Chemistry Atomic Structure and Chemical Bonding

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Lecture – 38

Variational Principle in Quantum Chemistry: Linear superposition Principle

Welcome back to the lectures in Chemistry and the topic of Atomic Structure and Chemical Bonding. My name is Mangala Sunder I am from the Department of Chemistry, Indian Institute of Technology, Madras.

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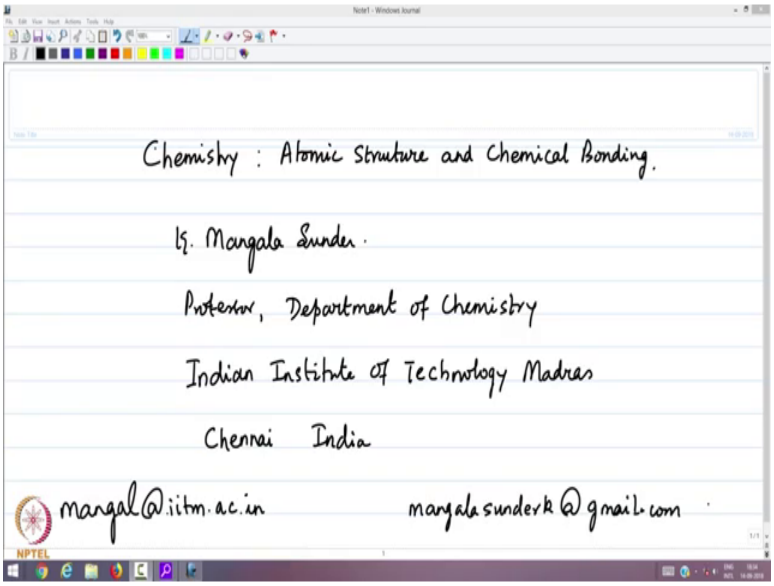

Chemistry : Atomic Structure and Chemical Bonding.

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My email coordinates ids are given here for you to contact me for any clarification ok.

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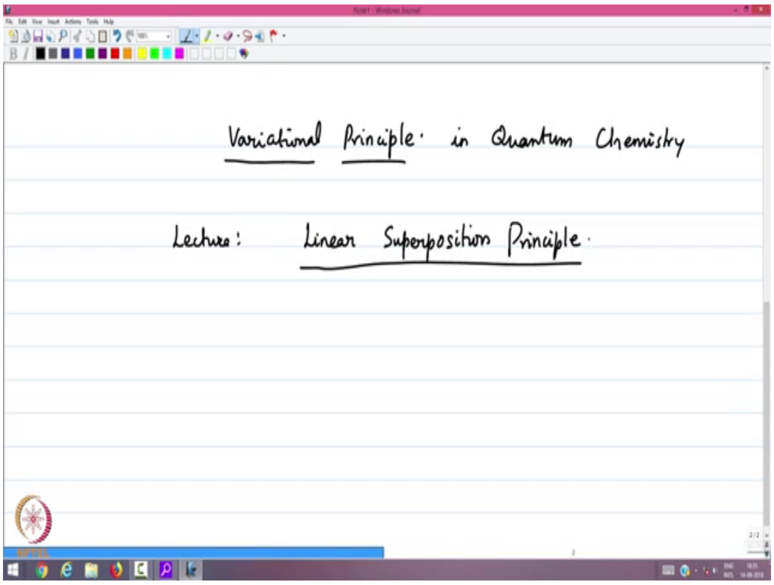

Variational Principle in Quantum Chemistry

Lecture : Linear Superposition Principle.

The set of lectures beginning today this lecture or this is on the Variational Principle in Quantum Chemistry and we will do it only in quantum chemistry we look at it non mathematically as much as possible. And this lecture title is Linear superposition of wave functions Principle. The subsequent lectures will provide you more details on the variational principle as well as some examples elementary examples from chemistry.

We will see what linear superposition principle means in our context.

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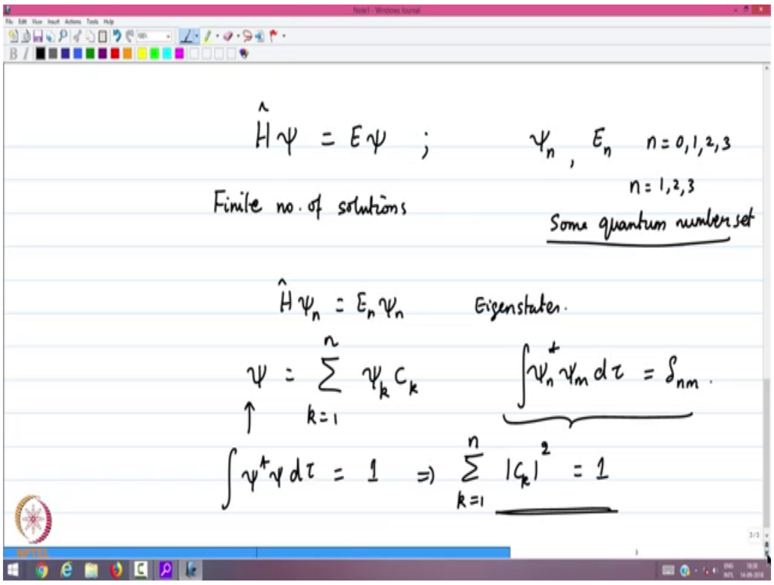

$\hat{H}\psi = E\psi$; ψ_n , E_n $n = 0,1,2,3$

$n = 1,2,3$

Finite no. of solutions

Some quantum number set

$\hat{H}\psi_n = E_n\psi_n$ Eigenstates.

$$\psi = \sum_{k=1}^{n} \psi_k c_k \qquad \underbrace{\int \psi_n^* \psi_m \, d\tau = \delta_{nm}}$$

$$\int \psi^* \psi \, d\tau = 1 \Rightarrow \sum_{k=1}^{n} |c_k|^2 = 1$$

The objective in quantum chemistry is of course to solve the Schrodinger equation, time independent most of the time H psi equal to E psi. And any such solution if we are able to do gives you a series of solution psi ns and energy is E ns where n can be 0; as in the case of harmonic oscillator 1 2 3 etcetera or n can be 1 2 3 etcetera; it is some quantum number set. Finite or infinite ok; let us first look at finite case finite number of solutions. So, what it means is that H on psi n is E n on psi n.

Now, these are eigenstates; however, if the system is not in an eigenstate and for some reason we are able to find out the eigen states of the system; then the arbitrary non eigenstate of the system is represented as a superposition of all the eigenstates with coefficients a n; where n runs from 1 to some finite number.

Let us call it as k or whatever or let me do the following try to the overall wave function as sum over k is equal to 1 to n; psi k with some linear combination coefficients C k. Usually this wave function psi ns which are eigenfunctions can be chosen as or often or orthogonal to each other. So, that you have psi n star psi n d tau is delta nm; therefore, using this orthogonality if we want to normalize this wave function; then we have psi star psi d tau is equal to 1 gives you the condition that the sum over the coefficients absolute square for all the values 1 to n, C k square is equal to 1.

So, this is it is a very straightforward integral to obtain.

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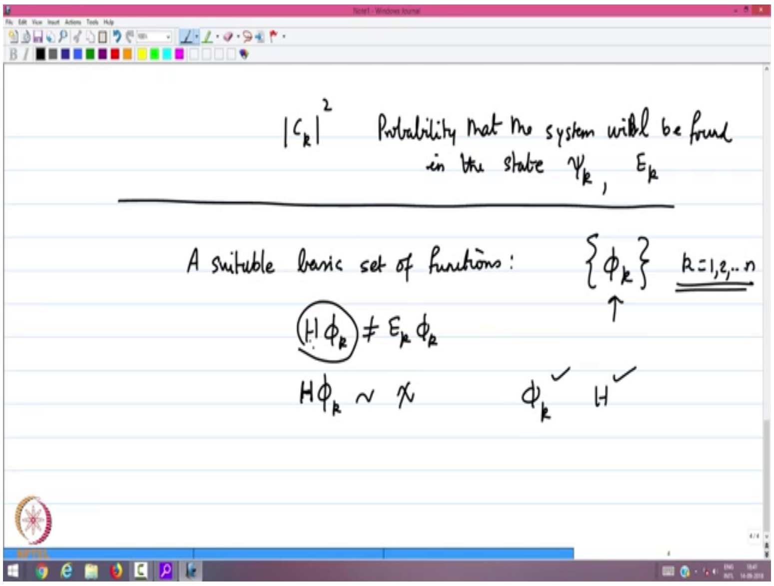

$|c_k|^2$ Probability that the system will be found in the state ψ_k, E_k

A suitable basic set of functions: $\{\phi_k\}$ $\underline{\underline{k=1,2,..n}}$

$\boxed{H\phi_k} \neq E_k\phi_k$

$H\phi_k \sim \chi$ ϕ_k ✓ H ✓

And I think I have discussed this enough in the previous lectures that I would assume that we use this condition that the coefficients are such that the absolute square C k is the probability that the system will be found in the state psi k will be found in the state psi k, if we have to make a measurement of the energy of the system and also the energy E k, the C k square gives you the probability.

The linear superposition is this one; now there are; obviously, many problems in fact, most of the problems in quantum chemistry. We do not know the psi ns that you see here will be write then down; we do not know the psi ns and our job is to first find out these psi ns. And if the state of the system is also arbitrary then what is the best description that we can provide for the state of the system and how do we obtain these eigenfunctions and the eigenvalues.

For this process, normally what one does is to choose a for every problem a suitable basis set of functions which we shall call them as phi k a full set k is equal to say 1 2 3; let us do a finite set k is equal to 1 2 n.

This is not an eigenfunction in the sense H on phi k is not equal to E k on phi k, but H on phi k gives you something else some chi; some other function. Therefore, using the fact that we can calculate the effect of the Hamiltonian on phi k because we know phi k, we know the Hamiltonian which is also a derivative operator and the potential energy operator. Therefore, it is possible for us to actually find the action of H on phi k; it will give you something probably different from the eigenfunction of the function itself.

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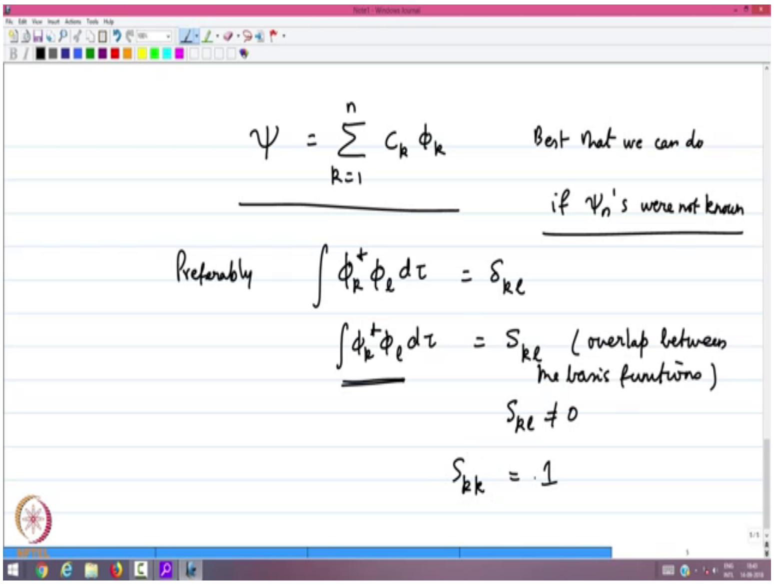

$$\Psi = \sum_{k=1}^{n} C_k \phi_k$$

Best that we can do

if Ψ_n's were not known

Preferably $\int \phi_k^* \phi_l \, d\tau = \delta_{kl}$

$\int \phi_k^* \phi_l \, d\tau = S_{kl}$ (overlap between the basis functions)

$S_{kl} \neq 0$

$S_{kk} = 1$

In that case, if we write the arbitrary state of the system using a linear combination coefficient set C k phi k and k is equal to 1 to n; this is the best that we can do; if psi ns where not known. Apart from all the model problems that I have solved already; the psi ns are generally not known for most of the problems. Therefore, we have to choose an arbitrary set of basis functions with preferably; we will have the basis functions phi k star phi l d tau whatever is the space available to the system; if it is 3 dimensional this will be some volume element.

And then the integral will tell you the entire volume in which the system is studied given that we probably would like to have a phi k star phi l is equal to delta k l. It may not also be possible to have these kind of functions if he chose certain types of functions; in which case phi k star, phi l d tau will be called S k l or overlap between the basis functions.

S k l is not 0, but we can always have S k l k k chosen to be such that it is 1 because these functions can be normalized. Therefore, if k is equal to l whatever that integral is called as kk we can choose it to be 1 ok.

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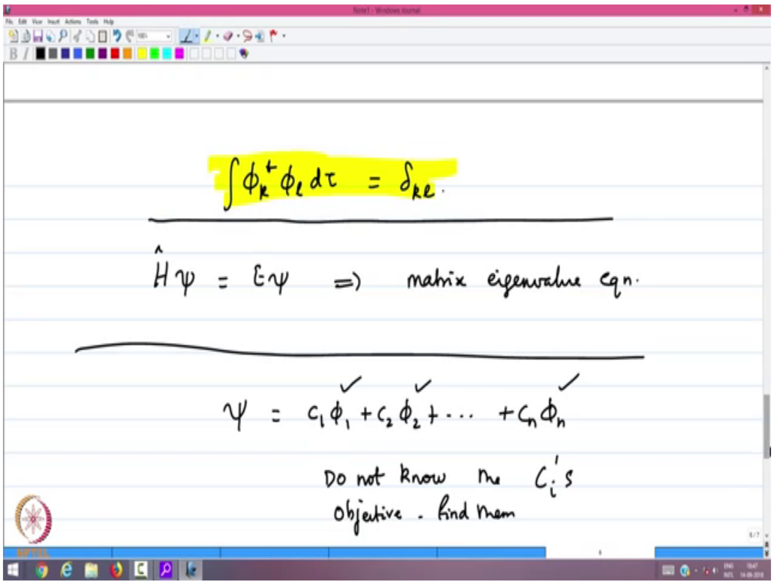

$$\int \phi_k^* \phi_l \, d\tau = \delta_{kl}.$$

$$\hat{H}\psi = E\psi \Rightarrow \text{matrix eigenvalue eqn.}$$

$$\psi = c_1\overset{\checkmark}{\phi_1} + c_2\overset{\checkmark}{\phi_2} + \dots + c_n\overset{\checkmark}{\phi_n}$$

Do not know the C_i's

Objective . find them

Let us first do the case where the study the case where phi k star phi l d tau is actually delta k l and see how this helps us to turn the Hamiltonian equation the Schrodinger equation H psi is equal to E psi into a matrix equation into a matrix eigenvalue equation.

So, to do this let us do the following algebra let us assume that the wave function psi is C 1, phi 1 plus C 2 phi 2 plus C n phi n. We know phi 1s, phi 2s phi ns etcetera because we have chosen them, but do not know the Cs; our objective is to find what they the Cs do not know the Cs the Cis right our objective is to find them.

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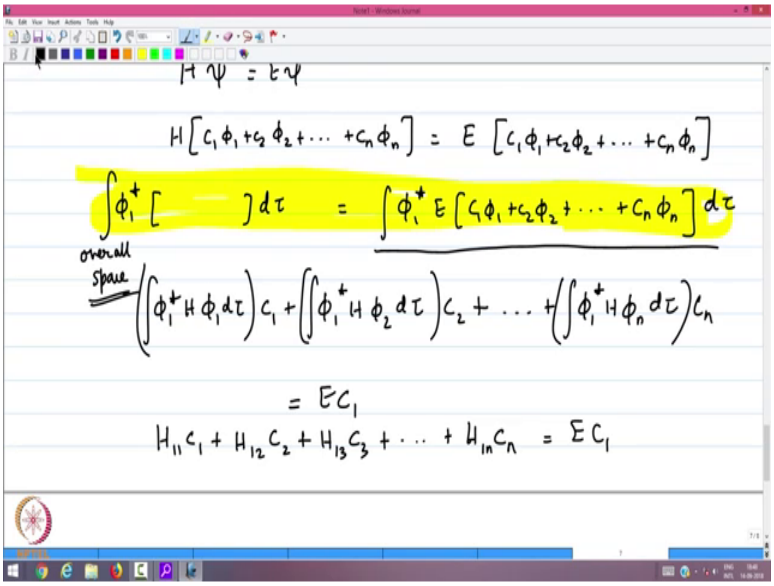

$$H\psi = E\psi$$

$$H\left[c_1\phi_1 + c_2\phi_2 + \dots + c_n\phi_n\right] = E\left[c_1\phi_1 + c_2\phi_2 + \dots + c_n\phi_n\right]$$

$$\int \phi_1^* [\quad] \, d\tau = \underline{\int \phi_1^* E\left[c_1\phi_1 + c_2\phi_2 + \dots + c_n\phi_n\right] d\tau}$$

overall space

$$\left(\int \phi_1^* H \phi_1 \, d\tau\right) c_1 + \left(\int \phi_1^* H \phi_2 \, d\tau\right) c_2 + \dots + \left(\int \phi_1^* H \phi_n \, d\tau\right) c_n$$

$$= E c_1$$

$$H_{11}c_1 + H_{12}C_2 + H_{13}C_3 + \dots + H_{1n}C_n = E C_1$$

Therefore, if we write H psi is equal to E psi if we write this it is H on C 1, phi 1 plus C 2 phi 2 plus C n phi n is equal to E on C 1, phi 1 plus C 2 phi 2 plus plus C n phi n to turn this into a matrix matrix equation; let us do the integration by first multiplying everything by phi 1 star and integrating with respect to the volume element and over all the space.

See over all space here means that for example, if you did the particle in the box the box land 0 to l; that is the integral limit. If it is a particle on a ring it is the value of the angle angular coordinate namely 0 to 2 pi; that is a limit. And in the case of hydrogen atom is the entire 3 dimensional volume xyz all going from minus infinity to plus infinity or the r theta phi in the hydrogen atom having all those values. So, this is what it means over all the space that is available to the system and the volume element is dependent on the dimension of the system that we have.

So, if we do this phi 1 star; then you can do the same thing on the right hand side the phi 1 star E C 1 phi 1 plus C 2 phi 2 plus C n phi n d tau. Now the left hand side is essentially phi 1 star; H phi 1 integral d tau times C 1 plus integral phi 1 star H phi 2 p tau times C 2 plus and so on.

You have integral phi 1 star H phi n; d tau C n and that is equal to E times the first one is of course, the phi 1 star phi one is a normalization integral and therefore, it is a constant C 1; that is a result. And the rest of it phi 1 star with phi 2; phi 1 star with pi 3 remember we chose the functions to be orthogonal to each other I have chosen that here; they are orthogonal. Therefore, all the other terms will go away from the right hand side and what you will have is only this. The left hand side each of this integral can be labeled as the matrix element of the Hamiltonian with respect to this ordering of the basis functions from 1 to n.

So, the first one is 1 1 C 1 plus the second one is 1 2 C 2 plus H 1 3 C 3 plus H 1 n C n is equal to E C 1, There is nothing specific about phi 1 star integration on this equation; we might as well do the same integration with phi 2 star and phi 3 star. And on the left hand side you will you see what we will get is the corresponding matrix element of the Hamiltonian; if you do it with the phi 2 star, you will get a H 2 1 and you will get a H 2 2; you will get H 2 3 and so on.

But on the right hand side what you would see is that if we do it with phi 2 star this integral phi 2 star keeps only the phi 2 term and all the other terms are 0 due to orthogonality therefore, it becomes E C 2.

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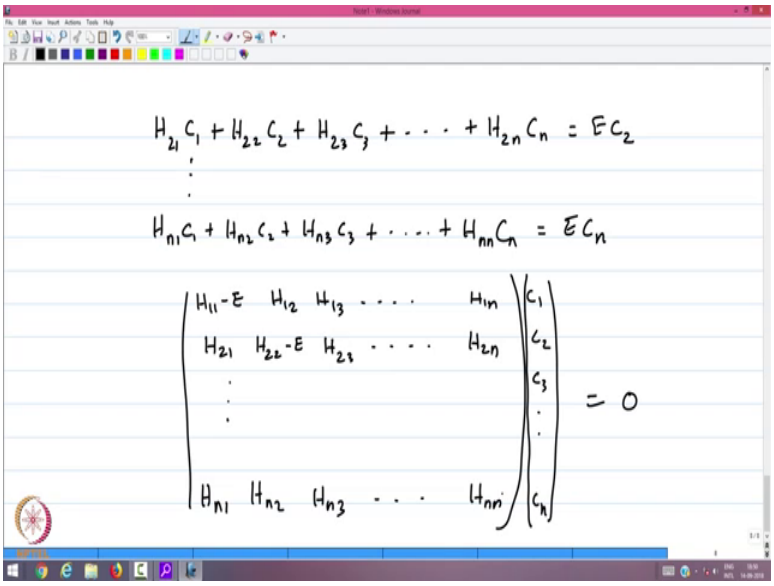

$$H_{21}C_1 + H_{22}C_2 + H_{23}C_3 + \cdots + H_{2n}C_n = EC_2$$

$$\vdots$$

$$H_{n1}C_1 + H_{n2}C_2 + H_{n3}C_3 + \cdots + H_{nn}C_n = EC_n$$

$$\begin{pmatrix} H_{11}-E & H_{12} & H_{13} & \cdots & H_{1n} \\ H_{21} & H_{22}-E & H_{23} & \cdots & H_{2n} \\ \vdots & & & & \\ H_{n1} & H_{n2} & H_{n3} & \cdots & H_{nn} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ \vdots \\ C_n \end{pmatrix} = 0$$

So, let me write that as the second equation H 2 1 C 1 plus H 2 2 C 2 plus H 2 3 C 3 plus H 2 n C n is equal to E C 2. And therefore, now you can write likewise n equations namely H n 1 C 1 plus H n 2 C 2 plus H n 3 C 3 plus plus H n n C n is equal to E C n.

Now, you can see immediately that this is nothing but a linear if you take the C 1 on this side this is becomes a linear homogeneous equation with the coefficients which are undetermined namely C 1 C 2 C 3 C n etcetera. So, what is that equation? If we write this as a matrix equation it is H 1 1 minus E times C 1 right and H 1 2 H 1 3 so on H 1 n and it C 2 C 3 C n that is equal to 0.

And likewise H 2 1 H 2 2 minus E H 2 3 this is H 2 2 minus E because of C 2 H 2 3 H 2 n and if we try to all the n equations you get H n 1, H n 2, H n 3, H n n. Now very often we choose the functions to be a real and therefore, these coefficients are the Hamiltonian coefficients are matrix elements are all real and if we restrict ourselves to this point to real matrix elements H ij then you know that H being a Hermitian operator or a symmetric operator here H ij is equal to H ji.

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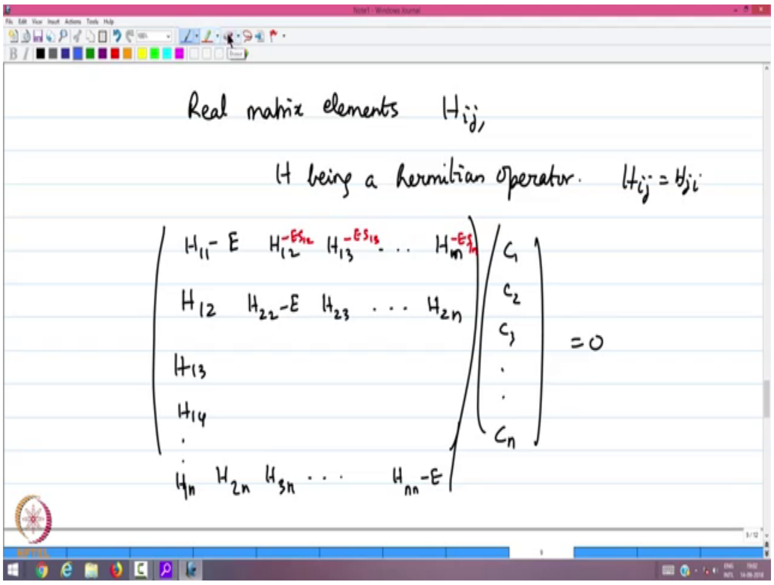

Real matrix elements H_{ij},

H being a hermitian operator. $H_{ij} = H_{ji}$

$$\begin{pmatrix} H_{11}-E & H_{12}^{-ES_{12}} & H_{13}^{-ES_{13}} & \cdots & H_{1n}^{-ES_{1n}} \\ H_{12} & H_{22}-E & H_{23} & \cdots & H_{2n} \\ H_{13} & & & & \\ H_{14} & & & & \\ \vdots & & & & \\ H_{1n} & H_{2n} & H_{3n} & \cdots & H_{nn}-E \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ \vdots \\ C_n \end{pmatrix} = 0$$

Therefore, you can see that the equation comes down to very simply H 1 1 minus E H 1 2 H 1 3 H 1 n; C 1, C 2, C 3 to C n is equal to 0.

And this will be also H 1 2 H 2 2 minus E H 2 3 on the way up to H 2 n H 1 3, H 1 4 and likewise H 1 n, H 2 n, H 3 n up to the last line H n n minus E equal to 0. So, the Schrodinger equation in the case of the unknown eigenfunctions assumes the form of using some known basis set functions.

The basis set functions are chosen carefully for different problems in different ways. The whole art of quantum chemistry is the right choice of the basis functions and also in almost all the cases, the basis functions are never finite I mean in principle there are infinite basis set functions. Therefore the generalization of this to the real matrix eigenvalue problem of quantum mechanics is direct and also immediate.

But you have turned the simple Schrodinger equation; we have differential equation containing the derivative operators in the Hamiltonian to that of solving a differential equation to a solving a matrix eigenvalue problem. Because you see the determinant of this matrix has to be 0 as this is nothing, but a linear homogeneous equation in n coefficients which are constants.

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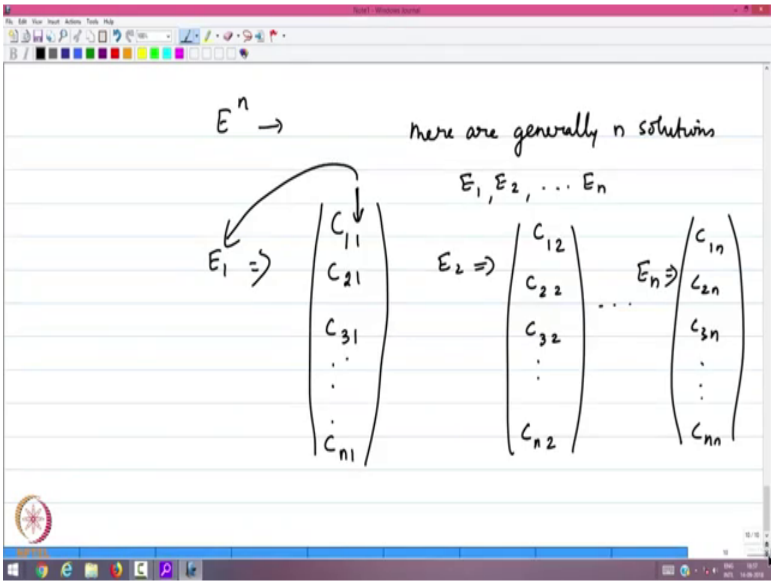

$E^n \rightarrow$ there are generally n solutions

$E_1, E_2, \ldots E_n$

$$E_1 \Rightarrow \begin{pmatrix} C_{11} \\ C_{21} \\ C_{31} \\ \vdots \\ C_{n1} \end{pmatrix} \quad E_2 \Rightarrow \begin{pmatrix} C_{12} \\ C_{22} \\ C_{32} \\ \vdots \\ C_{n2} \end{pmatrix} \cdots \quad E_n \Rightarrow \begin{pmatrix} C_{1n} \\ C_{2n} \\ C_{3n} \\ \vdots \\ C_{nn} \end{pmatrix}$$

Now the determinant of this if it is 0 it is going to give you a polynomial of E raised to n as the leading term and therefore, there are generally n solutions; n eigenvalues E 1 denoted as E 1, E 2 E n.

For each eigenvalue E you will have a column vector E 1, you will have a column vector C 1, C 2, C 3, C n, but this column vector is unique to the eigenvalue E 1. So, let us denote this as the following that if this is C 1, C 2 1, C 3 1, C n 1; where the second label 1 is the one to correspond to this energy eigenvalue E 1 and the C 1 C 2 C 3 the first label gives you the actual column vector.

Likewise for E 2 the eigenvector is going to be C 1 2 C 2 2 C 3 2 and so on and so you will have C n 2. So, you have all the eigen values and all the eigen vector correspondingly C 1 n C 2 n C 3 n up to C n n. So, the solution of the Schrodinger equation therefore, is that of the n by n matrix eigenvalue problem.

Now if the n is very large and if the n is infinite; obviously, the solution cannot be done even in the computer programming; using computer programming and using numerical methods it cannot be done. Therefore, we have to now find out what is the best basis set how many function basis functions that we have to choose and therefore, a whole lot of techniques come in.

Variational theorem is the starting point for the eigenvalue proposition and eigenvalue the problem of the Schrodinger equation; in that it puts an upper bound on the best possible solution that you can have. And that upper bound is the starting point that we usually called the exact solution to the ground state. And the variational method gives an exact upper bound to the calculation of the eigenvalue problem.

And any trial function that we can choose, any basis set that we can choose a trial basis set will never give you the exact lowest solution, but it will approach that. So, we will see the actual variational principle, but this as the background in the next lecture.

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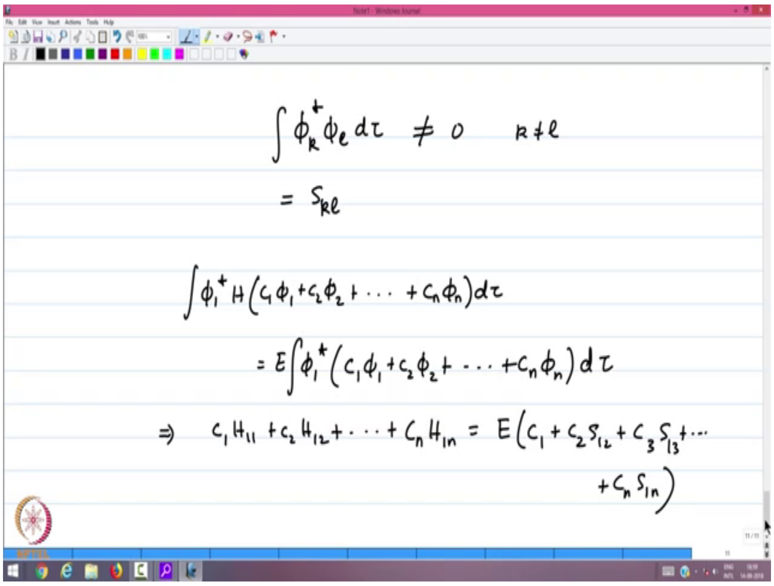

$$\int \phi_k^* \phi_\ell \, d\tau \neq 0 \qquad k \neq \ell$$

$$= S_{k\ell}$$

$$\int \phi_1^* H (c_1\phi_1 + c_2\phi_2 + \cdots + c_n\phi_n) \, d\tau$$

$$= E \int \phi_1^* (c_1\phi_1 + c_2\phi_2 + \cdots + c_n\phi_n) \, d\tau$$

$$\Rightarrow \quad c_1 H_{11} + c_2 H_{12} + \cdots + c_n H_{1n} = E(c_1 + c_2 S_{12} + c_3 S_{13} + \cdots + c_n S_{1n})$$

But let me complete this lecture with the possible case that the basis sets phi k phi l star d tau or not 0 even if k is not equal to l that is there is there is an overlap if you define this as S k l. How does this equation change? This one ok; we have integrated the Schrodinger equation H psi is equal to E psi using phi 1 star. And the term that we had kept is phi 1 star C 1 phi 1 E because phi 1 star phi 2 integral d tau is 0 and all these things are, but if they are not 0 each one will be denoted as a an overlap integral s 1 2 in this case s 1 3 in the next case s 1 n and so on.

So, let me just write down the 1 or 2 equations and the little generalize the matrix namely the integral phi 1 star H on C 1 phi 1 plus C 2 phi 2 up to C n phi n or some arbitrary n d tau is equal to the integral phi 1 star times E and C 1 phi 1 plus C 2 phi 2 plus C n phi n d tau.

And the equation is C 1 H 1 1 plus C 2 H 1 2 plus etcetera up to C n H 1 n is now equal to E the first one is C 1; the phi 1 star phi 1 d tau can always be chosen to be normalized; so, therefore, that is 1. And then you have plus C 2 S 1 2 plus C 3 S 1 3 up to C n S 1 n ok.

So, the same thing will happen for all the other equations that we have obtained by multiplying by phi 2 star or phi 3 star or any of them phi and so on there are n equations similar to this one there n equations. And the n equations will all have the SS coming in and therefore, what happens to this matrix? This matrix gets modified by default as follows; it gets modified into minus E S 1 2 minus E S 1 3 minus E S 1 n.

So, let me now write that.

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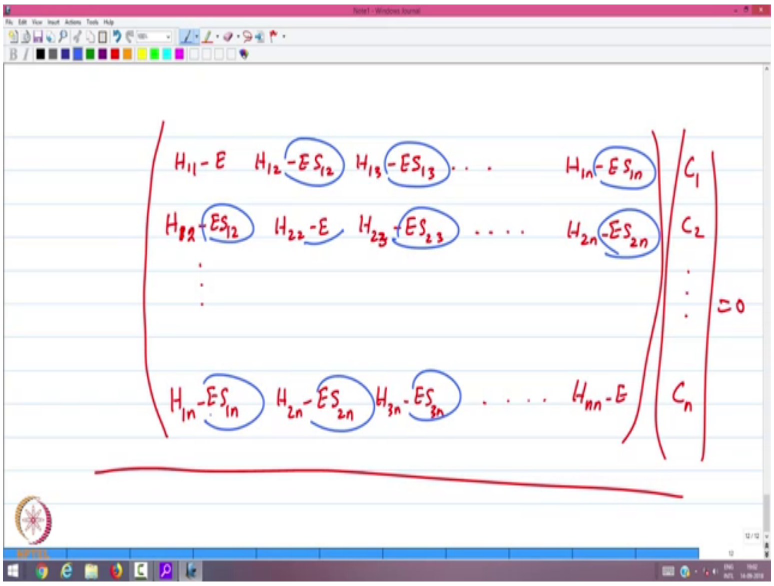

$$\begin{pmatrix} H_{11}-E & H_{12}-ES_{12} & H_{13}-ES_{13} & \cdots & H_{1n}-ES_{1n} \\ H_{12}-ES_{12} & H_{22}-E & H_{23}-ES_{23} & \cdots & H_{2n}-ES_{2n} \\ \vdots & & & & \\ H_{1n}-ES_{1n} & H_{2n}-ES_{2n} & H_{3n}-ES_{3n} & \cdots & H_{nn}-E \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ \vdots \\ C_n \end{pmatrix} = 0$$

You have H 11 minus E S 11 which is of course, 1 then you have H 1 2 minus E s 1 2 H 1 3 minus E S 1 3 you have H 1 n minus E S 1 n. And the second equation will be H 1 2 minus E S 1 2; again for real functions phi 1 star phi 2 or phi 1 phi 2 star they are both the same; therefore, you see that the overlaps are the same.

And you will have H 2 2 minus E H 2 2 minus E S 2 3; H 2 3 and so on H 2 n minus E S 2 n. And if you complete this it is H 1 n minus E S 1 n; H 2 n minus E S 2 n; H 3 n minus E S 3 n all the way up to H n n minus E; this matrix multiplied by C 1, C 2 C n this is 0.

So, the modification is that that you will have all the minus E S terms minus E S terms minus E S term everywhere this what this what and this what you can see that. So, the solution of the Schrodinger equation is either solving this one if the basis functions are chosen in a manner that; they are not actually orthogonal to each other or if the basis functions are chosen and they are orthogonal to each other solving this equation without the solving that.

So, this is the matrix eigenvalue problem and this is the direct result of assuming the wave function to be a linear superposition of some unknown that whose properties we understand. And whose integrals we can calculate we use that as a basis function therefore, the intelligent choice is to find the right set of basis function closed to what are possibly the eigenfunctions.

Of course, the eigenfunctions are what we want and the eigenvalues are what we are always looking for in the next lecture let me introduce the variational theorem with this as the background. And we will tell you a little bit about how to apply the variation theorem for some very elementary problems. The entire quantum chemistry program today depends so much on the fundamentals of variational principle; that it is important for us to follow through this in the course even in an elementary way. We will meet the next time with a little bit of introduction to the variational principle until then.

Thank you very much.