Ultrafast Optics and Spectroscopy
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Lecture - 35
Ab Initio Molecular Dynamics 2

Welcome to module 15 of the course Ultrafast Optics and Spectroscopy.

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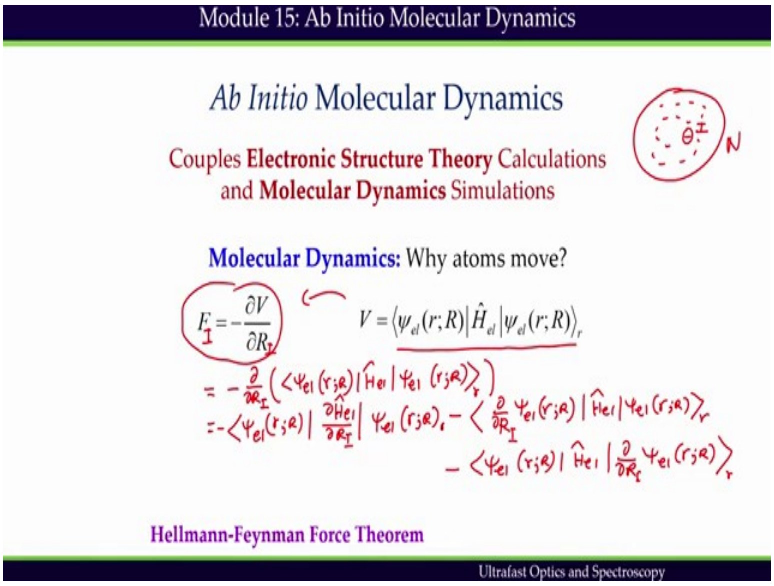

Module 15: Ab Initio Molecular Dynamics

Ab Initio Molecular Dynamics

Couples **Electronic Structure Theory** Calculations and **Molecular Dynamics** Simulations

Molecular Dynamics: Why atoms move?

$$\boxed{F_I = -\frac{\partial V}{\partial R_I}} \qquad V = \underline{\langle \psi_{el}(r;R) | \hat{H}_{el} | \psi_{el}(r;R) \rangle_r}$$

$$= -\frac{\partial}{\partial R_I}\left(\langle \psi_{el}(r;R) | \hat{H}_{el} | \psi_{el}(r;R) \rangle_r \right)$$

$$= -\langle \psi_{el}(r;R) | \frac{\partial \hat{H}_{el}}{\partial R_I} | \psi_{el}(r;R) \rangle_r - \langle \frac{\partial}{\partial R_I} \psi_{el}(r;R) | \hat{H}_{el} | \psi_{el}(r;R) \rangle_r$$

$$- \langle \psi_{el}(r;R) | \hat{H}_{el} | \frac{\partial}{\partial R_I} \psi_{el}(r;R) \rangle_r$$

Hellmann-Feynman Force Theorem

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Here, one question remains open. We said that nuclei will move in a system. Now, question is why nuclei should move in a system? Atoms move due to Hellmann Feynman force acting on them. The force which is nothing but negative of the potential gradient and the potential is nothing but is represented by this expectation value of the Electronic Hamiltonian.

And if we plug that in then what we get? We can get an expression for F and that is nothing but minus partial derivative with respect to R, this psi electronic r R Hamiltonian, electronic Hamiltonian psi electronic r R, integration over the electronic coordinate. So, if we take this first derivative that is the force then we can write as follows. Minus psi electronic r R, this is parametric dependence. <u>(Please look at the slides for mathematical expression)</u>

Then the first derivative of the Hamiltonian, then psi electronic r R this is one derivative, second derivative is going to be, second term is going to be the first derivative of the wave function which is R. So, we will consider this force acting on particular nuclei. So, let us say I have a system with N number of nuclei; N number of nuclei. We are talking about this nuclei denoted as I, that is why we are talking about I coordinate. So, with respect to I coordinate we are going to take a look at, this problem this is going to be I coordinate. (Please look at the slides for mathematical expression)

So, with respect to I-th nuclei we get the first derivative electronic r R electronic Hamiltonian psi electronic r R r minus psi electronic r R electronic Hamiltonian. This is the way we get 3 terms and we can simplify this terms, particularly last two terms you can simplify these two terms you can simplify as follows. We can rewrite these two terms as electronic expectation value. (Please look at the slides for mathematical expression)

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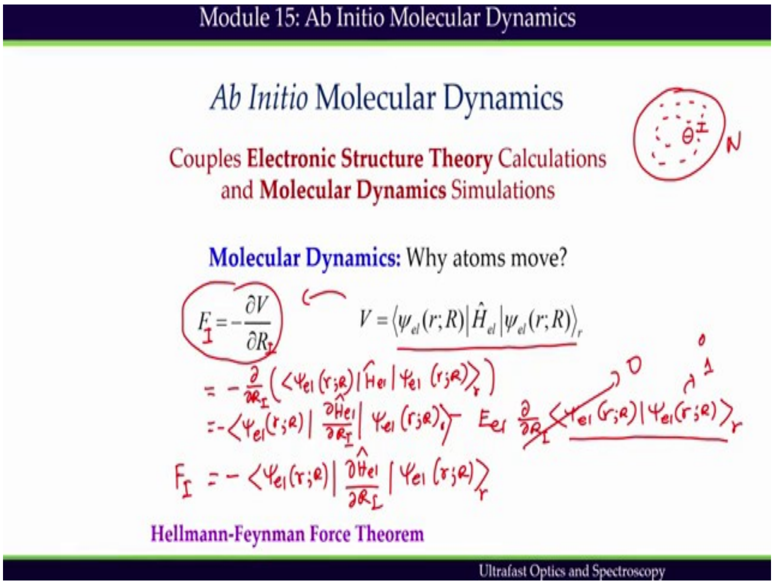

Module 15: Ab Initio Molecular Dynamics

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Molecular Dynamics: Why atoms move?

$$\boxed{F_I = -\frac{\partial V}{\partial R_I}} \qquad V = \underline{\langle \psi_{el}(r;R)|\hat{H}_{el}|\psi_{el}(r;R)\rangle_r}$$

$$= -\frac{\partial}{\partial R_I}\left(\langle \psi_{el}(r;R)|\hat{H}_{el}|\psi_{el}(r;R)\rangle_r\right)$$

$$= -\langle \psi_{el}(r;R)|\frac{\partial \hat{H}_{el}}{\partial R_I}|\psi_{el}(r;R)\rangle_r - E_{el}\,\cancel{\frac{\partial}{\partial R_I}\underline{\langle \psi_{el}(r;R)|\psi_{el}(r;R)\rangle_r}}\ \overset{0}{\ }\ \overset{0}{1}$$

$$F_I = -\langle \psi_{el}(r;R)|\frac{\partial \hat{H}_{el}}{\partial R_I}|\psi_{el}(r;R)\rangle_r$$

Hellmann-Feynman Force Theorem

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This is electronic energy to the respect to d dR I, psi electronic; psi electronic r. And what we see that this integral. So, this derivative can be written as follows and we can make this derivative to be 0 because orthonormal, we have taken orthonormal set for the electronic wave function and if it is a orthonormal then if they are the same electronic state is going to be 1 or 0. So, this is this integral it takes either 0 or 1 value and that is why the first derivative is going to be 0. (Please look at the slides for mathematical expression)

So, this term will be 0. Finally, what we get is that we get this force acting on I-th nucleus is going to be can be calculated as psi electronic wave function r R, the first derivative with respect to R, psi electronic r R. So, this is the; this is the expression for the Hellmann Feynman force and because of that force nuclei will always move, and the ultimate motivation in molecular dynamics is to reduce this force in a system.

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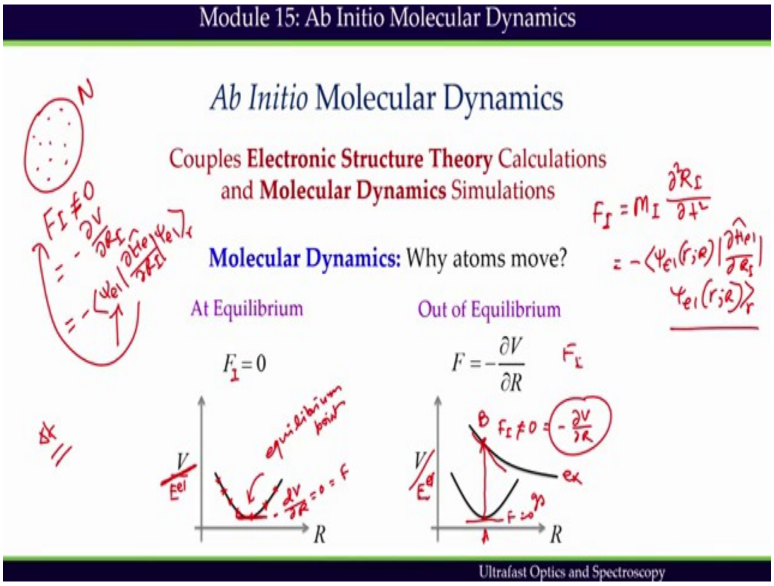

Module 15: Ab Initio Molecular Dynamics

Ab Initio Molecular Dynamics

Couples **Electronic Structure Theory** Calculations and **Molecular Dynamics** Simulations

Molecular Dynamics: Why atoms move?

At Equilibrium

$F_I = 0$

Out of Equilibrium

$F = -\frac{\partial V}{\partial R}$ F_I

$F_I = M_I \frac{\partial^2 R_I}{\partial t^2}$

$= -\langle \psi_{el}(r;R) | \frac{\partial \hat{H}_{el}}{\partial R_I} | \psi_{el}(r;R) \rangle_r$

$F_I \neq 0$

$= -\frac{\partial V}{\partial R_I}$

$= -\langle \psi_{el} | \frac{\partial \hat{H}_{el}}{\partial R_I} | \psi_{el} \rangle_r$

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At equilibrium when this is the potential energy V or, we can write down V electronic energy, anything is right; V or V electronic energy. So, we said that electronic energy can be calculated as a additive for different R, R behaves like a parameter here and we get the potential energy curve or potential energy surface. In the potential energy surface at the equilibrium point where the force at this point, at this point we know that the first derivative that is dV dR is going to be 0, that is why force is 0. So, this is this point is called equilibrium point.

So, at equilibrium F I on the I-th nuclei for that for the particular nuclei this force is going to be 0 and out of equilibrium, for out of equilibrium this force is not going to be 0. So, for example, when we excite a molecule to the electronically excited state, it will it reaches a potential energy surface which is entirely different from the ground state potential energy surface.

And at this point at this point we had force was 0, because the gradient of the potential gradient was 0, but at this point potential gradient is non-necessary to be 0 and in that case we get F on acting on the I-th nuclei is not going to be 0 and that can be calculated from the potential gradient at that point. (Please look at the slides for mathematical expression)

So, in mixed quantum classical picture, one can then write that F I force acting on I-th nucleus is going to be M I that is the mass of the nucleus and the acceleration acting on the I-th nucleus. This is, this can be calculated from this expression electronic wave function r R, the first derivative of electronic R I, psi electronic wave function r R r. So, this is the expression we can get. (Please look at the slides for mathematical expression)

Therefore, one photo excitation prepares system out of equilibrium ultrafast molecular dynamics can predict physical movement of atoms for a fixed period of time after photo excitation. Why molecule should move on the upper electronically excited state? So, this is your excited state, this is your ground state. And on the excited state it should move just because the force acting on it is not 0, it has certain force and because of that force nuclei will move. Force can be calculated from the derivative of the potential energy, the curve at that point.

So, in this figure we are showing that at a point A, this point is considered to be A let us say at point A atoms of the system will not move, but at point B, if we call this point to be B at this point atom should move because the system is out of equilibrium. Here, we note that mixed quantum classical approach is not the only way to deal with ultra fast quantum molecular dynamics.

Pure classical and pure quantum mechanical methods are also available. In a pure classical method, no well defined nuclear wave function is used and in pure quantum mechanical method well defined nuclear wave function which is vibrational wave function is used. We shall however, stay focused on them mixed quantum classical approach because this approach is easy to graphs for them for the beginners.

So, what is the basic idea in ab initio molecular dynamics, particularly following mixed quantum classical approach is that nuclei will move only when there is an force acting on them and force can be calculated directly from potential gradient. Potential can be calculated from electronic structure theory calculation. So, I have a system a system having N number of nucleus, nuclei this is N and this system will evolve which means that position and momentum of the of different nuclei will change because force acting on them is not 0.

And how do I get that force? Force can be calculated from the potential gradient. And this potential gradient can be calculated from electronic structure theory calculations because I need from electronic structure theory, I need this expression the electronic wave function I need. So, basically what I get is that from Hellmann Feynman theorem we get that this electronic wave function we get from electronic structure theory calculation psi electronic.

So, from this; so, this wave function we obtain from electronic structure theory calculation, from this wave function we get this force acting on it and once we know the force then using Hamilton equations we can get next position and momentum after delta t time and delta t is taken to be very short time. So, nuclei will move following classical equation of motion, but it will move on a potential energy surface depicted or provided by the electronic structure theory calculation that is called mixed quantum classical methodology.

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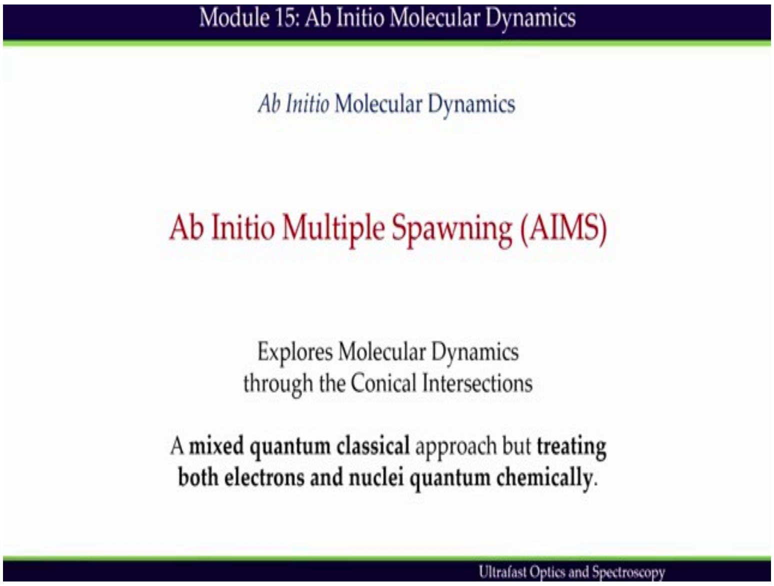

Module 15: Ab Initio Molecular Dynamics

Ab Initio Molecular Dynamics

Ab Initio Multiple Spawning (AIMS)

Explores Molecular Dynamics
through the Conical Intersections

A **mixed quantum classical** approach but **treating both electrons and nuclei quantum chemically**.

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Majority of the ab initio molecular dynamic simulations described in the literature assumes that Newtonian dynamics is sufficient for nuclei and electronics Schrodinger equation provides the potential energy surface. This approach is called mixed quantum classical approach and emphasizes the close relationship between the electrons that govern the form of the potential energy surface and the nuclear dynamics that occurs on this potential energy surface.

The mixed quantum classical approach to ab initio molecular dynamics is well justified by the fact that electrons are lighter than nuclei. This is why to a good approximation electron will rearrange quickly when nuclei move. However, the quantum mechanical nature of the nuclei becomes crucial for even a qualitative understanding of many chemical problems.

For an example, tunneling. An important chemical problem in which nuclei should be described quantum chemically is when the Born-Oppenheimer approximation breaks down, as is always the case in photo physics and photo chemistry involving conical intersection. In particular we will go over ab initio multiple spawning which explores molecular dynamics through the conical intersections.

AIMS method ab initio molecular, ab initio multiple spawning method is a mixed quantum classical approach, but treats both electrons and nuclei quantum mechanically. We will discuss this method ab initio multiple spawning method giving photo physics and photo chemistry in mind.

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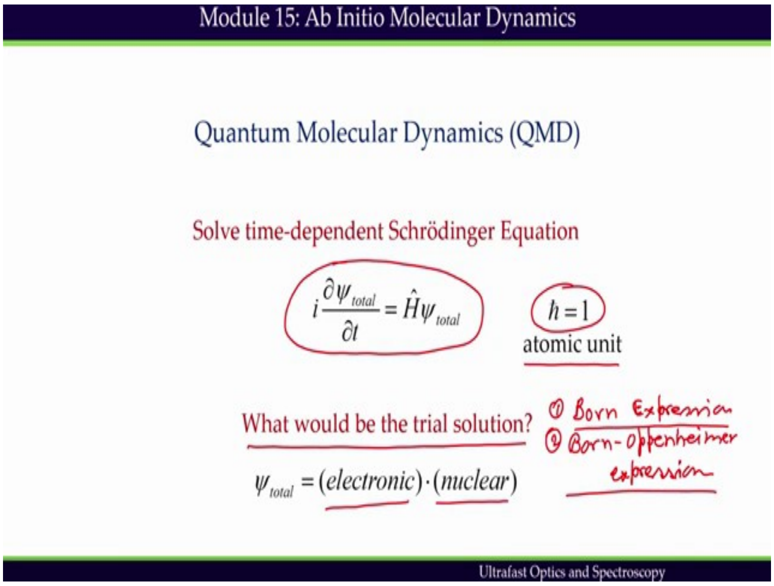

Module 15: Ab Initio Molecular Dynamics

Quantum Molecular Dynamics (QMD)

Solve time-dependent Schrödinger Equation

$$\boxed{i\frac{\partial \psi_{total}}{\partial t} = \hat{H}\psi_{total}}$$

$\boxed{\hbar = 1}$
atomic unit

What would be the trial solution?

① Born Expression
② Born-Oppenheimer expression

$$\psi_{total} = (electronic)\cdot(nuclear)$$

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In any quantum molecular dynamics, we begin with time dependent Schrodinger equation. Time dependent Schrodinger equation reads as follows, i the derivative with respect to t, the total wave function derivative of the total wave function is equal to the Hamiltonian and the total wave function. Here atomic immunity is used. And in atomic unit we consider it reduced Planck constant to be 1.

Now, for this time dependents Schrodinger equation, the first point we have to clarify is that what would be the trial solution for this. And in general either Born Expression or Born-Oppenheimer expression, so there are two approaches we follow to express the trial solution, trial wave function.

Either we use born expansion, what does it mean we will show very soon and or we use Born-Oppenheimer expression for the total wave function. In both expressions however, we use the product of electronic wave function and nuclear wave function that is quite common, but the expressions are slightly different depending on what kind of expression we use.

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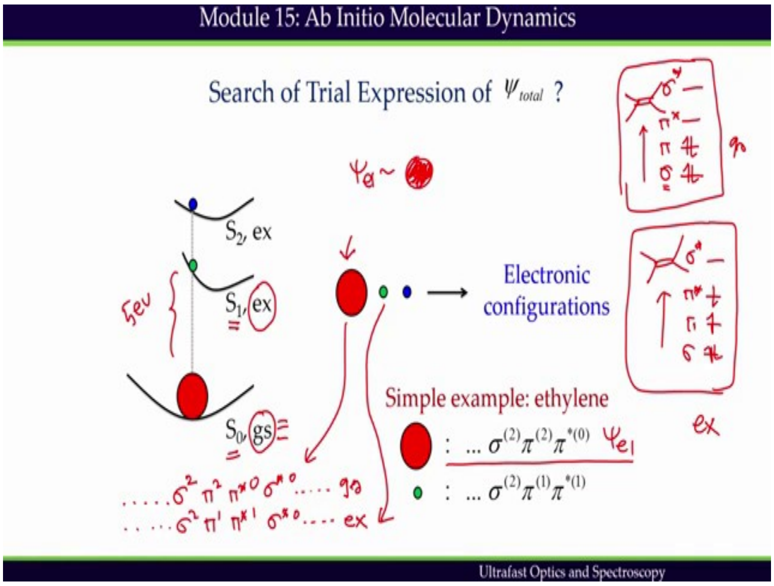

Module 15: Ab Initio Molecular Dynamics

Search of Trial Expression of ψ_{total} ?

Electronic configurations

Simple example: ethylene

: ... $\sigma^{(2)}\pi^{(2)}\pi^{*(0)}$

: ... $\sigma^{(2)}\pi^{(1)}\pi^{*(1)}$

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Let us first understand the electronic wave function. When electronically ground and excited states are well separated in energy, for an example the situation depicted here we show that the ground state potential energy surface is well separated from the excited state potential in each surface. Let us say this is your S 1 excited state, this is your S naught ground state and they are well separated. Let us say they are separated by 5ev energy difference.

So, if they are well separated, then one can easily assume that the total electronic wave function and if we say that system is in the ground state; in the ground state then one can easily assume the total electronic wave function adapts mostly single electronic configuration.

To understand this we can take an example of ethylene. Let us say ethylene molecule I have, we have ethylene molecule and in the ethylene molecule we have sigma bond, then we have pi, then we have pi star these are the orbital alignments let us say. And pi was doubly occupied sigma, doubly occupied and then pi star is not doubly occupied it is empty. And then we had sigma star as well like this empty orbitals. So, when we say electronic configuration, we mean this configuration how we, write down or feel the orbitals molecular orbitals.

So, we will say that if it is in the ground state, if ethylene in the ground state then we can write down the configuration as lower energy orbitals are shown in these dots, we are not writing explicitly. We are just writing the valence orbitals, high lying energy orbitals. So, sigma 2, we have 2 electrons occupied in the sigma orbital, then pi 2 and then pi star is going to be 0. So, this is going to be and then sigma star is also 0 and few dots because we have many other antimony orbitals as well.

So, this configuration we will call it a ground state electronic configuration. And ground state electronic configuration and then excited state configuration one can think of again dots then sigma 2, one electron from pi can be excited to the pi star and sigma star is still 0. This is going to be let us say one of the excited state electronic configurations.

So, this is the only difference in the excited state configuration where we have excited, so this is your ground state configuration then for the excited state configuration we will write down in a similar fashion, we have this pi star then sigma star and then pi and then sigma here, these are doubly, this is doubly occupied, this is now singly occupied, this is now singly occupied and then we will call it S. So, basically we should have electrons like this because it is a singlet excited state and we can say that this is excited state configuration.

So, this way one can think of creating many configurations and we will say that if the system is in the ground state we will assume that mostly the total electronic wave function component can be expressed by this and in other words pictorially here what we have is that there are balls we have shown. So, this big ball is presenting presented by the configuration this.

Then this green ball is representing configuration this. And we can say that the contribution of total wave function this high electronic wave function can be written as mostly this red ball. We will not have much contribution from the upper electronically excited states because their separations are long, this they have excited states and ground separation is very large.

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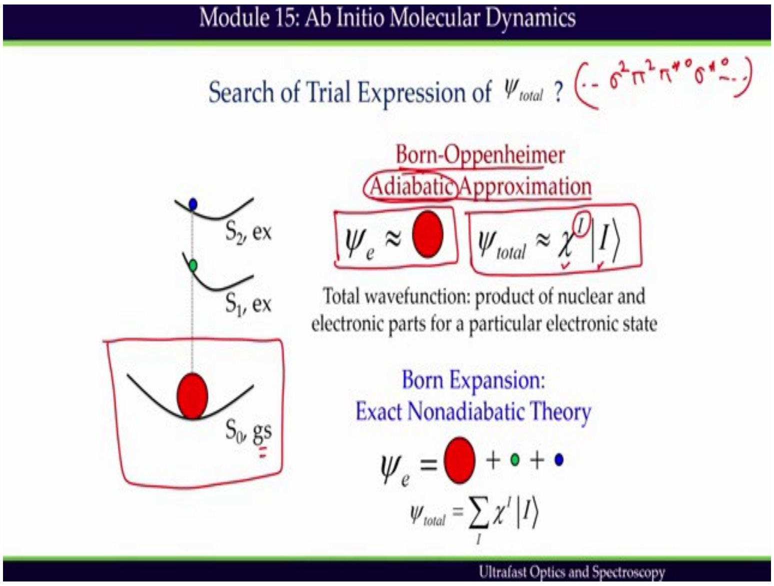
Module 15: Ab Initio Molecular Dynamics

Search of Trial Expression of ψ_{total} ? $(\cdots \sigma^2\pi^2\pi^{*0}\sigma^{*0}\cdots)$

Born-Oppenheimer
Adiabatic Approximation

$\psi_e \approx$ ● $\psi_{total} \approx \chi^{I}|I\rangle$

Total wavefunction: product of nuclear and electronic parts for a particular electronic state

Born Expansion:
Exact Nonadiabatic Theory

$\psi_e =$ ● + ● + ●

$\psi_{total} = \sum_I \chi^I |I\rangle$

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Now, if we consider the ground electronic state of ethylene, to a good approximation one can accept that ethylene ground state electronic wave function can be represented by the only big ball and that is exactly what we are trying to show. And big ball is a particular configuration, ground state configuration. And in that case, total wave function can be represented approximately like this, I have nuclear.

I said that in either born expansion or Born-Oppenheimer expansion we do Born-Oppenheimer expression of the total function we always take the product of nuclear wave function and the electronic wave function. So, we can consider a single electronic state, we are now blind to the other state, we are just seeing a single electronic state and we can write down a total wave function as the product of nuclear and the electronic depart.

This way of representing total wave function is called Born-Oppenheimer Adiabatic Approximation. So, this is called Born-Oppenheimer adiabatic approximation. In adiabatic approximation we do not see any other configuration. We only look at a single electronic state that is represented by I or in other words if it is ground state then if it is ground state.

In this approximation, it is assumed that electronic states are well separated in energy and total wave function can be expressed as the product of nuclear and electronic parts in a single electronic state. Under the adiabatic Born-Oppenheimer approximation, we stay blind to the other electronic state. We stay in a single electronic state and this is why we preserve the electronic configuration. Preserving electronic configuration in molecular quantum mechanics refers to the adiabatic approximation.

So, when you say adiabatic approximation it means that we are maintaining a particular electronic configuration. As I said that this big ball is represented by sigma 2 pi 2 pi star 0, sigma star 0 configuration. So, this configuration will be retained all the time for different nuclear configurations.

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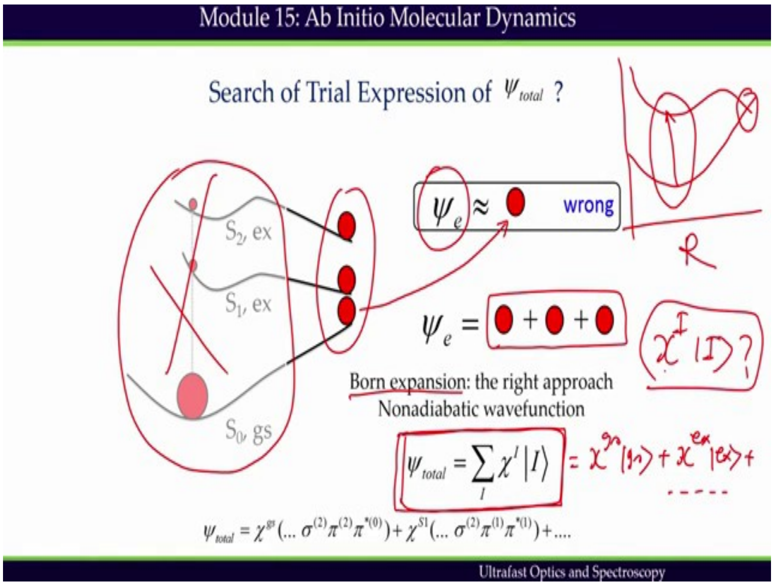

Module 15: Ab Initio Molecular Dynamics

Search of Trial Expression of ψ_{total} ?

$\psi_e \approx$ ● wrong

$\psi_e = $ ● + ● + ●

$\chi^I |I\rangle$?

Born expansion: the right approach
Nonadiabatic wavefunction

$$\psi_{total} = \sum_I \chi^I |I\rangle = \chi^{gn}|gn\rangle + \chi^{ex}|ex\rangle + \text{-----}$$

$$\psi_{total} = \chi^{gs}(\ldots \sigma^{(2)}\pi^{(2)}\pi^{*(0)}) + \chi^{S1}(\ldots \sigma^{(2)}\pi^{(1)}\pi^{*(1)}) + \ldots.$$

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But Adiabatic Born-Oppenheimer approximation breaks down, when if the electronic states are very close line. Let us say we are not in this regime anymore, we are in this regime. Let us we are not in this regime of the potential energy we are in this regime, where different electronic states are coming closer and they are very close line in that case one cannot say that this electronic part can be represented by a single configuration. It should be addition of multiple configurations.

So, total electronic wave function cannot be represented by a single electronic state, rather total electronic wave function has to be represented by summation of different electronic states. It means that I will some ground state ground state electronic wave function plus, then nuclear wave function of excited state multiplied by excited state the electronic wave function plus, all these summations we have to add and this kind of expansion is called born expansion which leads to non-adiabatic wave function. Non-adiabatic because we are mixing different electronic configurations.

So, Born-Oppenheimer approximation breaks down if electronic states are very close line. T hen representing total wave function with the help of only one electronic configuration is not appropriate, right approach is to take all important contributions. Above representation is called born expansion of the total wave function. In this case total wave function is no longer adiabatic rather it is non-adiabatic because we are now mixing electronic configurations.

Here, one important question is obvious. Do we need born or Born-Oppenheimer expression of the total wave function to deal with photo excited system? After a molecule undergoes vertical photo excitation, the electronically excited molecule evolves its structure on the electronically excited state surface and very often encounters surface crossing region, the region where potential energy surfaces cross each other. So, often potential energy surface is looks like this in the whole multi-dimensional space.

So, when we photo excite near the photo excitation regime, near the Franck Condon regime there potential energy surfaces can be well separated, but the moment nuclear start moving it may encounter a region where surface may cross each other. At the Franck Condon geometry electronic states may stay well separated, but as the electronically excited state species, approaches surface crossing region electronically excited states come closer, this is why if we want to explore the entire passage of a molecule from fc point to the surface crossing region we have to use born expansion. So, born expansion is very important for the photo excited system.

Our next question is how do we express psi, how do I express. So, if we understand that this is the final total expression, total the total we expression for the total wave function and that should include many excited states next question is how do we express nuclear wave function as well as electronic wave functions. So, if we know how to express it then we will be able to express total wave function.

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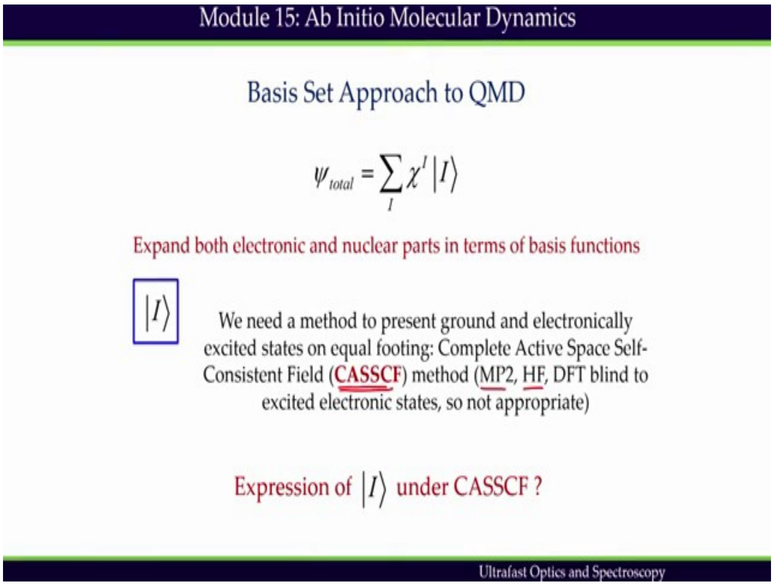

Module 15: Ab Initio Molecular Dynamics

Basis Set Approach to QMD

$$\psi_{total} = \sum_{I} \chi^{I} |I\rangle$$

Expand both electronic and nuclear parts in terms of basis functions

$\boxed{|I\rangle}$

We need a method to present ground and electronically excited states on equal footing: Complete Active Space Self-Consistent Field (CASSCF) method (MP2, HF, DFT blind to excited electronic states, so not appropriate)

Expression of $|I\rangle$ under CASSCF ?

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To represent electronic part we clearly need a method which can represent both the ground and electronically excited states on equal footing. For an example one can use complete active space self consistent field method CASSCF method, and by this method one can access electronically excited states. This method is not like single slater determinant approach like MP2 or Hartree Fock. In CASSCF method, one can access electronically excited states because we include the configurations, different configurations in the total electronic wave function.

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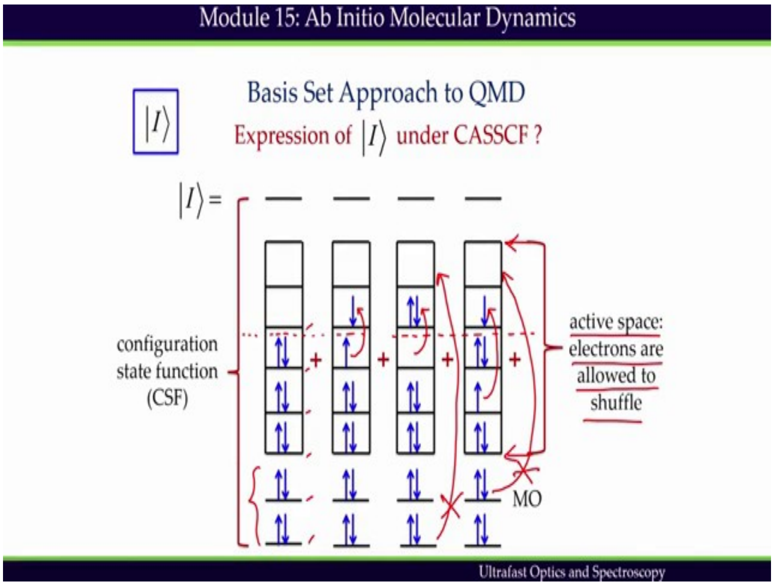

Module 15: Ab Initio Molecular Dynamics

$|I\rangle$

Basis Set Approach to QMD

Expression of $|I\rangle$ under CASSCF ?

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So, we will try to understand what does it mean by this CASSCF approach. Here, what we have drawn different configurations for electronic configurations. So, these are the levels which are corresponding to the molecular orbitals and we see that molecular orbitals are fully occupied below this level for the first configuration.

So, they are doubly occupied. So, this represents one configuration. Second, in the second configuration, in the second configuration what we have done we have excited one electron from this to the upper orbital. We have double excitation and then we have low lying orbital excitation as well. So, there are many other excitations one can include in this.

What is unique in CASSCF method? We consider that a particular set of orbitals are chemically important which is called active space. Electrons are allowed to shuffle in that active space only. So, we will not consider, once you once we define an active space which is chemically important molecular orbitals. We know that the molecular orbitals are involved in chemical bonding, and we will assume that, ok, this particular set which is shown in this box are representing the; representing the active space.

And if this is the active space then none of the electrons from low lying states from here to here this kind of electronic recitation will not be allowed or this kind of electronic excitation will not be allowed. These are not allowed. Only allowed electronic excitation or creating configurations different configuration would be within this box only. So, remaining electrons remain frozen or remain like not contributing to the electronic excitations.

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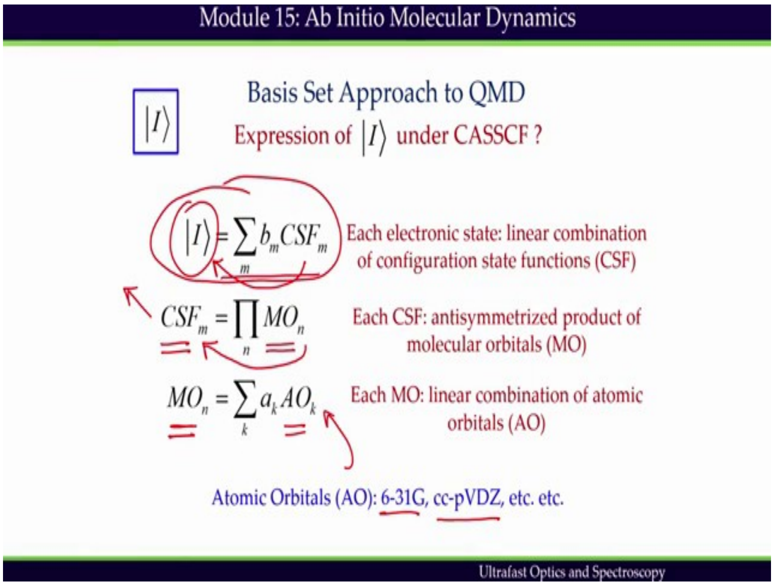

Module 15: Ab Initio Molecular Dynamics

$\boxed{|I\rangle}$

Basis Set Approach to QMD

Expression of $|I\rangle$ under CASSCF ?

$|I\rangle = \sum_m b_m CSF_m$ Each electronic state: linear combination of configuration state functions (CSF)

$CSF_m = \prod_n MO_n$ Each CSF: antisymmetrized product of molecular orbitals (MO)

$MO_n = \sum_k a_k AO_k$ Each MO: linear combination of atomic orbitals (AO)

Atomic Orbitals (AO): 6-31G, cc-pVDZ, etc. etc.

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So, this is all about CASSCF procedure. The hierarchy in the CASSCF method is following. In the CASSCF method, each electronic state is expressed by a linear combination of configuration state functions. Configuration state functions each configuration corresponding to the current configuration state function. So, we take the linear combination of the configuration state functions.

Each configuration state function is ant-symmetrized product of the molecular orbitals. So, this is nothing, but a product of molecular orbital, but particular kind of product where the anti-symmetric nature of the electron has to be preserved and that is why the product is called anti-symmetrized product of the molecular orbital. These are actually expressed in the determinant form.

This is called slater determinant. So, each configuration state function is a slater determinant and multiple configuration state functions we add and we get the final electronic wave function. In the single slater determinant approach, for example, MP2 or Hartree Fock in those methodology we do not use this expression, we only use a single configuration state function. And that is the only difference between CASSCF and other single slater determinant approaches.

And each molecular orbital is expressed as a linear combination of atomic orbitals. In computational chemistry atomic orbitals are represented by basis set such as popples, split valence, double g term, basis set 631G or Dunning's correlation consistent basis set like cc-pVDZ. There are many other basis sets which are available in computational chemistry.

So, with the help of this basis set one can express molecular orbital. Molecular orbital taking the antisymmetric product of molecular orbital we get the configuration state function. Each configuration state function will be added and to get the final electronic wave function. So, this is the hierarchy which is used for the CASSCF methodology.

We will stop here. And we will continue this module in our next lecture.