Quantum Chemistry of Atoms and Molecules
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Lecture-48
Variational calculation for particle in a box…..continued

As we know quantum mechanics is all about orthonormal functions. The way we use functions that we use are almost always when we talk about exact solutions they are either form an orthogonal basis or they are made by linear combinations of functions that form a complete orthonormal set. So, it makes sense at this stage of a discussion to see what happens when we express trial functions as a linear combination of orthonormal functions.

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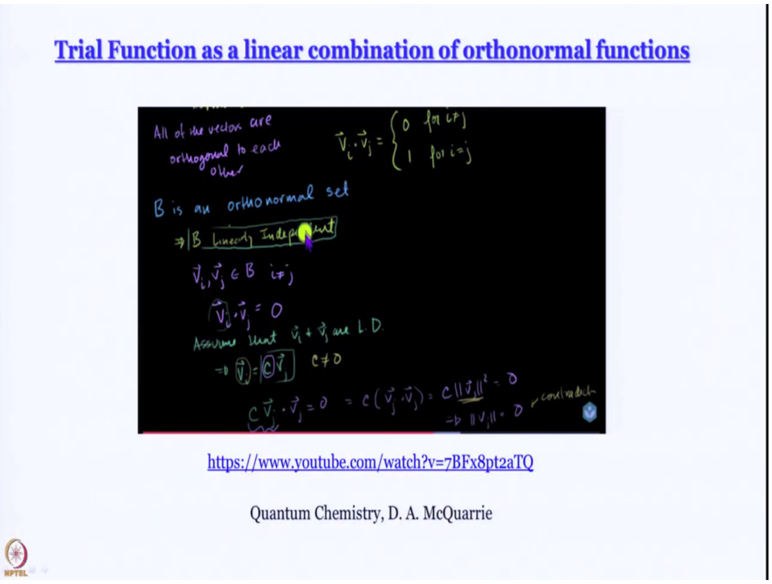

Trial Function as a linear combination of orthonormal functions

All of the vectors are orthogonal to each other

$$\vec{v}_i \cdot \vec{v}_j = \begin{cases} 0 & \text{for } i \neq j \\ 1 & \text{for } i = j \end{cases}$$

B is an orthonormal set

$\Rightarrow \boxed{B \text{ Linearly Independent}}$

$\vec{v}_i, \vec{v}_j \in B \quad i \neq j$

$\vec{v}_i \cdot \vec{v}_j = 0$

Assume that $\vec{v}_i$ + $\vec{v}_j$ are L.D.

$\Rightarrow \vec{v}_i = \boxed{c\vec{v}_j} \quad c \neq 0$

$c\vec{v}_j \cdot \vec{v}_j = 0 = c(\vec{v}_j \cdot \vec{v}_j) = c\|\vec{v}_j\|^2 = 0$

$\Rightarrow \|v_j\| = 0$ contradict

https://www.youtube.com/watch?v=7BFx8pt2aTQ

Quantum Chemistry, D. A. McQuarrie

And we know about the properties of orthonormal functions that are studied in the past.

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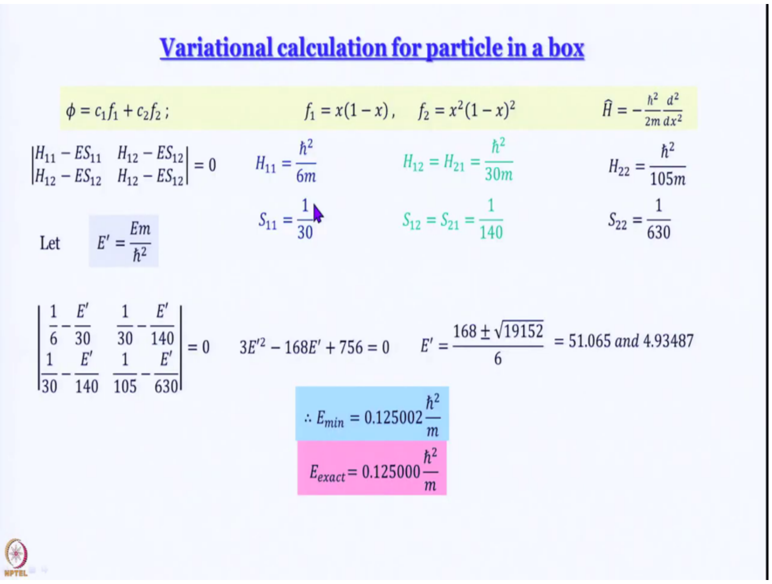

Variational calculation for particle in a box

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

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

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

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

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

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

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

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

So what will do this, we do that and will actually come back to particle in a box with little bit of twist when we talk about orthonormal functions. So let us quickly recap what we learnt in the previous module about variational calculation that you perform for particle in a box. There we had represented the wave function as c1 f1 + c2 f2 where f1 was x into 1 – x, f2 was x square into 1 - x whole square at the orthonormal you figure out.

But they definitely not the functions that we get by solving the Schrodinger equation exactly that we have done towards the beginning of this module of this course, so and this is the Hamiltonian – h cross square by 2m d2 dx2. So, what we did was that we wrote this secular equation and then we found out the expressions for all of these Matrix elements, H11 H 12 H 21 H 22 S11 S12 S 21 S 22 and then knowing these expressions and substituting E dash for E m by h cross square this secular determinant simplified into this form.

1 by 6 – E dash by 30 - 1 by 30 by E dash by 140 1 by 30 by 1 by 140 1 by 1 by 105 E dash by 630 that the determinant is equal to 0. This expands as a quadratic equation which has 2 roots 51.065 and 4.93487 of course out of these, this is a lower value and this is ground state energy and then what we did is we wrote this in terms of h cross square by m and we compare with this minimum value that we got of energy with the exact value of energy that we got earlier and we see the agreement is really, really good.

If you only if you go to the sixth place of decimal there is a difference between the calculated minimum value of energy and the calculated exact value of energy that is so we are good here. But then just because it has worked nicely for particle in a box does not mean that it will work if use arbitrary wave functions for more complicated systems.

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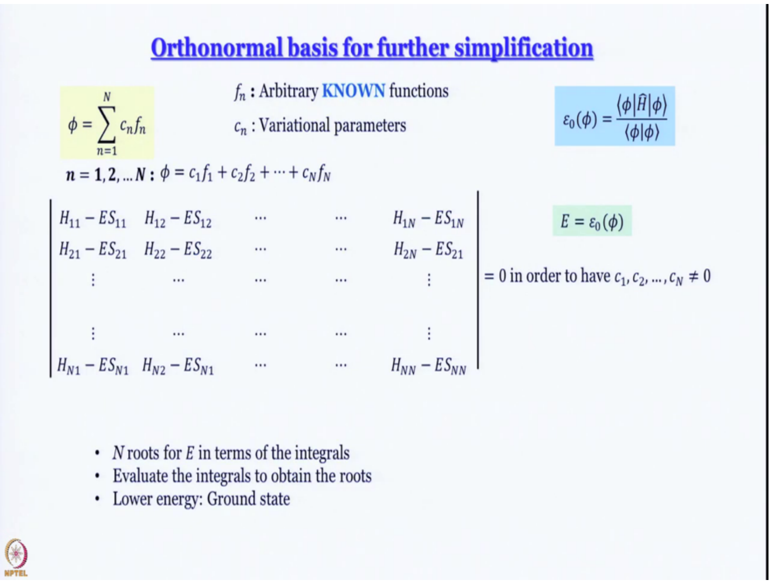

Orthonormal basis for further simplification

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

f_n **:** Arbitrary KNOWN functions

c_n : Variational parameters

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

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

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

$E = \varepsilon_0(\phi)$

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

You want to simplify that is why you want to talk about orthonormal basis. So, in this a linear combination that we have; you want to write this fm that are members of a complete orthonormal set. Of course even before going there if you simply write this expression that no matter whether fm's are orthonormal or not you will get this kind of a secular determinant. Last time we had just 2 by 2 determinants this will n by m determinant that is all.

And we will get n roots we have to evaluate integrals and one with lower then it will be the ground state. Now when we use orthonormal basis and we just touched upon this before closing the previous discussion the expressions becomes simpler. And expressions becomes simpler for the simple reason that S ij integral of fi star mj overall space all functions space is equal to delta ij you know that. Then i is equal to j then you get 1 by fi and fj are normal normalized.

And of course we are saying that they belong to orthonormal basis set so they are anomalies and if i is not equal to j then well once again remember they belong to orthonormal set. So if i is not equal to j then this integral become 0. So, what happens to the determinant in that case H 11 - ES

11 and this S 11 becomes 1. So this becomes H 11 minus this 12 position S 12 becomes 0 so the second term then vanishes completely left with only H 12 and that happens for all the other elements all the way until H 1n this S 1n also becomes 0.

And if you go from top to bottom in the first column all the second term vanishes because they are of S ij type. The 22 term what happens there S 22 is equal to 1 so you get H 22 – E, so what is that the diagonal elements all like H ii – E half diagonal elements are all H ij H ji type so this is what you get. H 11 – E H 12 H 13 so on and so forth then until it reaches H 1n when you go down H 11 – E H 21 H 21 so on and so forth until it reaches H 1n and diagonal elements H ii – E that is what you get.

And then already the expression has become simpler. What about H 12 and H 21? Can we say that there are 0, yeah, actually we cannot. Do you think that their 0 it is not necessarily correct. You going to encounter a situation where there is 0 but it is not the general case why because if you write this H ij any i any j write H ij that is equal to integral f i H f j ah the problem is fj usually would be the eigenfunction of the Hamiltonian of the system that is solvable exactly generally that what we chose.

So this Hamiltonian is different for example well we have not taken the example yet that when we take it we will see this Hamiltonian is not usually the Hamiltonian of this system for which we can solve Schrodinger equation exactly given that we can write the Hamiltonian. So, this is not necessary that f j is an eigenfunction of this Hamiltonian. So will not get an will not get a constant coming out of the integral always sometimes we can have special cases we will see.

So what will do it will keep H ij for now and we will said this S ij for i 0 is equal to 0 and we get this kind of a secular determinant.

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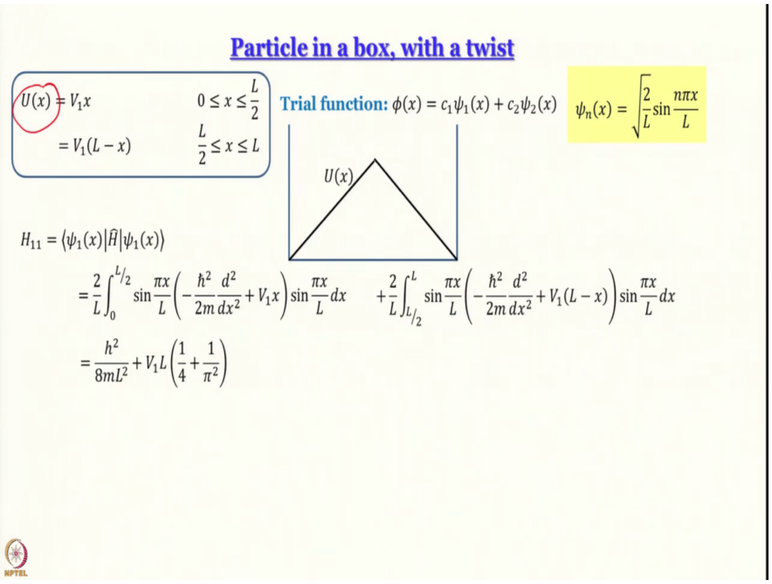

Particle in a box, with a twist

$$U(x) = V_1 x \qquad 0 \le x \le \frac{L}{2}$$

$$= V_1(L - x) \qquad \frac{L}{2} \le x \le L$$

Trial function: $\phi(x) = c_1\psi_1(x) + c_2\psi_2(x)$

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$$

$$H_{11} = \langle \psi_1(x) | \hat{H} | \psi_1(x) \rangle$$

$$= \frac{2}{L}\int_0^{L/2} \sin\frac{\pi x}{L}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_1 x\right)\sin\frac{\pi x}{L}dx \quad + \frac{2}{L}\int_{L/2}^{L} \sin\frac{\pi x}{L}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_1(L - x)\right)\sin\frac{\pi x}{L}dx$$

$$= \frac{h^2}{8mL^2} + V_1 L\left(\frac{1}{4} + \frac{1}{\pi^2}\right)$$

Now we take this example. We go back to a particle in a box but we include in it a twist or rather a bend we want to call it that. What is the bend and twist. We say that here potential energy is not 0 however, we see that potential energy is x dependent. For x lying between 0 and L by 2 half of the box the potential energy is V1 multiplied by x where V1 is a constant. For the other half for x ranging from L by 2 to L it is V1 into L – x.

What happens at x equal to L by 2 to take the first expression to get V1 into L by 2. If we take the second expression then also you get V1 into L by 2 right L – L by 2 that is L by 2 so there is no discontinuity in the function as such. There is a discontinued is so what does the potential energy look like then? Let us see this is my particle in a box for the first half from the left. Your potential energy will be a straight line with positive slope.

V1 into x for the second half it will be a straight line but with slope that is negative equal in magnitude, but negative. Now in this system let us use this trail function Phi of x is equal to c 1 Psi1 of x + c 2 Psi 2 of x what was Psi1 and Psi2 remember what you want to do you want to use an orthonormal function. And while using orthonormal function it makes sense to use of the orthonormal eigenfunctions of the Hamiltonian of the system for which we can Schrodinger equation exactly.

Then things will start making sense. I want to talk about particle in a box the orthonormal set that we use at least start with; it makes sense to take the wave functions of the Hamiltonian for a particle in a box in which the potential energy is 0 as long as a particle is inside box, and we know that the solutions are something like this Psi n of x is equal to root 2 by L sin n Pi x by L as we know ranges from 1 2 3 4 all the way up Infinity that is the contours of the quantum numbers.

So, remember when I say Psi1 of x essentially mean n equal to 1 put in this expression when I say Psi 2 of x I mean n equal to 2 put in this expression. So this is the formulation of a problem. As usual, I am not going to solve this please in fact this case you also do not need to solve every step you need to understand the logic. If you can solve it then it is even better. But as long as you understand the logic do not have to remember the final expression, please remember that.

A lot of things where you need to know the formula or anything you need to know only the very basic formulas that we already know by now, please do not try to remember that it makes no sense at all. Try to understand the logic. So, what will we do now, we know what the potential is. we know what the trial function is and we have expressed it as a linear combination of the orthonormal eigan functions of the Hamiltonian of particle in a box for which E is equal to 0 as long as the particle is within the box.

Now, we want to evaluate the matrix elements one by one. I show you some steps of H 11. How do we write H 11 integral Psi 1 x star in this case of course star is redundant just Psi1 x is fine because Psi1 of x is fine because it is real function. That left multiplying Hamiltonian operating on Psi 1 of x. Let me for the record will refer to it shortly, but let me even now write it once what is this Hamiltonian? What is the Hamiltonian for your particle in a box for which V equal to 0 intensity inside and V equal to 0 intensity outside.

It is of a kinetic energy term – h cross square by 2m a 1D box we might as well write the d2 dx2 that is for the particle in a box that we have studied earlier. In this case particle in a box with at least we have an additional potential energy term which itself changes its expression at x equal to L by 2 so to write the general expression I will write the Hamiltonian is – h cross square by 2m d2 dx2 plus let me just write U of x.

Depending on what x is, depending on what x is, we are going to use the appropriate expression for U of x the potential. So this is what will use depending on the value of x of course, we are going to get 2 terms is not it. When you expand this integral first of all there are 2 terms and secondly we have the second term is different for different ranges of x. Circulate 2 integrals one with limit from 0 to L by 2 the other with limits from L by 2 to L so that we can write this analytical form of U of x.

This is what I will write 2 by L where does 2 by L come from well Psi1 and Psi 2 remember in this case both are Psi 1 so root 2 by L root 2 by L so I take 2 by L outside and integral between limit 0 to L by 2 Sin phi x by L multiplying the Hamiltonian that everything written here in this case U of x is substituted by V1x because I am integrating only after L by 2 that operating on sin Pi x by L dx. what will the second integral be?

Same thing except well similar except the limits would be from L by 2 to L and instead of V1 x here I will write V1 into L - x this is what it is. So I have written down the expression for H 11. What do you get? What do you get if you try to say expand the first integer? That is the final answer let me write the first integral. So here writing this sin pi x by L – h cross by 2 m by d2 by dx2 sin pi x by L square and what I do is I bring this here also proved to be really here.

So this first one I can write it as i1 here will be equal to integral essentially Psi 1 of x well, do not forget the limit 0 to L by 2 this one is Hamiltonian ok since we know perturbation theory already I will use the language of perturbation theory here. I will write 0th order Hamiltonian, 0th order Hamiltonian means of a particle in a box in which potential energy inside the box is 0. Ok, so you can think that this is 0th order Hamiltonian. And this is the first order correction.

So I will just write like this operating on Psi 1 of x dx I already know what is H 0th operating on Psi 1 of x is that is basically the left-hand side of Schrodinger equation for n equal to 1. So it will be your E1 multiplied by Psi 1 n, for particle in a box with potential energy is 0 what is E1? x square by phi square m is it not. If L equal to 1. If L equal to L then it will be a L square. Ok. So this turns out to be just energy and then you integrate.

So, this is equal to something like I will write Epsilon 1 integral 0 to L by 2 Psi 1 of x whole square x dx. So, now tell me what is integral Psi 1 x whole square between limit 0 to L by 2. If I integrated from 0 to L what would have been? it would have been 1 total probability. So 0 to L by 2 for the symmetric wave function here that is going to be half. So this is how you expect. What about the second one; in well second term arising out of the first part here.

It will be V1 will come out here and then you will get integral 0 to L by 2 and I erase all this and I will write. What I am saying is I take root over 2 by L sin pi x by L and multiply it by V1x then again sin pi x by L will you agree that; I will call it L, i2 will be equal to integral 0 to L by 2 I can write again Psi 1 as we discussed earlier multiplied by x multiplied by Psi 1 dx and V1 will come out is it not V1 is a constant remember.

So this will be V1 integral 0 to 2 by 2 x into sin square Pi x divided by L dx, does that ring a bell or does this ring a bell? If I only change the limit from 0 to L by 2, 0 to L then this integral would be your average value of position. Here I am just integrating from 0 to L by 2. Now you know how to solve this integral using integration by parts. So that is what one has to do I am skipping all the steps but I told you. How to go about it and well I encourage you to do this by yourself.

When you do that and then when you do when you perform a similar treatment to the second term that is there then the final result that I show you is this is h square by 8 mL square. Remember what h square by 8m L queries is? h square by 8 m L square is essentially the energy of the particle in a box when potential energy inside is 0 potential energy outside is infinity. So that is what it is and the second term arises out of well, I will call it the second term because I written it as V1 into n multiplied by something that arises from the second terms of these integrals.

If you do it; it is a little long but it is definitely not undoable. So, this is the result we get this here is your H 11. And H 12 and H 21 turnout to be 0 and will discuss little later.

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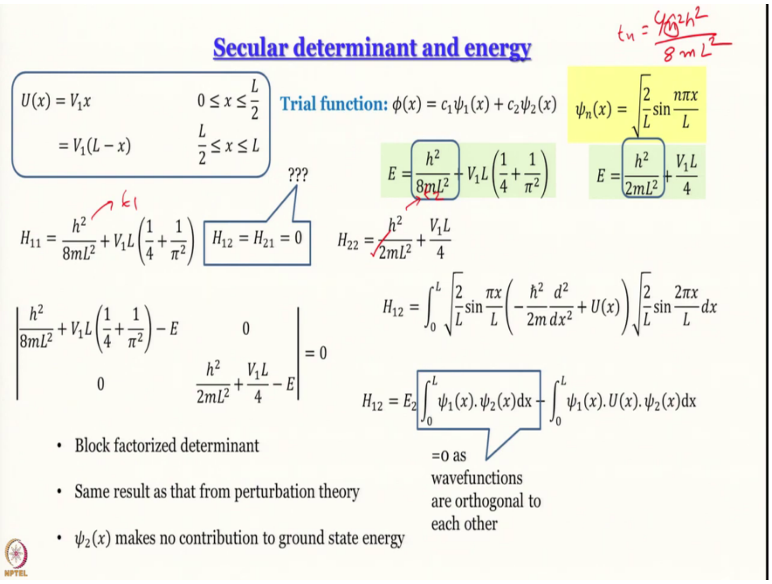

$\epsilon_n = \frac{4n^2h^2}{8mL^2}$

Secular determinant and energy

$$U(x) = V_1x \qquad 0 \le x \le \frac{L}{2}$$
$$= V_1(L-x) \qquad \frac{L}{2} \le x \le L$$

Trial function: $\phi(x) = c_1\psi_1(x) + c_2\psi_2(x)$

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$$

$$E = \boxed{\frac{h^2}{8mL^2}} + V_1L\left(\frac{1}{4}+\frac{1}{\pi^2}\right) \qquad E = \boxed{\frac{h^2}{2mL^2}} + \frac{V_1L}{4}$$

ϵ_2

???

$$H_{11} = \frac{h^2}{8mL^2} + V_1L\left(\frac{1}{4}+\frac{1}{\pi^2}\right) \qquad \boxed{H_{12} = H_{21} = 0} \qquad H_{22} = \frac{h^2}{2mL^2} + \frac{V_1L}{4}$$

ϵ_1

$$H_{12} = \int_0^L \sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)\right)\sqrt{\frac{2}{L}}\sin\frac{2\pi x}{L}dx$$

$$\begin{vmatrix} \frac{h^2}{8mL^2} + V_1L\left(\frac{1}{4}+\frac{1}{\pi^2}\right) - E & 0 \\ 0 & \frac{h^2}{2mL^2} + \frac{V_1L}{4} - E \end{vmatrix} = 0$$

$$H_{12} = E_2\boxed{\int_0^L \psi_1(x).\psi_2(x)\text{dx}} + \int_0^L \psi_1(x).U(x).\psi_2(x)\text{dx}$$

=0 as wavefunctions are orthogonal to each other

- Block factorized determinant
- Same result as that from perturbation theory
- $\psi_2(x)$ makes no contribution to ground state energy

Why is that they are equal to 0 remember they are not necessarily equal to 0 but will prove that they are equal to 0. H 22 turns out to be a h square by 2 m square multiplied by V1 L by 4. So, this h cross square by 8m L square that is energy of n equal to 1 right. So I think I have written it later but in case I have not, I write it like this Epsilon 1. Do you agree with me that this is epsilon 2, what is the epsilon n? Right here is equal to n square h square by 8m L square.

So if n equal to 2 then this becomes 4, 4 by 8 is half that is how you get this. So this is very nice is not it the first energy that we get it H 11 the first matrix element that we get that is essentially the energy of particle in a box for V is equal to 0 plus now again remembering or remembering what we learnt in perturbation theory plus we can see a correction term provided V1 is very small.

H 22 is energy of the second energy level plus correction term provided V1 is very small and the corrections are not exactly the same. Here tt is V1 L well for H 22 it is V1 L by 4 for H 11 it is L by 4 + 1 by phi square. We will see how this is important, let us go ahead and finish our discussion. The secular determinant we get is this and is very nice because it is a block factorised determinate since H 12 is equal to H 21 is equal to 0 we get a block factorized determinant.

And block factorized matrices and determinants a lovely because now see this solution becomes so easy, so what happens then is this, this is H 11 this is H 22 ideally you have to write H 11 into

H 22 is equal to 0 minus well H 11 into H 22 is equal to 0 that is what we get. If you do not have nonzero diagonal elements, then it would be H 11 into H 22 – H 21 to H 12 and you have to solve whatever equation you got.

Now it is H 11 into H 22 is equal to 0 directly gives you H 11 equal to 0 or H 22 equal to 0 so you do not have to even go into perturbation theory when H 11 equal to 0. I simply get E equal to h square b 8m L square + V1 L into 1 by 4 + 1 by pi square. So this thing that we get here is really one of the roots for energy. So what we see here is the one of the solutions is the energy for a H equal to for n equal to 1 plus a correction term that one of the roots.

The second root to get by equating H 22 to 0 is equal to h square by 2m L square + V1 L by 4 so once again energy of n equal to 2 plus a correction term that is very nice. We know that these two are the energies of n equal to 1 and n equal to 2 for the regular particle in a box that we have studied the earlier and that is really very nice. So, whatever energy we got earlier plus some correction term. So that is the advantage of having block factorize determinant.

You got the two roots which one is low energy which one is higher energy most likely this is lower energy unless this V1 L into 1 by 4 + 1 by pi square. This is really, really low energy if that happens then but then that it will add here also. So this is lower energy we can say that which with sufficient confidence. Ok. Now if you did this same treatment for perturbation theory which not doing explicitly, you get the same result.

And we should be willing to believe that also because the result is definitely I mean in line with what one gets perturbation theory 0th order energy plus first order correction right that is what you get these two theories are in agreement with this. Important thing here is that there is no contribution of Psi 2 in ground state energy. In ground state energy is the unperturbed energy if I can say plus a correction term this is small it is nowhere close to the energy of the second level.

And that happens because this H 12 and H 21 are 0. So now better discuss. Why is it that H 12 or H 21 must be equal to 0 in the case that we have discussed. Let us write it out H 12 is integral 1 to L now I can write 1 to L because I am writing the general expression for U of x I am not writing V1 x or V 1 into L - x depending on the range I choose I can substitute U of x as V1 x or V1 into L – x. So this is the general expression we get.

Of course we can break it down into two terms and when you do that in the first time again, what do I have I have Psi 1 then Hamiltonian unperturbed Hamiltonian operating on Psi 1. So, of course I get; unperturbed Hamiltonian operating on Psi 2 not Psi 1 I am not talking about H 11 any more I am talking about H 12 so eigen function that we have of the Hamiltonian gives me an eigenvalue of E2 when the unperturbed Hamiltonian operates on Psi 2 I get E 2 which is constant comes out of the bracket.

Integrate from 0 to L Psi 1 of x multiplied by Psi 2 of x dx what is that? That is definitely equal to 0 because Psi 1 and Psi 2 are orthogonal to each other. What about the second integral? Integral 0 to L Psi 1 of x U of x Psi 2 of x actually to evaluate it there is no need for me to write the explicit form of U of x. Because one thing I know for sure is that it goes up and goes down remember it is like a triangle. So, it is symmetric with respect to the midpoint.

So Psi 1 of x is symmetric that we know already a sin function that does not good for known. Psi 2 of x is antisymmetric like this nu of x is symmetric and we have studied this when we talked about particle in a box allow transition disallow transition what happens when the integrand is a triple product of two symmetric and antisymmetric functions, integrand is antisymmetric and we know by now that an integral of an antisymmetric integrand is equal to 0 is necessarily equal to 0.

So, both the terms of H 12 or H 21 for that matter would be equal to 0 that is why H 12 and H 21 is 0 in this case and that is what makes life very simple for us.

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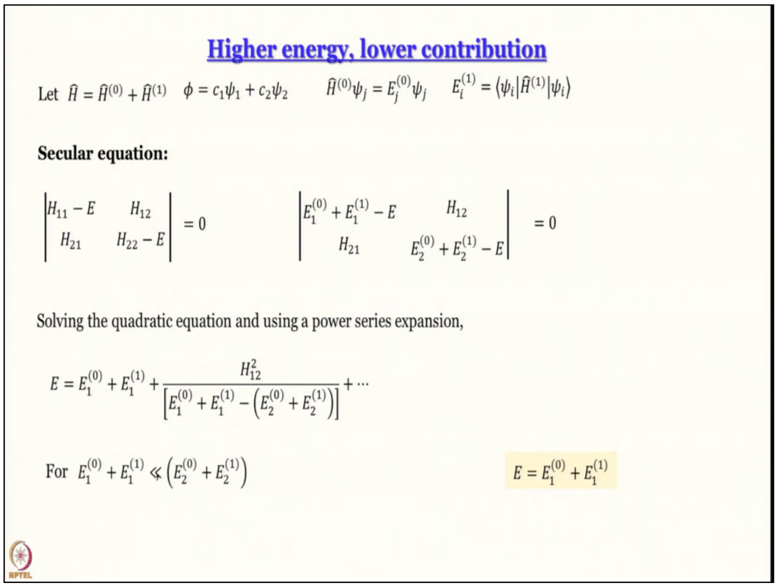

Higher energy, lower contribution

Let $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$ $\quad \phi = c_1\psi_1 + c_2\psi_2$ $\quad \hat{H}^{(0)}\psi_j = E_j^{(0)}\psi_j$ $\quad E_i^{(1)} = \langle\psi_i|\hat{H}^{(1)}|\psi_i\rangle$

Secular equation:

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0 \qquad \begin{vmatrix} E_1^{(0)} + E_1^{(1)} - E & H_{12} \\ H_{21} & E_2^{(0)} + E_2^{(1)} - E \end{vmatrix} = 0$$

Solving the quadratic equation and using a power series expansion,

$$E = E_1^{(0)} + E_1^{(1)} + \frac{H_{12}^2}{\left[E_1^{(0)} + E_1^{(1)} - \left(E_2^{(0)} + E_2^{(1)}\right)\right]} + \cdots$$

For $E_1^{(0)} + E_1^{(1)} \ll \left(E_2^{(0)} + E_2^{(1)}\right)$ $\qquad E = E_1^{(0)} + E_1^{(1)}$

This leads to this interesting observation that Psi 2 of x makes no contribution to ground state energy. Only Psi 1 of x makes the contribution to it. This is a general; this is sort of a subset of a more general phenomenon that when we express our trial wave function as a linear combination of orthonormal functions then functions with higher energy have lower contribution to the ground state. So, now let us slide again using the notation with plant in perturbation theory Hamiltonian is 0th order Hamiltonian plus first order correction phi.

This is what we written in our earlier treatment of variation variational treatment phi equal to c 1 Psi 1 c2 Psi 2. Now you are saying that this Psi's are eigen functions of 0th order Hamiltonian eigenvalues E j0. So the secular equation we get in this case. What would they be? They would be H 11 – c H 12 H 21 H 22 - c what we have learnt earlier. What is H ii we have H 11 H12 separately as just H ii. This is what H ii is, 2 terms the first time I hope you can see without much hassle you done it just now.

First term is a E 0th multiplied by integral Psi i star Psi i over all space which will be equal to 1 plus integral Psi 1 Psi i first order correction to Hamiltonian operating on Psi i. So, what is this, the second term? The first term of course is E i 0th and corrected energy second term as we have learnt in our perturbation treatment is the first order correction to energy. So we get E ith 0 plus first order correction to energy to that is what we use and this is what we get and then if you solve the quadratic equation and jumping steps here and if we use a power series expansion, then this is the approximate result to get.

Then you will few more terms but they will make progressively lower contribution to get E 1 equal to E 1 0th plus first order correction to E 1 plus this H 12 square divided by E 0th plus first E 1st minus so on and so forth. If you now remember the earlier problem of particle in a box with that triangular potential you will remember H 12 is equal to 0 there it automatically follows that E is equal to this 0th order energy plus the first order correction.

For other general solutions if you work in the regime that the energy levels are sufficiently; the spacing between the energy level successive energy levels is sufficiently large if you work in that regime, which is a reasonable approximation reasonable think to imagine then this difference is going to be large. If this is large, then this term will become smaller H 12 in a very large. Then approximately you get E equal to E 1 0th + E 1st so the higher terms do not even contribute to the ground state energy.

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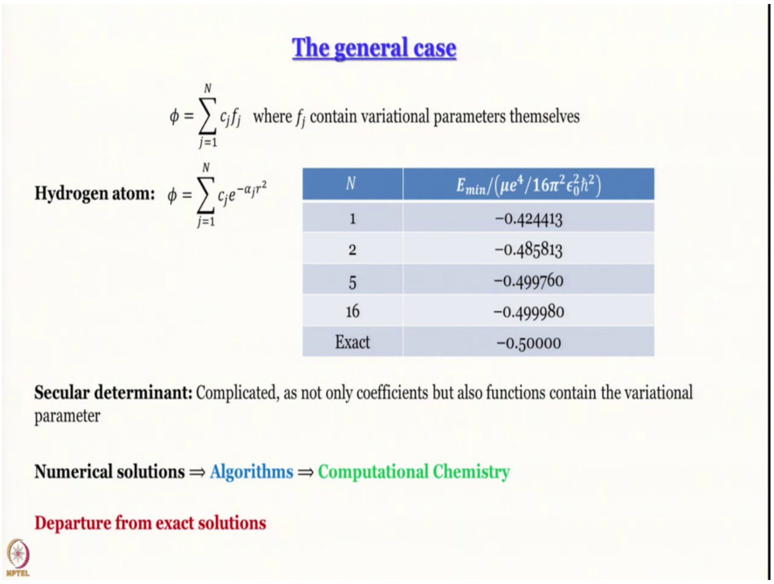

The general case

$$\phi = \sum_{j=1}^{N} c_j f_j$$ where f_j contain variational parameters themselves

Hydrogen atom: $\phi = \sum_{j=1}^{N} c_j e^{-\alpha_j r^2}$

N	$E_{min}/(\mu e^4/16\pi^2\epsilon_0^2\hbar^2)$
1	−0.424413
2	−0.485813
5	−0.499760
16	−0.499980
Exact	−0.50000

Secular determinant: Complicated, as not only coefficients but also functions contain the variational parameter

Numerical solutions ⇒ Algorithms ⇒ Computational Chemistry

Departure from exact solutions

So that is what we have and now to close this discussion let us just introduced the general case. We are talking about linear combination of orthonormal wave functions and what we have said so far is that it is the coefficient that is the variational parameters that is not necessarily the case. I can also have variational parameters within this orthonormal functions themselves the f themselves. For example for hydrogen atom we can write the function like this sum over j cj e to the power – alpha j r squared.

So this is this function here is similar to the one is wave function with the exception that this coefficient in the exponent is also a variational parameter so 2 variational parameters gives me greater flexibility of course you can play with number terms. so once again remember hydrogen atom is exactly solvable. But if you do a variational calculation using this kind of parameter, this kind of a linear combination and keep increasing the number of n's what you see is this if you use n equal to 1 this is the energy that you get -0.4 244413.

If you increase the numbers 1 go from 1 to 2 it becomes lower to phi even lower 16 -0.4 9980 now exact calculation that let me remind you in terms what is given here mu e to the power 4 by 16 square pi square epsilon 0 square x square, the exact calculation that we got earlier is -0.5. So now when you increase the number of terms to 16 you get very close to the exact solution. So what we learn from here is that in the general case, if increase number of terms you will closer to the energy.

And that is by using the power of variation theorem, upper limit theorem. One thing to understand here if we include the variation parameter in the functions themselves is that the secular determinant is complicated because the variation parameter is also there in the functions. In fact we will not be able to get an analytical solution like what we have been getting so far. You have to solve this numerical put in numbers for solution that you get changed the numbers see what solution that you get.

And you need different kinds of algorithms and this opens up the field of computational chemistry. I think I said this opens up field of computational chemistry once earlier will this really takes us into the domain of computational chemistry, but let us talk a little more about this later. Other thing that happens here is that also we are slowly started going away from the exact solutions. We have changed exact solution one is orbitals so by this introducing this variation parameter little more significant than what you have been doing so far.

So eventually you will reach a situation where you perhaps even do not have to start from exact solutions any kind of orthonormal set will do but this week for that. For now we close this discussion and finally we are now ready to resume our discussion of many electron atom the discussion will perform will be on helium.