Computational Physics

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Lecture – 41

Differential Equation for Quantum Mechanical Problems:
Variational Principle Part 01

So, in this module we are going to discuss about how using another numerical technique which is the Variational Principle, which we have already learned about in quantum mechanics in a basic quantum mechanics course, how we can solve the Schrödinger equation.

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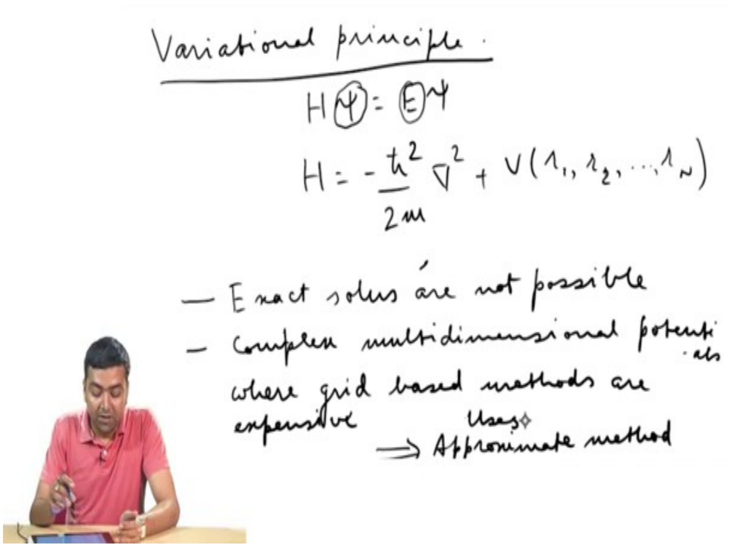

So, so if you recall it so what we are trying to solve is equations which are of this form H psi equals to E psi, where H is my Hamiltonian which has the following form minus H cot square by twice m grad square, which is the kinetic energy plus a potential which depends on different functions of positions. And our unknowns are these wave functions which are among this psi and this energy Eigen values.

So, in the numeral method which we seen so in the last module. So, there we solve the same equation for the one dimensional case where we numerically integrate this second order differential equation. However, when we go to multi dimensional problem or when we go to very complex problems it is impossible to solve it in that fashion so that method. So, that grid based method which if you remember in the numeral principle what we had is we divided our position space the r into several small grids. So, these type of grid based methods also become very inefficient.

So, when do we use this variational principle; the one is when you do not have exact solutions are not possible. The second is for complex systems complex multi dimensional potentials, where grid based methods becomes inappropriate or expensive. So, the way to go around solving these type of problems is to use some approximate method. So, one uses approximate method and one such approximate method is a based on my variational principle. So, what is the basic idea of variational principle?

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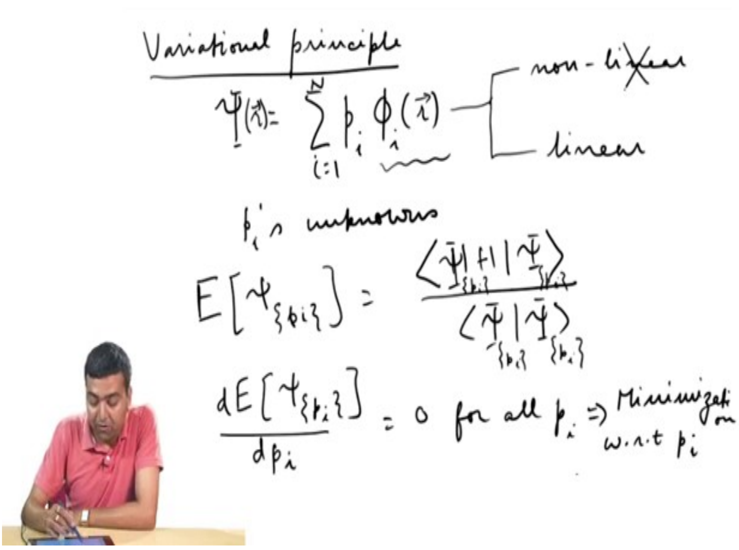

So, if I if we remember our basic quantum mechanics course, so what we are interested to know this wave function psi. So, what we do is we expand these wave functions in a particular basis functions phi i which are r and in some combination of the basis function i equals to 1 to n. So, where my pi s are the unknowns, so what I have done here is I have this wave function psi which is a function of r and I have done expansion of this wave function.

So, how the expansion is done is I expand them in a set of basis functions which are denoted by phi i here and pi are the coefficients. So now, this expansion you can do a non-linear or a linear expansion, but if you do a non-linear expansion then this becomes very difficult problem to solve. So, what people typically avoid the non-linear expansion and they do a linear expansion and of the wave functions.

So, once I have these wave functions, so what my variational principle still is that I can minimize my energy. So, I can write down my energy a in this fashion. So, my energy will be given by the expectation value of my Hamiltonian and with the normalization constant where the normalization is over psi.

Now. each of this psi s it denotes parametrically on pi which my p where my pi s are unknown. So, if I minimize this functional with respect to pi. So, what I will get is so what basically mathematically, what it means is my dE psi pi d pi is equal to 0 for all pi this is nothing but minimization with respect to pi ok, so this from using this minimization.

So, what I can get is I can get the values of pi s, now once I get the values of pi s. So, then I can I know the form of the wave function and then I can solve I can find out the corresponding also the Eigen values and I can also get the ground state energy of my system.

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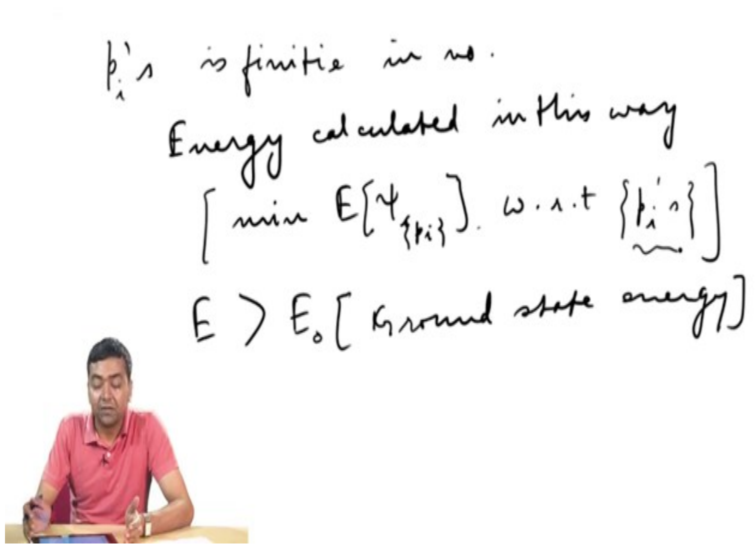

However our pi s now is finite in number because so since my pi is finite in number. So, my the basis in which I am expanding, so that what this implies is that the basis in which

I am expanding my wave function is now a finite basis. So, it does not spend a complete infinitely large Hilbert space.

So, what is this implies is that in this method the energy which we get calculated in this way that is minimizing E of psi with respect to the pi s this will if I call this energy as E. So, this will always be greater than my ground state energy where E0 is my ground state energy. So, what I can do is by increasing the number of pi s in my expansion I can gradually converge towards the ground state.

So, this is the basic principle of the Schrödinger of the variational principle and what this leads into is this will soon show that this leads into writing the Schrödinger equation in a matrix form. So now, what we will do is we will see how we can write down the we will go to the matrix formulation of Schrodinger equation.

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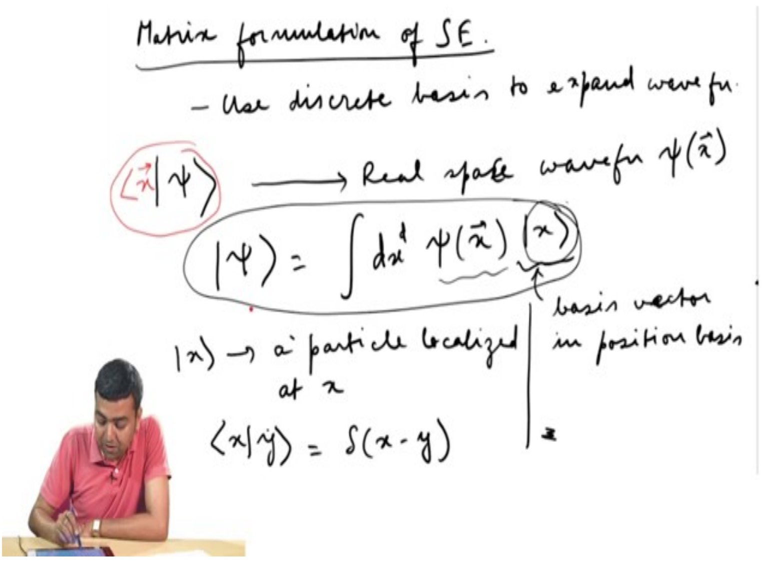

So, SE stands for Schrodinger Equation, so to so in order to cast the. So, what you should also remember that here what we are talking about is to solve the time independent Schrodinger equation for my system. So, basically my wave functions are stationary wave functions. So, in order to find out the so the unknowns which are my stationary wave functions.

So, in order to find out these stationary wave functions we need to expand them now in a discrete basis. So, what we do is we used discrete basis to expand wave function instead of using a continuous basis which is typically done when you solve it try to solve it analytically. So, if I if you recall so what I will use is I will use the bra-ket notation and I assume that you guys are familiar with bra-ket notations. So, in bracket notation wave functions psi can be related to its real space wave function, which I denote as psi x in using this following equation.

So, I have psi is an integral over so it is a d dimension it can be it is valid in one dimension two dimension three dimension and multiple dimensions. So, right as x so if you recall, now this my x is my basis vector in the position basis. What x represents is so basically what x represents is a particle localized at position x and what this implies is that if we compute, if you if we take any other basis vector y and we take the projection of y on x that will give me a delta function.

So, what it means is that this will give on nonzero value or you will find the particle at the position where only when my x is equal to y. So, using this relationship what we will do is we will now see how we can find out this psi x. So, if I want to try to find out psi x what I can do is I can take this function and project it on to the basis function which is my x here this basis function. So, if I do that what I will get is the following.

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$$\langle \vec{x}|\psi\rangle = \int dy^d\, \psi(\vec{y})\, \langle \vec{x}|\vec{y}\rangle \qquad |\psi\rangle = \int dx^d\, \psi(\vec{x})|\vec{x}\rangle$$

$$= \int dy^d\, \psi(\vec{y})\, \delta(x-y)$$

$$\langle \vec{x}|\psi\rangle = \psi(\vec{x})$$

So, what I am interested in is I will compute the projection of my psi on x and this will be given by the integral of psi. So, if I go back here ,so if I now try to compute this quantity. So, what I am computing is this quantity now in the next slide. So, if I try to compute this quantity here, so what it will do is this vector will operate on this one. But since we are projecting it on x, so this integral we have to do it on y. So, we use a different position basis instead of use representing it is base x, we represent it as y.

So, if we do that then what we will get is the following so this is my x. So, my psi i need to now represent in y and then I it will operate in this. So, again these represent d dimensional functions. So, if I do this integral, so now what I know is this will give me a delta function. So, what I can do is I can write this as in this fashion psi y delta x minus y now if I complete this integral, so this is nothing but my psi x.

So what this tells me is that if I want to find out. So, if I have my wave function in the if the relationship between my wave function in the bracket notation and in a continuous functional form if it is given by this expression, then if I want to find out this psi x. So, that will I can do by taking the projection of my wave function on the position on that particular basis function.

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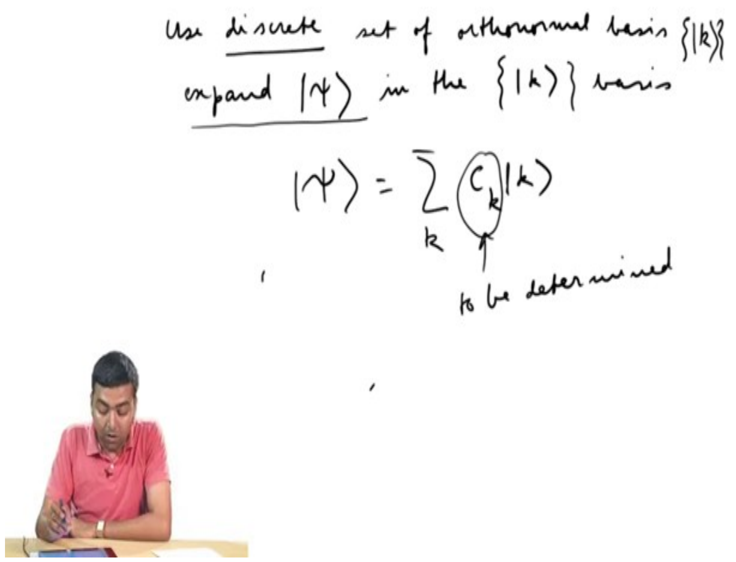

So, what we are we are going to use discrete set of orthonormal basis, which I am the whole family of this basis I am denoted it by k and expand my psi in the k basis. Again remember this expansion is this expansion which we are doing is a linear expansion. So, what I can write is my psi I can write as a sum of a linear combinations of c ks, where my c k s these are to be determined. Also we need to worry about the normalization of the wave function.

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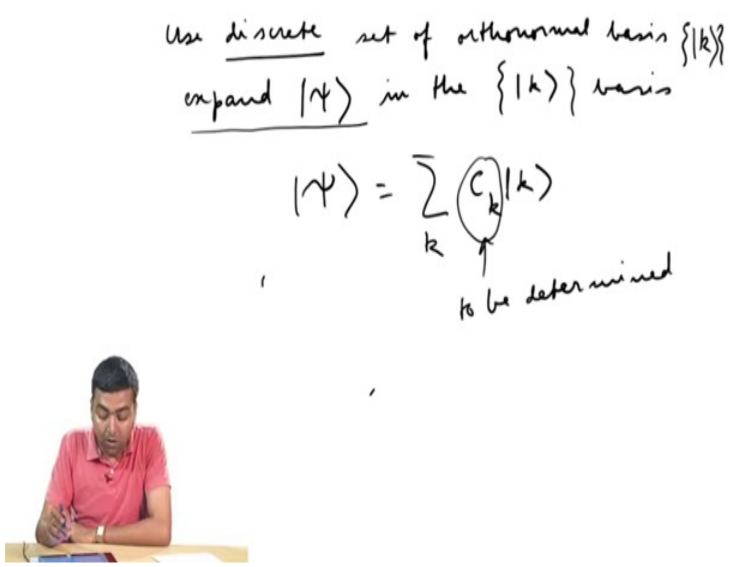

So, need to normalize my psi. So, if we impose the normalization conditions, so what one can show is that the sum over the square modulus of the coefficients should give me 1. Because I have assumed that my basis vectors these this k basis vectors this discrete basis set this is also normalized. Now, let us consider a real space wave function corresponding to the state k.

So, real space wave function corresponding to k, if we denote this as; if we denote this as phi with a suffix k x, then as before we can write k is equal to integration d x d phi k x k and since k are orthonormal. So, if I have another wave function p in the same basis. So, the overlap of p and k will be a delta function ok. Using this so what we can also show as in the previous case. So, now, if you remember my unknowns are my ck, so just for recapitulation.

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$$|\psi\rangle = \sum_k c_k |k\rangle \qquad \because \langle k|p\rangle = \delta_{pk}$$

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$$\langle k|\psi\rangle = \sum_p c_p \langle k|p\rangle = c_k \underbrace{\langle k|k\rangle}_{=1} = c_k$$

$$c_k = \langle k|\psi\rangle$$

So, what we are trying to do is we have this form I am writing as sum over k ck and we want to find what are this ck this is what we are going to find. So, as if you remember our one of the early examples where we were trying to find out the coefficient, so what we did is to find this unknown, we need to project it on my the basis set. So, what I will do is I will take any arbitrary vector which I it call as kp and then project it on that, but so if I do the same thing. So, what I do is I take a vector so I project it in this k basis.

So, what I will get is something like this, so this will be given by p say p. Now, if we look into this summation, so since my k and p this is a delta function as my vectors the basis vectors are orthonormal. So, this will survive only when for k equals to p. So, this will I will get c k and since these are orthonormal, so this will be equal to 1 so what I get is ck. So, my coefficients are nothing, but the projection of k on the wave function. So, this same thing I can write down in terms of wave functions of the scalar product, so which I will show in the next slide.

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$$\langle k|\psi\rangle = \int dx^d\, \phi_k^*(\vec{x})\langle\vec{x}|\int dy^d\, \psi(y)|y\rangle$$

$$= \int dx^d \int dy^d\, \phi_k^*(x)\,\underbrace{\psi(y)\langle x|y\rangle}_{\psi(x)}$$

$$= \int dx^d\, \phi_k^*(x)\,\psi(x)$$

So, what I have is my k psi this I can write as integration dx d. So, what I will do is I will plug in the value of k, I will plug in the value of psi. So, corresponding to this state k the wave function if you remember we had chosen as phi k and since it is the bra of that so I will take a complex conjugate.

So, hence I get phi k x cap x the position basis and then for my psi I can similarly write in dyd psi y in the y position basis. So, if I walk out this algebra, so what I would get is let me just bring out the integrals together d y d, then I will get 5 star k x psi y and I will get x y. Now, if we club in this following terms together, so the once which I am marking with red color.

So, if I take this if I perform this integral here, so what I will get is delta x minus y ok. So, if I do that then what I have is d x d I have phi star k x sorry I am sorry there is a mistake here, so this would not be this one so rather. So, this will give me a delta function the expectation the overlap of x with k will give me a delta of x minus y and if I do this whole integral what I will get is psi of x. So, I am integrating out the y degrees of freedom here. So, what I will we left with this psi x. So, this is what we can write this.

So, this thing if you remember this was my ck, the ck I can write in this form in the in the terms of the wave functions. So, this is nothing but the scalar product of the wave functions corresponding to the k vector and the psi vector. So, now what we will do is so from there we will see how do we now we apply this idea to the case of the Schrodinger equation.

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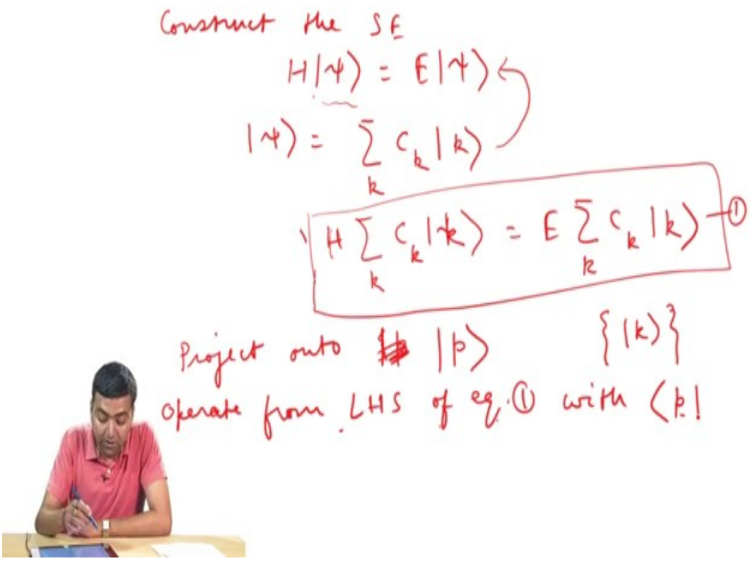

So, we will now construct the Schrodinger equation in the matrix form. So, remember we are looking into the matrix formulation of the Schrodinger equation. So, what we have is we start with h, so this is my Schrodinger equation now using the state the wave functions in the vector form psi a earlier we had it in the functional scalar form.

So, this psi you remember we have expand we are going to expand in a basis set c k. So, if we plug in the value of psi into this equation, so what I will get is H will act on psi which is nothing, but k and some of our k c k psi k and on the right hand side we will be having E sum over k ck k. So, as so now if you note that; so here we are using this k vectors, here as my basis vectors and this c ks are my are the functions, c ks are sorry these are not functions these are rather numbers this can be complex or real number depending on the problem which we are solving and H is also operator, so this whole equation. So, this is the equation of functions.

So, the way to solve these equations, so in principle what I have if I think of them as equations as the conventional equations, where you have numbers which are the as numbers. So, in that case so this whole equation here this represents infinite number of equations ok. Because I can impose a condition that for all value of r what I can do is I can say that this equation should be satisfied for all values of position for example.

So, the way to solve this is what you do is you project your equation onto an arbitrary sorry projected onto an arbitrary state p. So, this p remember belongs to one of the states which are contained in this family of states k. So, if we do the projection, so doing that what it means is if I call this as 1. So, we need to operate from left hand side of equation 1 with p ok.

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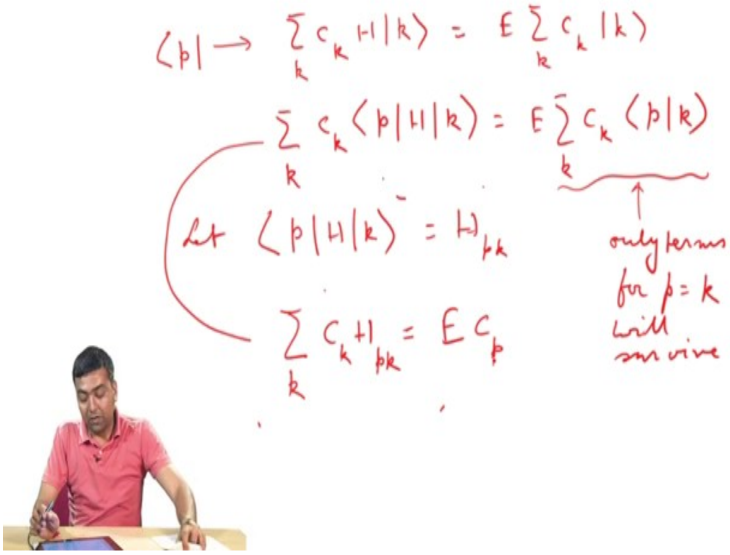

If we do that so let me just write down the equation once again we have ck H will act on k, this gives me E sum over k ck k. Now, if I on this equation I act as p. So, what I will get is sum over k ck then I have p H k plus equals to so E is a number you would not act on it c k is also a number; so we all get p k.

Now, let suppose let us call this thing as H of p k and on the right hand side of this equation that is this summation this summation only terms for p equals to k will survive, because my all the functions in the basis are orthonormal this is I have working this fault for an orthonormal basis. So, what we will get if we assume this, so this we can write in a slightly compact form which is given by ck H p k equals to E c p ok. So, look what does this mean?

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$$\{|k\rangle\} \rightarrow |1\rangle, |2\rangle, |3\rangle \cdots\cdots, |N\rangle$$

$$p=|1\rangle \quad \langle 1|H|1\rangle c_1 + \langle 1|H|2\rangle c_2 + \cdots\cdots + \langle 1|H|N\rangle c_N = E c_1$$

$$p=|2\rangle \quad \langle 2|H|1\rangle c_1 + \langle 2|H|2\rangle c_2 + \cdots\cdots + \langle 2|H|N\rangle c_N = E c_2$$

$$\vdots$$

$$p=|N\rangle \quad \langle N|H|1\rangle c_1 + \langle N|H|2\rangle c_2 + \cdots\cdots + \langle N|H|N\rangle c_N = E c_N$$

Set of N coupled differential equ.

Suppose if I have my k basis, so remember this was my k basis, suppose I represent this k basis in this form. So, I have these are my basis functions now and so on and so forth till N. So, if I go back so my recipe if you remember was I take any arbitrary basis vector which belongs to this family of basis vectors denoted by k and I project this whole equation on that.

So, suppose first I do with the same the projection taking this basis vector 1. So, if I project it using 1, so suppose my p is now equal to 1. So, what I will get is the set of numbers which are of this form 1 H 1 c 1 plus 1 H 2 H and the expectation value of H between 1 and 2 c 2 and plus and this will go on till we get as 1 H N. This is nothing but equals to 1 H N c N equals to E c 1. Similarly for p equals to 2 we can write, so this will be 2 H 1c 1 plus 2 H 2 c 2 plus so on and so forth plus 2 H N c N equals to E c 2.

Similarly we can repeat this and what we can do is for the in its basis function what we will have is this one. So, what we have here now is a infant set off. So, these are a set of; so these are set of coupled differential equations. Since the size of my basis set is N, so I have set of N coupled differential equations ok.

So, and each of these equations you see these are linear in cs in the cs which are our unknowns. So I have N plus 1 unknown, so that is n values of cs starting from c 1 c 2 to cn and then my energy Eigen values. So, the way to solve it is so you can write this whole thing in the matrix form.

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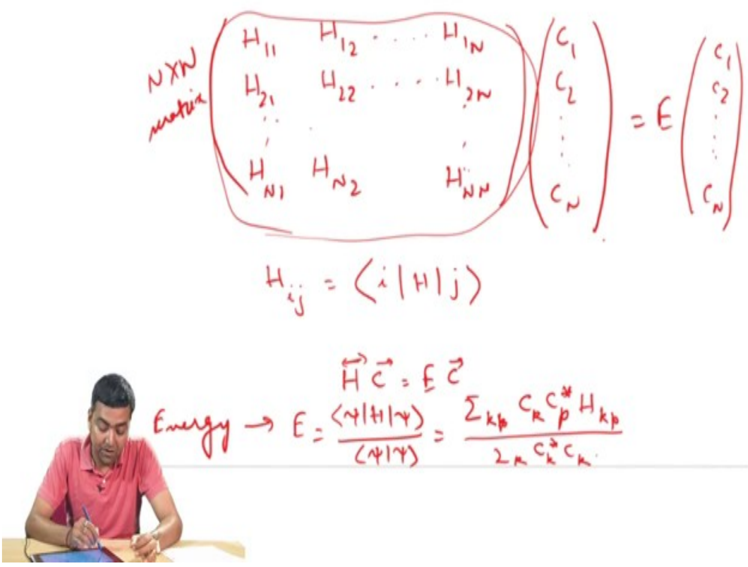

So, basically we will have you can write it as a, so this will be my N cross N matrix and this is some something like this I can write and this will go as H ok. So, where my H ij are of a this from i H j ok. So, what I have is a matrix equation which I need to solve. So, this matrix H acting on this vector c will give me E this c. So, basically what I have done is now in order to find out this vector c and this energy Eigen value; Eigen values E, what I need to do is I need to diagonalize this matrix this matrix.

So, if I am able to diagonalize this matrix then I will be able to solve the unknown problems. So, in this formalism your energy of the total system can now be given by is given in this form. So, if you remember my E is equal to psi H psi and then the expectation value of psi star.

Now, my so the psi s I am now doing I am expanding in this using a basis and I am doing a linear expansion of the psi s. So, if I plug it in there so what I will get is this my energy Eigen value this will be given by sum over k p ck c p star H k p divided by sum over k c k stars c k. So, this is what my energy Eigen values will be in this formalism.

So, far we have been saying that we need to so we choose our basis function a set of basis functions to expand our wave function. But till now we have not talked about what a good choice of the basis functions.

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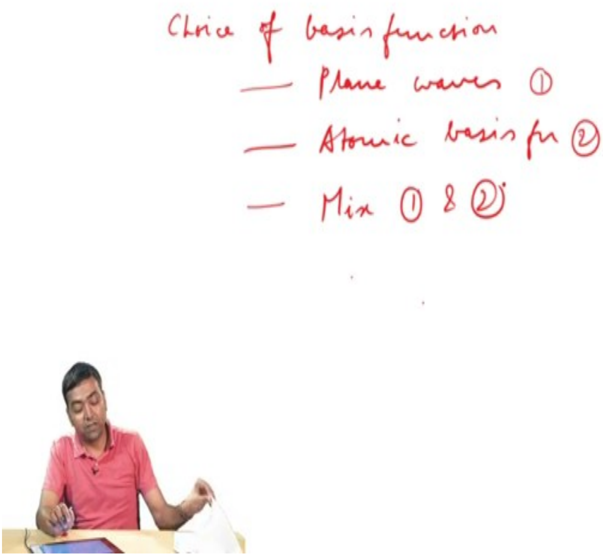

So, I mean the choice of basic functions can be in principle you can choose any type of functions. So, you can choose say for example plane waves as your basis functions, you can choose atomic wave functions as your basis function. You can mix as if I call this as 1 and you call this as 2, we can mix 1 and 2 and as a charge the basis function but in this. So, the example which we will do and in this lecture what I will restrict myself is to use momentum basis in a finite box.