Ultrafast Optics and Spectroscopy
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Lecture - 37
Ab Initio Molecular Dynamics 4

Welcome back to module 15 of the course Ultrafast Optics and Spectroscopy. We are continuing discussion on ab initio molecular dynamics which could be used to study ultrafast processes in molecular system, particularly following electronic excitation. In the molecular dynamics we can use three different approaches one classical approach which we have been discussed, another one is pure quantum mechanical approach which we have not discussed in this module.

The discussion is in this module is based on only mixed quantum classical approach. Where we move nuclei with the help of classical equation of motion and we get the potential from electronic structure theory calculations. So, molecular dynamics is mixed with the electron structure theory calculations. So, in this approach we have seen that the nuclei are represented by travelling Gaussian function.

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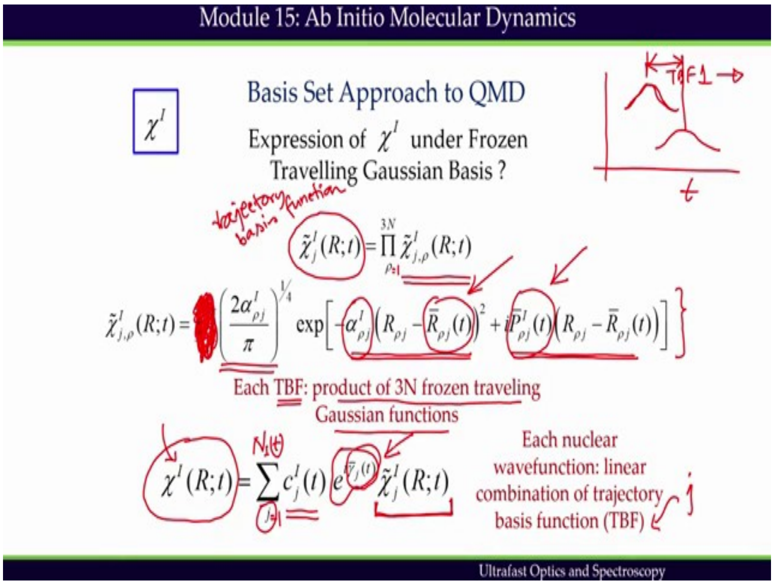

Module 15: Ab Initio Molecular Dynamics

$\boxed{\chi^I}$

Basis Set Approach to QMD

Expression of χ^I under Frozen Travelling Gaussian Basis ?

trajectory basis function

$$\tilde{\chi}_j^I(R;t) = \prod_{\rho=1}^{3N} \tilde{\chi}_{j,\rho}^I(R;t)$$

$$\tilde{\chi}_{j,\rho}^I(R;t) = \left(\frac{2\alpha_{\rho j}^I}{\pi}\right)^{1/4} \exp\left[-\alpha_{\rho j}^I\left(R_{\rho j} - \bar{R}_{\rho j}(t)\right)^2 + i\bar{P}_{\rho j}^I(t)\left(R_{\rho j} - \bar{R}_{\rho j}(t)\right)\right]$$

Each TBF: product of 3N frozen traveling Gaussian functions

$$\chi^I(R;t) = \sum_{j=1}^{N_I(t)} c_j^I(t)\, e^{i\bar{\gamma}_j(t)}\, \tilde{\chi}_j^I(R;t)$$

Each nuclear wavefunction: linear combination of trajectory basis function (TBF)

j

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And so far whatever we have shown that these earlier derivations are explicitly shown for students who are relatively new to quantum mechanics, this is why we have dealt with one dimensional problems so far.

Now, we will go back to three dimensional problem where I have n number of atoms. Now, when we have let us say one dimensional Gaussian one can think of the classical position of the atom represented by this point in space, this is let us say R space and it has a certain width. So, this is the representation of the travelling Gaussian which is travelling in R space. Now, this is one dimensional Gaussian the moment we make it three dimensional it becomes this let us say another R 1 and R 2 there are. If we take it two dimensional then I have one Gaussian like this another Gaussian should be like this so it makes a contour like this.

So, it is a it is more like localized in two dimensional space. Similarly three dimensional space is another Gaussian which will be along the z axis R3 axis. So and in order to get a localized function because we have to localize the Gaussian we cannot spread it over the space, in order to get the localized Gaussian function we take the product of individual Gaussian functions. So, this is called trajectory basis function, we prepared this trajectory basis function this is called trajectory basis function. We prepared this trajectory basis function by multiplying all the Gaussian functions.

Now, how many Gaussian functions I should have? I have three degrees of freedom Gaussian can move along x along y it can move along y and it can move along z direction. So, three different directions it can move and I have three I have N number of atoms. So, total I have 3 N number of Gaussian one dimensional Gaussian functions.

So, I am this product is going to be rho equals 1 2 3 N. So, 3 N number of Gaussian functions are multiplying and getting the trajectory basis function. Each Gaussian function we have represented, each Gaussian function is nothing but is represented by this we do not have this multiplication sign here this is just a Gaussian function.

So, each Gaussian function is represented by it is normalized Gaussian function, this represent this is the normalization factor which we have seen already and the it has both R components this is this is the Gaussian representation and this is the propagation. It represents that it is propagates along the direction R and R here representing the coordinate. It could be R 1 it could be R 2 it could be R 3 R 4 like this way is 3 N number of coordinates it is representing.

So, rho is the variable for that coordinate and this form of Gaussian is now known this is the particle form of the wave and that is the way we get that. In earlier lectures we have seen how to get this kind of form. So, what we have here is that I have trajectory basis function, I am forming trajectory basis function by the product of 3N frozen travelling Gaussian functions. And then I have to finally represent the nuclear wave function and nuclear wave function for a particular electronic state Ith state.

So, that nuclear wave function can be represented as summation of many such trajectory basis function, one can think about taking only one basis function one trajectory basis function and nothing wrong in it. But depending on what information we want to gather or what kind of dynamics we would like to explore, we might need to use many trajectory basis functions. So, when we take many trajectory basis functions clearly each trajectory basis function is representing one way of moving the overall system.

And so let us say again I will reduce this problem to one dimension. Let us say this is one trajectory basis function. Again trajectory basis function is a three dimensional wave function, but I will just for simplicity I will take one dimensional wave function. So, let us say I have one trajectory basis function this is trajectory basis function number one and another tragic. So, this is one way of reaction one outcome one each trajectory basis function has it is own outcome.

So, let us say one trajectory basis function is propagating along this way this is the time axis. Another trajectory basis function is propagating like this way there will be a phase difference between these two trajectory basis function and whenever we have a propagating event. When we have a propagating event or time dependent event then the relative position of each trajectory basis function with respect to the other has to be expressed and that relative position in time is expressed by the phase factor.

So, definitely we have to use a phase factor always time dependent phase factor which is showing how individual trajectory basis functions are relatively related and then because it is a summation of individual tragedy basis functions. I have to take the expansion coefficient as well for individual trajectory basis functions. So, j is the tri trajectory functions and depending on how many trajectory basis functions, I would like to take this number may change this j number may change. So, j is representing the trajectory basis functions.

By this way we represent the total wave function and the nuclear wave function on each electronic state is presented as a summation of multidimensional travelling frozen

Gaussian basis functions with time dependent coefficients. Here index j levels multidimensional travelling frozen Gaussian basis functions on electronic state I N I t which we show it here it should be actually N then I then t.

So, j is varying from one to N I t; N I t is a variable of time is a function of time. Because how many trajectory basis functions I need that can be then controlled as a function of time. Whenever the right time will come in the dynamic simulation one can introduce many trajectory basis function and that is the basis of the ab initio multiple spawning method. Where we can spawn or generate a new trajectory basis function as it is needed when the non adiabatic coupling would be very high.

We will show you what does it mean very soon. So, N t a sorry N I t shows the number of nuclear basis functions on electronic state I at time t, N I t is allowed to change during propagation this gives birth to spawning which will be discussed soon. The multidimensional travelling frozen Gaussian basis function is called trajectory basis function; each trajectory basis function is expressed as a product of one dimensional Gaussian basis function. And we have seen what does it mean by this one dimensional Gaussian basis function, rho represents the 3 N number of Cartesian coordinates of the molecule.

And alpha this alpha I rho j, this represents the time dependent width of the of the respective Gaussian function then R bar j t this one is representing the time dependent position, then p this one representing time dependent momentum and gamma this one is representing time dependent phase. And phase it means whenever we get the phase it means that I have multiple trajectory basis functions and question is how different trajectory basis functions are internally related, their relative propagation information is hidden in this phase factor.

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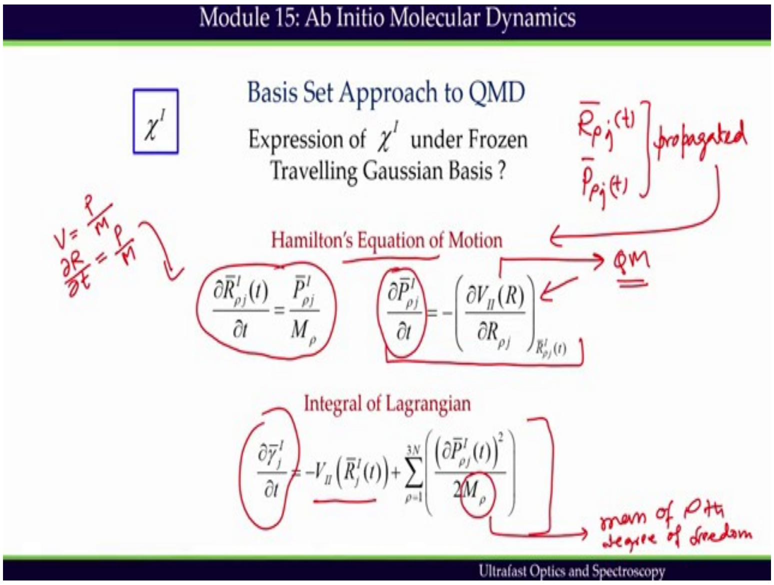

Module 15: Ab Initio Molecular Dynamics

$\boxed{\chi^I}$

Basis Set Approach to QMD

Expression of χ^I under Frozen Travelling Gaussian Basis ?

$\left.\begin{matrix}\bar{R}_{\rho j}(t)\\ \bar{P}_{\rho j}(t)\end{matrix}\right]$ propagated

$V = \frac{P}{M}$

$\frac{\partial R}{\partial t} = \frac{P}{M}$

Hamilton's Equation of Motion

$$\frac{\partial \bar{R}^I_{\rho j}(t)}{\partial t} = \frac{\bar{P}^I_{\rho j}}{M_\rho} \qquad \frac{\partial \bar{P}^I_{\rho j}}{\partial t} = -\left(\frac{\partial V_{II}(R)}{\partial R_{\rho j}}\right)_{\bar{R}^I_{\rho j}(t)}$$

QM

Integral of Lagrangian

$$\frac{\partial \bar{\gamma}^I_j}{\partial t} = -V_{II}\left(\bar{R}^I_j(t)\right) + \sum_{\rho=1}^{3N}\left(\frac{\left(\partial \bar{P}^I_{\rho j}(t)\right)^2}{2M_\rho}\right)$$

mass of ρth degree of freedom

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Now, in the in the previous slide we have seen that these are the ways you can express the nuclear wave function. But in order to express the nuclear wave function I have to depend on position momentum and phase this information I have to give and this information will come from the classical equation of motions.

For an example this R rho j bar t and p rho j t they are propagated following Hamilton's equation of motion. These are classical propagator and for this classical propagator one can write down this equations and this equation is very simple to understand because we know that v velocity is nothing but p momentum by mass and v is nothing but derivative of the distance which is d R dt equals p by M.

So, I get this equation on the other hand we know from the previously we have shown this Hamilton equation derivation for this propagation of the momentum. Propagation of the momentum will depend on this the gradient of the of the potential and the potential is coming from electron structure theory calculation. So, this is your quantum mechanical calculations, from where we get the potential we update the potential and then take the first derivative with respect to the position and then that negative of that derivative gives me the momentum propagator.

And nuclear phase is propagated at according to the integral of the Lagrangian this integral of the Lagrangian will not give the show the derivation. But this is also coming from the equation of motion. The first term of the above equation in this equation in the phase propagator, the first term corresponds to the potential energy of the I th electronic state and this m rho represents the mass of the rho th degrees of freedom; mass of rho th degree of freedom. So, in ms module this ab initio multiple spawning method, we are using classical propagator to propagate the nuclei.

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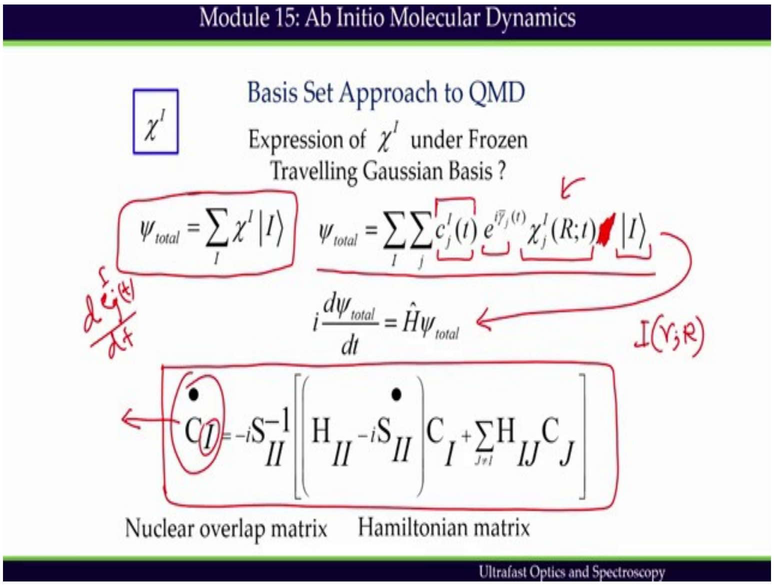

Module 15: Ab Initio Molecular Dynamics

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Basis Set Approach to QMD

Expression of χ^I under Frozen Travelling Gaussian Basis ?

$$\boxed{\psi_{total} = \sum_I \chi^I |I\rangle} \qquad \underline{\psi_{total} = \sum_I \sum_j c_j^I(t)\, e^{i\bar{\gamma}_j(t)}\, \chi_j^I(R;t)\, |I\rangle}$$

$I(r;R)$

$$i\frac{d\psi_{total}}{dt} = \hat{H}\psi_{total}$$

$\dfrac{d c_j^I(t)}{dt}$

$$\boxed{\dot{C}_I = -iS_{II}^{-1}\left[\left(H_{II} - i\dot{S}_{II}\right)C_I + \sum_{J\neq I} H_{IJ}C_J\right]}$$

Nuclear overlap matrix Hamiltonian matrix

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Finally the multi configurational nuclear wave function has the following form we have already pointed out that we have to use bond expansion of the total wave function and that is why the multidimensional form of the total wave function will be like this. Where this is trajectory basis function and this is a trajectory basis function and we do not have this is wrong. So, we have this trajectory basis function corresponding electronic wave function corresponding phase factor and corresponding expansion coefficient.

If we plug that in here in time dependence Schrodinger equation, then using the methodology which we have previously used similar kind of methodology one can use I am not explicit explicitly showing here. But one can use similar kind of meteorology and can get the matrix form of the of this coefficient the CI representing the coefficient matrix CI dot and this also gives us the population it is actually related to the population at the Ith state. So, depending on the value of C dot I will be able to get what is the population at the Ith electronic state.

Here I denote the electronic state and features the Ith electronic wave function. We note that the Ith the I here is actually depends on electronic coordinate and parametrically depend on nuclear coordinate and this chi I is the time dependent nuclear wave function associated with the Ith electronic state. As an unique nuclear wave function is associated with each electronic state qualitatively different nuclear dynamics can be allowed on different electronic state.

Once insert these expressions into time dependence Schrodinger equation a set of coupled equations for the temporal evolution of the coefficients of the trajectory basis functions of each electronic state are often. So, basically this is nothing, but d c j I d dt that is given here. So, this coefficient time dependent coefficient we get in the matrix notation we get this.

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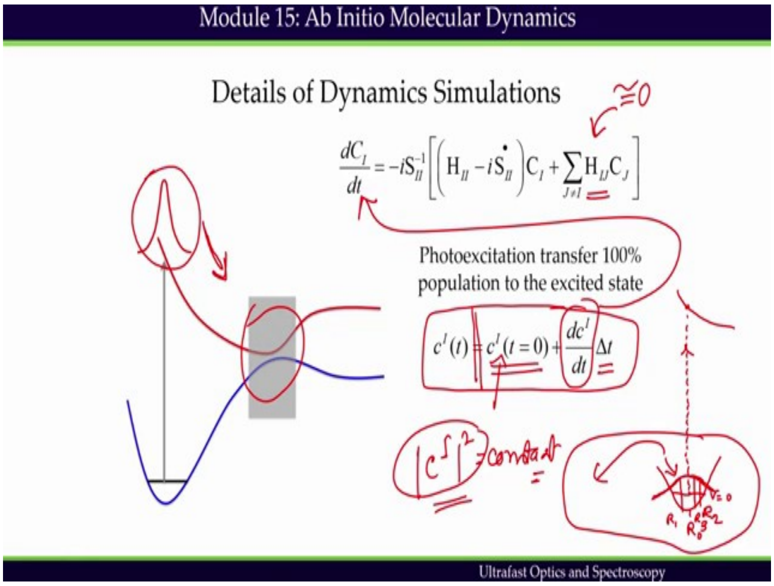

Module 15: Ab Initio Molecular Dynamics

Details of Dynamics Simulations

$$\frac{dC_I}{dt} = -iS_{II}^{-1}\left[\left(H_{II} - i\dot{S}_{II}\right)C_I + \sum_{J \neq I} \underset{=}{H_{IJ}} C_J\right]$$

Photoexcitation transfer 100% population to the excited state

$$c^I(t) = c^I(t=0) + \frac{dc^I}{dt}\Delta t$$

$$|c^S|^2 = \text{constant}$$

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Now, at t equals 0 all initial values of the coefficient and parameters which define the nuclear basis set position momentum and nuclear phase are provided randomly from the appropriate Wigner distribution, which features the combined distribution of the quantum particles coordinate and momentum in terms of the wave function.

So, when you prepare the one trajectory basis function let us say we are preparing one trajectory basis function in the upper electronic excited state. When you are preparing it I need the initial position momentum and phase information that information will come from Wigner distribution. So, what does it mean by this Wigner distribution? Let us assume that I am in the ground the vibrational state v equal state and ground vibrational state does not mean that it is energy is 0, because we know that any molecule cannot be made vibration less. Because zero point energy is a finite energy is not a zero energy. So, molecule will always be vibrating at the even at the zero point energy level.

Now, in the zero point energy level if we look at the wave function of the vibrational wave function it represents a Gaussian function under harmonic oscillator approximation. This Gaussian function actually representing the spread of different configuration. So, basically incident when we think about electronic excitation, we say that this geometry R naught equilibrium configuration or equilibrium geometry is excited to the excited state. But in reality that is not the case because we can have many others such different configurations representing the spread of the vibrational wave function.

So, I can have R 1, I can have R 2, I can have R3 ok. So, many other configurations can contribute to the initial geometry and that is why I have to what is the procedure for running this simulation, is that you take different initial configurations and prepare your initial states and then run those trajectories and then average them. We have to take the average of individual runs.

So this is done, but the taking the initial configuration different sample for the initial state is taken from the Wigner distribution. The Wigner function plays an important role in establishing the quantum to classical interface during photo excitation process a single trajectory basis function can be placed on the excited state surface, one electronic state is populated with position and momentum obtained from Wigner distribution of the ground state. This trajectory basis function can be propagated on the excited state surface following Hamilton’s equations classical propagator.

So, what we see that now I can again use Taylor series expansion and then use this as the as a propagator for the population and we see that for this propagator what I need I need the derivative. Because delta t is known delta t is the time step used in the molecular dynamics ab initio molecular dynamics that is known. Initial condition population is also known that is represented by CI, CI is not directly representing population it is actually C I square modulus is actually population.

So, it is related to population, so we know that what is the coefficient value at t equals 0 and after time delta t what is what would be the value of the coefficient that is that depends on this derivative and this derivative depends on this matrix elements. And these matrix elements are quantum mechanical effects because, it has a coupling term HIJ term and we know that HIJ term exist when we are near the conical intersection or surface crossing regime.

So, if you are away from surface crossing regime this becomes almost 0 this is almost 0 and because this is 0 this propagation is nothing but a single surface propagation. So, this trajectory basis function if I take step one trajectory basis function that will just propagate and population will not change at all, population will remain constant. This population in the upper excited state will remain constant because, nothing can change the population without this coupling vector this coupling matrix.

So, this propagation without HIJ this propagation is similar to propagation on a single surface, in which HIJ does not contribute to the complex expansion coefficient. Thus population on the Ith electronic state remains constant PI equals square modulus of this is the population in the excited state. However, during this propagation at each time step we calculate the effective non adiabatic coupling, effective non aromatic coupling we calculate and that non adiabatic coupling.

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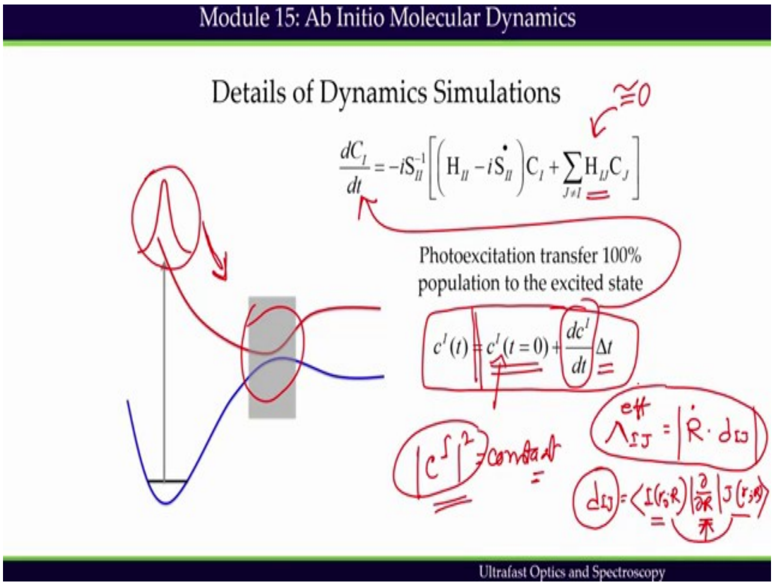

Module 15: Ab Initio Molecular Dynamics

Details of Dynamics Simulations

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$$\frac{dC_I}{dt} = -iS_{II}^{-1}\left[\left(H_{II} - i\dot{S}_{II}\right)C_I + \sum_{J \neq I} H_{IJ}C_J\right]$$

Photoexcitation transfer 100% population to the excited state

$$c^I(t) = c^I(t=0) + \frac{dc^I}{dt}\Delta t$$

$|c^I|^2 = \text{constant}$

$\Lambda_{IJ}^{eff} = |\dot{R} \cdot d_{IJ}|$

$d_{IJ} = \langle I(r;R)|\frac{\partial}{\partial R}|J(r;R)\rangle$

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I will show you what is the effective non adiabatic coupling this is represented by capital lambda I J, this is effective non adiabatic coupling. Which is nothing but modulus of this R dot dot d I J, where d I j is represented by this integral I R capital R J this is the coupling vector. What I will show here is that this integral representing and very interesting coupling J and I they are electronic state. But this is the nuclear coordinate what it what does it mean? It means is this coupling term is coupling two electronic states with the help of nuclear coordinate and that is the non adiabatic interstate coupling constant.

So, we always calculate; so we always calculate this we always calculate. So, we always calculate this effective non adiabatic coupling effective non adiabatic coupling constant and if we see that this effective non adiabatic coupling constant.

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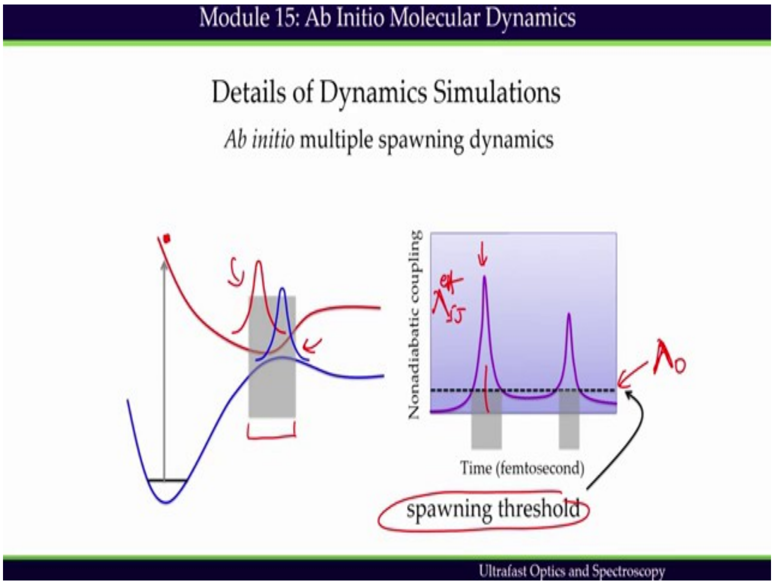

Module 15: Ab Initio Molecular Dynamics

Details of Dynamics Simulations

Ab initio multiple spawning dynamics

spawning threshold

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If the value of the effective non adiabatic coupling constant at a given time is larger than the predetermined threshold. So, let us saying during these calculations I started the propagation from the FC point which is Franck Condon point where the vertical excitation is going on, then it is propagating. During the propagation each time I will be calculating non adiabatic coupling term and if the non adiabatic coupling term here I am plotting each time, how non adiabatic coupling term is changing it is going beyond a threshold value. I will set that threshold value is a predetermined threshold value let us say lambda naught, this is lambda naught threshold value and this is lambda I am plotting.

So, if it is going beyond consider larger than the predetermined threshold value lambda naught, it is considered that excited state trajectory has entered a region of significant non adiabatic coupling. As pointed out earlier ms method adjust the size of the total wave function total number of trajectory basis functions aiming at describing quantum mechanical effects associated with electronic non adiabaticity.

A new trajectory basis function is spawned whenever the existing excited state trajectory passes through a region of significant electronic coupling to the lower electronic state. So, what does it mean? It means that the moment I have entered the Spawning regime; spawning regime is defined by a significant non adiabatic coupling. Wherever it is present it is called spawning regime and whenever there is a possibility whenever we see higher non adiabatic coupling, then what we do we spawn or generate a new trajectory basis functions.

So, now I have two trajectories functions let us say one trajectory basis function replaced on the upper state, another trajectory basis function will be replaced in the lower state. The spawning algorithm works in the following way first lambda naught parameter is defined to indicate entrance and exit coupling threshold values. Second lambda I J effective is computed at each time step, when lambda I J effective exceeds lambda naught this is levelled as t naught. Excited state trajectory basis function is propagated forward in time following Hamilton's equation of motion until lambda I J effective drops below lambda naught.

This time is labelled as tf in predetermine number of basis a predetermined number of bases functions is spawned within the time crossing time tf minus t naught. In the simplest case if only one trajectory basis function is spawned, a child trajectory basis function is created at the point of maximum non adiabatic coupling. So, at this point let us say of time I will spawn one child trajectory basis function in the lower electronic state. Because at this point that the lambda I J effective, this is lambda I J effective this value goes maximum and that is why we do that.

So, one can preserve the momentum and position when they are spawned. So, there are many methodologies one can use for the spawning mechanism. But this is nothing but or similar to stochastic hop or what is x discussed in surface hopping method. So, what we have a discussed so far is kind of a general idea of how spawning is done in ab initio multiple spawning dynamics and we will continue this session in the next lecture.