Ultrafast Optics and Spectroscopy
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Lecture – 28
Quantum Mechanical Model of Ultrafast Spectroscopy

Welcome to module 10 of the course Ultrafast Optics and Spectroscopy. In this module we will learn a simple Quantum Mechanical Model for Ultrafast Spectroscopy.

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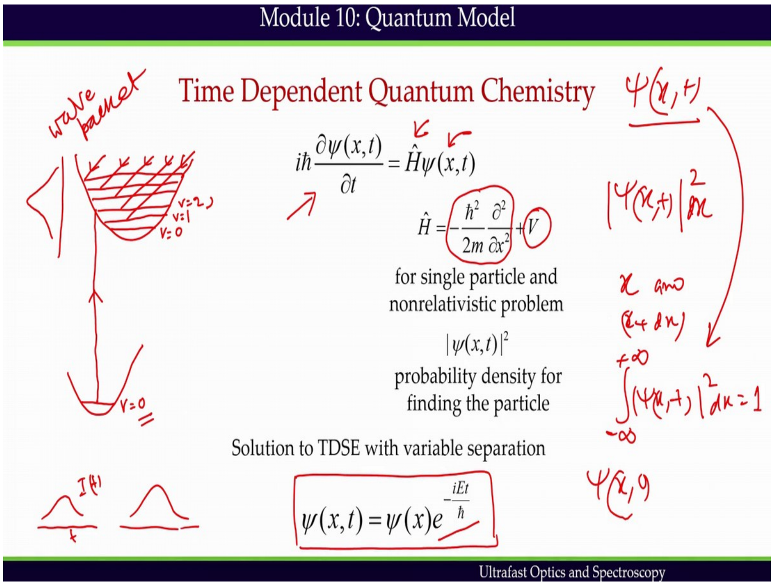

Module 10: Quantum Model

Time Dependent Quantum Chemistry

$$i\hbar\frac{\partial\psi(x,t)}{\partial t}=\hat{H}\psi(x,t)$$

$$\hat{H}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V$$

for single particle and nonrelativistic problem

$$|\psi(x,t)|^2$$

probability density for finding the particle

Solution to TDSE with variable separation

$$\psi(x,t)=\psi(x)e^{-\frac{iEt}{\hbar}}$$

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A description of basic ultra fast spectroscopy in which coherence is important begins with time dependent Schrodinger equation. The one which we have taken here, this is 1 dimensional the spatial dimension we have taken as x.

So, the wave function depends on x and t, and the term coherence is invoked here in the previous module we have discussed kinetic rate equations for different excitation processes. In those rate equations we have been discussed any coherence effect.

So, what does it mean by this coherence? A simple manifestation of coherence can be understood from following figure, let us say I have ground electronic state and a system is in the vibrationally ground state. And I am exciting the system to the electronically excited state. In the electronically excited state I have different vibrational states these are electronically excited states.

Now, when we undergo this transition with the help of a monochromatic photon, then we can excite from v equals 0 v equals 1, v equals 2 these are the vibrationally excited state. So, one can excite from v 0 of the ground state to the v 2 of the excited electronic state and that is possible only when I have a monochromatic excitation source. But when we are dealing with an ultra fast pulse a short pulse, then we know that a short pulse will always have this is intensity profile of the pulse we will always have a broad bandwidth.

So, instead of a monochromatic excitation we might have a number of excitation simultaneously. So, this is represented by the broad bandwidth which means I will be exciting these vibrational modes simultaneously. This kind of simultaneous excitation gives rise to coherence effect or we create a wave packet what does it mean? This will be revealed very soon we create a wave packet ok.

So, any kind of coherence effect can be understood from time dependence for injury equation where h is the Hamiltonian of the system here for simple representation we have used 1 dimensional problem and single particle problem we have only simple potential operator and the kinetic energy operator in 1 dimension.

Now, what does it mean by this psi x t[$\Psi(x,t)$]? This psi x t if we take this wave function, but if we take the modulus square of dx, then this represents the probability of finding the particle between x and x plus dx. In this regime what is the probability of finding that particle? And if it is normalized then we can write down psi xt dx equals 1 minus infinity to plus infinity over the full space. This psi x t modular square is called probability density for finding the particle at position x and at time t. (<u>Please look at the slides for mathematical expressions)</u>

If I know psi x 0 at 0 time if I know the wave function, then from time dependence or Schrodinger equation we will be able to get a complete solution from the problem which means anytime I can find out xt. And once I know wave function I will be able to find out the probability of finding those particles at a particular position in time. If we use them variable separation method which can be shown very easily one can separate the psi xt into its 2 different components. One can decompose wave functions psi x t into its components psi x and the time temporal component. Temporal component here in the wave function is given as a phase factor. This can be proved with the help of variable separation method and which we are not showing here.

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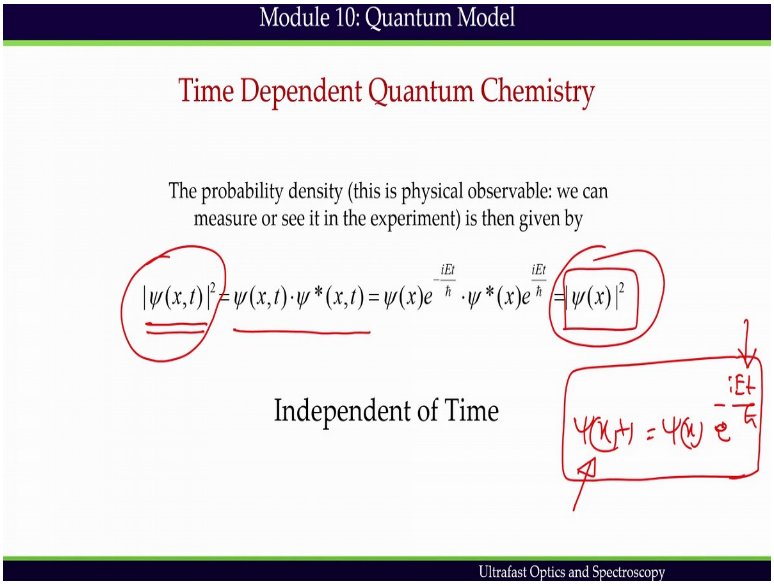

Module 10: Quantum Model

Time Dependent Quantum Chemistry

The probability density (this is physical observable: we can measure or see it in the experiment) is then given by

$$\underline{|\psi(x,t)|^2} = \underline{\psi(x,t)\cdot\psi^*(x,t)} = \psi(x)e^{-\frac{iEt}{h}}\cdot\psi^*(x)e^{\frac{iEt}{h}} = \boxed{|\psi(x)|^2}$$

Independent of Time

$$\boxed{\psi(x,t) = \psi(x)\, e^{-\frac{iEt}{\hbar}}}$$

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So, what does it mean? If we have this variable separation method then we see that psi x t can be expressed at psi x that phase component and the phase factor time dependent phase factor e to the power minus i Et by h cut E is the energy of that state. Now, if we if this is the general form of the wave function, if we have this general form of the wave function coming from time dependence or Schrodinger equation, all we need to understand that we do not observe wave function experimentally. What we observed all the physical observables are related to its density which is this square modulus. (Please look at the slides for mathematical expressions)

And if we if we take the density then the probability density is given by psi star psi which is finally, we get this. So, what does it imply? Probability density is independent of time this means that probability density does not change with time that is there is no effect there is no effective motion which can be observed. So, although wave function is time dependent corresponding probability density what we observed is time independent. (Please look at the slides for mathematical expressions)

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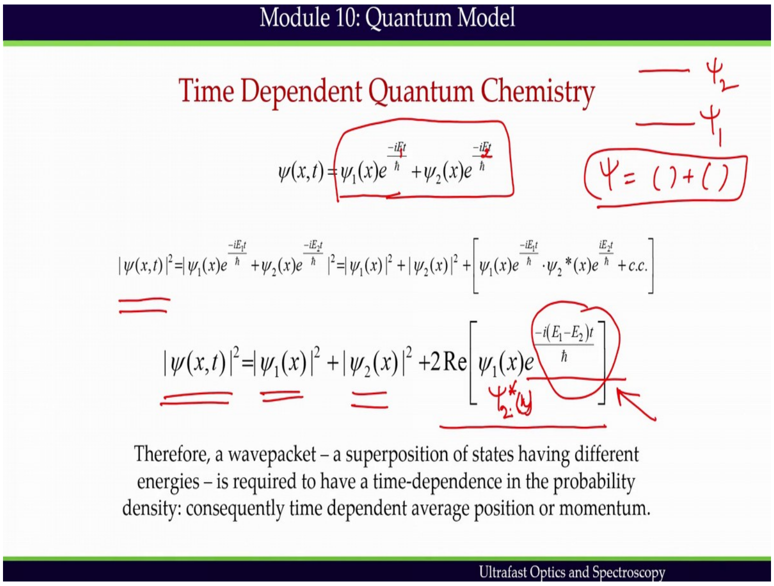

Module 10: Quantum Model

Time Dependent Quantum Chemistry

$$\psi(x,t)=\psi_1(x)e^{\frac{-iE_1t}{\hbar}}+\psi_2(x)e^{\frac{-iE_2t}{\hbar}}$$

$$|\psi(x,t)|^2=|\psi_1(x)e^{\frac{-iE_1t}{\hbar}}+\psi_2(x)e^{\frac{-iE_2t}{\hbar}}|^2=|\psi_1(x)|^2+|\psi_2(x)|^2+\left[\psi_1(x)e^{\frac{-iE_1t}{\hbar}}\cdot\psi_2{}^*(x)e^{\frac{iE_2t}{\hbar}}+c.c.\right]$$

$$|\psi(x,t)|^2=|\psi_1(x)|^2+|\psi_2(x)|^2+2\operatorname{Re}\left[\psi_1(x)e^{\frac{-i(E_1-E_2)t}{\hbar}}\right]$$

Therefore, a wavepacket – a superposition of states having different energies – is required to have a time-dependence in the probability density: consequently time dependent average position or momentum.

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So; however, if we look at the linear combination of the solution for an example instead of a single state if we consider at 2 states where I have this is psi 1 and this is psi 2 there are 2 states and total wave function is represented as a linear combination of this plus this both states together, then we will try to find out what will happen to the probability density. Any linear combination of particular solution is also a solution of the time dependence or injures equation. By forming linear combination of particular solution each with its own characteristic times time dependent phase factor, we only obtain the time dependence in the probability density how we will see that.

So, this is the first wave function, here there should be 1 because it is associated with energy of the first state, this is this should be 2 because it is associated with the second state and it is a superposition state which we create somehow we have to create a superposition state to get the time dependence in the probability density.

So, what I get is that, if we take the modular square then finally, we end up with an expression like this where this is missing here psi 2 star x is missing. So, what we get is that, the in such a situation where I have wave function represented as a linear combination of 2 states, then in that situation the probability density will depend on its own individual probability density plus there is an time dependent component and this time dependent component will control the time dependent variation of the density.

We note that this equation has three terms the first term the first 2 come from each particular solution associated with respectively 1 and 2 states and the third term arises from an interference term between the two. So, this is an interference term which is coming and this will modulate as a function of time as a function of time it will oscillate because this function this phase factor is an oscillatory function. This interference term is a result of having superposition of eigenstates with different energies a wave packet and this is called wave packet.

So, when we create an superposition state we call it is an wave packet. It is a not a pure state it is a 2 states together is a linear combination of 2 states and that is called the wave packet. Therefore, a wave packet a superposition of states having different energies is required to have a time dependence in the probability density and consequently in other observables such as average position average momentum of the particles.

So, this is a very important realization in quantum mechanics. In quantum mechanics if we have a pure state having only represented by its spatial and the temporal phase factors, that for a particular pure state we cannot have a time dependence in the density that and because it does not depend on time, it will the average momentum and average position of that particle will not change. But if we have a superposition state we create a wave packet then it will change.

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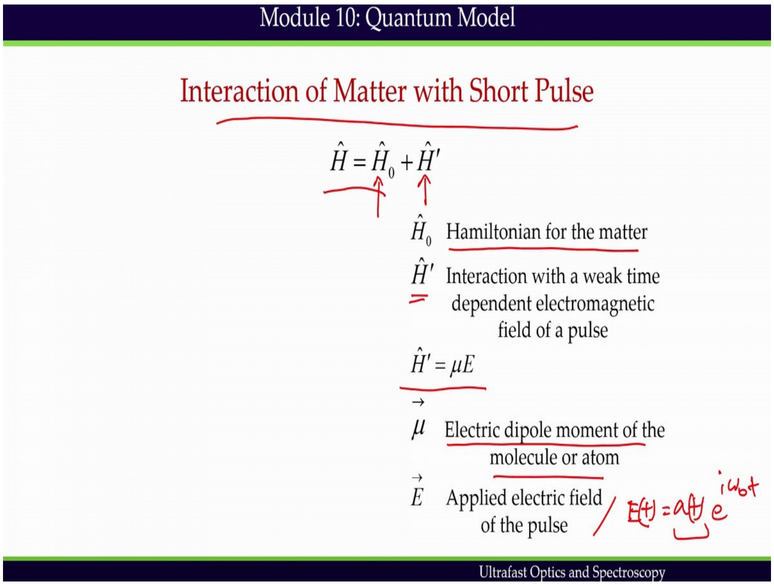

Module 10: Quantum Model

Interaction of Matter with Short Pulse

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

$\hat{H}_0$ Hamiltonian for the matter

$\hat{H}'$ Interaction with a weak time dependent electromagnetic field of a pulse

$$\hat{H}' = \mu E$$

$\vec{\mu}$ Electric dipole moment of the molecule or atom

$\vec{E}$ Applied electric field of the pulse

$$E(t) = \underbrace{a(t)} e^{i\omega_0 t}$$

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Now, we will look at the interaction, how to think about the interaction of matter with short pulse? For any interaction like matter interaction work we always decomposed

Hamiltonian total Hamiltonian into its without perturbation and with perturbation the both components will contribute.

So, H naught[H_0] is Hamiltonian for the matter without the interaction and H dash is interaction Hamiltonian interacting with the electromagnetic field of the pulse which is represented by mu E, and E is the applied electric field of the pulse we know how to represent such a pulse in time domain Et equals at that is the envelope function e to the power i omega naught t omega naught is the central frequency of the of the pulse and a t is the envelope function. And mu is the dipole of electric dipole moment of the molecule. So, electric dipole moment of the molecule is interacting with the dipole with the electric field of the applied beam.

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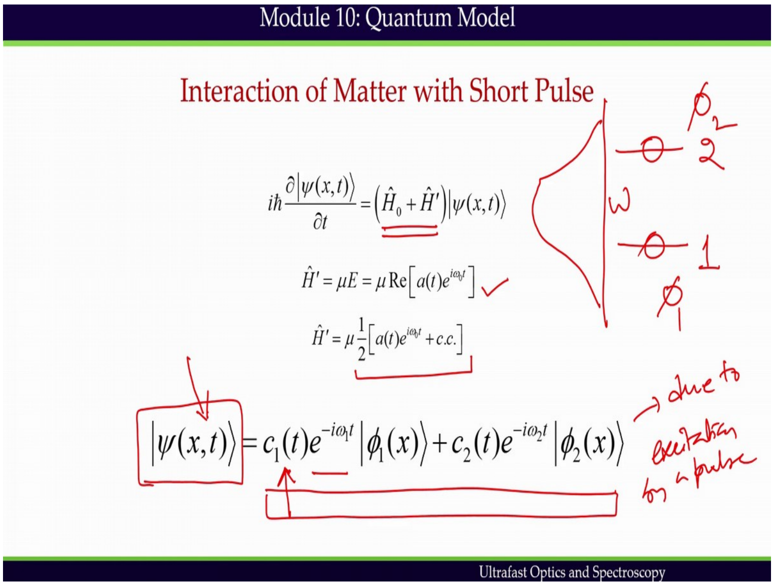

Module 10: Quantum Model

Interaction of Matter with Short Pulse

$$i\hbar\frac{\partial|\psi(x,t)\rangle}{\partial t}=\left(\underline{\underline{\hat{H}_0+\hat{H}'}}\right)|\psi(x,t)\rangle$$

$$\hat{H}'=\mu E=\mu\,\mathrm{Re}\left[a(t)e^{i\omega_0 t}\right] \checkmark$$

$$\hat{H}'=\mu\frac{1}{2}\underline{\left[a(t)e^{i\omega_0 t}+c.c.\right]}$$

$$\boxed{|\psi(x,t)\rangle}=\underline{c_1(t)e^{-i\omega_1 t}|\phi_1(x)\rangle+c_2(t)e^{-i\omega_2 t}|\phi_2(x)\rangle}$$

→ due to excitation by a pulse

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Now, the task is following we have to insert that perturbed Hamiltonian into time dependence Schrodinger equation and as I mentioned before this is the real part of the electric field and that has been represented in terms of its complex come its complex conjugate as well. And you we see that that the total wave function if we consider total wave function. So, now, we have a situation where the first state and this is second state. And when we are creating state due to excitation by a pulse we are creating a superposition of 2 states.

So, basically our bandwidth is such a way that is exciting both states simultaneously. This is the bandwidth of the pulse and that is why it is exciting both states simultaneously. If we are exciting both states simultaneously then we can say that there is a coefficient for this expansion, that is time dependent and this is the phase factor for corresponding state, this is we are calling it phi 1 and this is phi 2.

So, and that is the way you get a superposition's, that this superposition state is created due to due to excitation by a pulse and that is why we were representing the final expression and a tentative solution of that wave function is going to be superposition of these 2 states.

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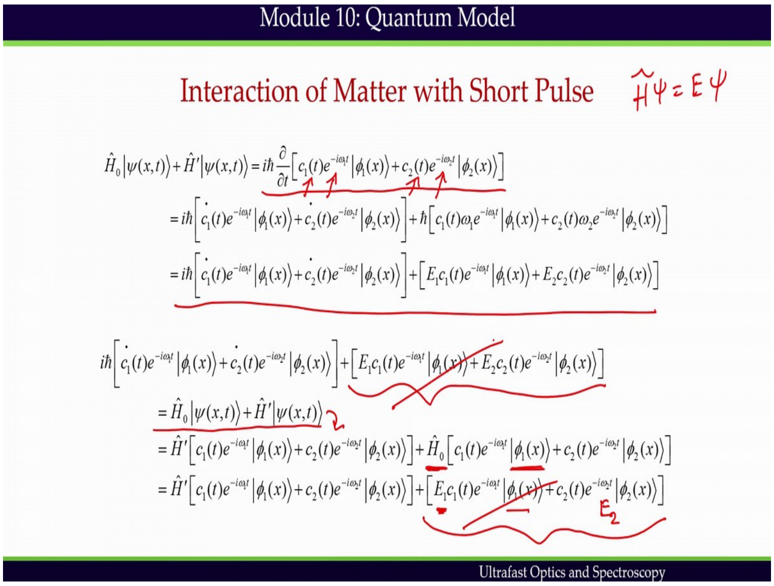

Module 10: Quantum Model

Interaction of Matter with Short Pulse $\hat{H}\psi = E\psi$

$$\hat{H}_0|\psi(x,t)\rangle + \hat{H}'|\psi(x,t)\rangle = i\hbar\frac{\partial}{\partial t}\left[c_1(t)e^{-i\omega_1 t}|\phi_1(x)\rangle + c_2(t)e^{-i\omega_2 t}|\phi_2(x)\rangle\right]$$

$$= i\hbar\left[\dot{c}_1(t)e^{-i\omega_1 t}|\phi_1(x)\rangle + \dot{c}_2(t)e^{-i\omega_2 t}|\phi_2(x)\rangle\right] + \hbar\left[c_1(t)\omega_1 e^{-i\omega_1 t}|\phi_1(x)\rangle + c_2(t)\omega_2 e^{-i\omega_2 t}|\phi_2(x)\rangle\right]$$

$$= i\hbar\left[\dot{c}_1(t)e^{-i\omega_1 t}|\phi_1(x)\rangle + \dot{c}_2(t)e^{-i\omega_2 t}|\phi_2(x)\rangle\right] + \left[E_1 c_1(t)e^{-i\omega_1 t}|\phi_1(x)\rangle + E_2 c_2(t)e^{-i\omega_2 t}|\phi_2(x)\rangle\right]$$

$$i\hbar\left[\dot{c}_1(t)e^{-i\omega_1 t}|\phi_1(x)\rangle + \dot{c}_2(t)e^{-i\omega_2 t}|\phi_2(x)\rangle\right] + \left[E_1 c_1(t)e^{-i\omega_1 t}|\phi_1(x)\rangle + E_2 c_2(t)e^{-i\omega_2 t}|\phi_2(x)\rangle\right]$$

$$= \hat{H}_0|\psi(x,t)\rangle + \hat{H}'|\psi(x,t)\rangle$$

$$= \hat{H}'\left[c_1(t)e^{-i\omega_1 t}|\phi_1(x)\rangle + c_2(t)e^{-i\omega_2 t}|\phi_2(x)\rangle\right] + \hat{H}_0\left[c_1(t)e^{-i\omega_1 t}|\phi_1(x)\rangle + c_2(t)e^{-i\omega_2 t}|\phi_2(x)\rangle\right]$$

$$= \hat{H}'\left[c_1(t)e^{-i\omega_1 t}|\phi_1(x)\rangle + c_2(t)e^{-i\omega_2 t}|\phi_2(x)\rangle\right] + \left[E_1 c_1(t)e^{-i\omega_1 t}|\phi_1(x)\rangle + c_2(t)e^{-i\omega_2 t}|\phi_2(x)\rangle\right]$$

So, all we need to do is that insert that expression into the time dependence Schrodinger equation, and we get first we will look at the right hand side this side which is the time derivative of this function if we do the time derivative of this function we end up with this expression. Here we remind ourselves that time dependent components are this expansion coefficient c and this phase factor.

Here also expansion coefficient and the phase factor both are time dependent that is why we are taking the first derivative with respect to the first derivative of those components only. And after doing that we can rewrite this equation one more time and we can here also we can insert the same expression for psi is a superposition state. When we insert that then we get certain value because here this H naught if it is employed on phi 1 state we get the E 1 multiplied by phi 1 that is time independence Schrodinger equation.

So, if I have H psi equals E psi is something like that. So, we are getting individual energies here. So, this is also true here also, but we have been we have missed this E 2 term here there should be 2 term and if we keep doing it then finally, what we see is that, on the left hand side I have a term which is equal to the term on the right hand side. (Please look at the slides for mathematical expressions)

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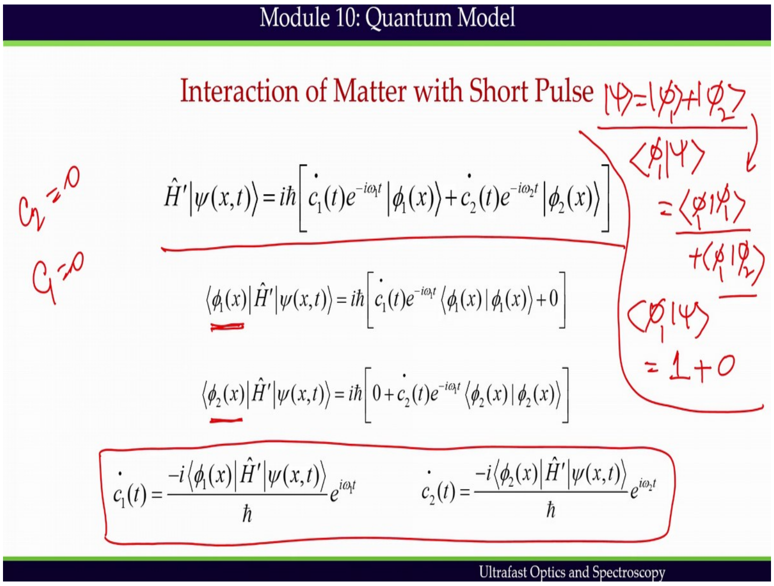

Module 10: Quantum Model

Interaction of Matter with Short Pulse

$|\psi\rangle = |\phi_1\rangle + |\phi_2\rangle$

$\langle \phi_1 | \psi \rangle$

$= \langle \phi_1 | \phi_1 \rangle$

$+ \langle \phi_1 | \phi_2 \rangle$

$\langle \phi_1 | \psi \rangle$

$= 1 + 0$

$c_2 = 0$

$c_1 = 0$

$$\hat{H}'|\psi(x,t)\rangle = i\hbar\left[\dot{c}_1(t)e^{-i\omega_1 t}|\phi_1(x)\rangle + \dot{c}_2(t)e^{-i\omega_2 t}|\phi_2(x)\rangle\right]$$

$$\langle \phi_1(x)|\hat{H}'|\psi(x,t)\rangle = i\hbar\left[\dot{c}_1(t)e^{-i\omega_1 t}\langle \phi_1(x)|\phi_1(x)\rangle + 0\right]$$

$$\langle \phi_2(x)|\hat{H}'|\psi(x,t)\rangle = i\hbar\left[0 + \dot{c}_2(t)e^{-i\omega_1 t}\langle \phi_2(x)|\phi_2(x)\rangle\right]$$

$$\boxed{\dot{c}_1(t) = \frac{-i\langle \phi_1(x)|\hat{H}'|\psi(x,t)\rangle}{\hbar}e^{i\omega_1 t} \qquad \dot{c}_2(t) = \frac{-i\langle \phi_2(x)|\hat{H}'|\psi(x,t)\rangle}{\hbar}e^{i\omega_2 t}}$$

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So, we can we can remove these 2 terms and finally, we get this expression and in many occasions when we are dealing with quantum mechanics we make use of ortho normalization condition to reduce an equation what does it mean? if I have let us say phi 1 plus phi 2 equals psi let us say this is an example.

If I have this situation a linear combination of these 2 states then what I do is that, I multiply this both side with the help of phi 1 let us say. So, this is the complex conjugate of phi 1, this phi 1. So, I get this expression on the left hand side and on the right hand side I get phi 1 phi 1 plus phi 1 phi 2. If I do that if I have this expression and if I do this kind of multiplication then we can make use of the ortho normalization condition where we will be able to simplify this expression simplify because this is going to be 1 plus this is going to be 0 is something like that. (Please look at the slides for mathematical expressions)

So, and in many occasions in quantum mechanics to reduce an equation we make use of this kind of orthonormalization condition and that is exactly what we have done here. We have 2 states that is why we can multiply by phi 1 in one step and another step we can multiply with phi 2 and then we get 2 equations time dependent equations where we are representing c 1 as a function of time and c 2 derivative of c 2 as a function of time these 2 equations. (Please look at the slides for mathematical expressions)

And we we can remind ourselves that c 1 and c 2 are the coefficient which means if I have c 1 equals 0, then there is no population in the 1 state and if sometimes if I have c 2 equals 0 then there is no population in the c 2 state. So, all we are interested in is that how the population is building up how we are building up the population in the first state and the second state depending on what is the coefficient for c 1 and c 2. So, that is this is the reason why we are interested in c 1 and c 2. (Please look at the slides for mathematical expressions)

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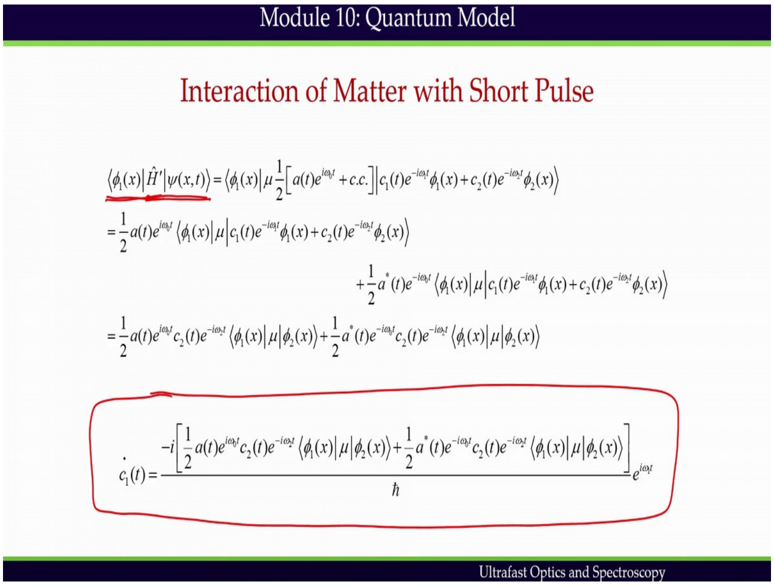

Module 10: Quantum Model

Interaction of Matter with Short Pulse

$$\underline{\left\langle \phi_1(x)\middle|\hat{H}'\middle|\psi(x,t)\right\rangle}=\left\langle \phi_1(x)\middle|\mu\frac{1}{2}\left[a(t)e^{i\omega_0 t}+c.c.\right]\middle|c_1(t)e^{-i\omega_1 t}\phi_1(x)+c_2(t)e^{-i\omega_2 t}\phi_2(x)\right\rangle$$

$$=\frac{1}{2}a(t)e^{i\omega_0 t}\left\langle \phi_1(x)\middle|\mu\middle|c_1(t)e^{-i\omega_1 t}\phi_1(x)+c_2(t)e^{-i\omega_2 t}\phi_2(x)\right\rangle$$

$$+\frac{1}{2}a^*(t)e^{-i\omega_0 t}\left\langle \phi_1(x)\middle|\mu\middle|c_1(t)e^{-i\omega_1 t}\phi_1(x)+c_2(t)e^{-i\omega_2 t}\phi_2(x)\right\rangle$$

$$=\frac{1}{2}a(t)e^{i\omega_0 t}c_2(t)e^{-i\omega_2 t}\left\langle \phi_1(x)\middle|\mu\middle|\phi_2(x)\right\rangle+\frac{1}{2}a^*(t)e^{-i\omega_0 t}c_2(t)e^{-i\omega_2 t}\left\langle \phi_1(x)\middle|\mu\middle|\phi_2(x)\right\rangle$$

$$\boxed{\dot{c}_1(t)=\frac{-i\left[\frac{1}{2}a(t)e^{i\omega_0 t}c_2(t)e^{-i\omega_2 t}\left\langle \phi_1(x)\middle|\mu\middle|\phi_2(x)\right\rangle+\frac{1}{2}a^*(t)e^{-i\omega_0 t}c_2(t)e^{-i\omega_2 t}\left\langle \phi_1(x)\middle|\mu\middle|\phi_2(x)\right\rangle\right]}{\hbar}e^{i\omega_1 t}}$$

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And then if we insert this if we if we if we insert this final expression for this for this part of Hamiltonian, then we get this expression and finally, we end up with this expression this is just simplifying this expressions and we get this. Now, when you get this is the expression for c 1 and this is the expression for c 1. (Please look at the slides for mathematical expressions)

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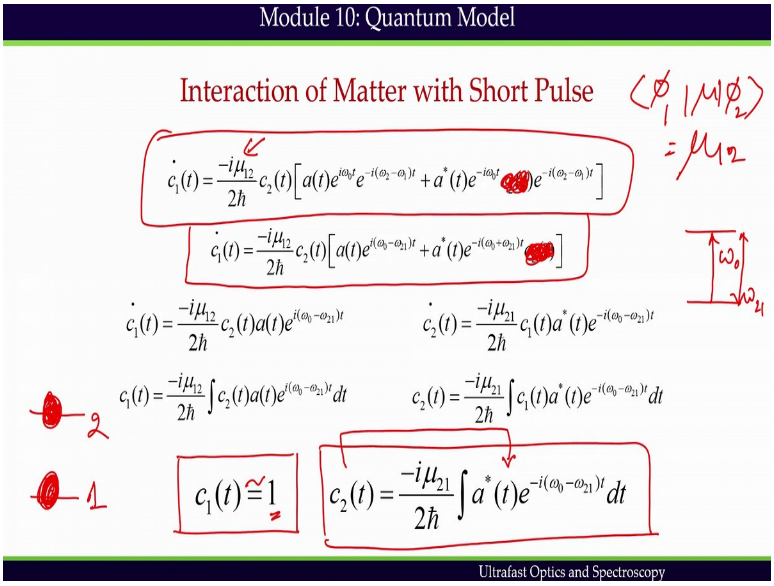

Module 10: Quantum Model

Interaction of Matter with Short Pulse

$\langle \phi_1 | \mu | \phi_2 \rangle = \mu_{12}$

$$\dot{c}_1(t) = \frac{-i\mu_{12}}{2\hbar} c_2(t)\left[a(t)e^{i\omega_0 t}e^{-i(\omega_2-\omega_1)t} + a^*(t)e^{-i\omega_0 t}\,[illegible]\,e^{-i(\omega_2-\omega_1)t}\right]$$

$$\dot{c}_1(t) = \frac{-i\mu_{12}}{2\hbar} c_2(t)\left[a(t)e^{i(\omega_0-\omega_{21})t} + a^*(t)e^{-i(\omega_0+\omega_{21})t}\,[illegible]\right]$$

$$\dot{c}_1(t) = \frac{-i\mu_{12}}{2\hbar} c_2(t)a(t)e^{i(\omega_0-\omega_{21})t} \qquad \dot{c}_2(t) = \frac{-i\mu_{21}}{2\hbar} c_1(t)a^*(t)e^{-i(\omega_0-\omega_{21})t}$$

$$c_1(t) = \frac{-i\mu_{12}}{2\hbar}\int c_2(t)a(t)e^{i(\omega_0-\omega_{21})t}dt \qquad c_2(t) = \frac{-i\mu_{21}}{2\hbar}\int c_1(t)a^*(t)e^{-i(\omega_0-\omega_{21})t}dt$$

$$\boxed{c_1(t) \cong 1} \qquad \boxed{c_2(t) = \frac{-i\mu_{21}}{2\hbar}\int a^*(t)e^{-i(\omega_0-\omega_{21})t}dt}$$

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And we can we can further simplify it and we can write down the expression for for c 1 like this where this mu 1 2 is nothing, but phi 1 mu phi 2 that is mu 1 2. So, what we see here is that this c 2 has been taken out. So, we do not have this c 2 anymore here and here also we have taken out this c 2 we do not have this c 2 here ok. (Please look at the slides for mathematical expressions)

So, we get the final expression like this, this is suggesting how the population in the first state is changing due to the interaction of matter with a short pulse and here we will take rotating wave approximation where we will approximately say that this we are almost in resonance with this phi naught and this is omega 2 1 is the difference this one this excitation they are they are almost in resonance with each other. And if they are almost resonance with each other then that the term which will contribute to this is going to be is going to be this c 2. (Please look at the slides for mathematical expressions)

And we are assuming here an unsaturation condition where we can approximately say that c 1 population does not change almost it remains to be the same. So, we are in the unsaturation limit and if we are in the unsaturation limit then we get the final expression for c 2. So, these two expression suggesting that in the ground state the first state and the second state we are creating a superposition state and we are saying that if we have a superposition state created by created by the excitation of our short pulse then we can say that the ground state population is remaining almost the same then that is why it is 1. (Please look at the slides for mathematical expressions)

But c 2 population is changing as a function of time this is unsaturation limit and c 2 c 2 population the sorry c 2 value will depend on this integral. So, this is an representation of how the population can build up the population can be build up in the x i the state as a function of time due to interaction within short pulse. (Please look at the slides for mathematical expressions)

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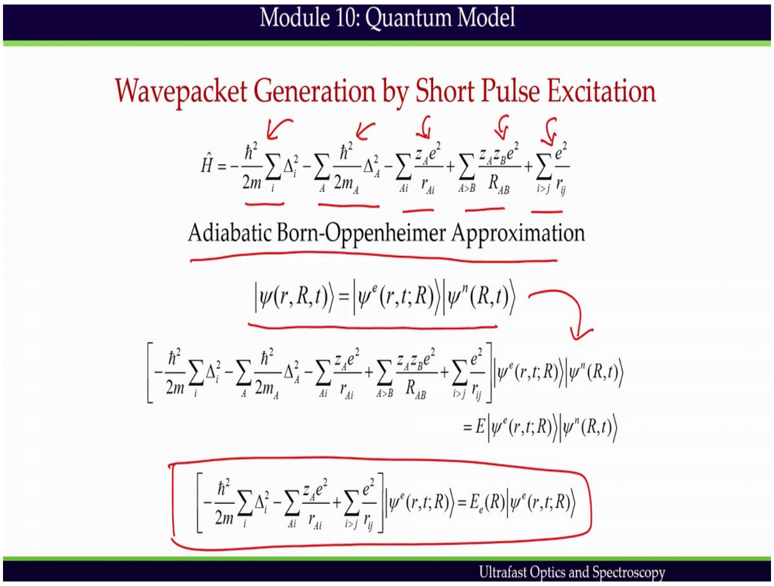

Module 10: Quantum Model

Wavepacket Generation by Short Pulse Excitation

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_i \Delta_i^2 - \sum_A \frac{\hbar^2}{2m_A}\Delta_A^2 - \sum_{Ai}\frac{z_A e^2}{r_{Ai}} + \sum_{A>B}\frac{z_A z_B e^2}{R_{AB}} + \sum_{i>j}\frac{e^2}{r_{ij}}$$

Adiabatic Born-Oppenheimer Approximation

$$|\psi(r,R,t)\rangle = |\psi^e(r,t;R)\rangle|\psi^n(R,t)\rangle$$

$$\left[-\frac{\hbar^2}{2m}\sum_i \Delta_i^2 - \sum_A \frac{\hbar^2}{2m_A}\Delta_A^2 - \sum_{Ai}\frac{z_A e^2}{r_{Ai}} + \sum_{A>B}\frac{z_A z_B e^2}{R_{AB}} + \sum_{i>j}\frac{e^2}{r_{ij}}\right]|\psi^e(r,t;R)\rangle|\psi^n(R,t)\rangle$$
$$= E|\psi^e(r,t;R)\rangle|\psi^n(R,t)\rangle$$

$$\boxed{\left[-\frac{\hbar^2}{2m}\sum_i \Delta_i^2 - \sum_{Ai}\frac{z_A e^2}{r_{Ai}} + \sum_{i>j}\frac{e^2}{r_{ij}}\right]|\psi^e(r,t;R)\rangle = E_e(R)|\psi^e(r,t;R)\rangle}$$

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Now, let us look at the creation of the wave packet. The Hamiltonian will be expressed explicitly in terms of nuclear contribution, electronic contributions all the contributions are included. So, here this one is electronic contribution, this one is nuclear contribution, this one is potential coming from interaction between nuclei and the electron this one is nuclear nuclei and this one is electron interactions.

And if we consider a adiabatic born Oppenheimer approximation where psi can be expressed as this is a is a product of nuclear wave function and electronic wave function, then if we plug that in we get this and we will be able to separate this 2 expression this is pure electronic with pure electronic component.

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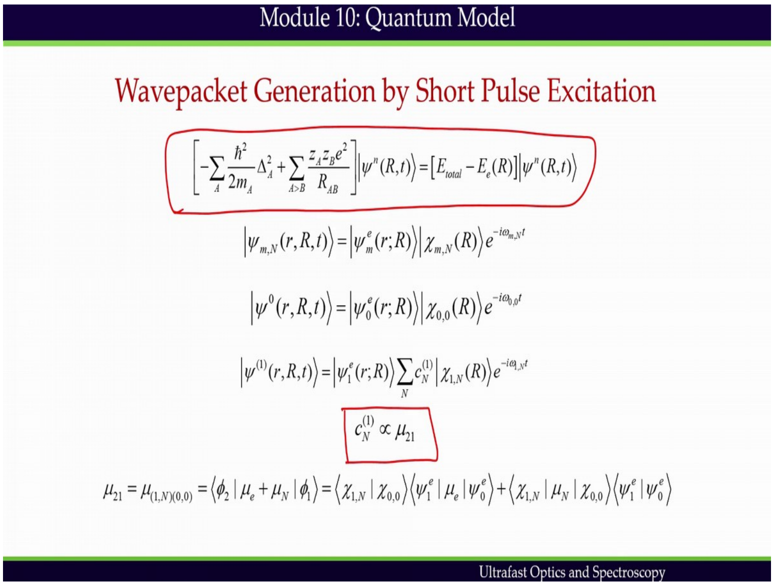

Module 10: Quantum Model

Wavepacket Generation by Short Pulse Excitation

$$\boxed{\left[-\sum_A \frac{\hbar^2}{2m_A}\Delta_A^2 + \sum_{A>B}\frac{z_A z_B e^2}{R_{AB}}\right]\left|\psi^n(R,t)\right\rangle = \left[E_{total} - E_e(R)\right]\left|\psi^n(R,t)\right\rangle}$$

$$\left|\psi_{m,N}(r,R,t)\right\rangle = \left|\psi_m^e(r;R)\right\rangle\left|\chi_{m,N}(R)\right\rangle e^{-i\omega_{m,N}t}$$

$$\left|\psi^0(r,R,t)\right\rangle = \left|\psi_0^e(r;R)\right\rangle\left|\chi_{0,0}(R)\right\rangle e^{-i\omega_{0,0}t}$$

$$\left|\psi^{(1)}(r,R,t)\right\rangle = \left|\psi_1^e(r;R)\right\rangle \sum_N c_N^{(1)}\left|\chi_{1,N}(R)\right\rangle e^{-i\omega_{1,N}t}$$

$$\boxed{c_N^{(1)} \propto \mu_{21}}$$

$$\mu_{21} = \mu_{(1,N)(0,0)} = \left\langle \phi_2 \mid \mu_e + \mu_N \mid \phi_1 \right\rangle = \left\langle \chi_{1,N} \mid \chi_{0,0}\right\rangle\left\langle \psi_1^e \mid \mu_e \mid \psi_0^e\right\rangle + \left\langle \chi_{1,N} \mid \mu_N \mid \chi_{0,0}\right\rangle\left\langle \psi_1^e \mid \psi_0^e\right\rangle$$

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And next one this is pure nuclear the contribution from nuclear motion. And if we then insert this contributions into the previous c N equation then we can say that this is proportional to mu 2 1 and that is an expression which we need to find that out and mu 2 1 expression is given.

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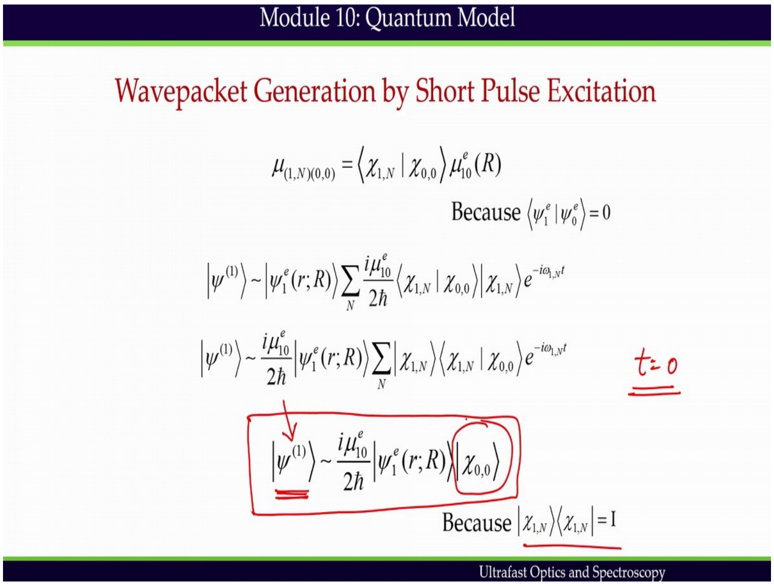

Module 10: Quantum Model

Wavepacket Generation by Short Pulse Excitation

$$\mu_{(1,N)(0,0)} = \left\langle \chi_{1,N} \mid \chi_{0,0}\right\rangle \mu_{10}^e(R)$$

Because $\left\langle \psi_1^e \mid \psi_0^e \right\rangle = 0$

$$\left|\psi^{(1)}\right\rangle \sim \left|\psi_1^e(r;R)\right\rangle \sum_N \frac{i\mu_{10}^e}{2\hbar}\left\langle \chi_{1,N} \mid \chi_{0,0}\right\rangle\left|\chi_{1,N}\right\rangle e^{-i\omega_{1,N}t}$$

$$\left|\psi^{(1)}\right\rangle \sim \frac{i\mu_{10}^e}{2\hbar}\left|\psi_1^e(r;R)\right\rangle \sum_N \left|\chi_{1,N}\right\rangle\left\langle \chi_{1,N} \mid \chi_{0,0}\right\rangle e^{-i\omega_{1,N}t}$$

$t=0$

$$\boxed{\left|\psi^{(1)}\right\rangle \sim \frac{i\mu_{10}^e}{2\hbar}\left|\psi_1^e(r;R)\right\rangle \boxed{\left|\chi_{0,0}\right\rangle}}$$

Because $\left|\chi_{1,N}\right\rangle\left\langle \chi_{1,N}\right| = \mathrm{I}$

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If we simply insert it and simplify the expression with the help of the identity operators like this we finally, get an expression for the excited state. What we get this expression for the excited state suggests that the excitation at 0 time. So, t equals 0 when just the interaction is happening at that time, the wave function which I have created is nothing, but the ground state wave function of the ground state nuclear wave function.

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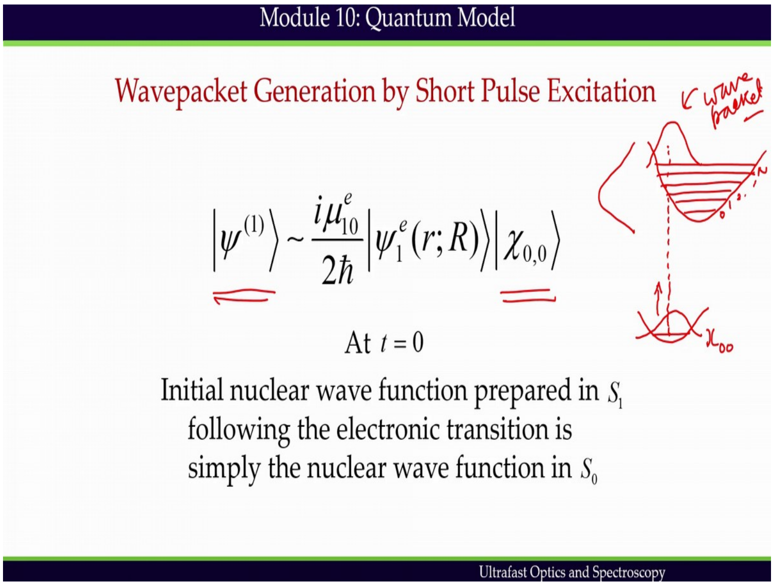

Module 10: Quantum Model

Wavepacket Generation by Short Pulse Excitation

$$\underline{\underline{|\psi^{(1)}\rangle}} \sim \frac{i\mu_{10}^{e}}{2\hbar}|\psi_1^{e}(r;R)\rangle\underline{\underline{|\chi_{0,0}\rangle}}$$

At $t = 0$

Initial nuclear wave function prepared in S_1 following the electronic transition is simply the nuclear wave function in S_0

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So, what does it suggest? And suggest that let us say at t equals 0 only. So, let us say I have the ground state which is represent ground electronic state and this vibrational state is represented by this chi 0 0 this vibrational state and we know that the wave function of this state is going to be if the simple harmonic oscillator, then its going to be and gaussian wave function. On the other hand we are exciting the system to the electronically excited state and with the help of an ultra fast pulse and in that state, we have a number of vibrational states and we have assumed that we have taken linear combination of n number of states here.

So, the final wave function how does it look like? It will be a superposition of all states n number of states we are considering 0 1 2 blah blah blah blah n number of states we are considering that. So, you are taking n number of linear combination and finally, if we take the n number of linear combination then this final wave function would look like just like the ground state wave function which means that this wave function would be coming on this surface only and this is called wave packet.

So, we have created a wave packet in the upper excited state due to excitation by an ultra fast pulse, this wave packet definitely could evolve in time why? Because it is a superposition wave packet is created due to superposition of different states and we know that the moment we create a superposition state it will definitely its density will definitely evolve with respect to time. How a web packet will evolve on the potential energy surface that is the part of discussion for wave packet dynamics which can be very interesting to learn although in this module we will not discuss that we will just end this module.

In this module we have studied we have represented quantum mechanical model which can be very suitable for understanding for the first time, understanding ultra fast spectroscopy and we have discussed how and wave packet is created and wave packet in a simple form is nothing. But when we undergo an electronic excitation with the help of an ultra fast pulse the wave packet we create is nothing, but the ground state wave function placing on the upper excited state. We will meet again for the next module.