Time Dependent Quantum Chemistry
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Lecture No. 04
Optical Analogy to Quantum Superposition

Welcome back to module 1 of the course time dependent quantum chemistry.

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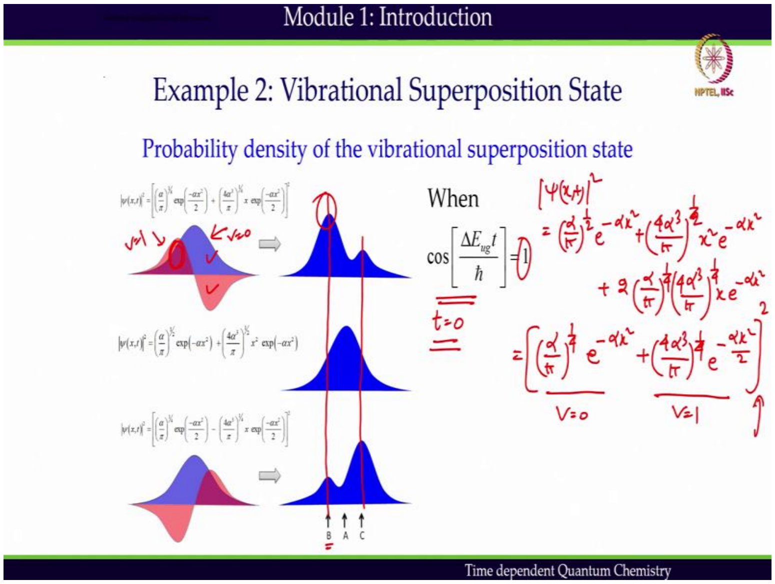


Module 1: Introduction

Example 2: Vibrational Superposition State

Probability density of the vibrational superposition state

$$|\psi(x,t)|^2 = \left[\left(\frac{\alpha}{\pi}\right)^{1/4}\exp\left(\frac{-\alpha x^2}{2}\right) + \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x \exp\left(\frac{-\alpha x^2}{2}\right)\right]^2$$

$$|\psi(x,t)|^2 = \left(\frac{\alpha}{\pi}\right)^{1/2}\exp(-\alpha x^2) + \left(\frac{4\alpha^3}{\pi}\right)^{1/2} x^2 \exp(-\alpha x^2)$$

$$|\psi(x,t)|^2 = \left[\left(\frac{\alpha}{\pi}\right)^{1/4}\exp\left(\frac{-\alpha x^2}{2}\right) - \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x \exp\left(\frac{-\alpha x^2}{2}\right)\right]^2$$

When

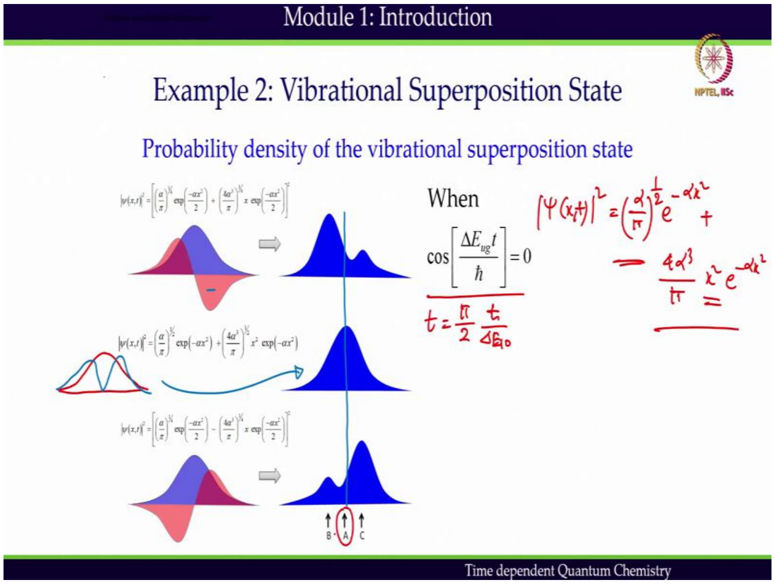
$$\cos\left[\frac{\Delta E_{ug} t}{\hbar}\right] = \boxed{1}$$

$t=0$

$$|\psi(x,t)|^2 = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} e^{-\alpha x^2} + \left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{2}} x^2 e^{-\alpha x^2} + 2\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}\left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{4}} x e^{-\alpha x^2}$$

$$= \left[\underbrace{\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\alpha x^2}}_{V=0} + \underbrace{\left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}}}_{V=1}\right]^2$$

Time dependent Quantum Chemistry



Module 1: Introduction

Example 2: Vibrational Superposition State

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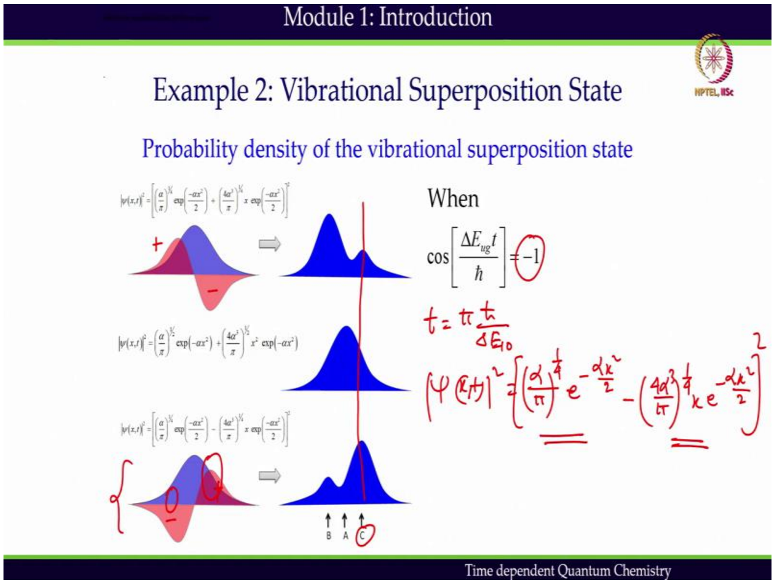
When

$$\cos\left[\frac{\Delta E_{ug} t}{\hbar}\right] = 0$$

$$t = \frac{\pi}{2}\frac{\hbar}{\Delta E_{10}}$$

$$|\psi(x,t)|^2 = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} e^{-\alpha x^2} + \frac{4\alpha^3}{\pi} x^2 e^{-\alpha x^2}$$

Time dependent Quantum Chemistry



Module 1: Introduction

Example 2: Vibrational Superposition State

NPTEL, IISc

Probability density of the vibrational superposition state

$$|\psi(x,t)|^2 = \left[\left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(\frac{-\alpha x^2}{2}\right) + \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x \exp\left(\frac{-\alpha x^2}{2}\right)\right]^2$$

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$$|\psi(x,t)|^2 = \left[\left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(\frac{-\alpha x^2}{2}\right) - \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x \exp\left(\frac{-\alpha x^2}{2}\right)\right]^2$$

When

$$\cos\left[\frac{\Delta E_{ug} t}{\hbar}\right] = -1$$

$$t = \pi \frac{\hbar}{\Delta E_{10}}$$

$$|\psi(x,t)|^2 = \left\{\underline{\underline{\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}}} e^{-\frac{\alpha x^2}{2}} - \underline{\underline{\left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{4}}}} x e^{-\frac{\alpha x^2}{2}}\right]^2$$

Time dependent Quantum Chemistry

We have been discussing vibrational superposition state, and we have shown that for the for cos equals cos function equals 1, which means that at t equals 0 at the beginning of the superposition, we have proved that the density will be localized or more at a particular point, which is we are defining as B point in the space.

And we will look at what will happen next, if we make the cos value 0 and if we make the cos value 0, it means that I have $t = \frac{\pi}{2}\frac{\hbar}{\Delta E_{10}}$. So, I have this

$$|\psi(x,t)|^2 = \left[\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} e^{-\alpha x^2} + \left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{2}} x^2 e^{-\frac{\alpha x^2}{2}}\right]^2$$

So, I have these two functions adding and if we add these two functions, what we have is that all would be positive.

And adding these two functions it means that I have all are square basically. So, I do not have I have this function, then I had another function, but it is no squared that is why it will not have any phase like this negative phase like this. So, and if we add them together, we finally, get this, which means that the density has now come maximum density has come to this middle point which is defined by A at this time.

Similarly, if we continue and use minus 1 value, which means that $t = \pi \frac{\hbar}{\Delta E_{10}}$ then what I get is that

$$|\psi(x,t)|^2 = \left[\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}} - \left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{4}} x e^{-\frac{\alpha x^2}{2}} \right]^2$$

It suggests that first we have to subtract these two wave functions.

So, now, we are subtracting this to a function that is why you have changed phase previously here the phase was positive and negative here. Now, we have negative here positive here and we are subtracting, If we subtract it, then what will happen? This two needs to be added now. And if we add them, then clearly this portion of the wave function will be magnified and this portion will be destructively interfering and that is why we have now total density move to maximum density has moved to the position C.

So, what we see from this time dependent change in the density the position of the atom, we see that the density is changing from B position to A position to C and again it will be oscillatory. So, C will come back to A and B and this is the way density is changing and that is exactly manifesting the molecular vibration. So, coherence has now allowed to observe the change in density as a function of time, which can be experimentally observed.

The same frequency with the same frequency of the molecular vibration, but if it was staying at V equals 0 state that was a stationary state, there is no way we could observe this change in density or this frequency of vibration. So, coherence has a beautiful effect in the experiment and one can make use of the coherence to observe certain thing which cannot be observed if it is in stationary state.

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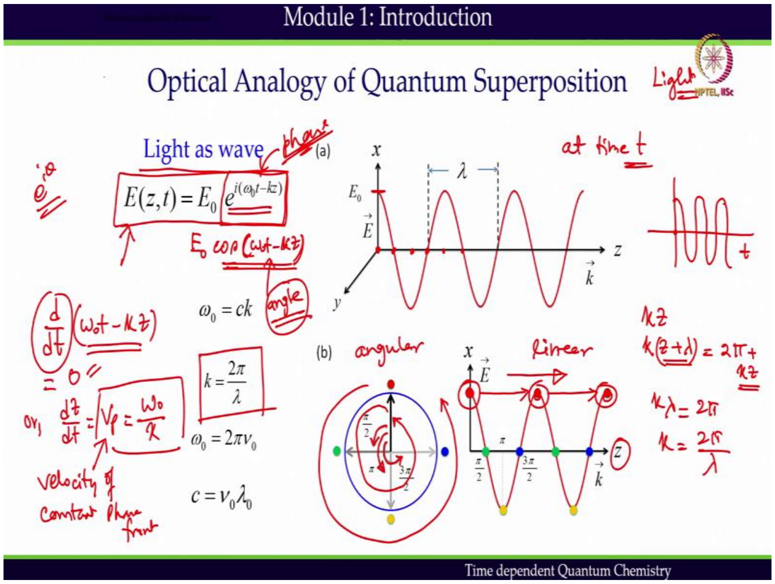

Module 1: Introduction

Optical Analogy of Quantum Superposition

Light as wave

$$\boxed{E(z,t) = E_0 \boxed{e^{i(\omega_0 t - kz)}}}$$

$$E_0 \cos(\omega_0 t - kz)$$

$$\omega_0 = ck$$

$$\boxed{k = \frac{2\pi}{\lambda}}$$

$$\omega_0 = 2\pi \nu_0$$

$$c = \nu_0 \lambda_0$$

$$\frac{d}{dt}(\omega_0 t - kz) = 0$$

$$\text{or, } \frac{dz}{dt} = \boxed{V_p = \frac{\omega_0}{k}}$$

velocity of constant phase front

$$kz$$

$$k(z+\lambda) = 2\pi + kz$$

$$k\lambda = 2\pi$$

$$k = \frac{2\pi}{\lambda}$$

Time dependent Quantum Chemistry

So, far we have talked about quantum superposition and there is a in optics, often we talk about superposition and by taking superposition of optical waves, that is the plane wave, we can create the pulse and often we discuss that pulse and it is important to introduce that immediately because very soon the superposition state quantum superposition state which is nothing but a wave packet we will be discussing wave packet and getting an idea from optical interference can help us understand better what does it mean by the wave packet in its propagation.

Light has dual nature when light exhibits wave nature it propagates as an electromagnetic wave. On the other hand, when light is a particle, we consider is propagating as a particle. So, life has a dual character, the kind of character we are considering here is the wave character of light. So, light as a wave we have to see and that moment we see light as a wave, we express its electric field in this following form.

Here also just like wave function, we see that there is a phase factor the temporal and spatial phase factor, which is nothing but $e^{i\theta}$ kind of an expression phase factor. And once we see that phase factor, we understand that it is changing the phase as a function of time all the time. This is complex notation in real notation, one can express as $E_0 \cos(\omega_0 t - kz)$ it this is the real part, and this is an oscillatory part.

So, maximum field strength is oscillating as a function of space and time. So, this this is a picture which is taken at a time, let us say, t freeze that time at a particular time. Suddenly, if we think that we are used to magnetic wave propagating through space, and at a particular time I would like to know, how the field strengths are as a function of distance we see that at this distance field strength is maximum and this distance field strength is 0, at this distance field strength is maximum, but in the opposite direction.

At this distance field strength is 0. And so on like this way, field strength distributions are. Similar pattern can be observed for time at a particular distance at a particular point of space. If I try to plot the how electric field is changing as a function of time, this is also similar way different time at a particular point its field strength is changing and that is the manifestation. We are talking about electric field because generally electromagnetic wave has both electric fields and magnetic fields, but magnetic field strength is weaker than electric field.

And that is why we are neglecting magnetic field strain field oscillation here, we are only considering the electric field oscillation. Now, when something is propagating, there is a very easier way to consider so this this phase factor is nothing but $\cos(\omega t)$ and cos within bracket everything should be angle this is going to be an angle. So, what we can do is that when electromagnetic wave is propagating in a linear space, we can represent its propagation in a circular dial that can be used and that is the way this angle the phase angle will be defined.

For an example here we are starting from here at this point, and then when we reach so basically from here to here, when we reach here, we make an advancement linear advancement, but angular advancement made by $\pi/2$ from here to here, when you go there, in this linear scale, we make another angle advancement which is π, and when we come here, from this point to this point, we make $\frac{3}{2}\pi$ angular advancement. On the other hand, when you come back here, it is the 2π angular advancement we create. So, this linear motion is linear advancement and angular advancement they are correlated and how it is correlated that is something which I am going to show here this k z is the term which is controlling the linear advancement. So, if I advance $z+\lambda$ wavelength total wavelength, then angular advancement would be 2π + k z.

$$k(z+\lambda) = 2\pi + kz$$

$$k\lambda = 2\pi$$

$$k = \frac{2\pi}{\lambda}$$

These are the relations which are important for all this plane waves. And as I mentioned before that $\omega_0 t - kz$ this part is called the phase of the electric field.

And that is very important phase is very important physical quantity, it is important physical quantity because, if you think about this phase red one color represented by the red color, we see that this red color is repeating after a certain distance again is repeating. Which means that let us say I am in a space light is propagating through the medium when light propagates through the medium, electric field is oscillating in the medium, and we have somehow managed to find out a red color light which will be turned on whenever the electric field is maximum.

Which means that I am collecting the phase this one, this one and this one. So, red color will be blink, after certain time red color blink, after certain time red color blink and question is with what velocity this whole thing is propagating? We can find out by taking the constant phase front you see, the phase front here is repeating so, it is constant phase front and if I take the constant phase front, it means that the time derivative of that phase $(\omega_0 t - kz)$ it is actually time wave length at the phase that is going to be 0.

$$\frac{d}{dt}(\omega_0 t - kz) = 0$$

$$\frac{dz}{dt} = V_p = \frac{\omega_0}{k}$$

Or in other words, dz/dt that is the velocity that is called phase velocity of the constant phase front velocity of constant phase front that is V_p equals nothing but $\frac{\omega_0}{k}$. So, this is the way we define the velocity. This is an important concept we have developed the how we define the velocity of a plane wave or light plane wave of the velocity is related to the phase that is the phase given here.

So, I have been telling that phase is an important concept phase has information of the velocity. How do you get that velocity information? It is the constant phase front velocity. That is why the phase is taken to be constant and with respect to time, derivative of a constant is going to be always 0 and that is the way we find out the phase velocity. So, this concept will be used very soon in the superposition.

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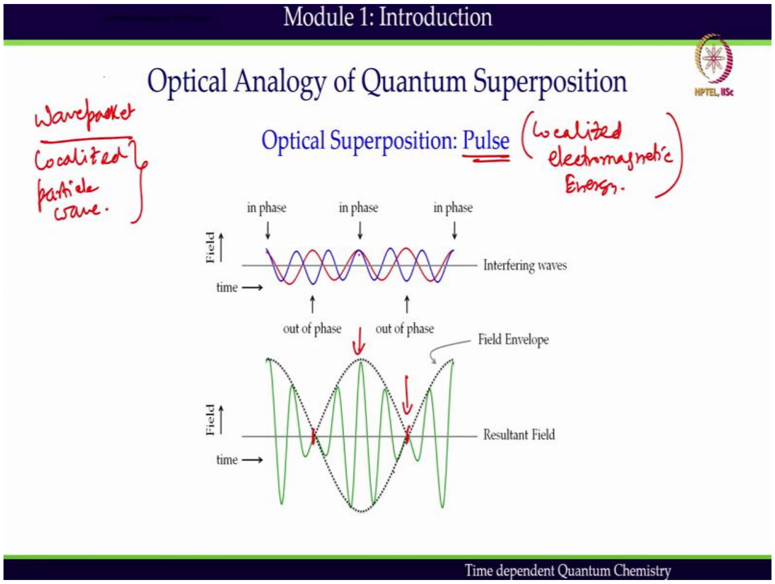
Module 1: Introduction

Optical Analogy of Quantum Superposition

Optical Superposition: Pulse (localized electromagnetic Energy.)

Wavepacket

Localized particle wave.

Time dependent Quantum Chemistry

Optical superposition which creates the pulse localized electromagnetic energy, wave packet on the other hand it is the localized particle wave.

So, this is a two conceptually different, but they have very close similarity and how do you create that, we create optical superposition by considering two slightly different frequency components, they are interfering with each other and there are places where they will be interfering constructively, they are places where they will be constantly destructively interfering in the end, the final pulse should look like this. A pulse, which is localized electromagnetic energy in space.

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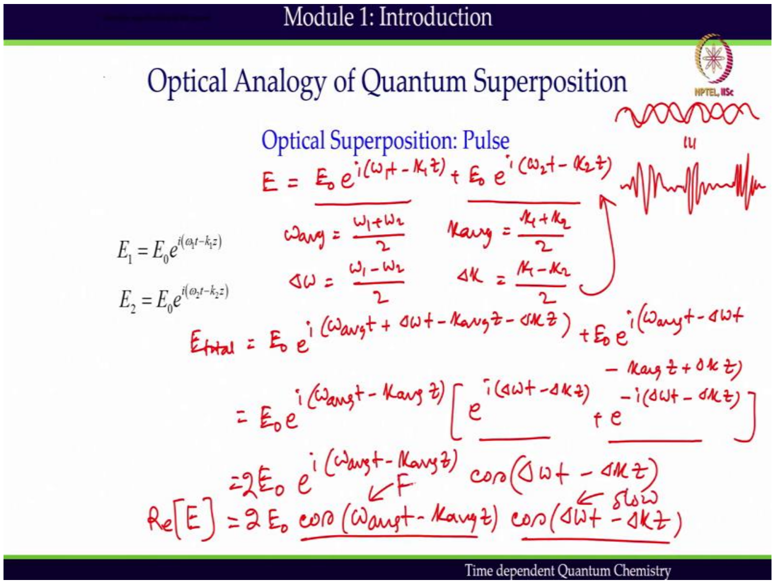

Module 1: Introduction

Optical Analogy of Quantum Superposition

Optical Superposition: Pulse

$$E = \underline{E_0 e^{i(\omega_1 t - k_1 z)}} + \underline{E_0 e^{i(\omega_2 t - k_2 z)}}$$

$$E_1 = E_0 e^{i(\omega_1 t - k_1 z)}$$

$$E_2 = E_0 e^{i(\omega_2 t - k_2 z)}$$

$$\omega_{avg} = \frac{\omega_1 + \omega_2}{2} \qquad k_{avg} = \frac{k_1 + k_2}{2}$$

$$\Delta\omega = \frac{\omega_1 - \omega_2}{2} \qquad \Delta k = \frac{k_1 - k_2}{2}$$

$$E_{total} = E_0 e^{i(\omega_{avg} t + \Delta\omega t - k_{avg} z - \Delta k z)} + E_0 e^{i(\omega_{avg} t - \Delta\omega t - k_{avg} z + \Delta k z)}$$

$$= E_0 e^{i(\omega_{avg} t - k_{avg} z)} \left[\underline{e^{i(\Delta\omega t - \Delta k z)}} + \underline{e^{-i(\Delta\omega t - \Delta k z)}} \right]$$

$$= 2E_0 e^{i(\omega_{avg} t - k_{avg} z)} \cos(\Delta\omega t - \Delta k z)$$

F

slow

$$Re[E] = 2E_0 \underline{\cos(\omega_{avg} t - k_{avg} z)} \, \underline{\cos(\Delta\omega t - \Delta k z)}$$

Time dependent Quantum Chemistry

And when we look at this, the optical pulse creation, we will be able to define it because electric field total electric field will be defined in following way total electric field is

$$E = E_0 e^{i(\omega_1 t - k_1 z)} + E_0 e^{i(\omega_2 t - k_2 z)}$$

Two electric fields two plane wave propagating along the same direction, but they have slightly different frequency and how the total electric field is changing.

So, this is equivalent to or creating a pulse like this is. So, we are considering only two electric fields. And if we define now,

$$\omega_{avg} = \frac{\omega_1 + \omega_2}{2}$$

$$k_{avg} = \frac{k_1 + k_2}{2}$$

$$\Delta\omega = \frac{\omega_1 - \omega_2}{2}$$

$$\Delta k = \frac{k_1 - k_2}{2}$$

If we do that, then I will be able to plug that in here.

And I will be able to express this total electric field as

$$E_{total} = E_0 e^{i(\omega_{avg} + \Delta\omega t - k_{avg} z - \Delta kz)} + E_0 e^{i(\omega_{avg} - \Delta\omega t - k_{avg} z + \Delta kz)}$$

If we simplify it to some extent, we will be able to get this

$$E_{total} = E_0 e^{i(\omega_{avg} - k_{avg} z)} \left[e^{i(\Delta\omega t - \Delta kz)} + e^{-i(\Delta\omega t - \Delta kz)} \right]$$

This is complex conjugate of each one.

$$E_{total} = 2E_0 e^{i(\omega_{avg} - k_{avg} z)} \cos(\Delta\omega t - \Delta kz)$$

So, and if we take the real part of it

$$\mathrm{Re}(E_{total}) = 2E_0 \cos(\omega_{avg} - k_{avg} z) \cos(\Delta\omega t - \Delta kz)$$

We get two different oscillation one is slowly varying one another one is fast varying component.

ω_{avg} is higher frequency so, fast varying component very quickly changing $\Delta\omega$ I told you that the frequencies are very small difference. So, $\Delta\omega$ is going to be very small and that is why this is going to be your slow varying component. This is going to be a fast varying component.

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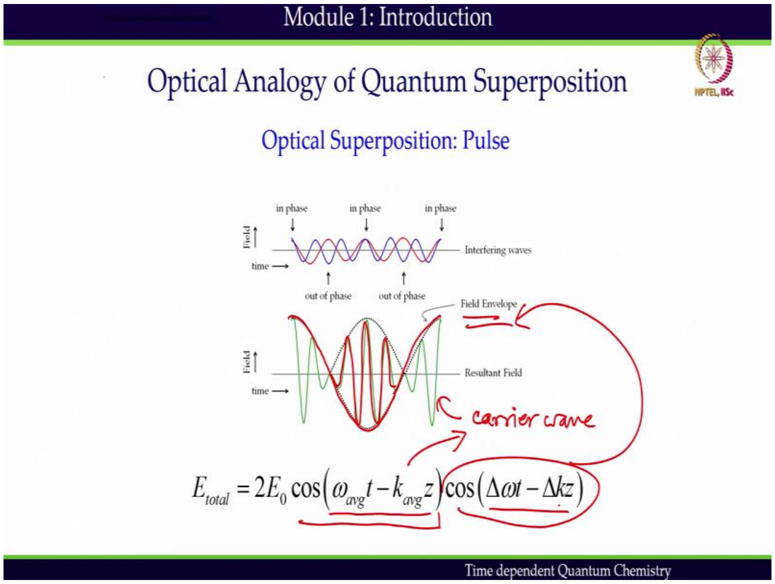

Module 1: Introduction

Optical Analogy of Quantum Superposition

Optical Superposition: Pulse

$$E_{total} = 2E_0 \cos\left(\omega_{avg} t - k_{avg} z\right) \cos\left(\Delta\omega t - \Delta kz\right)$$

Time dependent Quantum Chemistry

So, there are two with the variations we see and that is exactly as shown here. This one is slowly varying component which is defining the field envelope, but this one is fast varying component which is defining the result in the carrier wave this is called carrier wave. So, this part is carrier wave and the slow part is defining the envelope part. And if we look at these two, then it is clear that for a pulse I have because two different phases, the phase is defined by this part and this part.

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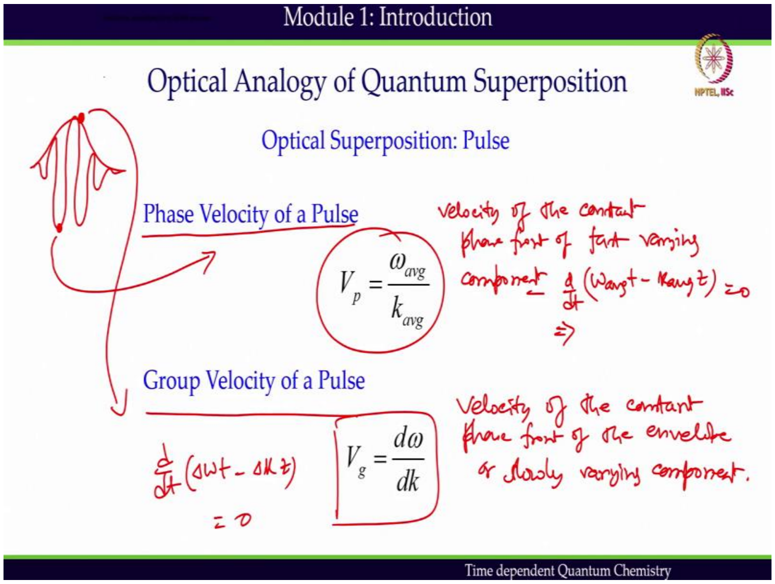

Module 1: Introduction

Optical Analogy of Quantum Superposition

Optical Superposition: Pulse

Phase Velocity of a Pulse

$$\boxed{V_p = \frac{\omega_{avg}}{k_{avg}}}$$

velocity of the contant phase front of fast varying component $\frac{d}{dt}(\omega_{avg}t - k_{avg}z) = 0$

$\Rightarrow$

Group Velocity of a Pulse

$\frac{d}{dt}(\Delta\omega t - \Delta k z) = 0$

$$\boxed{V_g = \frac{d\omega}{dk}}$$

Velocity of the contant phase front of the envelope or slowly varying component.

Time dependent Quantum Chemistry

So, two different phases will be defining two different velocities again velocity will be defined. So, phase velocity of the pulse will be defined by the velocity of the constant phase front of fast varying component. How can I get that? Clearly, I had phase $(\omega_{avg} - k_{avg} z)$ this is the phase I take the first derivative to be 0. If I take first derivative constant phase front will repeat that is why first derivative is 0, it is the phase it is the velocity of the constant phase front.

So, if I take that, then I get the phase velocity

$$V_p = \frac{\omega_{avg}}{k_{avg}}$$

on the other hand group velocity of the pulse what does it mean? It means the velocity of the constant phase front of the envelope or slowly varying component. For that I will take the first derivative of this one this phase to be 0 and we get this group velocity.

$$V_g = \frac{d\omega}{dk}$$

So, what does it mean phase velocity and group velocity is that when I have a pulse, I have an envelope function slowly varying envelop function and I have the fast varying components which is called the carrier wave.

Both are actually propagating through the medium question is what is the velocity of this envelope function and what is the velocity of this carrier wave these two components are different and these two components will have independent velocities. So, sometimes it may have been that they are together they have the same velocity, sometimes it may so, happen that they have different velocity that is why one is proceeding quickly than the other.

So, I will plot this pulse one more time this oscillation is moving through the phase velocity, but this one which is part of the envelope function going through group velocity collectively, what is the velocity they are moving forward individual average component how they are moving forward. So, these are the two components, it is very important, and we will be using these kind of concepts very soon in wave packet dynamics in the later different modules.

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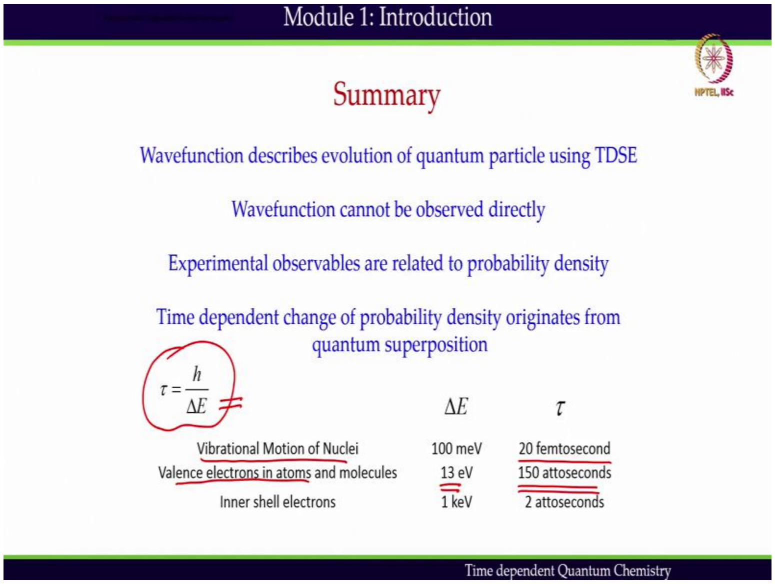

Module 1: Introduction

Summary

Wavefunction describes evolution of quantum particle using TDSE

Wavefunction cannot be observed directly

Experimental observables are related to probability density

Time dependent change of probability density originates from quantum superposition

$\tau = \frac{h}{\Delta E}$

	ΔE	τ
Vibrational Motion of Nuclei	100 meV	20 femtosecond
Valence electrons in atoms and molecules	13 eV	150 attoseconds
Inner shell electrons	1 keV	2 attoseconds

Time dependent Quantum Chemistry

We have come to the end of this module. In this module, we have introduced time dependence Schrodinger equation we have tried to understand the meaning of wave function, we have tried to understand what you observe experimentally that is the density which you observe and in order to observe the density I need to see time dependent density which is nothing but the superposition state.

So, if a particle staying in a stationary state, its wave function is time dependent, but its density is not time dependent and that is why it is stationary state. In order to observe quantum dynamics I need to have superposition state and further for absorbing superposition state one key information the time versus ΔE this is inversely proportional to each other.

So, if I create a superposition state or vibrational superposition state because vibrational spacing is very small, it is time would be much longer, longer than the electronic superposition state. Electronic superposition state delta is much larger. And that is why it is much faster timescale of the density oscillation we should observe. So, with this we will end this module, we will continue discussion of time dependent quantum chemistry in next module.