Introductory Quantum Chemistry
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Lecture - 43
Hydrogen Molecular Ion – continued

So, this is essentially continuation of my previous lecture and I have derived expressions for these integrals the integral here and the integral there. And I have removed everything that I do not need from the previous lecture. And I am left with this expression for the numerator in here and that expression for the denominator.

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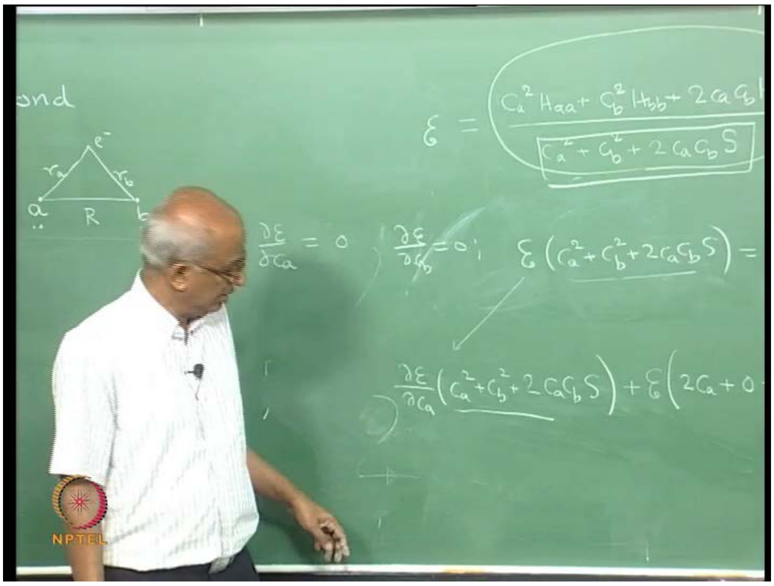

So, therefore, if you substituted this expression you are going to get c a square H a a plus c b square H b b plus, divided by c a square plus c b square plus 2 c a c b into S. For what is S? I would like to remind you, what it is? S is defined to be integral d Tau 1 s a 1 s b. Product of 1 s a and 1 s b and often there is this question, why is it that this integral is not 0, because you normally learn that if you multiplied any two atomic operates and intergraded it them over the entire space the answer is actually 0.

Now if the orbitals belong to the same atom; that means, if I have taken, let us say 1 s a and multiplied it by 2 s a, where 2 s a is an atomic orbital on the same atom and integrate over the entire space the answer will be equal to 0, but 1 s a and 1 s b are not on the same atom they are on different atoms. And further what is the shape of 1 s a? 1 s a is having this kind of the shape and how is 1 s b, well this is 1 s b right. So, therefore, in these integral what you are actually doing is, maybe I will use different colours this is 1 s a and that is 1 s b. And remember every where the both the functions are positive, this is positive. 1 s a is positive 1 s b also is positive.

So, therefore, you are actually multiplying two functions which are positive and therefore, what will happen? The product will actually be positive and you integrate, is integration is just a process of summation. So, some over all points in space what is the result? The result can only be positive it cannot be 0. And further when you multiply that two functions, where is that the product has the largest value. Well if you are thinking of a point somewhere here, see their one, the distance from nucleus a is not large and therefore, 1 s a will have the fairly appreciable value, but the distance from the other nucleus is large and therefore, 1 s b will have a small value and therefore, what will happen? The product will have a very small value at this point, over at that point.

Because you see, the distance from nucleus b is large. Similarly if you think of a point here, there again the product will have a very small value, because the distance from nucleolus a is large. But if you are thinking of this region, which is in between there the values of 1 s a and 1 s b are appreciable, because the distance from nucleus a and nucleolus b both of them are not large. And therefore, when you think of the product, the product will have a large value in the inter nuclear region. That is the region where the two orbitals we say over lap.

So, essentially this integral is a measure of how strong the overlap between the two atomic orbitals is. And because of that, this integral capital S is referred to as the overlap integral. And it gives an idea of how strong the interaction between the two orbitals is basically. So, now we will do is having defined this overlap integral, let us proceeds we have our expression for script E and what should I do now, I have to find out or I have to think of c a and c b right. I have to think of script E as a function of c a and c b and then find the maxima or minima of this function right. I should find the minimum of this function, how will I do that, the answer is that I will have to put dou E by dou c a equal to 0, I think it is already written here.

I will have to put that equal to 0. I shall also have to put dou e by dou c b is equal to 0 right. These are the two conditions to have a minimum now; this means that I have to take this expression. Write this expression I will have to take and differentiate that with respect to c a put the derivative equal to 0 and then differentiate that again and once more with respect to c b and put that derivative equal to 0. Now this looks like a tedious thing because you have to differentiate a ratio, but what we will do is a simplifying trick, my script E given by this expression. So, instead of differencing that expression what I will do is little bit difference. I will first multiply this function by this; I will multiply this equation throughout by this factor.

So, if you did that multiplication what is their equation that you are going to get? You will get script E into c a square plus c b square plus 2 c a c b into S is equal to c a square H a a plus c b square H b b plus 2 c a c b H a b this is what you will get right. Now, having got this equation, what I will do is, I will just go ahead and differentiate. Because after all I just want a difference find a derivative of script E.

So, now, with this equation suppose I differentiated this equation with respect to c a partially, then what is the result that I am going to get, well from the left hand side you are going to get dou E by dou c a into c a square plus c b square plus, oh yeah this is correct, thought I had made a mistake right. If you differentiated the left hand side you will get derivative of script E with respect to c a plus script E into the derivative of this term with respect to c a remember I am differentiating partially with the respect to c a.

So, derivative of this term will be 2 times c a and remember you are differentiating partially with respect to c a; that means, the derivative of this term will be equal to 0. And what will be the derivative of this term; it will be 2 times c b into S. So, that is the derivate of the left hand side what will be the derivate of the right hand side? It is going to be 2 c a H a a. I am differentiating this term, if I differentiated this term you will get the answer to be 0, because that term does not depend upon c a. And the last term will give me 2 c b H b b fine.

Now, if I want, I can rearrange this expression I can take this to the right hand side and then divide throughout by that term and get an expression dou E by dou c a, if I want, but that is unnecessary. Because afterword I going to put this equal to zero so, straight away in this equation I can put this equal to 0. And so, I get one equation what is that equation? I put this equal to 0 and I get that, this must be obeyed. And in that equation I can make simplifications because 2 is common. So, remove that 2. And further you take the terms on left hand side to the right hand side so, what will happen? If you did that, take this terms to the other side then, you are going to get H a a, what is this term H a a into c a, but one more term will come because, you have script E into c a. That I am taking to the other side.

So, therefore, this minus script E will be the first term. And then there are two terms actually which involves c b, what will they be, the term which is already there. There is my mistake. This is actually you are differentiating this with respect to c a and the answer should have been c b H a b not H b b here right. This term give you the answer 0, while you had this term if you differentiated that, you will get c b times H a b. So, therefore, what will happen is that? You will have H a b minus script E into S that is the other term right. And these two things added together must give you the answer 0. So, how did I obtain this equation?

I would obtain this by putting dou E by dou c a equal to 0, this implied that I have such an equation. In a similar fashion if you took the derivative of script E with the respect to c b and put it equal to 0, what is the answer that you are going to get? It is fairly easy to write it down, you do not have to actually work it out you can write by analogy and the answer is going to be H a b minus script E into S into c a plus H b b minus script E into c b is equal to 0 correct.

If you did exactly the same procedure you are going to get this equation. And what should I do? I have to solve these two equations and if I solved this equations what is the good thing? The good thing is that, I shall get the best possible values of c a and c b. Now instead of directly solving it, I am going to write it in a fancy form. What I will do is I will write this as a matrix equation.

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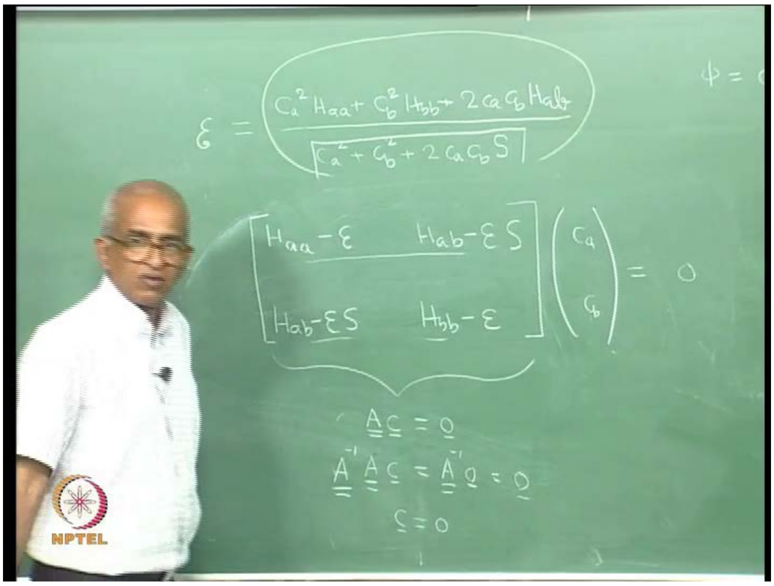

You will realize when I have write this and after I have written this, that this is nice, I am writing a matrix which is a 2 by 2 matrix. If I strictly speaking, I should put a column matrix on the right side saying that there is a 0 here and there is a 0 there because, if you look at this, you will realize that when you multiply these with that and put it equal to 0 you will get the first equation. And if you multiplied this with that and put it equal to 0 you will get the second equation.

Now many a time if you pulled on usually write 0, 0 here, but instead write by just write the 0, which I actually means that you have a column matrix there. Now this is, what is done in the slide also. This can be written these two equations can be written I am in a matrix form and that is nice. The matrix form is shown here, but why do I say that it is nice? Well this matrix equation is actually of the following form. See you have a square matrix here and this is a column matrix.

So, I can write it in this following form, I have a square matrix. A square matrix I shall indicate with double underlining and this is the column matrix this A stands for this whole matrix and the other matrix which I shall denote by the symbol C with one underling indicating that this is a column matrix. So, therefore, this is the form of this equation A into C is actually equal to 0, strictly speaking I should put an underline there to indicate that it is a column correct, it is a column of 0 and 0.

So, you have a square matrix, multiplying a column matrix equal to 0 that is the form of this equation. So, then what will happen is that I can say imagine I am multiply from the left hand side with the inverse of A right. So, I would have A A inverse and on the right hand side you would have A inverse multiplying 0 which after all, you see multiplying anything by 0 you are going to get 0.

So, you are going to get 0 still, but what has happen to the left hand side? You have A inverse A. A Inverse is identity and therefore, what is the result that you get, you will get this the result is that C is equal to 0 correct. Now if C is equal to 0, what is the C? C is actually this object, C is this column matrix. If you say that, that C is equal to 0, that implies c a is equal to 0 and c b also is equal is to 0 right. And therefore, what happens to your trail function c a is equal to 0 c b is equal to 0.

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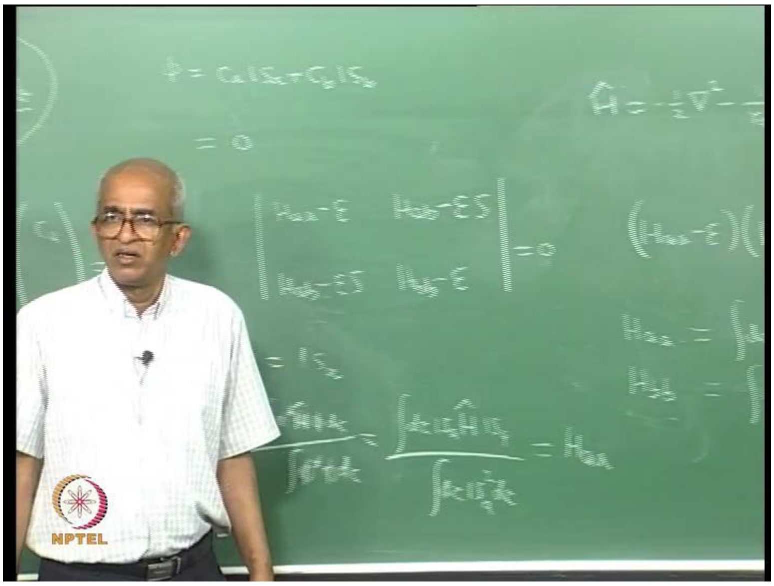

So, you have trail function identically equal to 0, is that acceptable? It is definitely not acceptable because, this means that your wave function for your electron is 0 everywhere and therefore, the electron is not anywhere right. So, I mean this is the kind of comment that one can make. If phi is equal to 0 your electron is not anywhere and therefore, definitely there is not acceptable.

So, what is wrong with this analyzes, see I have assumed that A has an inverse. If A has an inverse then definitely C must be equal to 0 by this argument. So, therefore, what is the conclusion, the matrix A must be such that it does not have an inverse. So, when is that the matrix does not have an inverse, the answer is very simple, if the determinant of the matrix is equal to 0 then, it does not have an inverse. If the determine is not 0 then, you can always find an inverse. So, the conclusion is that if this equation is to give you sensible answers for c a and c b then the determinant of this matrix must be equal to 0. So, let us take this determinant and put it equal to 0.

So, what is the determinant? The determinant actually is magnitude of sorry, determinant of H a a minus E, H a b minus script E into S, H a b minus script E into S, H b b minus script E this determinant must be equal to 0 right. Now this is very nice, why is it very nice because, originally I had two equations c a and c b, I had two equation, one for c a and the other for c b and the problem was to solved for c a and c b. And once I had obtained though best values of c a and c b, I would have to put them in here and find the value of script E. But now, look at this I have obtained an equation for script E directly I have actually eliminate c a and c b from the problem, I have just an equation for script E.

So, if I solved this, I will get the best possible value of script E. So, I do not have to actually solve for c b and c a, that is why the matrix analyses is nice. And so, all that I need to do now is just solve this equation right. Now if you expanded this, if you expanded the determinant what will you find? You will find that a quadratic expression in script E. And you are saying that the quadratic expression script E is actually equal to 0.

If you solved that you are going to get two different values of script E right. And then you have the problem what will you do with these two values, will the answer is that you will look for the one that is lower because, that will be the best approximation for the ground state of the system. So, let us expand this determinant and see what happens. So, this determinant I can expand, what I will get is H a a minus script E into H b b minus script E minus H a b minus script E into S, let we multiply these two and from the product you subtract the product of these two and this and that are identical.

So, you will get H a b minus script E into S the whole square is equal to 0 and this is the quadratic equation, if I solve the quadratic equation I am going to get two answers. Now, the analyses that I have carried out is fairly general, even if I did not have a 1 s b atomic orbital here. It is here, I have assumed that this is 1 s a and 1 s b and I have assumed that the two nucleus are identical. But imagine I have a situation, where I have may be one nucleus is a helium nucleus and the other nucleus, the first one nucleus is a helium nucleus and the other is a proton. Even for that, if I assumed that it I may take linear combination like this. All the analyses that I have carried out can be pushed through without any difficulty you will get this as the answer even for a more complex system which has only two atomic orbitals. But now, I am going to make use of the fact that the two nuclei are identical right. I know that, the two nuclei in this case, in the case of two plus, they are identical and therefore, it is possible for me to use that fact and make some simplifications.

So, you think of H a a and you think of H b b. What is H a a? Well H a a is actually integral d Tau 1 s a H 1 s a and H b b is actually integral d Tau 1 s b H 1 s b right. Now suppose, I say that I am going to try the function 1 s a as a trial function, suppose I am going to say I am not take this linear combination c a 1 s a plus c b 1 s b, but instead I just want to use the atomic orbital as my trial function; that means, I am going to try phi to be equal to 1 s a. Then what will be the value of energy that I will get? The energy that I will get is, integral phi star phi sorry, integral phi star H phi d Tau divided by integral phi star phi, this is the expression for energy that I will get.

But now, I am going to say, now my trial function is not such a combination, but is just 1 s a and what will happen, I will get d Tau 1 s a H 1 s a divided by integral d Tau 1 s a square d Tau right. If for a movement you are going to say that, the wave function for the electron is just 1 s a, it is not a linear combination, but it is just 1 s a then, the expression for energy that you will get is actually d Tau 1 s a H 1 s a divided by integral d Tau 1 s a square d Tau, but this integral is unity and therefore, this is nothing but equal to H a a. Now, this gives me the simple physical interpretation for this integral imagine that, I have this H 2 plus molecule and imagine that one electron is force to sit in the atomic orbital 1 s a then, it is energy would have been this integral and therefore, I can say that H a a is the energy of an atomic orbital right, which is in a molecule.

So, it is the energy of an electron in the molecule, but force to sit in the atomic orbital 1 s a. And if I extended this same argument to H b b would be the energy of an electron, which is forced to sit in 1 s b, but I know that 1 s a and 1 s b are identical because, the two nuclei are equal lent the orbitals are equality therefore, whether I put the electron in 1 s a over 1 s b this is tem should have the same energy. And this simple argument convinces me that H a a and H b b must be the same. Can actually evaluated by actual integration you will find that, they are equal, but this physical argument tells me that, H a a and H b b must be the same and therefore, what should I do, I can put that here H b b must be equal to H a a and hence this equation becomes even simpler.

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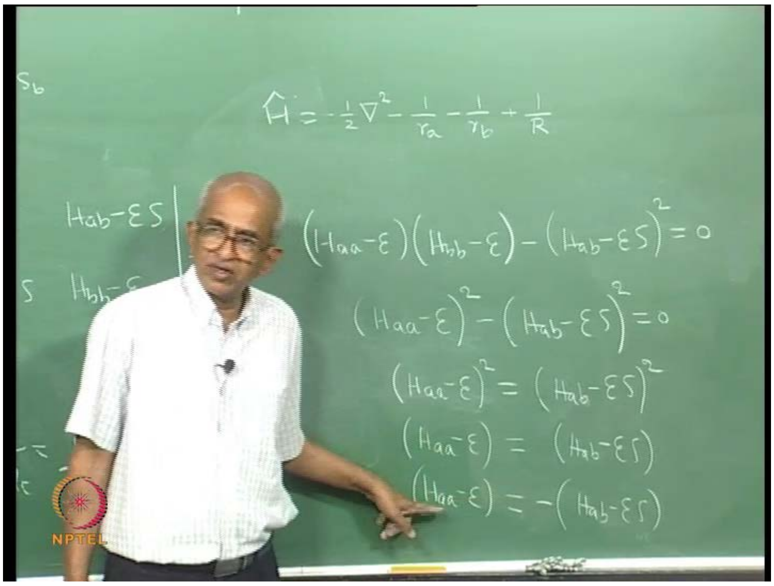

The left hand side becomes H a a minus script E the whole square because, this and that are identical, minus H a b minus script E into S the whole square is equal to 0 correct. Now, this is a quadratic equation, but this is a particularly simple quadratic equation because, what I can do is, I can take this terms to the other side. And write this equation as H a a minus script E the whole square is equal to H a b minus script E into S the whole square.

And if I wanted to find the value script E all that, I need to do is I take the square root of both the sides. So, when you take the square root, I shall get H a a minus script E is equal to H a b minus script E into S, that is only one possible square root, one possible solution right. But you have another solution where you will say that H a a minus script E may be the negative of the other term; that means, you would have minus of H a b minus script E into S.

So, this single equation is equivalent to one of these two equations right, either this or that has to be obeyed. And if you took the first equation you will get one of the possible solutions while if you took the other sign you will get the other solution. So, we will look at the negative sign first. So, what does that gives me H a a minus script E is equal to minus of H a b minus script E into S right.

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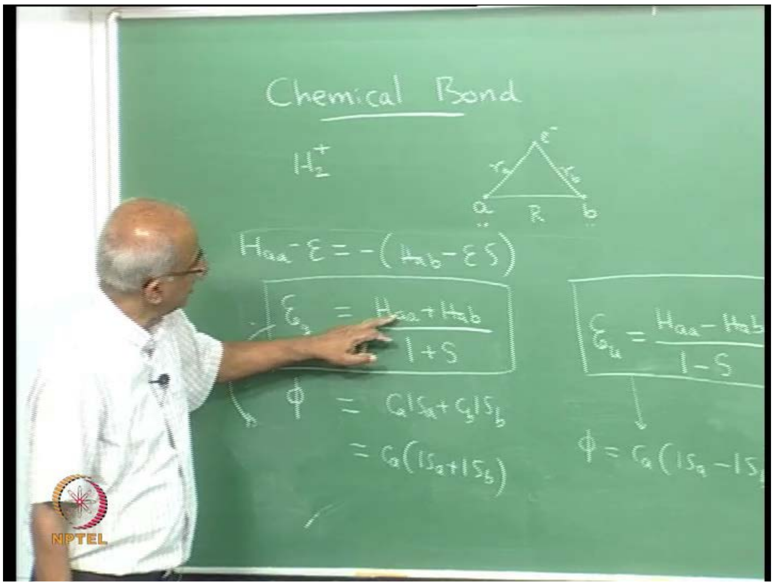

If I took the negative sign this is the answer that I will get. So, I can rearrange and get an expression for script E, what is the expression? H a a plus H a b divided by 1 plus S is the answer you will get. And for reasons which I will explain later, see I am going to get one more solution for script E. So, I will like to distinguish between this solution and the other solution and this solution I will put a subscript g. The reason will become clear later. And if you took the other one, the other solution this one and sold for script E you will get a different answer, let me write that answer.

I will put a subscript u for that and if you did the rearrangement and solving you will find that it is given by H a a minus H a b divided by 1 minus S fine. So, these are the two possible answers for script E, one I have denoted has E g and another one I have called E u. And out of these two which one would you expect is the best approximation for the ground stage. Well the way it is written it would appear as if this is lower than that because, you see there is the negative sign here and you would except this is lower.

But in actually what happens is that all this quantities H a a, H a b they are all negative, which is not surprising because, if you think of the energy of the hydrogen atom, it is actually minus 13.6. So, therefore, all these integrals H a a, H a b they all negative and therefore, what happens is that, this is the one, that is actually lower and this is higher.

Now the next thing that I would like to do is, I would like to find the corresponding wave function, it is not enough to say that this is the best energy, I should also know why this is the best energy correct, that I should know.

So, therefore, I want to find the wave function, I want to look at the wave function and how will I do that? Well I know that c a and c b actually satisfy this matrix equation, I could satisfy this matrix equation that also our starting points. So, in that matrix equation I will imagine that this equation is obeyed because, that is my solution that is of interest this equation is obeyed correct. And that will actually give me the value E g.

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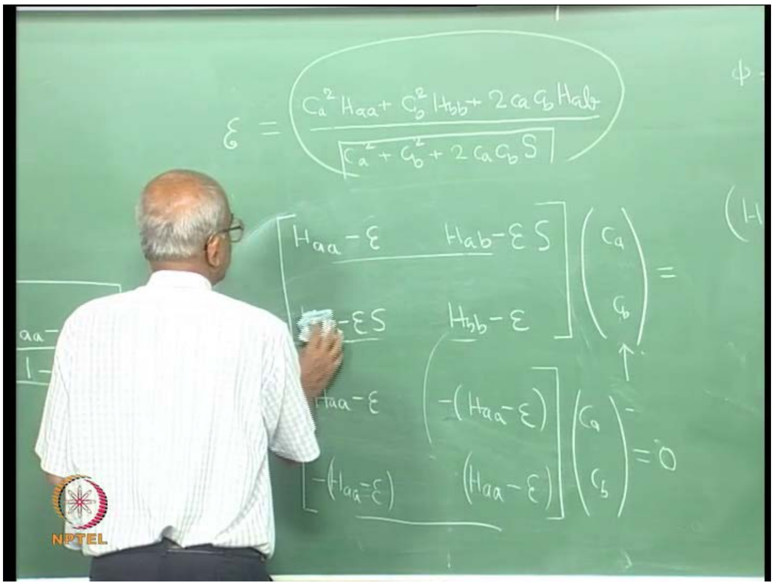

So, therefore, if I want to find out the trial function corresponding to this energy this script E, I should take this equation and use it in my matrix equation. So, if I use that what is the answer that, I am going to get H a a minus script E into S right. This equation tells me that this object multiplied by minus 1 is actually equal to H a a minus script E. So, therefore, the quantity that is occurring well there is no S here, H a a minus script E then this one is actually the negative of the same object correct.

This is just the negative of this, that is what that equation says and if you looked at the second thing, this part H b b is actually equal to H a a. So, this may be written has H a a minus script E and this object is just the negative of that. So, therefore, this one will come minus H a a minus script E correct. So, you realize that these elements are all simple and this multiplying c a c b is actually equal to 1 correct. oh thank you this is equal to 0. So, let us multiple things out and see what happens. So, if you multiply this, you are going to find H a a minus script E into c a minus H a a minus script E into c b must be equal to 0, that is my first equation.

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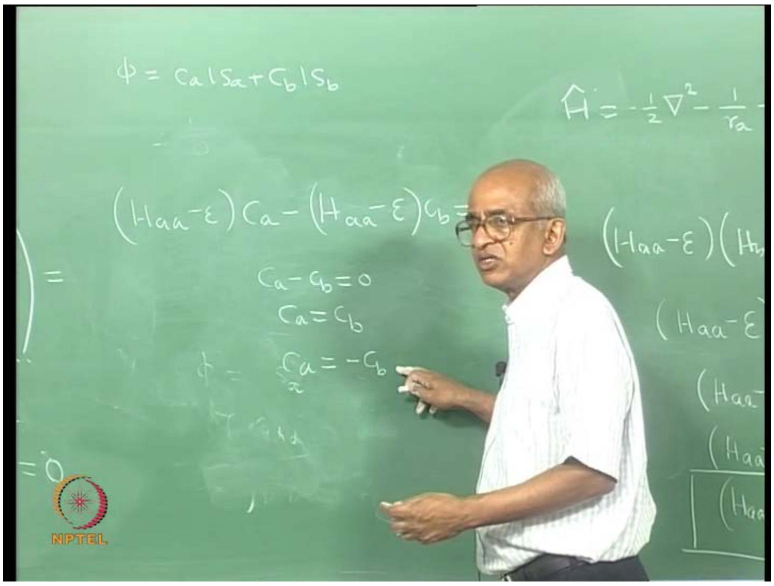

But H a a minus script E is communed. So, you can divide throughout by that and therefore, what does it give you? It gives you the result that c a minus c b is equal to 0, which implies that c a must be equal to c b correct. So, as far as this value of script E is concerned c a must be equal to c b. And now, suppose I multiplied this row with that column and put it equal to 0, what is the answer that you are going to get? The answer that you are going to get is, exactly the same you will get the answer c a is equal to c b.

So, even though it appears as if you have two separate equations, they are both the same and therefore, the only answer that, you will get is c a must be equal to c b. Now if suppose, you look for the other solution, how will you look for the other solution, the other solution would have instead of negative sign it would have a positive sign; that means, instead of this negative sign, you are going to have a positive sign instead of this also you are going have a positive sign.

And so, if you multiplied, what will happen is that you will get the result c a plus c b equal to 0 therefore, for the other solution, we will have what it would have c a equal to minus c b right. So, in one solution what has happened c a is equal to c b while in the other solution c a is equal to minus c b that is all. So, what are those solutions, let me just write them. In this case phi is equal to, well our expression for phi is, it is actually c a into 1 s a plus c b into 1 s b, but as far as this solution is concerned we found that c a is equal to c b. So, therefore, this will become c a into 1 s a plus 1 s b while for the other case, for this case you will find that phi is actually given by c a into 1 s a. So, in this case c b is the negative of c a.

So, therefore, the solution becomes c a into 1 s a minus 1 s b that is the another solution fine. Now what we can do is, we can evaluate while the expression for c a, you can find the expression for H a a and H a b just for the sake of completeness. I will write the expressions, I am not going to derived them and these expression are slightly more complicated, they are rather difficult to derive it needs quite a bit of algebra. We will now, look at expression for H a a and H a b they are not very difficult to evaluate in this particular case. So, let us look at them. So, that will be the expression for H a a and in this expression the R of course, as you know is the inter nuclear distance R is the inter nuclear distance. And here is the expression for H a b so, the expression contains S and delta which are define in this slide.

So, this is the expression for S, S is actually the overlap integral and delta is defined by this expression. So, I have written this expressions just to demonstrate to you that it is possible to evaluate H a a and H a b and express them as functions of inter nuclear distance. So, therefore, if I use this expressions in here, I would have E g as a function of the inter nuclear distance. And once I get that what can I do? I can plot this energy against R, against capital R that is what is done in my mathematic yeah file, which you will see in a seconds and once you have obtained that you can actually plot right.

You can plot the energy as a function of inter nuclear distance and this blue curve which is seen in the mathematic f note book is a plot of script E right. Script E with the subscript g as a function of R. R actually in this figure it is plotted has a function of R which is given in angstrom. So, the horizontal axis is in angstrom, the vertical axis is actually in atomic units that mean, you will take that value and multiply it by that is in atomic units.

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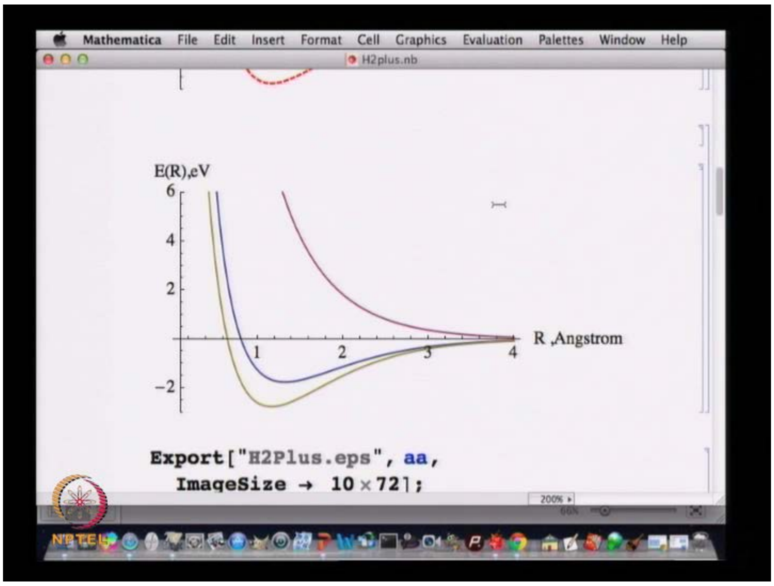

So, it is multiplied by 27.2 and that is your vertical axis. Horizontal axis is not in atomic units, it is in angstroms and then you find that you get this blue curve, what is this blue curve? The blue curve actually shows that as you bring the two spaces together the energy of the system, you can see it is decreasing it reaches a minimum and this point. Where the energy is minimum must be the equilibrium inter nuclear distance of s 2 plus molecular ion.

So, therefore, theoretical by making this plot it is possible for may to find out the inter nuclear separation and then you may ask me what is this yellow looking curve, this curve the answer is that there is a much more accurate calculation then what I have done here, this is approximate has I have told you. It is possible to use a variation method and do a much better calculation. And if you did that much better calculation this is actually the result. And you can do the same thing with the other state the one that you called E u right, you can substitute the expressions and then plot E u also has a function of R and if you did that you are going to get this magenta curve.

So, therefore, what is the conclusion? Well the conclusion is, this is the very accurate calculation much better than the calculation that we have done, but our calculation gives this curve. And if the system is actually having this as the state, if this is the state of the system then, there is the formation of a bond. But if you are thinking of the wave function for the electron to be not this function, but instead you say that the wave function is this, I have the distinguish between this two.

So, therefore, this function I will call it phi g and this function, I will called phi u then, the reason for this notation, I will explain. If this, the wave function is given by phi g then, there is a lowering of energy, while if the wave function is given by phi u, you find that there is no lowering of energy. And therefore, no bond is formed, if that is the way it is. So, now we have to look at phi g and phi u, but before I look at them in detail. I should know what this c a is? And what this c a must be, I will find them, that will be my next problem and how will I find them, the answer is that any wave function it has to be normalized.

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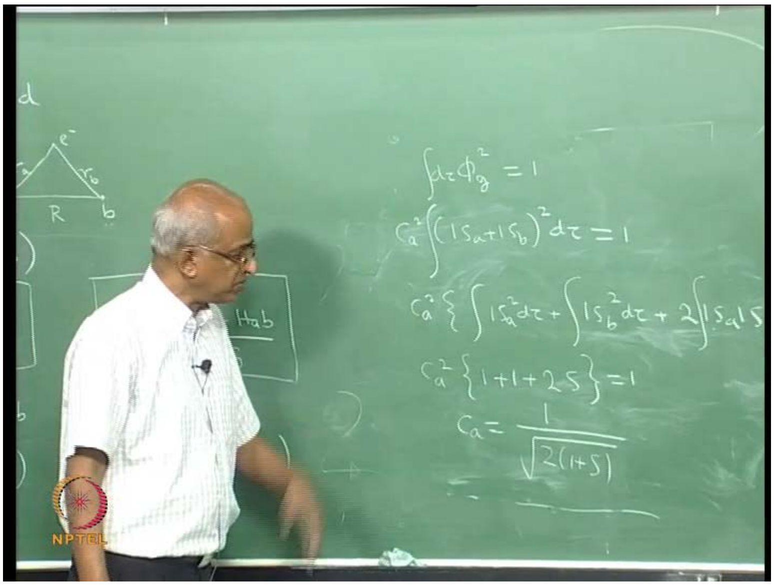

So, therefore, what will I do, I will find c a in such a fashion that phi g is normalized. And I will find this c a in such a fashion that phi u is normalized that should be the procedure. So, how will I carry out the process of normalization? Well what I am saying is that take phi g multiplied by its own complex conjugate integrate over the entire space, but here it is not necessary to worry about complex conjugation because everything is real. So, therefore, you just take phi g square it integrate over the entire space, the answer must be 1.

So, if this is your phi g what will happen is that I would have c a square 1 s a plus 1 s b the whole square d Tau integrate over the entire space right, c a is just a constant. So, this must be equal to 1. So, if you took the square what will happen? You will get c a square into integral 1 s a square d Tau plus integral 1 s b square d Tau plus 2 times 1 s a 1 s b d Tau integrated over the entire space, this must be equal to 1 correct. And as we have seen previously 1 s a is an atomic orbit, there is normalize.

So, this integral must be 1. 1 s b also is normalized, so, this integral must be 1 right. This integral is actually non 0, it is the thing that we have denoted by symbol capital S. And hence, what do I find? I find that c a square into 1 plus 1 plus 2 time S must be equal to 1, which implies that c a must be equal to 1 by square root of 2 into 1 plus S right, I mean, if you add this 1 with 1 you will get 2 so, and c a must be equal to that. And hence my phi g it may remove this c a and say and put it there.

So, this phi g must be equal to 1 by square root of 2 into 1 plus S. Now in an exactly similar fashion I can determine this c a, this c a will be determine in such a fashion that, this orbital is normalized. And if you did that it is fairly straight forward, you will find that this c a must be equal to 1 by square root of 2 into 1 minus S instead of a plus and then of course, you will have 1 s a minus 1 s b correct. So, this is my other function and we will look at the nature of these two functions in the next lecture.

Thank you for listening.