Ultrafast Optics and Spectroscopy
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Lecture - 36
Ab Initio Molecular Dynamic 3

Welcome back to module 15. We are continuing Ab Initio Molecular Dynamics discussion on ab initio molecular dynamics which is relevant to ultrafast processes. We have primarily interested in the dynamics associated with photo physics and photo chemistry. What we have discussed so far is mix quantum classical approach in mixed quantum classical approach we propagate nuclei with the help of classical propagator which is nothing, but Newton's second law, but we take the potential which provides the force acting on the nucleus. We get the potential from electronic structure theory calculations.

And in the problem of photo physics and photo chemistry, we have seen that we have to express electronic wave function in terms of CASSCF wave function that is one way of thinking of it.

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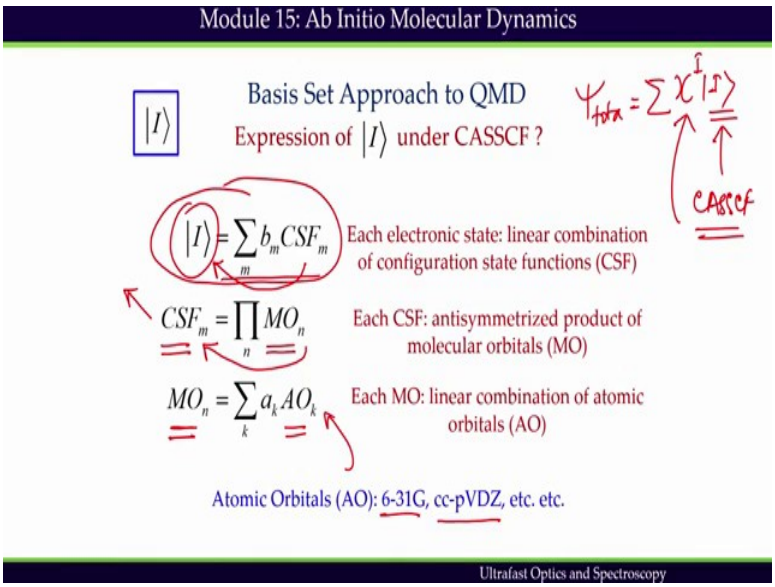

And we have shown here the hierarchy of the CASSCF wave function. CASSCF wave function is the electronic wave function the expression of the electronic wave function. But the total wave function we have seen that total wave function is nothing, but the

summation of nuclear product of nuclear wave function and electronic wave function. So, electronic wave function we know how to represent this has to be represented with the help of CASCCF methodology, but how do you express this nuclear wave function? That is an important question right now.

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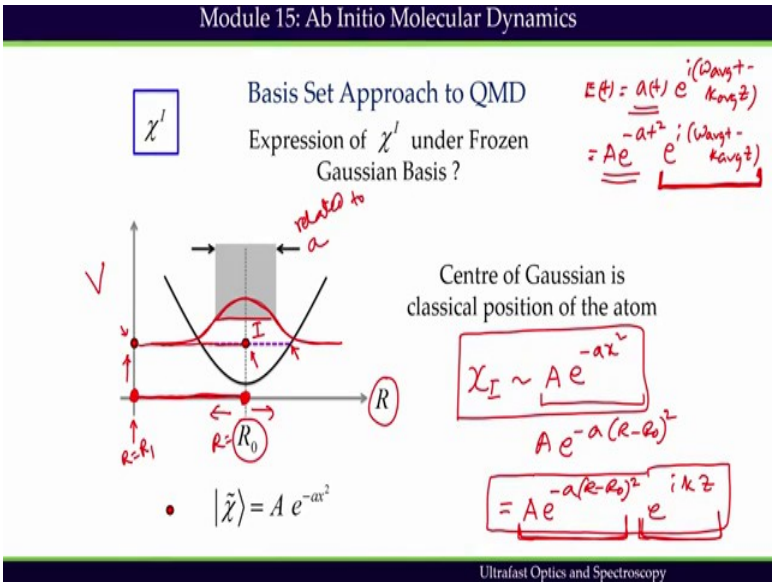

So, our next question is that how do we express time dependent nuclear function in terms of basis set that is called basis set approach to QMD Quantum Molecular Dynamics. What kind of basis set would be suitable to represent nucleus? The kind of basis set which we have used in the expressing electronic wave function is that atomic orbitals which is nothing, but a basis represented by the basis set.

And many basis sets which are available 631-G basis set is one of the commonly used basis set to express electronic wave function, but question is how do you express nuclear wave function in terms of basis set. To understand that we will first look at the harmonic oscillator; atoms are not classical point particle. For any classical point particle both position and momentum can be exactly determined at any point of time. Quite on the contrary atoms are quantum mechanical particles for which position and momentum cannot be precisely known simultaneously.

This is a consequence of the Heisenberg's uncertainty principle. A quantum mechanical particle is described by a wave function under the simple harmonic oscillator approximation vibrational wave function for a simple diatomic molecule has a width.

So, let us say I have a diatomic molecule and the way we express diatomic molecule is that one atom is anchored on this axis on this y axis, it will be anchored it will not move along this way or this way; it will not move along this way.

It will only move along the y axis and another molecular another atom will be moving along this direction either this way or this way. So, this is the diatomic molecule. So, this x axis is representing the inter nuclear distance. Under the simple harmonic oscillator approximation vibrational wave function for a simple diatomic molecule has a width.

So, what does it mean? Even if I am in the zeroth energy level, this is this dotted line is representing the zeroth energy level of the vibration the nucleus is like this and its intern nuclear distance is R naught which is that equilibrium distance, we call it equilibrium distance. But there is an if we say that this atom is anchored on the y axis which is the potential energy surface axis potential energy axis. On this axis if it is anchored here, then sorry it is anchored at this R value R equals certain value that say R 1, then this position will change.

So, at this position it is R equals R naught and it can change, the position of this nuclei will change as its vibrating. So, when it is vibrating, we it is quite clear that even in the zeroth energy level, there is an uncertainty of the position. So, this width of the vibration; this width of the vibrational wave function represents the position uncertainty of the atom. The ground vibrational wave function under simple harmonic oscillator approximation represents a Gaussian wave function.

Centre of the Gaussian represents the classical position of the atom. These are the very well known facts from preliminary quantum mechanics. For the sake of simplicity, we can consider one dimensional problem here. We can assume a Gaussian representing the vibrating atom centre of the Gaussian represents classical position of the atom, but we note that this function does not represent a traveling function.

So, what we can do is that one can say that I have to express this wave function nuclear wave function. So, I will consider the I'th nuclei which is here which is here; I'th nuclear I can express like this way I can say that it is nothing, but a Gaussian function a x square and a is related to its width. This width is related to a this width is related to a related to a.

So, I can use a Gaussian function to represents Gaussian basis to represents the nuclei nuclear position. But the problem is that if we represent it, then we know that the Gaussian function, this is not a propagating function; this is not a propagating function. This is always centred at x equals 0. So, for the given problem one can rewrite this expression as minus a R minus R naught whole square, then it is; then it is centred at R equals R naught. (Please look at the slides for mathematical expresion)

And we have seen this in our previous lectures that we had a Gaussian pulse and if the Gaussian pulse has to be centred at R equals R naught, then we know that this is going to be the expression. But this expression does not indicate that this function will move along a particular direction. In order to get something moving or propagating, we know that we have previously expressed our ultrafast pulse as follows. (Please look at the slides for mathematical expresion)

The expression for ultrafast pulse was E t equals a t multiplied by i omega average t minus k average Z. So, that was the expression and we said that this envelope function can be expressed as some kind of Gaussian function minus a t square in the time domain we are representing that is minus a t square e to the power i omega average t minus k average z. (Please look at the slides for mathematical expresion)

So, this was the expression we used. So, what we what is what was quite clear that this envelope function is propagating because of this additional term. So, this term is representing a propagating wave or propagating component. So, one so in the space domain if we want to express it as a propagating traveling wave, then what we need to do is that e to the power minus a R minus R naught whole square. This is a Gaussian function, then it has to be multiplied by e to the power i k Z. (Please look at the slides for mathematical expresion)

If we multiply by e to the power i k Z, then this is an expression which is showing that it is a traveling Gaussian nuclei should move centre of the; centre of the Gaussian is going to be the classical position of the nucleus. And it can move it can move because this is representing the Gaussian function and this is indicating that this part is indicating that it will be propagating along the Z direction with the k vector. Now, question is for a nucleus, it is a nucleus it is not up it is a point part; it is a particle. (Please look at the slides for mathematical expresion)

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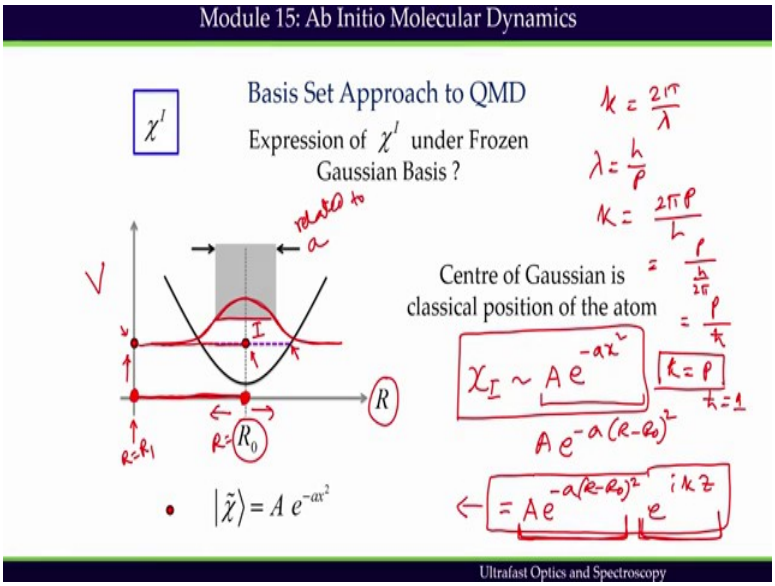

And we know that for any k this k can be expressed as 2 pi by lambda. For any k and we know that we are dealing with nucleus and that is why we have to deal with the particle wave or De Broglie matter wave which can be expressed as lambda equals h by P where P is the momentum. Thus wave vector in momentum space can be given as k equals 2 pi P by h or in other words P by h by 2 pi which is given me reduced Planck constant and in atomic unit then k becomes P because h cut is 1; it is taken to be 1 in atomic unit. (Please look at the slides for mathematical expresion)

So, k is nothing, but P. So, I can rewrite this expression as follows, I can then express the express the travelling Gaussian function as follows it is going to be e to the power minus a R minus R naught square representing the Gaussian.

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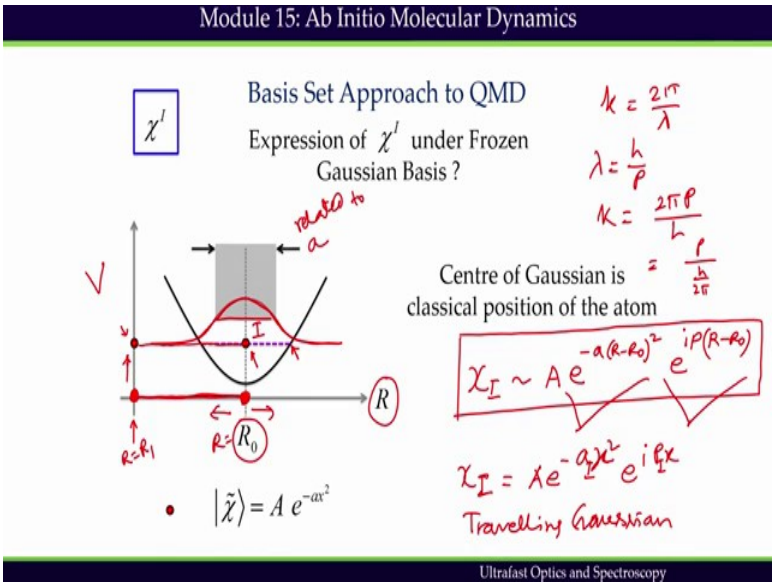

And the traveling part is going to be this wave component is going to be i then P and x P and Z will consider as R minus R naught. This z is nothing, but the distance and that can be represented by this. So, final expression for a traveling Gaussian for a particular nuclei is going to be this. This the first part the first component the this is representing the Gaussian part and this is representing the propagating wave part matter wave part.

Now, if we have this kind of expression or one can express in for simplicity, one can keep this form as well e to the power minus a x square multiplied by e to the power i Px. If it is Z, you can express in terms of Z as well that is not the problem, we are just expressing in terms of x. So, this is the expression for a traveling Gaussian and each nuclei i'th nuclei can be expressed in terms of traveling or Gaussian. So, this a should have an subscript I and P should have a subscript I as well because it is associated with ith nuclei.

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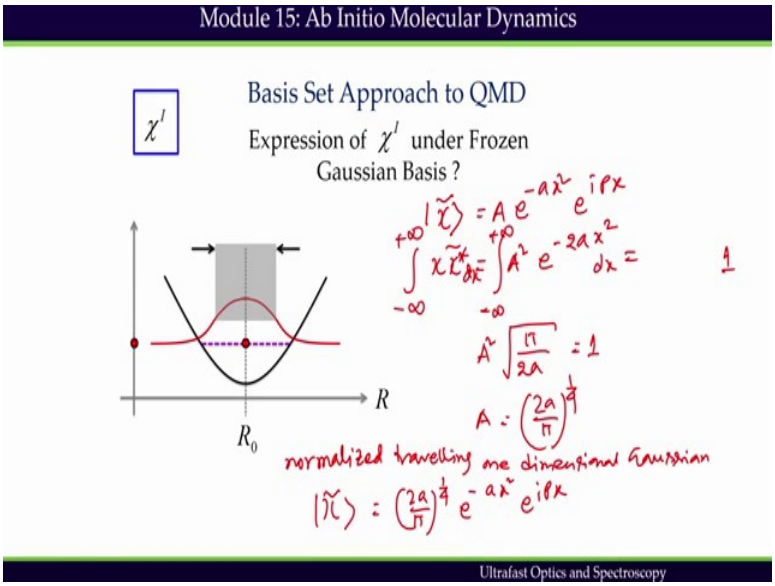

So, we can definitely normalize this kind of function. So, we are taking the nuclear wave function as in this form e to the power minus a x square e to the power i P x. So, we can take the magnitude which is nothing, but. So, this and we which we get it a square e to the power minus 2 a x square and this is the this is magnitude square and what we get is that now we will do the normalization. (Please look at the slides for mathematical expresion)

And for normalization will take minus infinity to plus infinity integration over d x which we get to be 1 minus infinity to plus infinity dx and we get the integration to be 1. If it is a normalized function and this gives me A square and this integration we get from a standard integral Gaussian integral we get 2 pi by 2 a which is 1 or A equals 2 a by pi square root of 2 a by pi. (Please look at the slides for mathematical expresion)

And sorry this is not going to be square root A is going to be 2 a by pi to the power 1 by 4 and so, the normalized one dimensional. So, one can write down normalized traveling one dimensional Gaussian. We can write like this is nothing, but 2 a by pi to the power 1 by 4 e to the power minus a x square e to the power iPx. So, that is the expression for the nuclear one nucleus normalized traveling which the nucleus has been expressed in terms of normalized traveling one dimensional Gaussian. (Please look at the slides for mathematical expresion)

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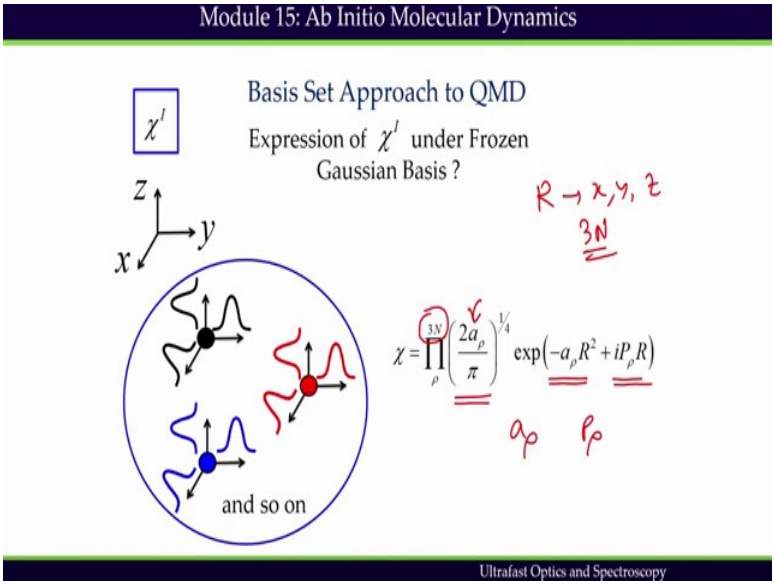

Now, if we have n number of system like same and then I have 3N number of total degrees of freedom total degrees of freedom I will have and because each atom can move along x y and z direction. If the system with n atoms needs to be represented by traveling Gaussians, one can take product of one dimensional Gaussians. Each dimension is represented by R and rho represents the 3N Cartesian coordinates. So, what we need to do is that we have to use a localized Gaussian that is why we are taking a product.

So, we the product has to be this is a product of 3N number of one dimensional Gaussian, each Gaussian is represented by its a which is and so, this is a normalization constant and its exponential part having this a R square. This part is the Gaussian part and this part is the propagating wave part which is the similar expression we have seen.

Here we have changed the variable from x to R; R representing either x y or z component. So, how many such R? We have 3N number of such R we have and R is representing the general variable along this particular direction. We note that different width that is the a rho and different momentum has been assigned to each one dimensional traveling Gaussian.

So, if I have 3N number of degrees of freedom, then we should have 3N number of this one dimensional Gaussian propagating Gaussian and we should take the product of each Gaussian to represent the nuclear wave function.

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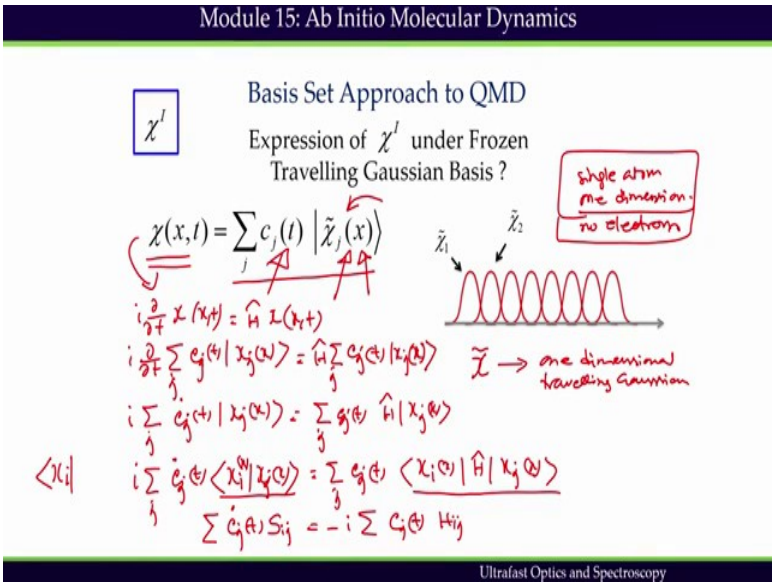

To develop a basic understanding instead of n atoms, one can stick to one atom for the time being and one can also assume the one dimensional problem, we have no electrons and we can also assume that we have no electrons as well. We are just trying to play with the nuclear wave function. Nuclear wave function will depend on space and time x and t which can be expressed as a linear combination of many trajectories and it is something like that.

So, many trajectory what does it mean it means that you can have a trajectory like each trajectory is represented by one dimensional traveling Gaussian. So, I will consider this chi is nothing, but one dimensional; one dimensional traveling Gaussian. We do not have any product of different Gaussian because we have only single atom and one dimension. Under this approximation, one can express the total nuclear wave function in the basis of traveling Gaussian and one can say that this individual traveling Gaussian is not time dependent, but its expansion coefficient is time dependent.

So, if we have this situation, then what we are going to do? Here also we are not considering any electron we do not have any electrons. So, we do not have electronic wave function. It just an assumption under this assumption. We will try to understand what is going on if we plug that in the into the time dependence Schrodinger equation. Time dependent Schrodinger equation reads like this which is the total wave function.

Now, here total wave function, we will consider that chi that is x t equals H chi that is x t; this is my total wave functions. So, I will insert that one, I will have considered that no electrons are there. So, that is why no electronic wave function I have been included I have just included the nuclear wave function. So, if I have this situation, then I can plug that in here and what I can write is that I partial derivative with respect to t summation of c j that is the index as a function of t, then that is the j that is expression like this and equals this is H summation of c j t. This is j then chi j x.

We have assumed that this traveling Gaussian function or trajectory is not time dependent. In our next derivation, we will consider it to be time dependent, but in this derivation we are not considering it to be time dependents. So, if we have that then we can do this time derivative and we can write down this expression as j. This is going to be then c j dot; dot is expressing the time derivative with respect to time, then j x equals this is going to be nothing, but c j t then H then j x.

Now in quantum mechanics often we use we make use of ortho normalization condition. However, it is not necessary here that this Gaussian functions are orthonormal, but we can still multiply by this chi i from the left hand side. So, I can get rewrite this expression as c j that is the dot time derivative, then integration is going to be i j x both are function of x equals summation of j c j t then chi i x H chi j x.

So, we can write this and this expression can be simply written as summation of C j the first derivative then this integral will write down S ij equals minus i summation of C j t and this integral, we will call it H ij.

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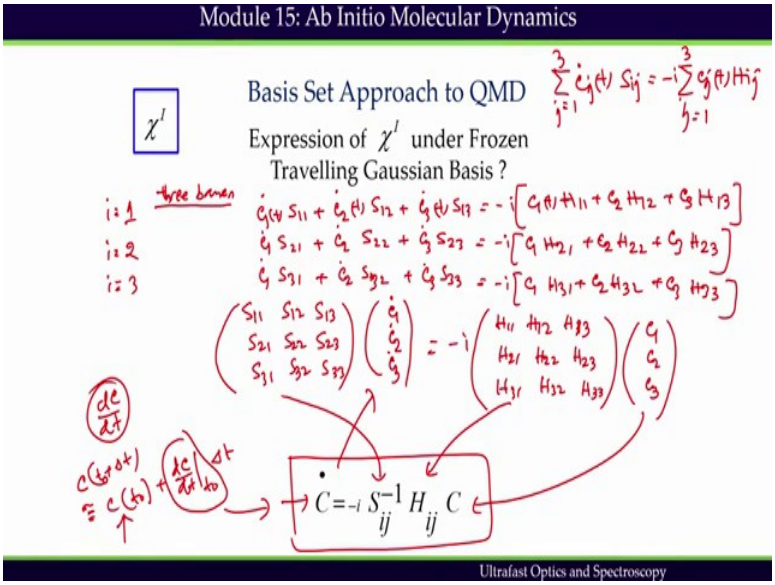

Considering now three basis, one can then I will write down this expression one more time we have written C j t its first derivative then S ij equals minus i summation of C j t H ij that is the expression we have. Now, if I consider 3 basis, then one can write down C 1 t which means j would be 1 to 3. So, j is going to be 12 3; in that case, one can write down C 1 t S 11 plus C 2 t S 12 plus C 3 t S 13 equals minus i C 1 t H 11 plus C 2 H 12 plus C 3. I am not writing as a function of time of this coefficients just to quickly express it 13. (Please look at the slides for mathematical expresion)

So, this is one equation we get and then one can write down one can write down this is i equals 1, then i equals 2 and i equals 3 I have to write. And for i equals 2, I can write down C 1 S 2 1 plus C 2 S 22 plus C 3 S 23 equals minus i C 1 H 2 1 plus C 2 H 22 plus C 3 H 2 3. And again i equals 3, I can write down C 1 S 31 plus C 2 S 32 plus C 3 S 3 3 equals minus i C 1 H 31 plus C 2 H 32 plus C 3 H 3 3. So, this is can be these three equations can be expressed in the matrix form. (Please look at the slides for mathematical expresion)

And how do I express in the matrix form? I can express it matrix form S 11 S 12 S 13 S 2 1 S 22 S 23 S 31 S 32 S 33 is multiplied by C 1 dot C 2 dot and C 3 dot equals minus i of H 11 H 12 H 1 3, then H 2 1 H 22 H 23 then H 31 H 32 H 33, then C 1 C 2 C 3 which can be rewritten as in the matrix forms can be rewritten as this. So, this is suggesting this part this matrix is we have taken here and this matrix is here and this coefficient is here. So, we can rewrite we can rewrite this one as in this matrix form. (Please look at the slides for mathematical expresion)

So, finally, what we are getting is that a value for dC dt and why we need this value for dC dt? Because we if we want to propagate it for a particular state, what is the population that will be controlled by dC dt. So, if we find out if we want to know t plus delta t after time t plus delta t what is the coefficient C, what trajectories exist and what trajectory population we should consider that is going to be C at t naught plus dC dt at t naught del multiplied by delta t. If the delta t is very very small this is that the up to first derivative, we are called expanding Taylor series expansion.

So, this dC dt, one can get it from the time dependence Schrodinger equation because the first initial coefficients is known for a particular expansion, next onwards in time its unknown and that unknown coefficient can be calculated directly from the from this time derivative. So, in this expression in this derivation, what we have considered? We have considered time independent basis; now we can consider time dependent basis.

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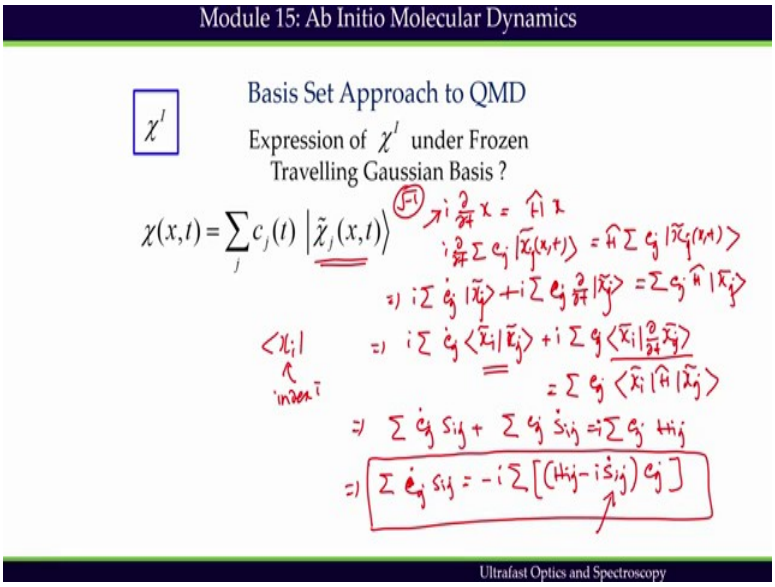

And if we consider time dependent basis, then again we have to plug that in into the time dependent Schrodinger equation which is the partial derivative of chi equals H chi and it is nothing, but i del del t summation of C j then chi which is now a function of x and t that is the way we are taking. (Please look at the slides for mathematical expresion)

And in that case H is going to be summation of C j, then chi it is now function of x it is a function of now x and t. So, we will get additional terms because now when can write down that this is nothing, but summation of C j dot multiplied by this function plus I

have to also consider the other derivative which was not present in the previous expression. This is going to be C j and the first derivative of this one equals now summation of C j, then the H then nuclear base basis set this one which can be rewritten as i summation of now following the previous procedure, we can multiply by this is going to be j actually. (Please look at the slides for mathematical expresion)

So, there is an index j here is index j here is index j here, index j here. So, this we previous we have seen we have multiplied by chi i like this way. So, we can do the same thing. Now we can multiply with this chi i and then this is chi j plus i C j then chi i was derivative of chi j equals summation of C j and this is chi i H chi j. (Please look at the slides for mathematical expresion)

So, this is the expression we finally, get. So, we know that this is we are going to write down. So, this whole expression can be reduced in the well known form that is the C j dot then this is S ij plus i here we remind that this i is not the index i here. This is an index i and this is nothing, but the complex number square root of minus 1. (Please look at the slides for mathematical expresion)

So, i this can be written as C j, then this is we are saying S ij dot. S ij dot this expression is S ij dot which is nothing, but minus i sorry not minus i we still have this summation C j, then this is called H ij. Now I can take this I from here and place it on the right hand side by minus i and then one can write down this expression as C j dot S ij equals minus i summation of H ij minus i S ij dot then C j; this is the way one can express. (Please look at the slides for mathematical expresion)

So, final expression for the time dependent coefficient we get like this. In the previous expression, we did not have this term, but now we have additional this term.

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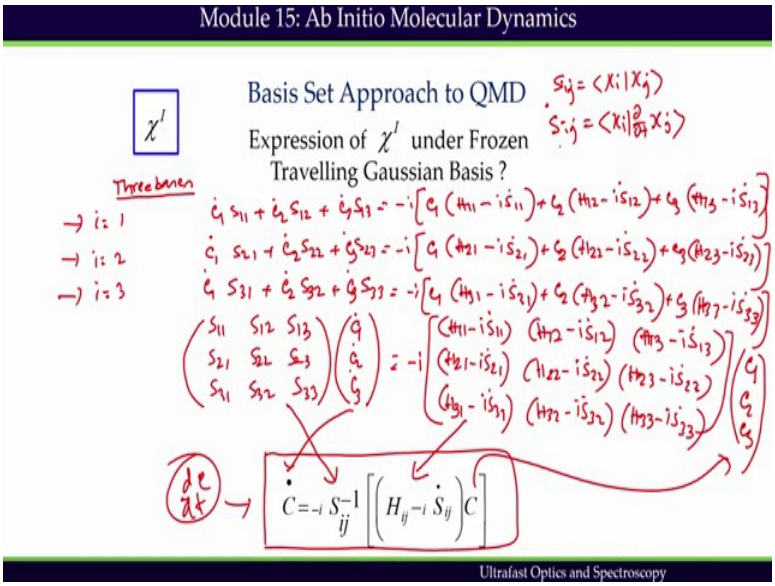

And if we take now again 3 basis, then one can write down like following way. We can rewrite that expression again here for us to remember that is the C j dot t S ij equals minus i summation of H ij minus i S ij dot, then C j that was the expression. So, taking again 3 basis again 3 basis, one can consider i equals 1 i equals 2 and i equals 3. If i consider that then what I get is that i get C 1 dot S 11 plus C 2 dot S 12 plus C 3 dot S 13 equals minus i C 1 H 11 minus i S 11 plus C 2 multiplied by H 12 minus i S 12. (Please look at the slides for mathematical expresion)

These are dots plus C 3 into H 1 3 minus i S 13 dot. This is the expression we get for the first one, i equals 1 then i equals 2 the procedure is exactly the same. Procedure we are following the same procedure which we have followed previously this is going to be S 2 1 plus C 2 dot S 22 plus C 3 dot S 23 equals minus i into C 1 H 2 1 minus i S 2 1 dot plus C 2 H 22 minus i S 22 dot plus C 3 H 23 minus i S 23 dot. (Please look at the slides for mathematical expresion)

Similarly, for i equals 3, I get C 1 dot S 31 plus C 2 dot S 32 plus C 3 dot S 33 equals minus i into C 1 H 31 minus i S 31 plus C 2 into H 32 minus i S 32 dot plus C 3 into H 3 3 minus i S 33 dot. So, these are the expressions we get. Finally, in the matrix form if we want to express 1 can do it S 11 S 12 S 13 S 2 1 S 22 S 23 S 31 S 32 S 33 C 1 dot C 2 dot C 3 dot equals minus i H 11 minus i S 11 H 12 minus i S. These are dots 12 dot H 13 minus i S 13 dot. (Please look at the slides for mathematical expresion)

This is an expression, then multiplied by C 1 C 2 C 3 and the second term here H 21 minus i S 21 H 22 minus i S 22 H 23 minus i S 23 H 31 minus i S 31 H 32 minus i S 32 H 33 minus i S 33. So, these are the expressions we get. Finally, the matrix form can be represented by this equation where the first derivative of this coefficient can be expressed as follows here. This is the inverse matrix, this is the Hamiltonian this is the matrix represented by this and this is represented by this. (Please look at the slides for mathematical expresion)

So, we get and this is here. So, we can express like this way. Two different kind of equations we get and what we see here we should remind ourselves that this S ij; this S ij is like an overlap matrix; this S i j is like an overlap matrix is nothing, but chi i then chi j. But S ij dot is not ddt of chi the time derivative of the overlap matrix, it is not like this rather it is as we have defined before it is chi I, then the first derivative of chi sorry this is chi j. This is the expression and then H this is the this is something which we should remember that is was S dot here is not the time derivative of the overlap matrix. (Please look at the slides for mathematical expresion)

We will stop here and we will continue the discussion of the quantum molecular dynamics which is important in ultra to understand ultrafast processes and we will continue the discussion on the Gaussian basis to express the nuclear wave function. We will meet again for the next lecture.