 minus 1 by 2 π squared times h squared by 4 which gives you roughly a number close to this but greater than this number h by 4 π. So you see – just numerically you can check this up. It's greater not greater than or equal to. It's greater than h by 4 π.

Therefore, the smallest uncertainty which is obtained for n equal to 1 is already greater than h by 4 π and for all other values of n both these terms are increasing therefore they will be definitely much greater than h by 4 π. So this is Heisenberg's formula.

$$\left[\langle \Delta x\rangle\langle \Delta p\rangle\right]^2 = \left(\langle x^2\rangle - \langle x\rangle^2\right)\left(\langle p^2\rangle - \langle p\rangle^2\right)$$

$$= \left[\left(\frac{\cancel{L^2}}{3} - \frac{\cancel{L^2}}{2n^2\pi^2}\right) - \frac{\cancel{L^2}}{4}\right]\frac{h^2 n^2}{4\cancel{L^2}}.$$

$$= \left(\frac{1}{12} - \frac{1}{2n^2\pi^2}\right)\frac{h^2 n^2}{4} \geq \left(\frac{h}{4\pi}\right)^2$$

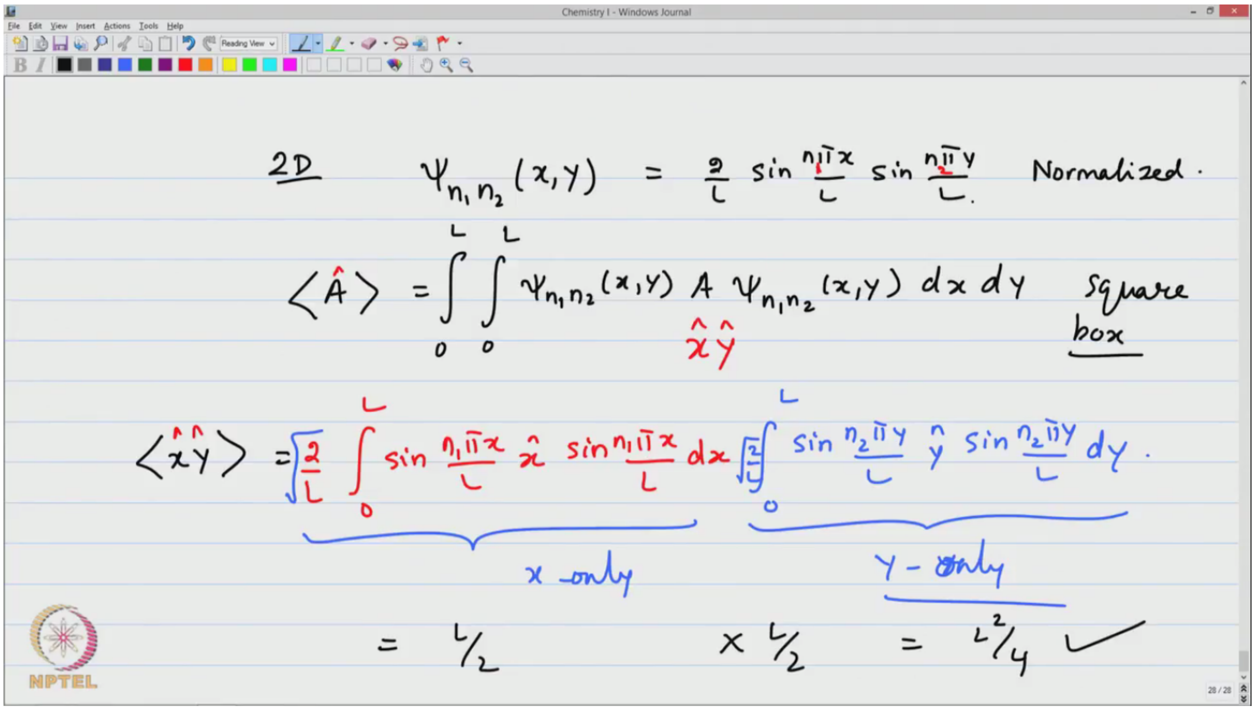
$n=1$

$$\left(\frac{1}{12} - \frac{1}{2\pi^2}\right)\frac{h^2}{4} \geq \left(h/4\pi\right)^2 \checkmark$$

Heisenberg's formula.

I think that's what we wanted to verify in that problem. Yeah show that it verifies the Heisenberg's uncertainty principle. In the lecture itself we will see that why this is the formula for the uncertainty but we – given this as the uncertainty how do you calculate them is what I explained the problem.

The next problem says for the free particle in a two dimensional box we have to calculate the expectation values for the product of the position coordinates x and y, the product of the square of x the average value for the square of x, the average value for the square y and then a particular peculiar quantity which is like minus h bar x dou by dou y, y dou by dou x. if you look at it carefully this will be xpy minus py px times y. It will be a cross product of position and momentum so it is something like an angular momentum and we can see that the answer is actually 0, okay for that. Let's look at the [Indiscernible] [00:10:49] box. So 2-D box. You recall that the formula for the wave function φ is given in terms of two quantum numbers n1, n2 and in terms of the two coordinate variables x and y and that is 2 by L sin n π x by L sin n π y by L. Therefore if you calculate any average value A, you have to do the following integral namely φ n1, n2 x, y star is not needed because these are real function then the operator A acting on the function φ n1, n2, x, y except that now the difference the integral is over both dx and dy because x goes from 0 to L and why also goes from 0 to L for a square box. So this is the quantity we have to calculate. The denominator is 1 because the wave functions are normalized. So if you want to calculate the average value x,y if you put x,y here the operators because they are all operators [Indiscernible] [00:12:14] mechanics. If you put x,y here you see that the integral is expressed in terms of functions products of x and products of y, this is also a product of x and y and so is this one therefore the integral separates out into two integrals namely 0 to L keeping 2 by L outside, sin n π x by L I should say this is n1 and this is n2. So n1 π x by L x operator times sin n1 π x by L dx this is one integral for the x. This is the other integral for the y 0 to L sin n2 π y by L. The operator y sine n2 π y by L dy. So it separates out into two integrals x only integral y only integral and if you have to write this as 2 by L and L by L then you know exactly that this is the particle in one dimensional problem for the x coordinate. Therefore, the answer for this is L by 2 the average value for the position of the particle is L by 2 and this is, except for a coordinate change this is also a particle in the one dimensional box with the coordinate y. This also is L by 2. Therefore the average x,t is L square by 4. It's easy.



So separation of variables and separation of the functions as products of functions of one variable times products of functions of another variable helps you in also separating out the average value calculations as one-dimensional integrals. Such things are important in mathematics and physics and also in chemistry when you calculate more and more complicated system properties it's important to see the superability of these integrals as much as possible. This is just an illustration to do that. What about the quantity x square? The average value x square for the state φ n1n2. It's also easy you can see it immediately that this integral is to 2 by L 0 to L dx sin n1 π x by L x square sin n1 π x by L is this one integral from the x part of it and the other integral doesn't have the operator. It is 0 to L sin n2 π y by L sin n2 π y by L dx because this operator x square obviously acts only on multiplies the x square or any function which is dependent on x and therefore the integration is done with the x variable only. This you already did in the previous problem. You calculated this as you recall the answer was L cube by 3 minus there is this L square by 2 n square π square, sorry this should also be L square. This is x square so this should be L square. So you calculated this. This is of course a normalization integral. This is equal to 1. So the average value of x square in the function doesn't change, in this representation doesn't change. In a similar way the average value of y square all that you do is you associate y square with this term there is no x square here and therefore this is a normalization integral and this will give you exactly the same result after all the integration, sorry this integration variable is dy. The integration here will be x with no function and the information with y contains the y square if you want to calculate the average by φ n1, φ n2 is identical and the answer is also the same.

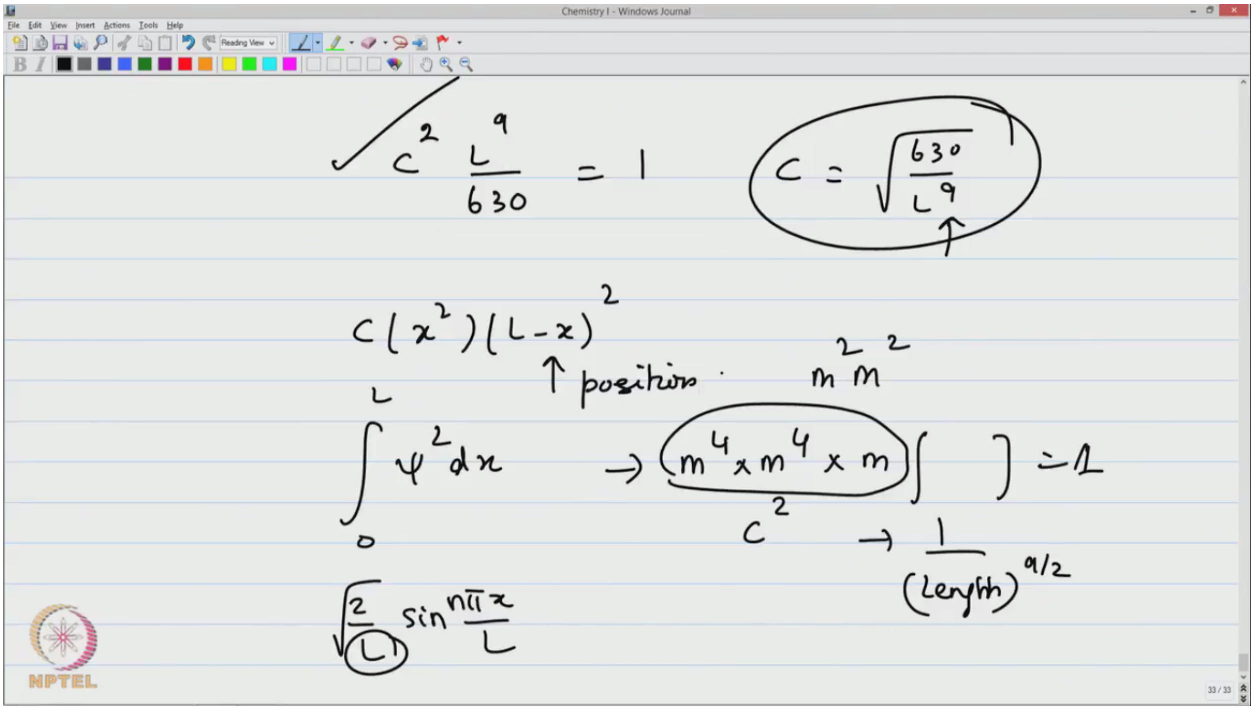
The last one is this quantity expectation value of minus ih bar x dou by dou y minus y dou by dou x. Recall that minus ih bar dou by dou y is py and minus ih bar dou by dou x is px. Therefore this integral is xpy minus pyx. The average value that's what you wanted to calculate in the state phin1, n2. You see that this is x only. This is y only therefore you can see that the first term xpy will be 2 by L sin n π x by L x sin n π n1 n1 π x by L dx. This is the x part of it and then the y part is 2 by L sin n2 π y by L and py is the derivative minus ih bar d by dy sin n2 π y by L dy and the limits are 0 to L for the square box. Then you know that this is nothing but the average value for the position which is L by 2. This is the average value for the momentum indeed coordinate representation corresponding to the wave function. Therefore it is 0. The average value for the momentum is 0. we saw some previous problem. Therefore, xpy is is 0 and likewise this is also 0 there is no angular momentum. The plane of motion does not contain the two dimensional box motion does not lead to any other motion like an angular motions or there is nothing called this is called the angular momentum in two dimension – in two dimensions and the direction of the angular momentum is perpendicular to the plane but this is 0 for the [Indiscernible] [00:19:29] 2-D box. So this is problem 8.

Problem 10 is a conceptual it's an introduction to a concept called the linear combination of wave functions are also acceptable in quantum mechanics of their functions. So what we have here is an arbitrary normalized wave function for a particle in a box is given by this formula x square into L minus x square and we are asked to find of the normalization constant C and secondly we are asked to express this wave function as a linear combination of all eigenfunction of the particle in the one dimensional box. Root 2 by L sin n π x by L is the eigenfunction with an eigenvalue en and it asks you to obtain an expression for the coefficient Cn and also what is meant by the absolute square of Cn summed over all such ns. And finally what is the average only for the energy of the particle in the state.

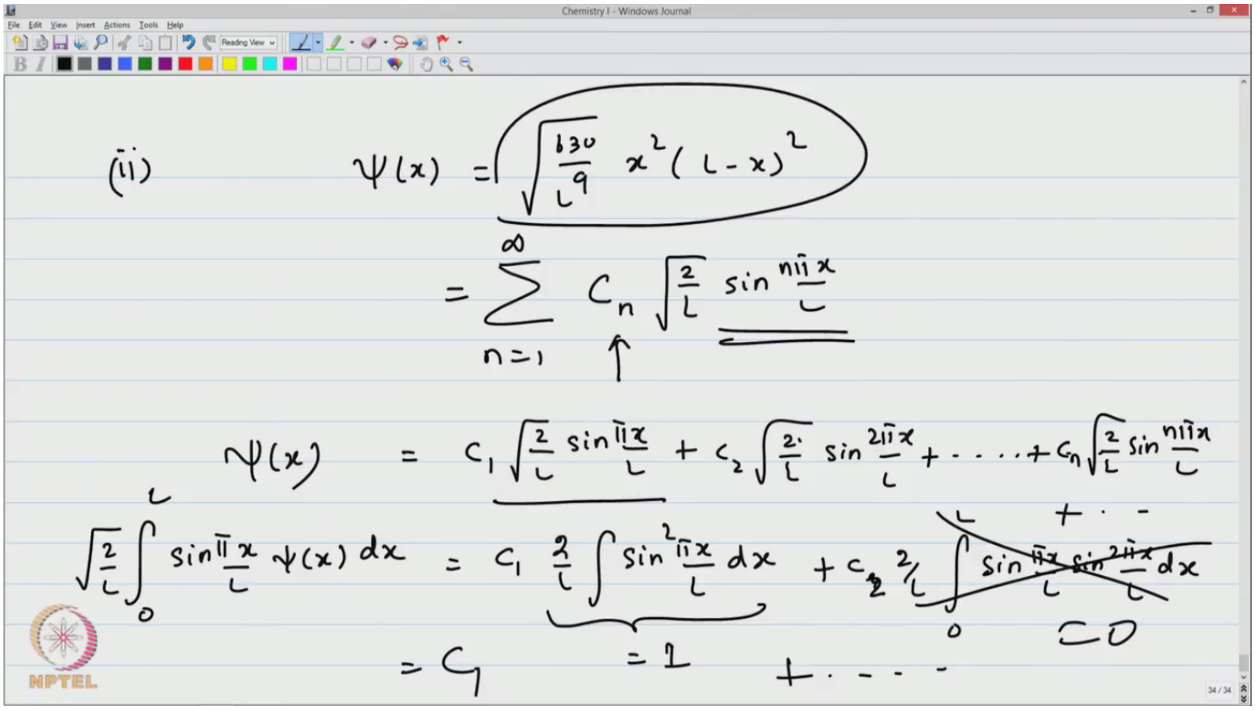
The concept in this problem is general for all of the relativistic quantum mechanics therefore please try and understand this very very carefully. First of all we write the wave function φ of x is equal to C x square into L minus x whole square. Now it's acceptable because it's normalizable. Second boundary conditions are valid. What is the boundary condition φ of L and φ of 0 they both should be 0 okay which is true in this case. Therefore this function satisfies the boundary condition. It's an arbitrary function. If you ask H on φ of x it will not give you an e on φ of x. It will give you something else because this is the second derivative. Remember it's d square by dx square the minus h bar square by 2 m and that will act on x square into L minus x square this is a polynomial. So it will give you a reduced polynomial. It won't give you the same function. Therefore this is not an eigenfunction. This is called an arbitrary state which we do not know what it is but if you try to measure the energy associated with the state we will get one of the eigenstates which the particle in the box tells us as the result and those eigenstates eigenvalue are h square by 8 m square 1, 4, 9, 16, 25, and so on so when you make your measurement you will get only one of them but unlike other regular measurements where you expect the same result for the same measurement for the same system you won't get that here. If you make another measurement on an identical system you make it different eigenvalue with a different probability and that's not different in a sense that you have a coin with two states head or tail every time you throw the coin you don't necessarily get head all the time. You get head sometimes you get tail sometimes not both one or the other and if you have a die with six phases when you throw the die exactly the same way each time you don't get the same result you get different. So there's nothing special about that part of it that this is not an eigenfunction therefore when you make a measurement you get a different energy eigenvalue each time you make a measurement. How do we incorporate that in our description of the particles of the state of the particle? That's what this is when we say C x square into L minus x whole square be expressed as a linear combination of all eigenfunctions Cn root 2 by L sin n π x by L. So this problem is to suggest that any arbitrary state can in repeated measurements if you have n number of copies of them infinite number of copies of them each one of them can give a different eigenvalue when energy is measured and therefore what is the probability that we get a particular energy when we make the measurement that information is contained in this coefficient not in the coefficient itself but in the square of the coefficients. This problem illustrates our idea.

Let us first of all normalize this function. So the normalization essentially means is φ of x square because these are all real 0 to L dx we want that to be one which means it's going to be C square square X raise to 4 into L minus X raise to 4 dx should be 1. So if you expand this C square times integral x raise to 4 it is L raise to 4 minus 4 L cube x plus 6 L square x square minus 4 L x cube plus x raise to 4 dx is equal to 1. It's a fairly simple integral to do except that there are numerous terms. The first term is for example the first term 0 to L is the limit, 0 to L the first term is x raise to 4 L raise to 4 dx and that is L raise to 4 times x raise to 5 by 5 between the limits is L raise to 5 by 5. So that's the first term. The second term for example is 4 L cube times integral x raise to 4, 5 sorry, x raise to 5 dx between 0 to L. So if you calculate this this is x raise to 6 by 6 between the limits it gives you 4 L cube by times L raise to 6 by 6, 3 by 2, 2, 2, 3. So likely as you can calculate all the individual terms and you just add all these fractions.

When you do that the answer turns out to be C square L raise to 9 divided by 630 that will be 1, that's the answer you will get when you do the arithmetic. Therefore, C is square root of 630 by L raise to 9. What is special about L raise to 9? Is it right or wrong? Look at the function C x square L minus x whole square. This is position. So the unit here is say distance or meter or whatever it is. so let us write this in the form of meter so it is meter square and this is a meter also square and then you take the integral φ squared dx you are integrating over the position. So you are integrating over quantities which are meter 4 times meter 4 times a meter, times some number that is equal to 1 okay. Therefore the normalization constant C square must have the inverse of this dimension in order for the integral to be a number, no physical dimension associated with that. Now for the dimension of C should be the square root of it one by the square root of this. Therefore it should be 1 by the length to the 9 by 2. This is also a fundamental result in quantum mechanics that if the wave function depends on a position variable in one dimension the wave function dimension will be 1 by square root of the length. You have already done that because you see the particle in the 1d box you have 2 by L sin n π x by L square root of L in the denominator. L to the half distance length to the half. So if it is a three-dimensional wave function for example for hydrogen atoms you have [Indiscernible] [00:28:41] three coordinates are there. Therefore you have you see the integral is R square, D or D theta, D5 sin theta. So the volume element is length q and the wave function is wave function and its square therefore the wave function squared must have the dimension of length to the minus 3 so the wave function should be 1 by L to the 3 by 2. So the dimension of the problem if the dimension is n, the wave function should have the unit 1 by L to the n by 2. That's what that is. This represents therefore the normalization constant that root 630 by L raise to 9 should be understood with not only the number 630 but why the number of the power of L being 9 inside the square root should be associated with the integrals that you do. Problems tell you many more things that cannot be told in the lectures. Therefore it's very very important that you solve these problems and you analyze them in greater detail.

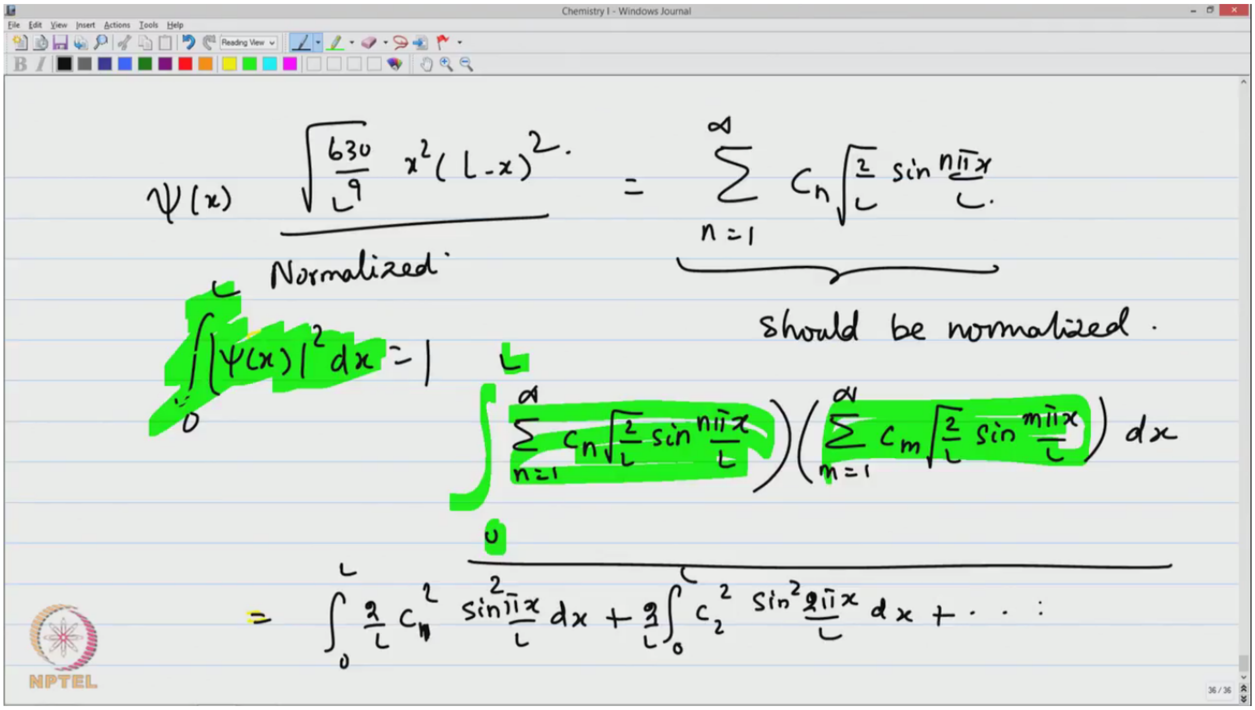


Now let's continue to the second part. We write φ of x which is now we have normalized it so 630 by L raise to 9 x square L minus x whole square we want to write this as a sum over n of all wave functions a numerical coefficient Cn which we don't know what it is root 2 by L sin n π x by L. So how do we find out Cn? It's very simple. Sine n π x by L root 2 by L they are all normalized wave functions. They are also orthogonal. For example this is nothing other than C1 times root 2 2 by L sin π x by L plus c2 root 2 by L sin 2 π x by L plus etcetera plus infinity, Cn times root 2 by L sin n π x by L and it continues and you have φ x here which is that namely this number, this function. So suppose you multiply this integral the left hand side with sin π x by L and a root 2 by L and you do φ x multiply this and then integrate between 0 and L dx then you see on the right hand side the first term gives you C1 2 by L integral sin squared φ x by L dx, okay, which you know is nothing but normalization therefore it is equal to 1. What about the next term? It is C2 2 by L integral sin φ x by L sin 2 π x by L dx between 0 to L plus other terms likewise all the other terms. You multiply every term with the sin π x by L square root 2 by L and then you do the integration. The first term gives you C1. What about the other terms? You remember that these wave functions are orthogonal to each other therefore sin π x by L is orthogonal to the sine 2 π x by L. goes to 0. What about every other term? All of them go to 0.



Therefore the general formula Cm is integral 0 to L φ m of x if it is complex conjugate if it is a complex function you should always have a star, sorry this is φ of m, this is root 2 by L sin m pie x by L star actually that's what we should be doing but anyway the star is the same as the without it φ of x dx. Therefore this m orthogonal function, orthogonal function fix the coefficient on projects the wave function to give you that coefficient Cm. So the general expression for Cm is therefore integral 0 to L root 2 by L so let me also put the other factor namely 630 by L raise to 9 0 to L dx sin n π x by L multiplying the φ of x which is x square into L minus x whole square. That's the exact formula for Cm. There are two more parts of this problem. Let's finish this and then we will some of this part of it the next the other problems will be done in the next part.

The next problem is what is the sum Cn squared? Now the wave function you know if given by this formula namely root 630 by L raise to 9 x square into L minus x whole square this is normalized. φ of x so that φ of x square dx between 0 to L is 1 okay. And on the right hand side you have sum over n equal to 1 to infinity Cn root 2 by L sin n π x by L. Okay. Therefore this also should be normalized in the sense that if you take this function sum over n equal to 1 to infinity Cn root 2 by L sin n π x by L this is an infinite sum and therefore the next infinite from that is φ 8 φ we shall write is as m equal to 1 to infinity Cm root 2 by L sin m π x by L dx 0 to L . that's what this term is. φ x square, this one sorry, the φ x square dx 0 to L. is φ x square 0 to L.



Now you can see immediately that when you expand the right-hand side with these two functions one is n π x by L the other one this goes from 1, 2, 3 to infinity this also goes 1, 2, 3, to infinity if you take the one function sin π x by L the only one that will survive this integral here is the other function namely sin π x by L. Therefore this term will turn out to be the sum will be 0 to L 2 by L C1 square sin π x by L square dx plus 0 to L C2 square sin squared 2 π x by L 2 by L dx plus etcetera. No cross terms will be possible. Cn. Cm where N and m are not the same remember that sin functions are orthogonal to each other therefore that integral is 0. So no cross term. Therefore and each one of these terms itself gives you only the coefficient C1 square because the rest of it is equal to 1 the base functions are normalized. Therefore the eigenfunction expansion gives you the orthonormal eigenfunction expansion of any arbitrary function gives you sum over m Cn square is the normalization of that function φ x φ x dx 0 to L and that's one. And the sum over Cn square is 1 therefore the quantities Cn square divided by the sum over all of them, m2 gives you the probability that the state of the system when measured for its energy for energy gives you the energy En. This is a probability and the probability is different for different n and the state itself will become root 2 by L sin n π x by L. The probability that the state φ of x which is arbitrary, it's a combination of all of them. But when you measure what is the probability that you will get eigenstate with this eigenvalue that is given by square of the co-efficient therefore that the interpretation for the linear combination coefficient the coefficients are not important they give rise to what are called the probability amplitudes and interference but the square of the coefficients tell us about the probabilities to use for the results the outcomes the measurement of the state or a given energy given eigenvalues, given eigenfunctions and so on. That's the interpretation for this. Now you know immediately you can verify that the average value energy for the system since the probability is C1 square for the state one and when it is 1 the energy measured is E1 you can see that the probability for the energy 2 is C2 square. The probability for energy 3 is C3 square and so on. Therefore the average value is n equal to 1 to infinity Cn square I will just put the C without the absolute values but they are the absolute values times En. This is the average value. Now you can see that if it is eigenstate then all coefficients are 0 except one and that means it's that energy therefore the energy measured for an eigenstate is always the eigenvalue. If it is not an eigenstate any one of the energies are possible and the probabilities which this happen or given by these coefficients for this problem is extremely important in understanding the conceptual generalization of a simple eigenvalue, eigenfunction of a particle in a box the arbitrary wave function, the normalization of an arbitrary wave function and the expansion of an arbitrary wave function in terms of the basis are the eigen basis; all these concepts are tied up in this one problem. We will continue with the remaining problems in the next part.