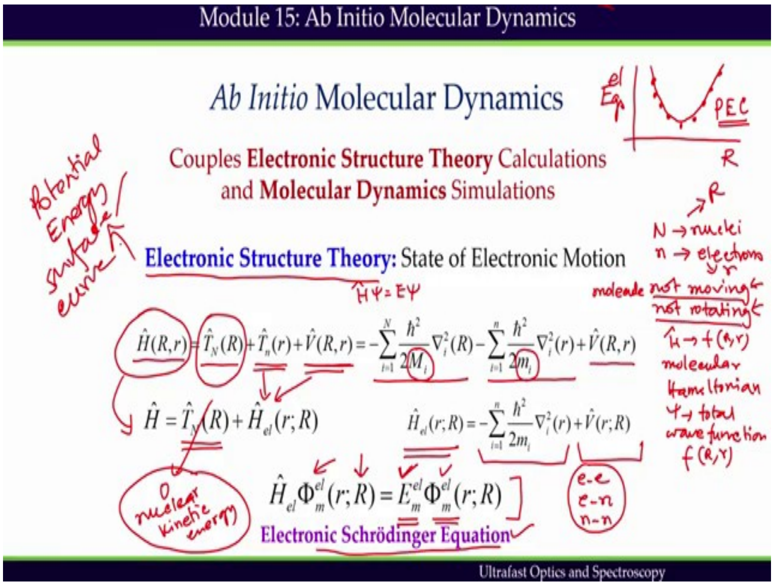
Ultrafast Optics and Spectroscopy
Dr. Atanu Bhattacharya
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bengaluru

Lecture - 34
Ab Initio Molecular Dynamics 1

Welcome to module 15 of the course Ultrafast Optics and Spectroscopy. In this module, we will go over Ab Initio Molecular Dynamics for photochemistry and photo physics. These are, these dynamics are relevant to the ultrafast processes, which occurs in a molecular system after photo excitation.

(Refer Slide Time: 00:52)



Module 15: Ab Initio Molecular Dynamics

Ab Initio Molecular Dynamics

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

Electronic Structure Theory: State of Electronic Motion

$$\hat{H}(R,r) = \hat{T}_N(R) + \hat{T}_n(r) + \hat{V}(R,r) = -\sum_{i=1}^{N}\frac{\hbar^2}{2M_i}\nabla_i^2(R) - \sum_{i=1}^{n}\frac{\hbar^2}{2m_i}\nabla_i^2(r) + \hat{V}(R,r)$$

$$\hat{H} = \hat{T}_N(R) + \hat{H}_{el}(r;R) \qquad \hat{H}_{el}(r;R) = -\sum_{i=1}^{n}\frac{\hbar^2}{2m_i}\nabla_i^2(r) + \hat{V}(r;R)$$

$$\hat{H}_{el}\Phi_m^{el}(r;R) = E_m^{el}\Phi_m^{el}(r;R)$$

Electronic Schrödinger Equation

Ultrafast Optics and Spectroscopy

Ab initio theory refers to a theory which is not based on any experimental parameter. Ab Initio Molecular Dynamics couples electronic structure theory, calculations and molecular dynamics simulation. Ab initio molecular dynamics is particularly important when we are interested in molecular dynamics, on the femtosecond and picosecond timescales.

As ab Initio molecular dynamics couples electronic structure theory calculation and molecular dynamics simulation, it is quite instructive that we go for these two topics very quickly. We will begin with the electronic structure theory. In the electronic structure theory, we study the state of electronic motion in the electrostatic field created by stationary nuclei.

While dealing with AIMD Ab Initio Molecular Dynamics electronic wave function is assumed to be time independent, because electrons are lighter than nuclei and this is why it is less differently assumed that when electron, when nuclei move, electrons can quickly reorganize themselves. Let us consider a non moving, non rotating molecule with N number of nuclei.

And so, we will consider N number of nuclei and small n number of electrons and the molecule is non moving, is not moving, molecule is not moving which means it does not have any translation as well as not rotating. Then we can write the time independence Schrodinger equation as H psi[HΨ] equals E psi[EΨ], that is the time independent Schrodinger equation for the molecular system, where H is the molecular Hamiltonian, H is molecular Hamiltonian and psi is the total wave function; psi is the total wave function.

Here, H and psi are function of both nuclear coordinates nuclear coordinate is represented by R capital R and electronic coordinate is represented by small r. So, this is a function of both R and r, this is also function of capital R and small r, electronic ordinate and nuclear coordinate. E is the total energy.

Hamiltonian for the molecular system, for this whole molecular system, this is the Hamiltonian of the molecular system, which can be written as, which can be decomposed as follows we have nuclear kinetic energy, we have electronic kinetic energy and the total potential contribution. This is electrostatic potential contribution. So, nuclear kinetic energy operator is written here, then electronic kinetic energy operator is written here, and the potential, total potential contribution we have written here.

Here, capital M and represent the mass of the specific nucleus and small m represents the mass of the electron. The molecule is assumed to be not rotating and not moving in space, they are not moving and they are not rotating; however, mole the molecule can vibrate. Therefore, the kinetic energy operator term of the nuclei that T N, this is the kinetic energy operator term of the nuclei originates from the vibrational motion in the molecule.

It is to be noted carefully, that if the centre of mass of the molecule is moving, the molecule is allowed to rotate in space. Additional terms, coupling electron and nuclear rotation and translational motions arises which are neglected in the present derivation.

So, we are assuming that the molecule is not rotating, molecule is not translate not undergoing any translation it is, but it can undergo vibration.

So, the molecular Hamiltonian this molecular Hamiltonian, total molecular Hamiltonian, this can be now rewritten as follows; we have separated nuclear kinetic energy part and rest of the total potential as well as the electronic kinetic energy components has been included in this H electronic Hamiltonian, where H electronic Hamiltonian as representing the kinetic energy operator for the electrons and the total potential, potential including everything.

Potential which includes the electron, electron interaction, electron nuclei interaction as well as nuclei interaction all are included in electronic Hamiltonian. This H el call electronic Hamiltonian, which does not contain any kinetic energy operator of the nuclei, but all other terms this is why it is called electronic Hamiltonian and we should note here that electronic Hamiltonian includes electron potential term, then electron electron nucleus potential term as well as nucleus nucleus potential term all this all the potential terms are included in the electronic Hamiltonian.

By setting the nuclear kinetic energy to 0, so, when we say that nuclear kinetic energy is 0, which means this is 0 neglected nuclear kinetic energy. You said that 0, it means that we are not allowing the molecule to move or rotate. So, this is the assumption which has been mathematical implemented here. So, if you use this to be 0, it means that molecule will not move or rotate, in that case the we get Hamiltonian for frozen nuclei.

So, the Hamiltonian which we get, this electronic Hamiltonian is the Hamiltonian for the frozen nuclei, clamped nuclear Hamiltonian. For a fixed value of the parameter R it is eigan value this is the eigen value we get and eigen function we get. So, this is called electronics Schrodinger equation; electronic Schrodinger equation gives me electronic wave functions, but here R depends parametrically, what does it mean? I will show you very soon.

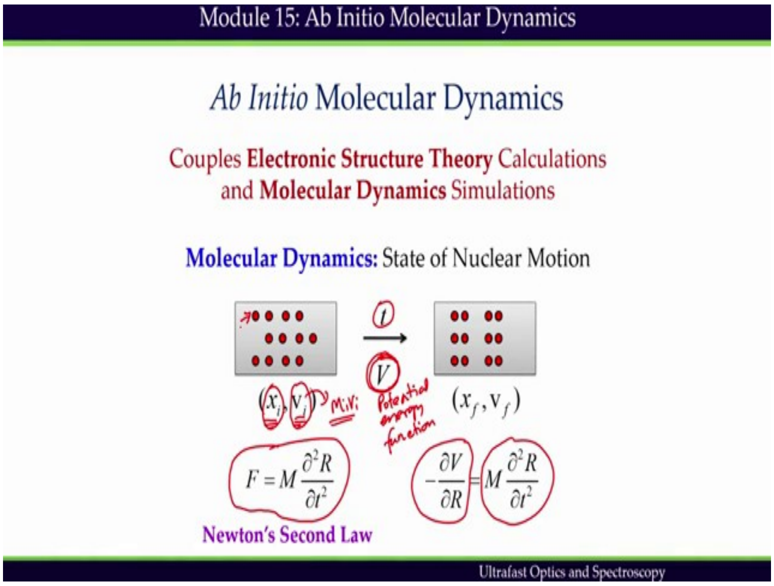
We use electronic Hamiltonian and from the electronic Hamiltonian we get electric wave function as well as electronic energy. So, what does it mean by this parametric dependence is that if we, what does it mean? It means that if I try to for a particular R, I will be able to calculate the electronic energy. This is the E electronic energy, let us say for the ground state electronic energy.

So, this electronic energy, I will be able to get for a particular R. So, for individual R, I get this kind of plot and if I continuously connect them, then what I get is the potential energy curve, potential energy curve or potential energy surface in multi dimension. So, parametric dependence what does it mean? It means that for a particular R I solve this equation and I get this eigen value electronic energy and I get the point for a particular R.

So, for different R I will be able to get a number of points and I can connect them and that curve which is representing this electron the variation of the electronic energy as a function of R is representing the potential energy curve or potential energy surface in multi dimensional. So, that is why the electronic Schrodinger in the electronic Schrodinger equation R has parametric dependence.

It is not a variable, the variable is R in electronic Schrodinger equation and so electronic Schrodinger equation we get after setting the nuclear kinetic energy 0. This is the clamped Hamiltonian approximation. So, in electronic structure theory in the end what we do is that; we get electronic energy of a system or in other words, I get the potential energy surface or potential energy curve for a particular system. So, electronic structure theory ultimately provides me potential energy surface or curve.

(Refer Slide Time: 11:53)



Module 15: Ab Initio Molecular Dynamics

Ab Initio Molecular Dynamics

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

Molecular Dynamics: State of Nuclear Motion

$$F = M\frac{\partial^2 R}{\partial t^2}$$

Newton's Second Law

$$-\frac{\partial V}{\partial R} = M\frac{\partial^2 R}{\partial t^2}$$

Ultrafast Optics and Spectroscopy

As stated earlier that ab initio molecular dynamics couples electronic structure theory calculations and molecular dynamics. So, we will now look at molecular dynamics. In molecular dynamics you study physical movement of atoms, for a fixed period of time, giving a view of the dynamical evolution of the system. A dynamical simulation requires a set of initial coordinates and velocities, velocities on the other hand momentum.

So, velocity is the is corresponding to its momentum. Momentum can be M i V i that is the momentum and the initial coronate is xi. So, in any molecular dynamics what we need? We need to start with an initial position and momentum or velocity and the potential energy function for the nuclei and the potential energy function for the nuclei, under which potential it will move and so, this is the potential energy function; this is potential energy function for the nuclei.

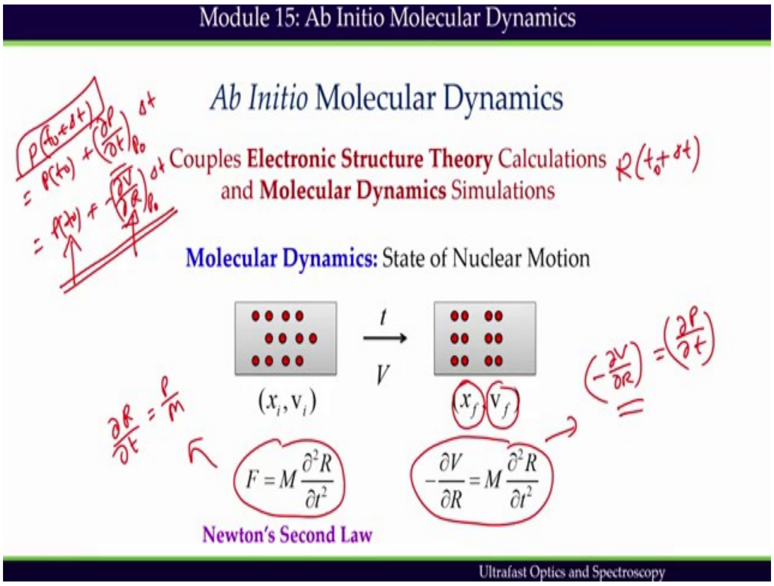
By taking a large number of very smalls time steps, the temporal behavior of the system by taking a large number of very small time steps the temporal behavior of the system is obtained. At each time step position and velocities are updated and new potential energy is calculated. So, in molecular dynamics what we need?

We need one initial coordinate, one its initial velocity or momentum and the potential on which nuclei will move and remember, in electronic structure theory calculations we get the potential. So, this potential can be taken from electronic structure theory calculation and we can move this initial position and momentum as a function of time and this is all about molecular dynamics. Nuclei are heavy point particles and to a good approximation we may assume that they behave like classical point particles, in that case that dynamics can be simulated by solving Newton's second law, classical equation of motion.

So, the force which is nothing, but mass into acceleration that is the second, Newton's second law and one can use this equation to calculate the force and we know that the force is related to the potential gradient minus dV dR. This potential gradient is giving the force acting on individual particle and due to this force is moving.

So, considering potential energy V, the above differential form can be rewritten as minus dV dR which is nothing, but M d 2 R d t 2, where V is the potential energy at position R. Minus d V d R represents the negative of the potential energy gradient, which is the force acting on the particles in some cases it is useful to rewrite above equations in other forms.

(Refer Slide Time: 15:39)



Module 15: Ab Initio Molecular Dynamics

Ab Initio Molecular Dynamics

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

Molecular Dynamics: State of Nuclear Motion

$(x_i, v_i) \xrightarrow[V]{t} (x_f, v_f)$

$F = M\frac{\partial^2 R}{\partial t^2}$

Newton's Second Law

$-\frac{\partial V}{\partial R} = M\frac{\partial^2 R}{\partial t^2}$

$P(t_0+\delta t) = P(t_0) + \left(\frac{\partial P}{\partial t}\right)_{P_0}\delta t = P(t_0) + \left(\frac{\partial V}{\partial R}\right)_{P_0}\delta t$

$R(t_0+\delta t)$

$\left(-\frac{\partial V}{\partial R}\right) = \left(\frac{\partial P}{\partial t}\right)$

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

Ultrafast Optics and Spectroscopy

For any example; one can rewrite this equation as minus dV dR equals dP dt and this equation was rewritten as dR dt equals P by M and we have seen that how to calculate next position after t plus delta t time t naught plus delta t time that we have seen already. Now, we are discussing how to get the next momentum. So, momentum can be obtained as P t naught plus delta t which is nothing, but P t naught under same approximation that delta t is very small, we get dell P dt at P naught delta t.

So, this time derivative can be written as minus dV dR. So, P t naught plus minus dV dR at P naught initial time delta t. So, if we know the derivative, this potential energy gradient, if you know the potential energy gradient from the electronic structure theory calculations and if we know the initial momentum, then will be able to calculate our next momentum at t naught plus delta t time and this is the wave we get the temporal behavior of the next position momentum we get.

Numerical implementation of this approach in molecular dynamics is called violet algorithm. We will stop here and we will continue this module in our next lecture.