Chemistry Atomic Structure and Chemical Bonding
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Lecture – 46
Video Tutorials on Angular Momentum (Orbital and Spin) and Variational Method
Part – II

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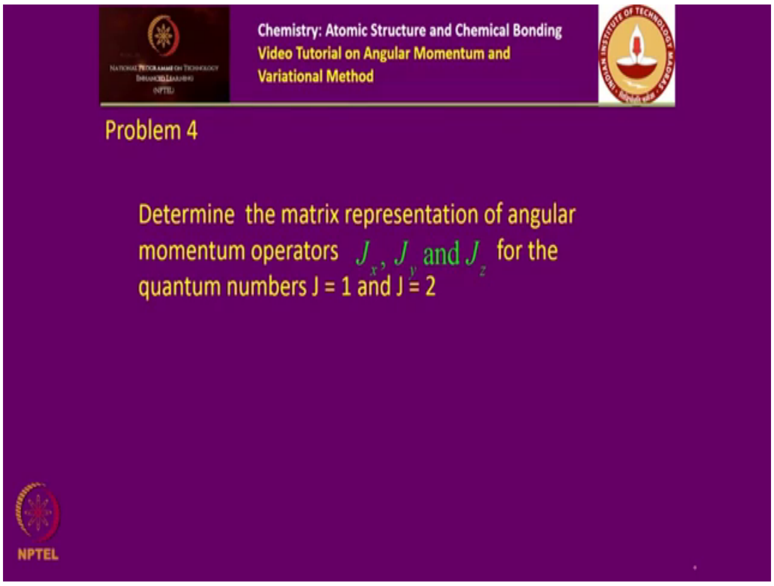

So, we shall continue from the process where we left; namely we representation for the angular momentum operators x y and z within the basis set for J is equal to 1. And the basis set for J is equal to 2 is identical in principle for the calculations.

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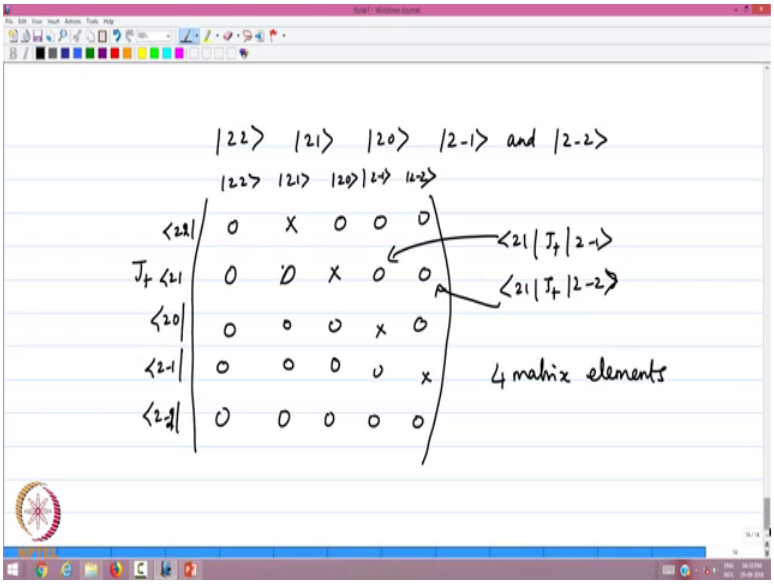

But there are 5 basis functions and the basis set is given by the basis set is given by this 5 basis functions 2 2 2 1 2 0 2 minus 1 and 2 minus 2. Therefore, following the same argument that we had, if we write J plus as a 5 by 5 matrix remembering that the basis functions where ordered in this form 2 minus 1 and 2 minus 2 and in the last state, they were ordered this way 2 2 2 1 2 0 2 minus 1 2 minus 2.

You can see that this element is 2 2 J plus on 2 2 this will be 0 and J plus acting on 2 1 will give you a 2 2 therefore, this is nonzero and all the others will only step up once, but this is already more than one step away therefore, this is 0 this is 0 this is 0. And J plus operator is stepping up. Therefore, 2 1 2 2 is not possible J plus 1 2 2 is 0 and diagonal element is also 0 and so, what we have is this and the other 2 are also 0 these are 2 steps away from each other the J 2 1 and this is for example, 2 minus 1 and this is 2 1 2 2 2 2 minus 2 2 1 J plus 2 minus 1 and 2 1 J plus 2 minus 2.

That is this element and this is this element and they are; obviously, 0. So, if you continue this you can see right away the diagonal of diagonal form that this is what you will have you know and all the 5 elements are 0, because none of them will give you 2 minus 2 when they J plus x on them. So, this is 0 therefore, you have to calculate 4 matrix elements only and you have to use the same formula that we had.

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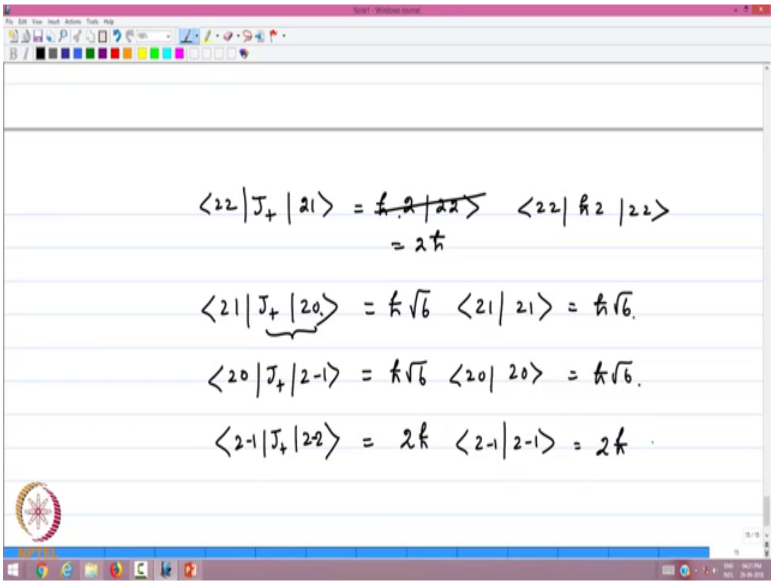

J plus on 2 1 is going to give you h bar in the last representation I omitted the h bar.

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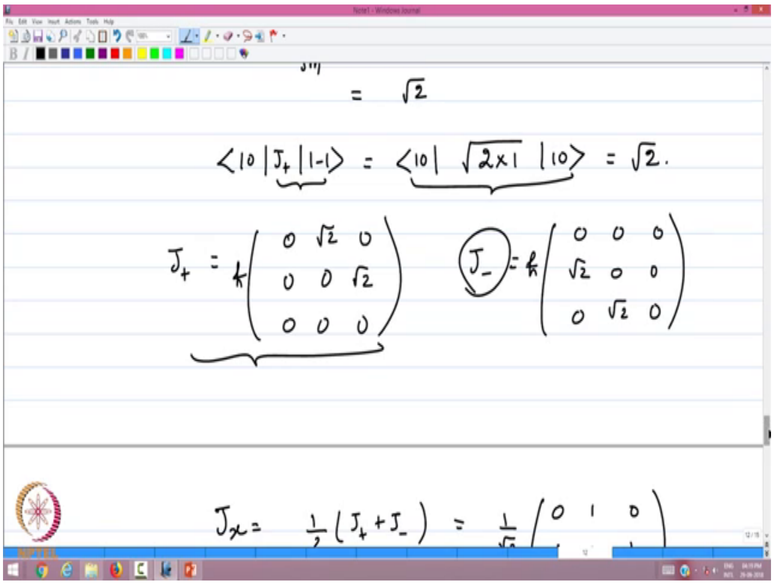

So, you must put the h bar here, and you must put the h bar here in the representation of this angular momentum.

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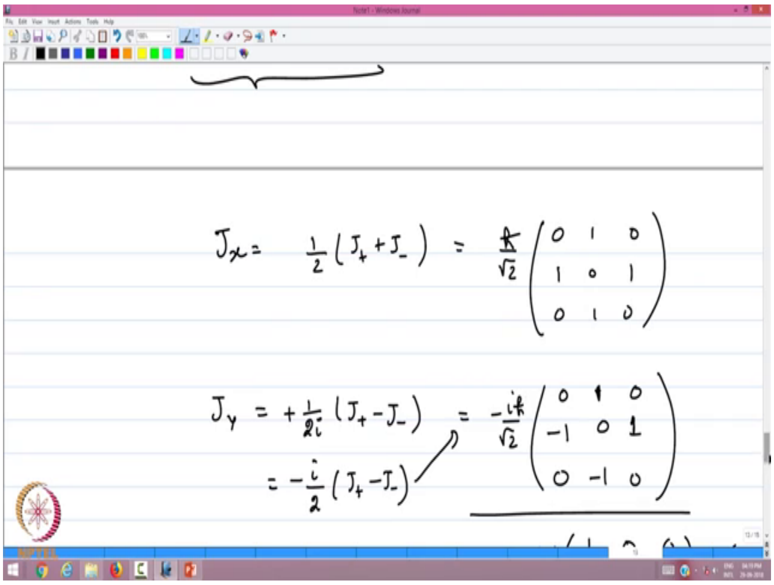

And like ways this is also h bar by 2 and this is minus i h bar by root 2 please keep this in mind so, on yeah. And if we do the same thing here J plus on 2 1 you have h bar J minus m which is 1, J plus m plus 1 is 4 therefore, it is 2 and then the state is 2 2. Therefore, the state 2 2 acting on this will give you 2 2 h bar 2 acting on 2 2

So, we answer is 2 h bar likewise the element 2 1 J plus acting on 2 0, gives you this is square root of J plus m which is 2 J plus J j minus m which is 2 and J plus m plus 1 which is root 3 therefore, this gives you root 6, and the state will be 2 1 after the action of this and therefore, it is h bar root 6 2 0 J plus on to minus 1 will give you again the same thing, J minus m will be 3 and J plus m plus 1 will be 2.

So, it will give you h bar root 6 2 0 2 0 and this will also be h bar root 6 and the last is 2 minus 1 J plus on 2 2 2 minus 2; and you can see that J minus m is 4 J plus m plus 1 is 1 therefore, this will give you 2 h bar 2 minus 1 the state 2 minus 1 into h bar.

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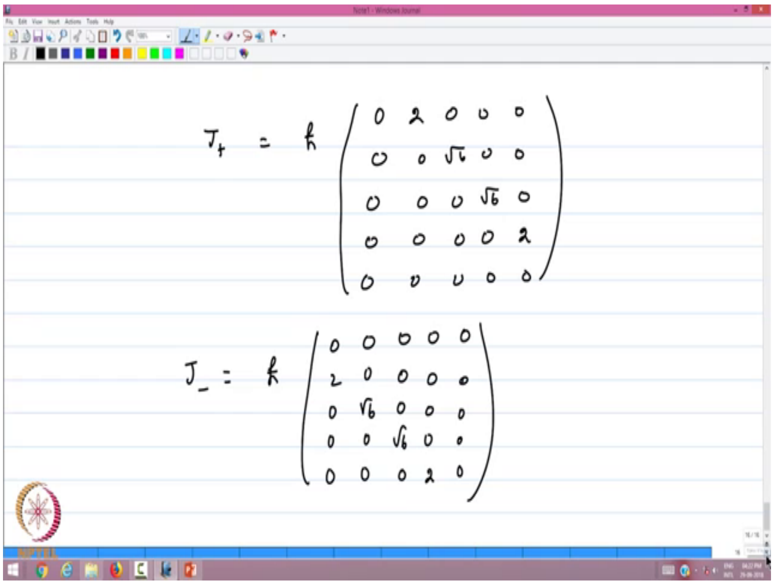

So, the matrix element for J plus is immediate that it is h bar 0 2 0 0 0 0 0 root 6 0 0 0 0 0 root 6 0 and 0 0 0 2 and its 0 0 0 0 0.

Therefore you can see the matrix for J minus is the Hermitian adjoint of course, these are real numbers therefore, you have simply 0 2 0 0 0 the adjoint the transpose of the row, and the transpose of the second row is 0 0 root 6 0 0 the transpose the third row is this, and the transpose of the fourth row is 2 and the transpose of the fifth row is all 0. So, this is J minus.

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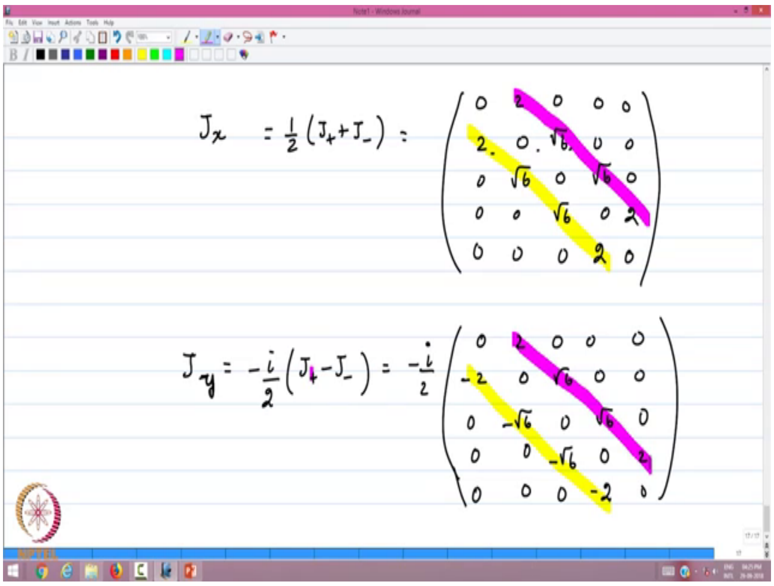

And therefore, you can see immediately that J x is 1 by 2 times J plus plus J minus and so, you can see all the elements which are not 0 0 2 and of course, this is a J x is a Hermitian matrix you can see it right away and this is root 6 0 0 0 and you can see that this is 0 0 0 and this is root 6.

So, you will have 2 0 root 6 here 0 0 0 and this element is root 6 0 0. Therefore, its Hermitian the transpose of that will be root 6 0 and this will be 0, and this is 2 2 1 2 3 I have a next column here that is what I am what happened. So, 0 2 0 0 0 2 0 root 6 0 yes this is correct and now this will be 2 and this is 0. So, this is J x J minus is minus i by 2 J plus minus J minus therefore, you can write this as minus i by 2 and this component is all J minus please remember this is all J minus component

This is all J plus component; the J plus component remains unchanged of course, minus i by 2 has been taken out therefore, J minus can be written very the J z sorry J y' J y can be written immediately as this way and so, what you have is 0 2 0 0 0 minus 2 0 root 6 0 0, and then you have minus root 6 0 root 6 0 because all of this is J plus and then the minus is there is a minus 2 here let me write fourth one this is 0 0 this is 0 0 and then you have 1 2 3 4 5 all these things are there. So, you have root 6 0, and you have a root 6 here with a minus sign and you have a minus 2 here this is what you will get.

So, this is all from the sorry this is all from the J minus with a minus sign and all of the others are from the J plus with the plus sign. So, J x J y and of course, J z is very simple because its diagonal and its simply the m value.

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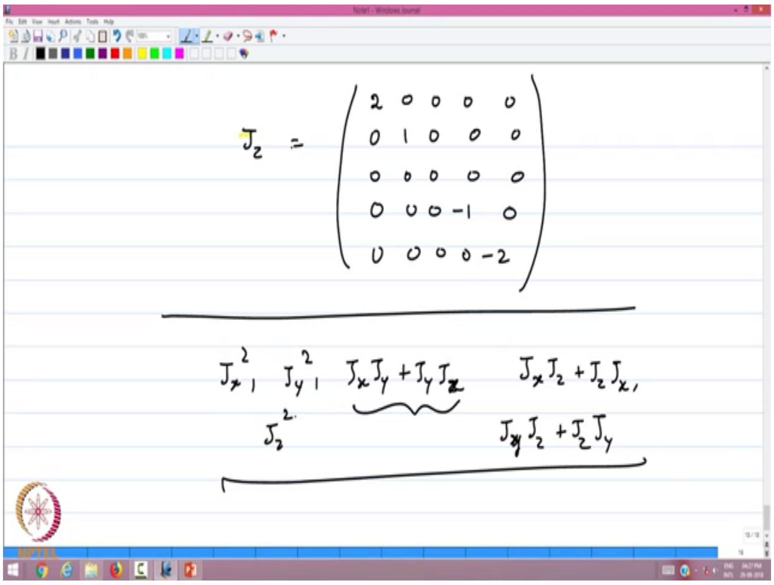

So, J z is immediately written as you know m being 2 0 minus 1 minus 2 1 0 minus 1 minus 2. So, you have 2 1 0 minus 1 minus 2 and so, you have these zeros of all these things 1 2 3 4 this is diagonal. So, you have 1 2 3 4 there are 5 of these and that is that is the J z operator.

Once you know these operators is possible for you to write J x square, J y square, J x J y plus J y J x this is a Hermitian in combination J x J z plus J z J x and J y J z plus J z J y; you can simply multiply the matrices that you have to get the operator form of the the matrix form of the operators given here and also J z square ok. So, this is a very simple way of representing angular momentum matrices, for the angular momentum operators using the basis functions which are diagonal for the operators which are diagonal or the J square operator and the J z operator. This is problem 4.

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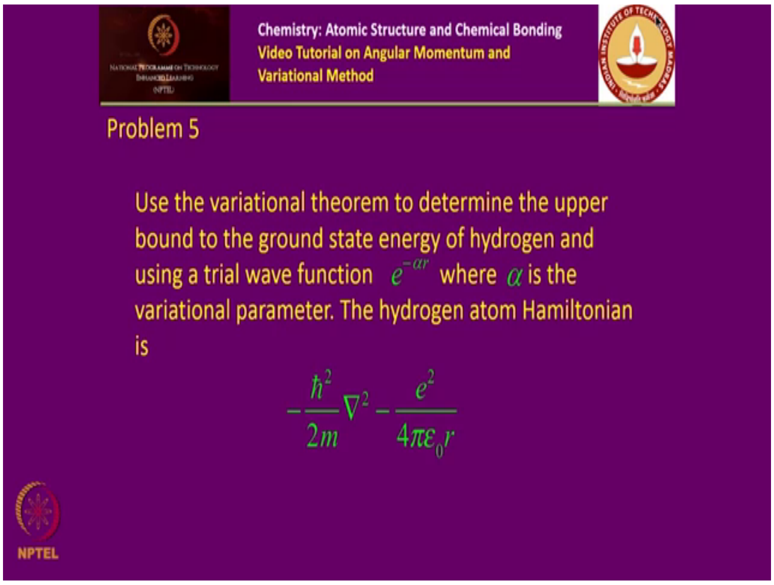

Now, theorem to determine the upper bound to the ground state energy of hydrogen, and using a trial wave function exponential minus alpha r where alpha is the variation parameter. The hydrogen atom Hamiltonian is minus h bar square by 2 m del square minus e square by 4 pi epsilon naught r.

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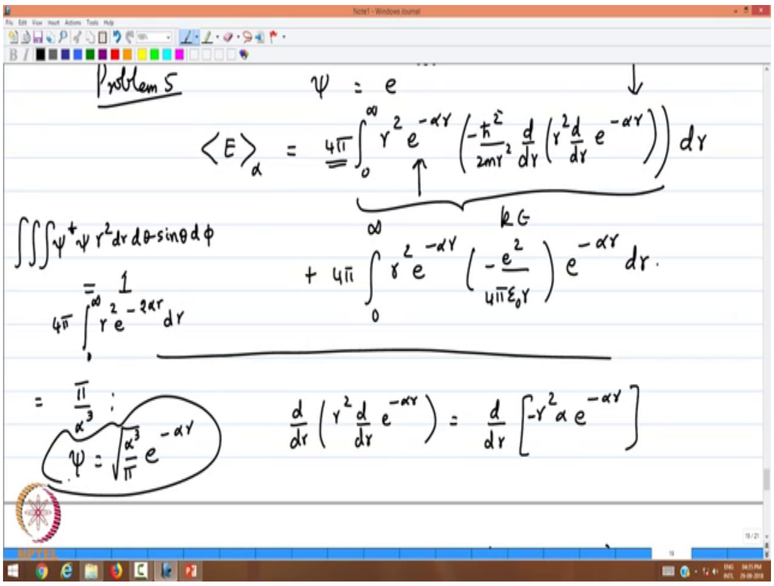

Psi given as e to the minus alpha r and the expectation value you were supposed to calculate as a function of the parameter alpha is for the operator from 0 to infinity r square e to the minus alpha r and the hydrogen atom Hamiltonian that you need to worry about is only the radial part minus h bar square by 2 m r square d by d r r square d by d r acting on e to the minus alpha r d r all the angular parts the integral gives you only 4 pi.

Because the function does not contain any angular variable therefore, the rest of the Hamiltonian containing the angular variables acting on the exponential minus alpha r will give you 0. If there is no need for them, and the integration of the angular variables over 0 to 2 pi and 0 to pi sin theta d theta d pi will give you 4 pi for this is all that you have to calculate this is for the kinetic energy, and a corresponding term that you have to calculate this 4 pi 0 to infinity r square e to the minus alpha r minus e square by 4 pi epsilon naught r e to the minus alpha r d r.

This is the expectation value for the energy e, using the Hamiltonian and the wave function the exponential minus alpha r therefore, this is a function n of alpha. In fact, you would see that once what is you calculate the e of alpha, I would only write 2 or 3 steps because its again a straightforward integration problem. So, you should be able to calculate this quantity for example.

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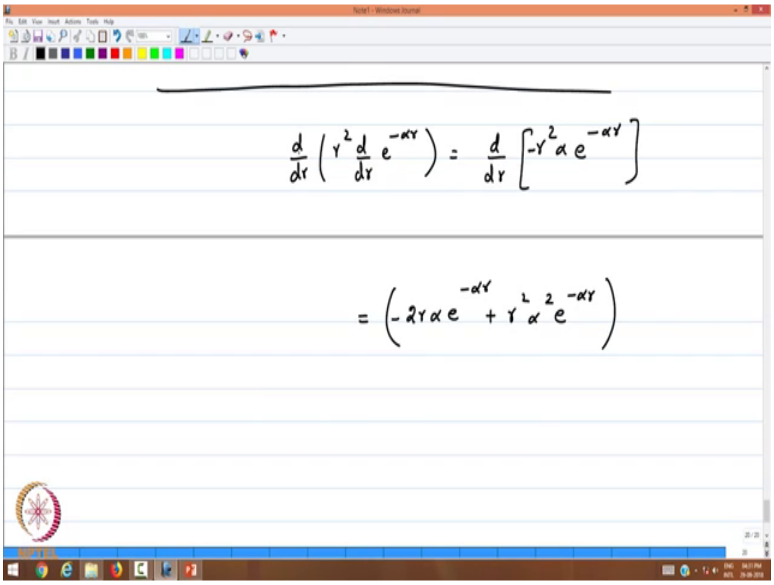

Ah 1 by r square d by d r let us leave the 1 by r square out because that anyway gets cancelled with the r square part of the integral itself.

So, if you write this d by d r, r square d by d r of exponential minus alpha r then what you have is it is a d by d r r square minus r square alpha e to the minus alpha r. And you can see that the second derivative gives you this result minus that is also you have minus 2 r alpha e to the minus alpha r and then you have a plus r square alpha square e to the minus alpha r. So, this is everything that is in the derivative form, but for this minus h bar square by 2 m r square ok.

So, you can substitute that and do the integral.

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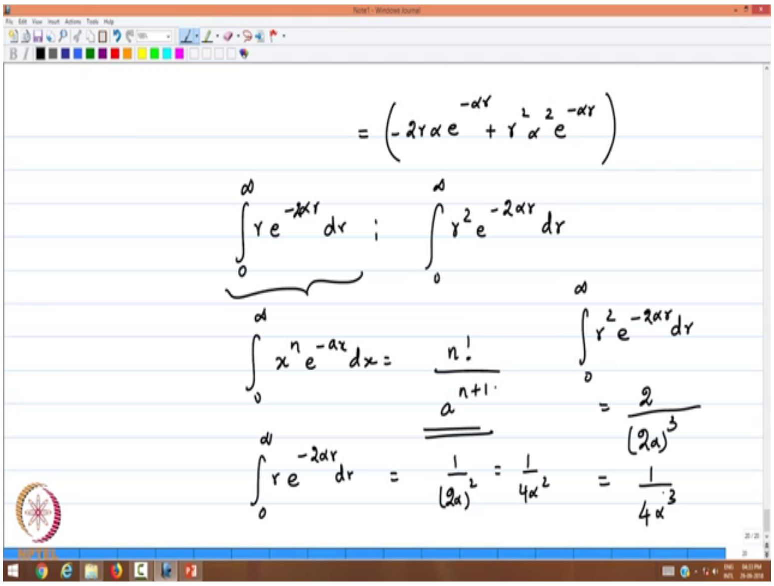

The integral that you need to do or the following or e to the minus alpha 2 alpha r d r from 0 to infinity, and the other integral that you have to do is 0 to infinity r square e to the minus 2 alpha r d r. This integral is a standard integral please recall that we use this in one of the problem sets earlier, that this is x raise to n e to the minus a x d x is n factorial by a raise to n plus 1.

Therefore this will give you the integral from 0 to infinity or e to the minus 2 alpha r d r will give you n is 1 and a is 2 alpha therefore, you will have 1 by 2 alpha square, which is 1 by 4 alpha square. And the other integral that you will get namely r square e to the minus 2 alpha r d r from 0 to infinity is n is 2 therefore, its 2 factorial which is 2 divided by a is minus a is to alpha raise to n plus 1 is 2 alpha cube and therefore, it will give you a 1 by 4 alpha square 4 alpha cube. So, sorry 4 alpha cube.

These are the only 2 integral details that you need to know in order to calculate this, and if after some time maybe about half an hour if you do not make any mistakes or probably less than that if you are first enough the integral that you calculate of course, there is also one more item that I have missed here, the wave function should be normalized therefore, you need to do psi star psi r square d r d theta sin theta d phi; this should be set equal to 1 and this will be the answer to this will be 4 pi that comes from the angular integration and the integral is 0 to infinity r square e to the minus 2 alpha r d r and that would give you, you remember this gives you 2 factorial divided by 8 alpha cube therefore the answer you will get is pi over alpha cube..

Therefore, psi is square root of alpha cube by pi e to the minus alpha r; this is to be used in your calculation. The result of doing those integrals would be is it just algebraic x step.

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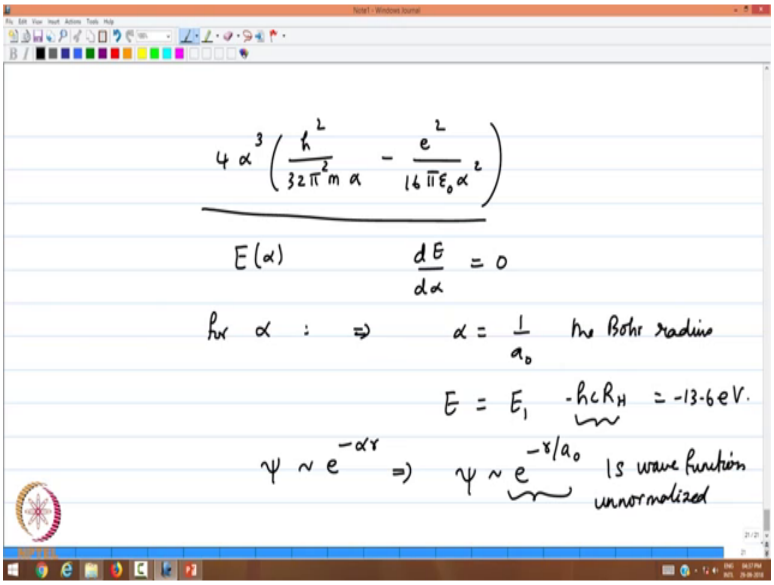

So, let me give you the answer that you will get 4 alpha cube h square by 32 pi square m alpha minus e square by 16 pi epsilon alpha square ok. Now you have to remember the to equate this, if this is to be given as a the E of alpha. Then you have to set to the d E with respect to d alpha to be 0 and then obtain an expression for alpha

And if you take the derivative of this expression and you set the derivative to be 0 and you want to minimize this so, that the energy is the lowest energy, you will see without any specific difficulty you would see that alpha is exactly 1 by a naught the Bohr radius. At which point the energy that you get will be exactly the energy E 1 which is minus h c Rydberg constant and that is minus 13.6 e V. The very reason for choosing the the very reason for choosing the wave function psi to be exponential minus alpha r for the ground state   is to make you recognize that psi which is exponential minus r by a naught is the 1 s wave function unnormalized.

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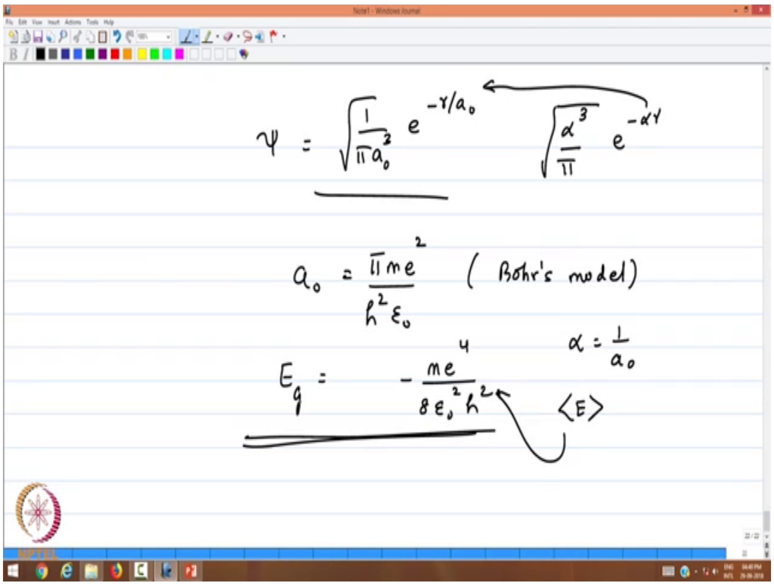

And if it is normalized you will see that psi is 1 by pi a naught cube e to the minus r by a naught. They call the similarity of this with the term that you have alpha cube by pi square root e to the minus alpha r.

You see that alpha is 1 by a naught, gives you immediately the ground state exact ground state therefore, the wave function that was given to you is for you not to do the whole calculation, but to guess the answer that alpha has to be 1 by a naught and then therefore, the wave function is that and the energy that you obtain is minus h c Rydberg constant r minus thirteen 13.6 c V you what you might be what you might have to also remember is the following formula for the coefficients a naught and the energy e. A naught is pi m e square by h square epsilon naught this is from the Bohrs model. And the E that you calculate is minus m e raise to 4 by 8 epsilon square h square. This is what you will get when you realize that alpha is 1 by a naught and therefore, the average value e is exactly the ground state this is the ground state energy.

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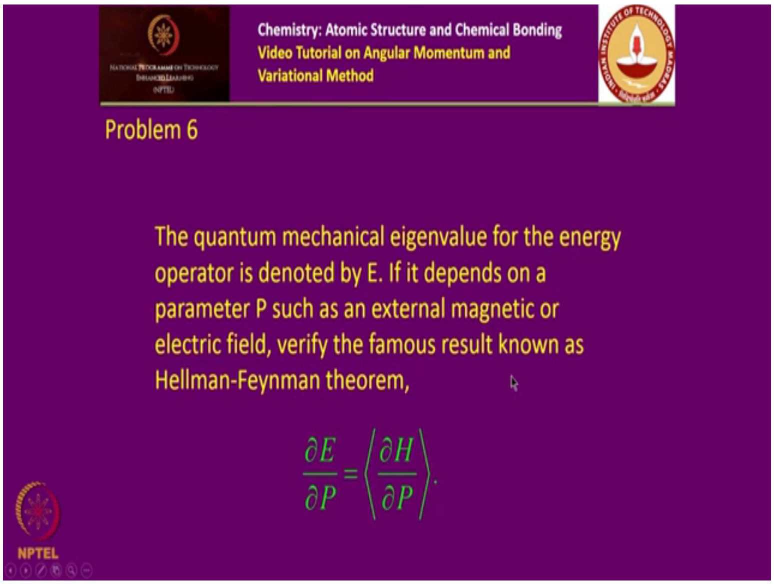

The next problem is an important result in all of quantum chemistry and it is fairly a straightforward and simple result first given by the Hellman and working with Richard Feynman and this is known as the Hellman Feynman theorem. The problem states that the quantum mechanical eigenvalue for the energy operator is denoted by E which is the eigenvalue for the operator H. If the eigenvalue depends on a parameter P such as an external magnetic field or electric field verifying verify that the famous result that was given as Feynman theorem namely, the derivative of the eigenvalue E with respect to the parameter is equal to the expectation value of the derivative of the Hamiltonian which is a function of P. This is the angular brackets tell you that this is the expectation value of course, what you have on the side is a number and therefore, you must actually get a number here and h is a Hamiltonian expressed as a function of P and so, the number that you get out is the expectation value now for the average value of the energy eigenvalue is nothing, but the expectation value of or the average of the Hamiltonian operator this is problem 6.

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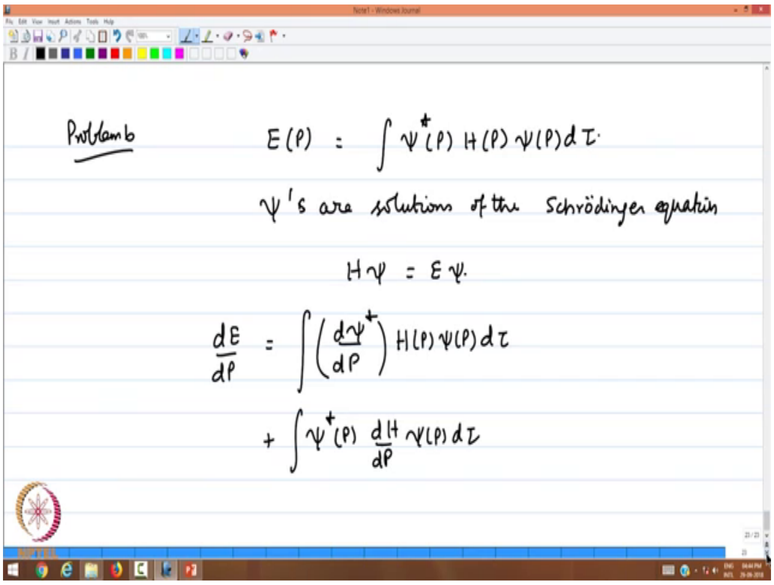

The energy is written as a function of parameter P as psi star of P H of P and psi of P d tau. Let us assume that psi are the solutions of the Schrodinger equation and its easier ok. So, if psi is a solution then H on psi is going to give you E on the psi. Now let us calculate to the derivative d E by d P when what you have is, the integral the derivative goes inside the integral it calculates the d psi star d P then its H of P psi of P d tau that is a first term then there are 2 other terms which are derivatives which are functions of P and therefore, you have psi star of P d H by d P of psi of P d tau.

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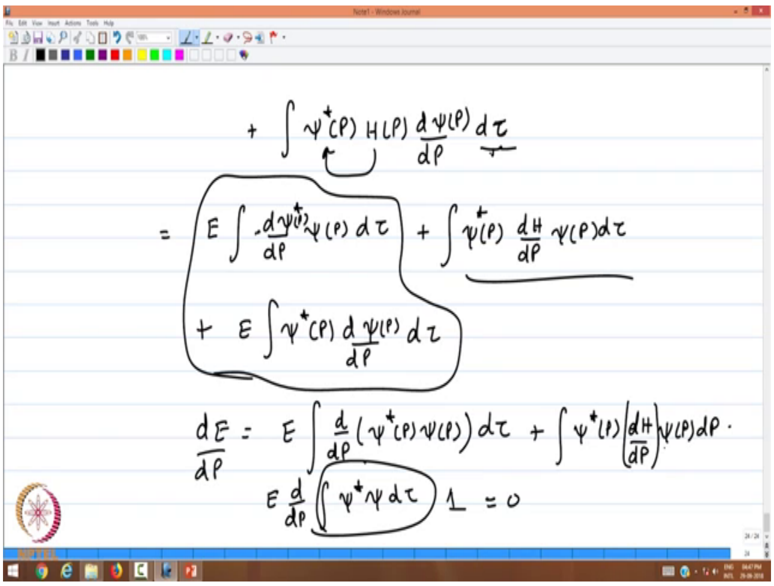

And last one plus integral psi star of P H of P d psi of P by d P d tau this is the volume space integral ok. P is some parameter on which the Hamiltonian depends on and therefore, the expectation value also depends on that parameter. Now the H acting on P because H is a Hermitian operator you know that this is going to give you real values and likewise the H acting on P is going to give you the real value eigenvalue e. So, if you write the next step we have E times d psi star by d P psi of P d tau that is the first term. The second term is; obviously, psi of P star d H of d P over d P and psi of P d tau and the third term taking into account hermiticity, you have E psi star of P d psi of P by d P d tau.

You can see that these 2 terms immediately add as nothing other than the derivative d E by d P as nothing other than this derivative E the integral d by d P of psi star psi, d tau and the term which is not disturbed is this one psi star of P d H by d P psi of P d P. And this is of course, you know d by d P P is a parameter that is not controlled by the integral therefore, this is nothing other than E d by d P of the entire integral psi star psi d tau this is 1 normalized or is it a constant therefore, its independent of P therefore, this is equal to 0.

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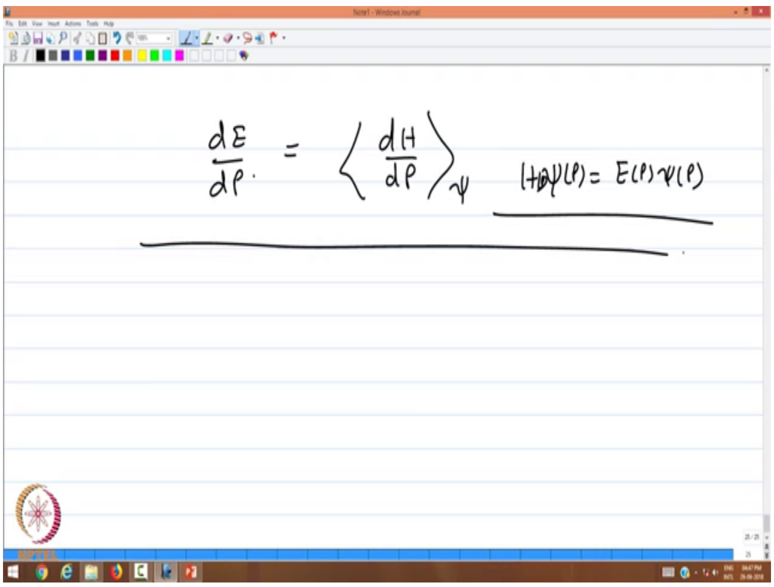

And what you see here is nothing, but the average value for the operator called d H by d P and that is why it is written as the expectation value d H by d P on psi as the d E by d P where H on psi E gives youE E on psi which is also a function of P when we direct proof or direct verification of the Hellman Feynman theorem.

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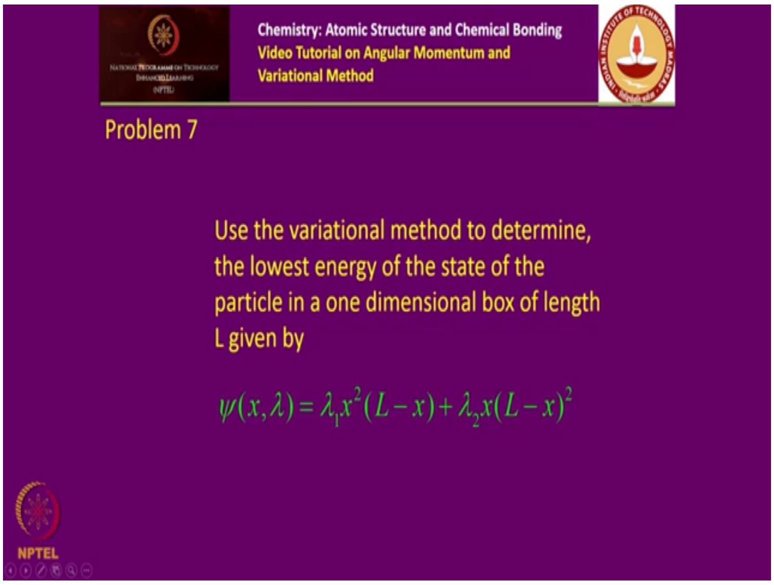

Let us look at the next problem, this is a algebraically it is a long problem, but the methods are extremely simple I have given an exact calculation in the theory in one of the lectures the earlier, and this problem is on the variational method and its used to determine the lowest energy of the state of the particle in a one dimensional box given by the formula given by the state.

The state is an arbitrary state psi x comma lambda, lambda is basically lambda 1 and lambda 2 as a variational parametric set of lambda 1 and lambda 2, with 2 basis functions x square into L minus x and x into L minus x whole square ok. Both the wave functions satisfy the particle in a 1 dimensional box boundary condition, L is the length of the box therefore, I might want to say that somewhere here one dimensional box of length L L given by this formula.

Now, I have done this precisely for a 2 2 by 2 2 matrix problem earlier. So, let me recall the mathematical steps for you to calculate.

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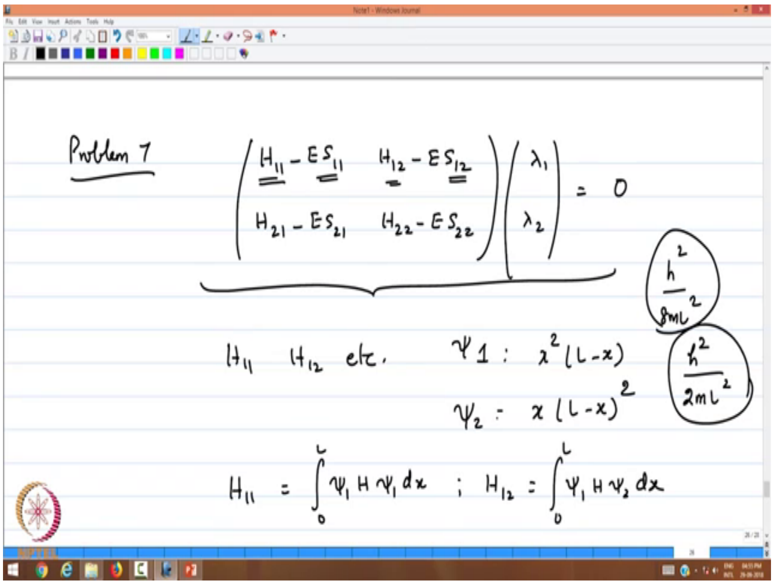

In one of the lectures earlier I did mention that one must variationally minimize this determinant H 1 1 minus ES 1 1 H 1 2 minus ES 1 2, H 2 1 minus ES 2 1 and H 2 2 minus ES 2 2 this is what we had said into the coefficients here its of course, lambda 1 and lambda 2 is equal to 0

We wanted to find out lambda 1 and lambda 2 in such a way that E is minimum, but this is what you have to do in order to get this and if you solve the determinant you will get 2 eigenvalues and the smaller of the 2 eigenvalues is the one that is closest to the ground state eigenvalue. Therefore, the calculation involves recognizing the matrix elements and the overlap integrals, and for H 1 1 H 1 2 etcetera what is 1 and what is 2? One is given by this function namely go back and look at the function this is the first function x square into L minus x that is 1 1 the function psi 1 is x square into L minus x. The function psi 2 is x into L minus x whole square see the x into L minus x whole square.

So, essentially this is the same as you are this is the same as you are c 1 times phi 1 and c 2 times phi 2, and H 1 1 is given as the corresponding 1 phi 1 H phi 1 and H 1 2 is phi 1 H phi 2 and so, on so. Now let us look at this therefore, if we call psi 1 as this, H 1 1 is the integral psi 1 H psi 1 d x between 0 and L and H 1 2 is the integral 0 to L psi 1 H psi 2 d x.

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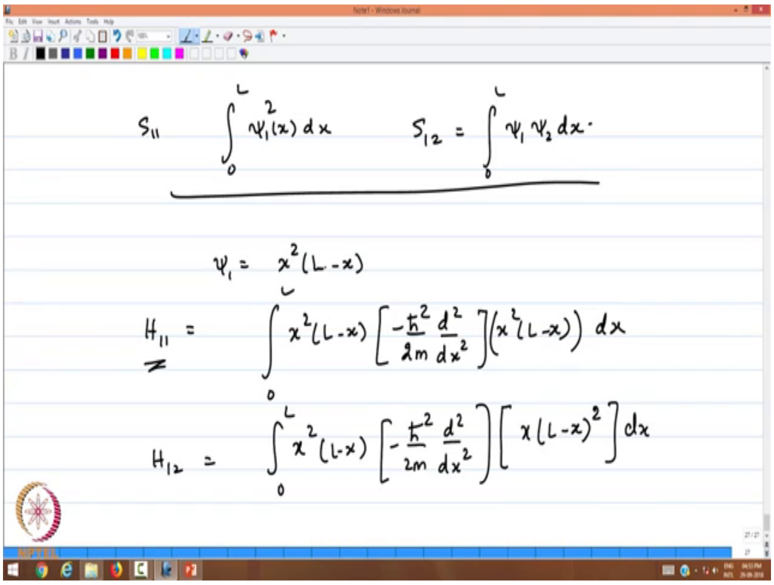

And the integral S 1 1 is psi 1 of x square 0 to L d x and the overlap integral the S 12 is the integral 0 to L psi 1 psi 2 d x.

All these functions are extremely simple, namely psi 1 is x square into L minus x therefore, let us just do one element calculation H11 is nothing other than x square into L minus x, times the Hamiltonian for the particle in a box which is minus h bar square by 2 m, d square by d x square acting on the function x square into L minus x d x between 0 to L this is H11 and what is H 1 2? H 1 2 is 0 to L the first function is still x square into L minus x and the Hamiltonian is minus h bar square by 2 m d square by d x square. But the second function is x into L minus x whole square d x.

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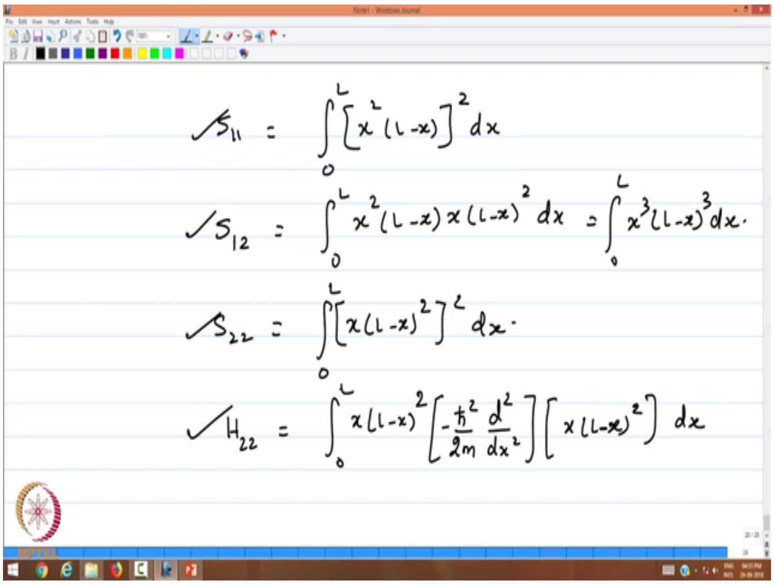

Likewise S 11 is the integral 0 to L, x square i think yeah x square into L minus x whole square d x and S 12 is the integral 0 to L x square into L minus x times x into L minus x whole square d x, which is 0 to L x cube into L minus x whole cube d x. And likewise S 2 2 is the integral for the second function namely x into L minus x whole square between 0 to L, d x. I guess we have defined all the integrals that need to be yeah that is also one more H 2 2, which is 0 to L x into L minus x whole square times minus h bar square by 2 m d square by d x square acting on the function x into L minus x whole square d x

So, we know this we can calculate all these things are very simple integrals you have to just sit down and do the algebra, they are elementary integrals the derivative and polynomials is so, easy to calculate, that its possible for you to calculate all these things 1 2 H 1 1 and H 2 2, and you simply substitute that in this determinantal are the in this Hamiltonian matrix and take the determinant to be 0, you get 2 answers for e the lowest of the 2 is the 1 that is closest to the ground state function. Please remember the ground state function for the particle in a box is h square by 8 m L square and the next energy state for the particle in a box is h square by into m square m is 2 therefore, it is 2 m L square.

So, you can see that how much e 1 differs from this answer, and how much e 2 differs from the e 2 gives you an idea whether your model wave function is approximately is is good or is it really a bad approximation so, on. But of course, in a particle in one dimension box we know the solutions therefore, this is purely it to illustrate how to handle such things using known methods therefore, this is a fairly simple enough exercise I have not solved this into the numerical form because all the integrals that I have left for you have to calculate you can calculate.

Now, I think that brings to the end of this particular video tutorial of 7 problems, and again as i have said earlier this time I have not even given the final solutions therefore, that is enough room for you to sit down and time for you to sit down and work out the answers for familiarizing yourself with the mathematical techniques, and also the basic algebraic calculations ok..

We will continue with the particle with the the linear combination of atomic orbitals for the molecular orbital definition for the diatomic molecules, and starting with the hydrogen. I think we looked at hydrogen molecule already what we will look at the other homonuclear and heteronuclear diatomic molecules until then.

Thank you very much.