Quantum Chemistry of Atoms and Molecules
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Lecture-47
Secular Equations for Particle in a Box

In our discussion of variation method we have taken a few examples now we go back and see how we can nicely represent functions as linear combinations of other functions and how this gives us a better result for energy in case of our good old particle in a box.

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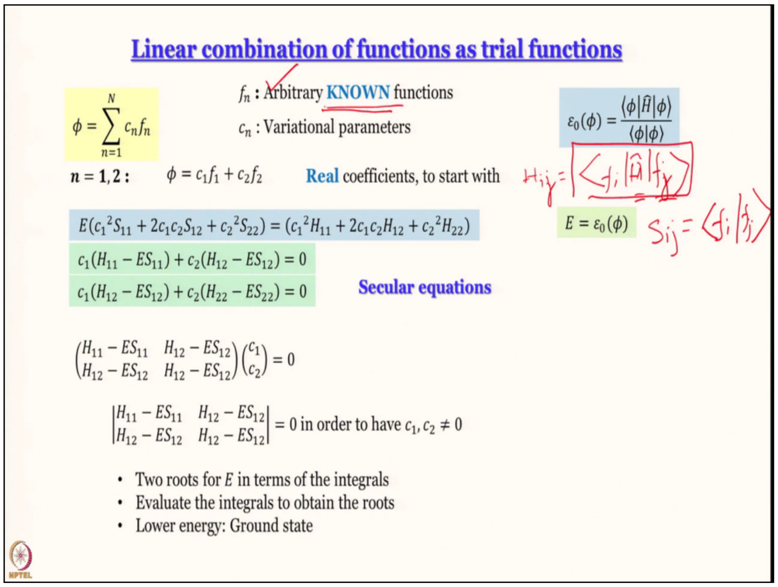

Linear combination of functions as trial functions

$\phi = \sum_{n=1}^{N} c_n f_n$

f_n : Arbitrary KNOWN functions

c_n : Variational parameters

$\varepsilon_0(\phi) = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle}$

n = 1, 2 : $\phi = c_1 f_1 + c_2 f_2$ Real coefficients, to start with

$H_{ij} = \boxed{\langle f_i|\hat{H}|f_j\rangle}$

$E = \varepsilon_0(\phi)$ $S_{ij} = \langle f_i|f_j\rangle$

$E({c_1}^2 S_{11} + 2c_1c_2S_{12} + {c_2}^2 S_{22}) = ({c_1}^2 H_{11} + 2c_1c_2H_{12} + {c_2}^2 H_{22})$

$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0$

$c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0$

Secular equations

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{12} - ES_{12} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{12} - ES_{12} \end{vmatrix} = 0 \text{ in order to have } c_1, c_2 \neq 0$$

- Two roots for E in terms of the integrals
- Evaluate the integrals to obtain the roots
- Lower energy: Ground state

So, this is something we have covered already we have said that it is possible to express trial functions as linear combinations of other functions. And in this case what we said is that we are going to work with fixed functions and we are going to use the coefficients as the variational parameters which means that we are not suppose we are using a lot of Gaussian functions we are not going to change the full width of maximum or position of the Gaussian functions.

For each Gaussian functions those parameters will be fixed what the only thing that will change is the coefficient c n so this is our variational parameter. And what we said is that by changing this will try and get the minimum value of the function on epsilon 0 and that is going to provide an upper bound to the ground state energy. And we have demonstrated this with a simple example where there are only 22 terms in the summation.

So phi equal to c 1 f 1 + c 2 f 2 and also now we have kept only real coefficients but actually the mathematics is not very vastly different if the coefficients are not real imaginary coefficients are a reality I mean it is a strange way of saying things perhaps but that is actually correct. So, you do have imaginary coefficients does not matter you always end up taking their complex conjugate when you talk about contribution.

So what we have shown is that for this system we have been able to construct the secular equations for the 2 variational parameters the 2 coefficients and we have written these written these equations in terms of H 11 S 11 H 12 S 12 and S 22 H 22 so these are essentially integrals what integrals are these I actually should have written here sorry for having forgotten but I hope you have not forgotten H ii.

Let me write in general term is equal to integral f i H f i so H ij would simply mean I have to close this, this and S ij I think ij is a more general way to write because I can always be equal to j that is simply integral f i star f j over all space. So, we have formulated these secular equations in terms of these integrals and see these integrals are numbers and the good thing about working with these integrals is this.

Let me underline this word here these functions f in terms of which we have expressed our trial function these are arbitrary fine of course they are but they are known. Arbitrary in the sense that they may not be the correct functions I mean there is no particular reason like we had used a particular function E to the power i phi that was the eigen function of this p z operator. So, when we try to construct the phi dependent part of the wave function of hydrogen atom we had taken a E to the power i m phi.

And that made perfect sense here it mean well it has to make some sense but it may not make perfect sense to use some particular function f that way they are arbitrary but they are known. so if I use a Gaussian function I know where the maximum is I know where the what the full width of maximum is. If it is an exponential function I know what is the constant associated with that exponential decay so on and so forth.

So I know the functions also I know Hamiltonian so if the function is an eigen function of the Hamiltonian I can hope to actually work out the value of this integrals and if i can do that well this is c 1 a variable multiplied by a number plus c 2 a variable multiplied by a number. So, it is just plain good old 2 linear 2 set of 2 simultaneous linear equations that is all. It is just that it might look a little scary for somebody whose new because you are writing enigmatic things like H 11 - E S 11 and so on so forth.

Nothing to worry about that now see when you take secular equations you could do 2 things. First is you can try to find the coefficients after all coefficients are the parameters here but do not forget 1 thing we do not know yet is E. So, what we do is now we do not worry about coefficients that might be the story for another day if you go through our lectures in symmetry for example, there is this Nptel course that we taught in symmetry.

There we have actually found out this coefficients as well for pi molecular systems but here we do not bother about coefficients. Our goal now the only goal is to determine the ground state energy. So, E is our target and to target E what we do is we write it in matrix form like this and if you study the theory of linear equations for this to be for the c 1 c 2 to be nonezero that would give a trivial solution this secular determinant of this matrix that must be equal to 0 that is very well known from mathematics that existed that has existed for a long time.

So this secular determinant equal to 0 that is what you have to solve. And now see H 11 I can figure out and we will for particular box S 11 we can H 12 S 12 H 12 everything the only unknown now in this determinant is E. So, I will expand the determinant equate it to 0 I will get in this case I will most likely get a quadratic equation and I will solve it to get the answers so this is what we do. We will get 2 roots of E be if it is a quadratic equation they will be in terms of the integrals.

If I can find values for the integrals which we will for particle in a box then we will get 2 roots as particular numbers or defined quantities. Then we can evaluate the integrals as I said out of these 2 roots the 1 which has a lower energy corresponds to the ground state energy that is all.

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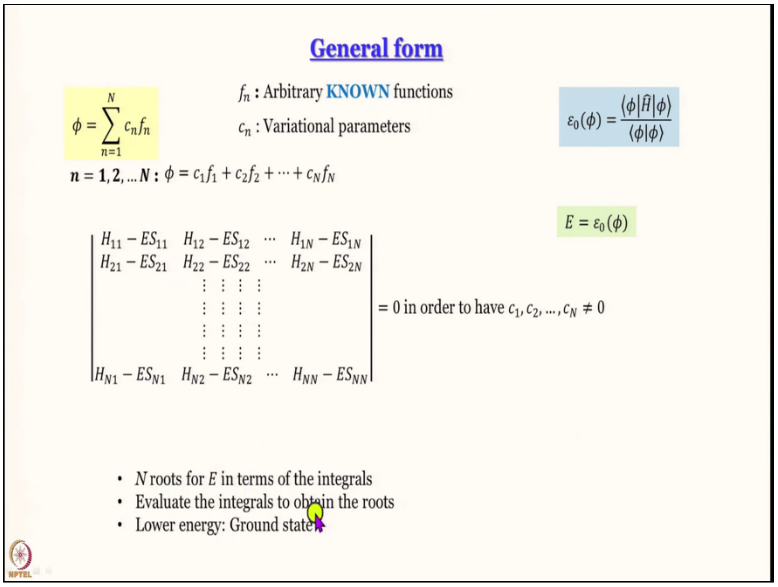

General form

$$\phi = \sum_{n=1}^{N} c_n f_n$$

f_n : Arbitrary **KNOWN** functions

c_n : Variational parameters

$$\varepsilon_0(\phi) = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle}$$

$n = 1, 2, \ldots N$: $\phi = c_1 f_1 + c_2 f_2 + \cdots + c_N f_N$

$E = \varepsilon_0(\phi)$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ & \vdots & \vdots & \\ & \vdots & \vdots & \\ & \vdots & \vdots & \\ & \vdots & \vdots & \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0 \text{ in order to have } c_1, c_2, \ldots, c_N \neq 0$$

- N roots for E in terms of the integrals
- Evaluate the integrals to obtain the roots
- Lower energy: Ground state

And this is the general form it is not necessary that small n will be restricted to 1 and 2 it can go all the way up to any number N, so this is what the function will be at that time capital phi equal to c 1 f 1 + c 2 f 2 so on and so forth plus c N f N in that case we will just get a bigger perhaps more intimidating secular determinant but this is a secular determinant of nth order. So, if we expand it of course it is going to be tedious once again but if we can do it if we want to do it we can.

So if you can expand it we are going to get n roots for E and once again the lowest energy I should not say lower energy here, lowest energy should be the ground state energy.

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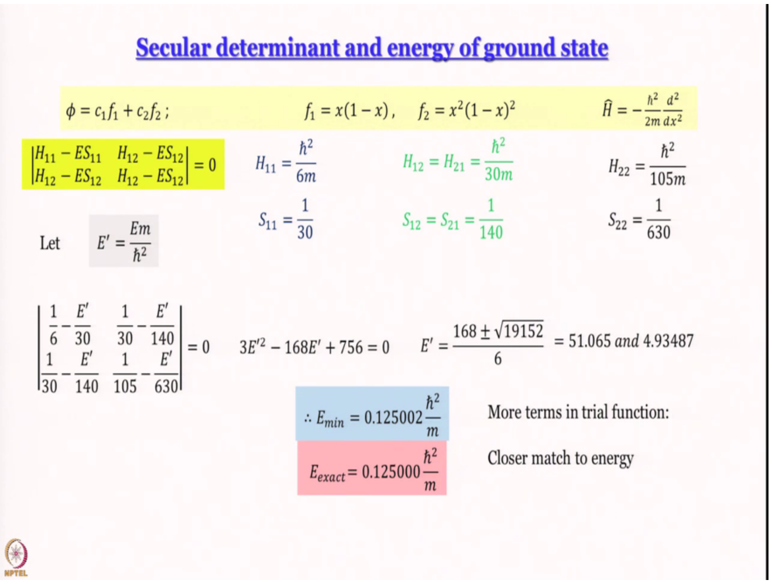

Secular determinant and energy of ground state

$\phi = c_1 f_1 + c_2 f_2$; $f_1 = x(1-x)$, $f_2 = x^2(1-x)^2$ $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{12} - ES_{12} \end{vmatrix} = 0$$

$H_{11} = \frac{\hbar^2}{6m}$ $H_{12} = H_{21} = \frac{\hbar^2}{30m}$ $H_{22} = \frac{\hbar^2}{105m}$

$S_{11} = \frac{1}{30}$ $S_{12} = S_{21} = \frac{1}{140}$ $S_{22} = \frac{1}{630}$

Let $E' = \frac{Em}{\hbar^2}$

$$\begin{vmatrix} \frac{1}{6} - \frac{E'}{30} & \frac{1}{30} - \frac{E'}{140} \\ \frac{1}{30} - \frac{E'}{140} & \frac{1}{105} - \frac{E'}{630} \end{vmatrix} = 0 \qquad 3E'^2 - 168E' + 756 = 0 \qquad E' = \frac{168 \pm \sqrt{19152}}{6} = 51.065 \textit{ and } 4.93487$$

$\therefore E_{min} = 0.125002\frac{\hbar^2}{m}$

$E_{exact} = 0.125000\frac{\hbar^2}{m}$

More terms in trial function:

Closer match to energy

Now with that background let us see how we can use this kind of wave function linear combination of functions in particle in a box and does that improve the situation at all. You might remember in 1 of the previous modules we had actually tried to do a variational calculation of ground set energy of particle in a box and there we obtained a an over estimation by 4% and that time we said 4% is good but not good enough.

So with that background can we improve upon that 4% if we use this kind of a linear combination of functions as a as our trial function. To do that what we do is we use f 1 equal to x into 1 - x f 2 equal to x square into 1 - x whole square. The choice of these wave functions is inspired by the discussion we had the last time we talked about trial functions for particle in the box. Remember we are said that the functions have to be symmetric with respect to l by 2.

And here we have set l to be equal to 1 which means whatever we write is in terms of l. So, there is an l square in the denominator for energy that has been set to 1. If you want the absolute value just bring that n square back in the appropriate position. So, we need a function we need functions that are symmetric with respect to the midpoint and also they must vanish at the boundaries x into 1 - x as well as x square into 1 - x whole square both satisfy these conditions.

I request you to recall what we had obtained in the earlier treatment remember which function which trial function we had used earlier. We had used phi equal to x to the power alpha into 1 - x square I think something like this and that alpha had come out to be I think 0.862 or something like that let us remember that result. Now we are trying to improve upon that 4% over estimation that we had by using a linear sum of 2 functions both of the which are sort of inspired by the function that were used in the previous function.

And this here is our Hamiltonian you might remember that in the last time we had used Hamiltonian written Hamiltonian in terms of atomic units well here we are not using atomic units I am doing it intentionally because we should actually be equally conversant equally comfortable with all kinds of units. So, this is our Hamiltonian now the next thing to do is to see whether we can make this secular determinant any simpler and that can be done if you can work out the expressions for all these integrals.

Or you can say the matrix elements remember we talked about it these are all matrix elements let us try to do that. What I will do is I will show you the steps for 1 well the easiest one H 11 and then I leave it to you to work out the rest if you want you do not have to work out all but work out at least 1 or 2, one of the H's and one of the S's that will be good. So, Hamiltonian is - h cross square by 2 m d2 dx 2 - h cross square by 2 m comes out I am integrating now between 0 and 1 because I have set l 2 equal to 1.

So, what do I have inside 3 phi multiplied by d 2 d x 2 phi so this is the first term that I will get this will be H 11 because this is f 1 remember H 11 essentially means integral of f 1 star H f 1 over all space all x in this case. So, x into 1 - x into d2 dx 2 of x into 1 - x simple so this x into 1 - x essentially is x - x square so first of all we will find the first derivative of x into 1 its very simple perhaps many of you would have worked it out by the time I do it.

So essentially I am trying to get d dx of x - x square and without having to know rocket science I think we can see that this is going to be 1 - 2x so the second derivative is such that we have to find the derivative we have to differentiate the this thing that we got the first derivative 1 - 2 x and we have got - h cross square by 2 m outside the integral what is d dx of 1 - 2x I not even bother writing it is simply -2.

So that minus sign comes out and the 2 cancels with the 2 in the denominator so I am left with H cross square by m multiplied by integral from 0 to 1 x - x square is that yes again this is also very simple I will not even go through the steps I just show you the answer this is the answer I am showing this step only so that you can check in case you go wrong somewhere the answer that we get is h cross by 6 m beautiful.

Let me erase all that bad handwriting so H 11 as promised has been worked out and it turns out to be h cross square divided by 6m so it is up to you to prove that H 21 equal to H 12 is equal to H cross by 30m H 22 is h cross by 105 m S 11 equal to 1 by 30, S 12 equal to S 21 remember S ij equal to S ji because it is just integral of a double of a direct product and H 12 equal to H 21 by using turnover rule remember H is a hermitian function hermitian operator this is S 22.

What do I do next I take all these expressions and I plug them into this secular determinant. While doing that it helps if I work in terms of E cross E dash which is E m by h cross square and you can see why H 11 what is H 11 H cross by 6 m - E into S 11 so - E by 30. So, naturally this m will go up and so the expression just becomes a little simpler if i write E dash equal to E m by h cross square and this is the determinant I get that is equated to 0 I am going fast intentionally because there is no point in me reading out every step.

But what you do is you just multiply diagonally then subtract the product of the other diagonal the terms of the other diagonal and you get this quadratic equation 3E dash square - 168 E dash + 756 is equal to 0 we all know how to solve quadratic equations - E + - root over b square -4ac by 2 a use that and we get E dash equal to 168 + - root over 19152 by 6 which translates as 51.065 and 4.93487 do not forget we have set l to be equal to 1.

So remembering that when we go back to E min E min the minimum value of epsilon 0 turns out to be 0.125002 h cross by m now that might not mean much to you but it will when I show you the exact result in the same kind of expression. So, the exact result that we had got for your particle in a box written in the same way for l equal to 1 turns out to be 0.125000 h cross by m see this number is 0.125002 and this is 0.125000.

So if you are wondering why we are writing so many decimal points does it make sense? Yes it does so remember earlier when we use that phi equal to x to the power alpha 1 - x square kind of function the agreement that time seem to be good now it seems to be horrible yeah we had 4% over estimation and we said only 4% over estimation. Now look at this you stop at the third decimal place or fourth decimal place or fifth decimal place the match is perfect.

Only in the 6th decimal place the exact value is 0 and the calculated value is 2. So, this is a good match in fact it can get better. So, what we see is that if you use more terms in the trial function then we can get a better match to energy and that opens up a tremendous possibilities. First of all you do not care well you do a little bit but you do not care about being absolutely right on what kind of functions to use. See we are talking about wave functions here.

We know that wave functions have to satisfy Born interpretation right bound conditions, boundary conditions. So, they have to become 0 eventually they cannot go to infinity anywhere they cannot be 0 in all places they have to be continuous. So, we are only going to use that kind of wave functions that kind of functions f will choose that kind of f's only but the good thing is as long as that happens you do not really have to care whether you should use a Gaussian or a log normal or an exponential which function.

You use whatever function gives you a good match that is the beauty of our variation method that the nitty-gritty is not even required you do not need to know the wave function all that well. Now think what we had said at the beginning we said the wave function had all the information about a system you make the Hamiltonian operate on it that is a question you ask the wave function gives you the answer here we are going beyond that.

We do not even know the wave function we are making up some kind of a wave function and we are just changing it until we get close to the right answer. Here we are doing test cases exact solutions are known. So, that is what gives us the confidence that yes it works we are getting close to the value that we had got earlier using the exact solution. Next we are going to talk about systems for which you cannot find exact solution.

And that is where the promise will be fulfilled. So, it is a I do not know if you can call it enigmatic I say this is a an amazing situation in Schrodinger equation the only thing you know is Hamiltonian you do not know the wave function you are making it up you are changing it you are doing all sort of things you do not know energy. By doing all sort of things to the wave function the method takes you close to the value of the actual energy.

And in the process if you work out the coefficients as well for that value of energy you will also have a particular form of wave function and that is something that you can plot and you can see what it looks like and using it you can draw these maximum probability contours and what not even though you cannot solve the equation. So, you might remember that this is this cliche people pull the legs of quantum chemist saying that these people have only one equation and they do not even know how to solve it.

Now let me say that that is that sounds very tongue-in-cheek smart thing to say but it is absolutely unfounded because here we have a situation where we do not have to solve directly we can get the solutions by using beautiful approximation methods. And in doing that we actually get important parameters that we are going to use later also this H ij H ji S ij S ji everything is going to come back and everything is going to be useful in many different applications of quantum chemistry, quantum mechanics all in good time.

But for now the take home message is that if you increase the number of terms in trial function you get a closer match to energy.

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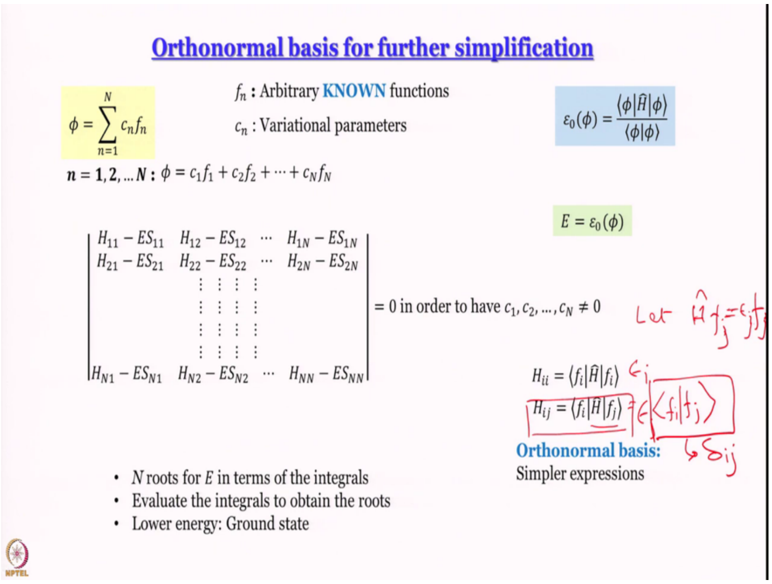

Orthonormal basis for further simplification

$$\phi = \sum_{n=1}^{N} c_n f_n$$

f_n **:** Arbitrary **KNOWN** functions

c_n : Variational parameters

$$\varepsilon_0(\phi) = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle}$$

$\boldsymbol{n = 1, 2, \dots N:}$ $\phi = c_1 f_1 + c_2 f_2 + \cdots + c_N f_N$

$$E = \varepsilon_0(\phi)$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & \vdots & \vdots \\ H_{N1} - ES_{N1} & H_{N2} - ES_{N2} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0 \text{ in order to have } c_1, c_2, \dots, c_N \neq 0$$

Let $\hat{H} f_j = \epsilon_j f_j$

$H_{ii} = \langle f_i|\hat{H}|f_i\rangle$ ϵ_i

$\boxed{H_{ij} = \langle f_i|\hat{H}|\underline{f_j}\rangle} = \epsilon \boxed{\langle f_i|f_j\rangle}$

$\hookrightarrow \delta_{ij}$

Orthonormal basis:
Simpler expressions

- N roots for E in terms of the integrals
- Evaluate the integrals to obtain the roots
- Lower energy: Ground state

So, before we can close this discussion and go over to actual multi electron atom system we need to discuss 2 more things one of them I have sort of summarized in this slide. First of all see the functions that we had used earlier remember were arbitrary even though known. Now I can choose a set of functions that are orthonormal are not they can I, what happens when I choose an orthonormal function?

Especially when I am faced with this daunting task of working out this kind of a humongous determinant, does it help? Well as you can see what do we work with? We work with these and I have not written S similarly I can write S ii and S ij. So, here if i use these first of all if I use eigen functions of Hamiltonian and if I use if I choose such eigen functions that form an orthonormal set basis means this is what I am working with.

This is the set of functions on which I am doing all my calculations based on which this base is set. So, if I choose an orthonormal basis where all these f functions are orthogonal to each other and are they themselves normalized then what happens then I know very well what H f i will be I am choosing eigen functions I will write the others as well. So, let us work with this H ij let us say let us say Hamiltonian operating on f i gives me what will I write epsilon i this epsilon that epsilon are not the same.

Different epsilon i f i so this turns out to be so Hamiltonian operating on f j will give me epsilon j f j good old eigen value equations. So, what will H ij be this will be integral f i star I know what H fj is it is epsilon j fj and epsilon j is a constant so it can come out f j remains inside the integral and this is what I get. Now see if I have chosen an orthonormal basis do not you know that this is going to be delta ij this integral is going to be equal to 1.

If i equal to j and equal to 0 if i is not equal to j so what I am saying is that many of these hij integrals well all hij integrals where i is not equal to j they will become 0 and H ii integrals will boil down to just epsilon i so this entire determinant is going to become so simple you are only going to have this some epsilon term and you are going to have 0's everything will be written in terms of those. So, that is what we are going to study in little more detail in the next module.

So let us conclude today by saying that if you use orthonormal basis we actually get simpler expressions and it the secular determinant becomes a little easier to handle. There is another advantage but let us talk about that after we have discussed what happens when we after we discuss how orthonormal normal basis simplifies the problem further for us. Because remember the whole idea here is that we do not want too tedious as a calculation we want it to be as simple as it can get.

Next day we are going to see how beautifully this problem plays out if we use an orthonormal basis. Another advantage let me say this at least think of an orthonormal basis that we know think of say orbitals hydrogen atom that is an orthonormal basis suppose I write a multi electron system wave function as a linear combination of hydrogen atom orbitals then what happens? We know exactly how to go about this yeah and we can actually hope to think we already know so much about orbitals.

The moment we bring in those orbitals then we know exactly how to proceed and we sort of know what to expect eventually that is a very important paradigm in talking about not only one electron atoms but also molecules. So, remember the reason why we are allowed to use this linear combination is that variation method allows us to add as many terms as you want to the trial wave function and vary no matter what we do we can never do better than the best.