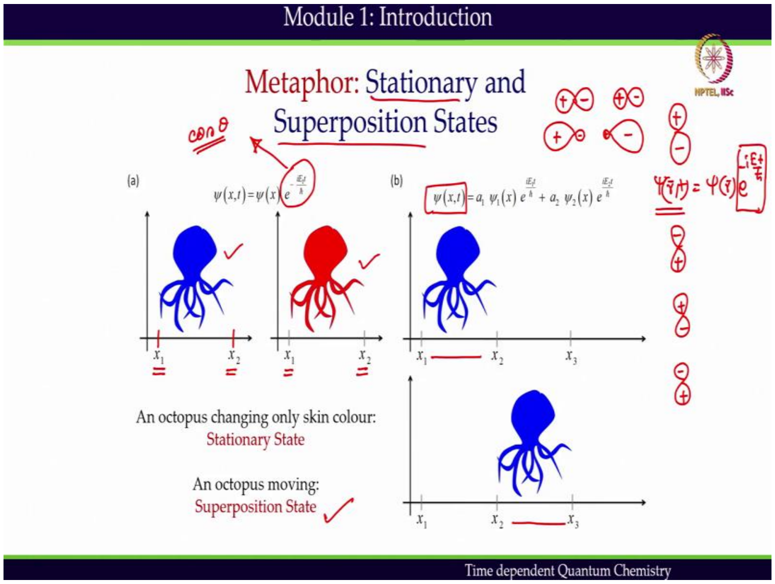
Time Dependent Quantum Chemistry
Professor. Atanu Bhattacharya
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bengaluru
Lecture No. 03
Electron and Vibrational Superposition States

Welcome back to module 1, we have discussed a time dependence Schrödinger equation and then with the help of variable separation method, we have been able to get them wave function. We have got the idea of stationary state and superposition state. Superposition state is absolutely needed to observe the temporal change in the probability density, which is all about the quantum dynamics. Because that is the only way we can observe the motion of quantum particle.

(Refer Slide Time: 00:55)



Module 1: Introduction

Metaphor: Stationary and Superposition States

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

(b) $\psi(x,t)=a_1\,\psi_1(x)\,e^{-\frac{iE_1t}{\hbar}}+a_2\,\psi_2(x)\,e^{-\frac{iE_2t}{\hbar}}$

An octopus changing only skin colour: Stationary State

An octopus moving: Superposition State ✓

$\Psi(\vec{r},t)=\Psi(\vec{r})e^{-\frac{iEt}{\hbar}}$

Time dependent Quantum Chemistry

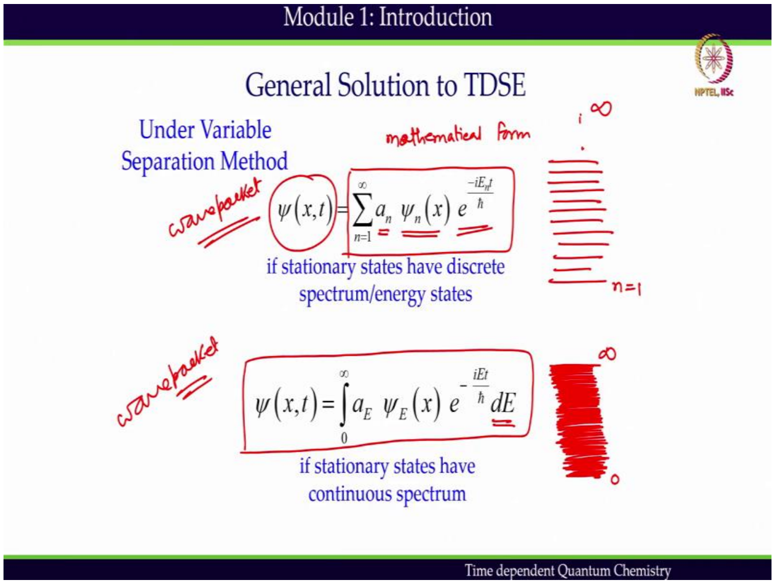
Now, we have said that the phase is very important factor. And, because phase is an important factor, let us say I give an example here, p orbital, we often express as positive and negative lobes like this way. Now, if I consider this p orbital and express the orbital, the wave function total wave function, then I would express like this way, it is going to be this is 3 dimensional. So, instead of x I will consider r here as vector and x I will consider r here.

And then its characteristic phase factor $e^{-\frac{iEt}{\hbar}}$. So, what it suggests that if I, if I try to observe, it is with function p orbital wave function, and somehow if I can manage to get how does it look like as a function of time, I will see that after a certain time, it has changed its phase, again, after a certain time, it has changed its phase again, after certain time it change its phase. But total density does not change. And that is the meaning of the stationary state.

This phase becomes important when we talk about combining two different wave functions for an example we know that this wave function if they are combining like this way, so they do not combine because of this negative and positive phase. They do not combine and that is why they form kind of anti-bonding state and bonding state is just the reverse one.

So, phase becomes very important phase is a physical quantity, which describes it is the wave function motion. But its density may not depend on that phase, unless we create the superposition state.

(Refer Slide Time: 03:09)



Module 1: Introduction

General Solution to TDSE

Under Variable Separation Method

$$\psi(x,t) = \sum_{n=1}^{\infty} a_n \, \psi_n(x) \, e^{\frac{-iE_n t}{\hbar}}$$

if stationary states have discrete spectrum/energy states

$$\psi(x,t) = \int_0^{\infty} a_E \, \psi_E(x) \, e^{-\frac{iEt}{\hbar}} dE$$

if stationary states have continuous spectrum

Time dependent Quantum Chemistry

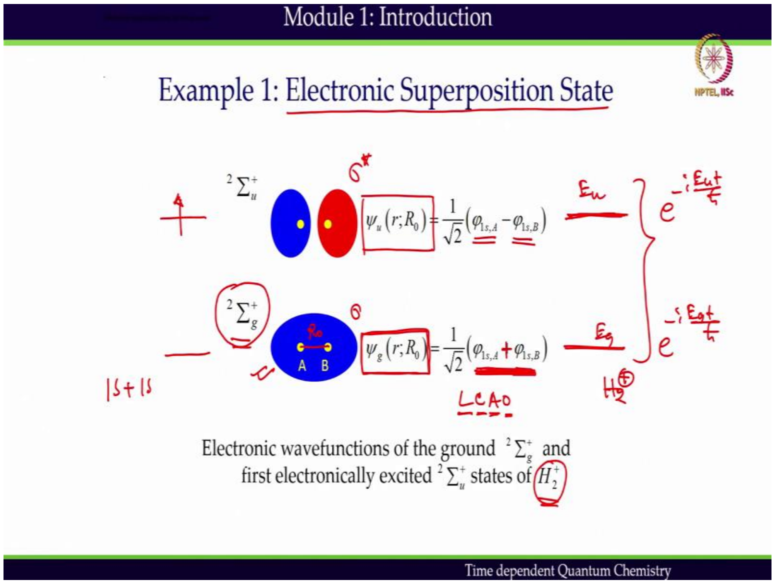
We after having understood this ideas, one can now introduce more rigorous mathematical definition of the wave function, the time dependent wave function. Obviously, it is going to be a superposition wave function because that is exactly where we are interested in quantum dynamics, it has to be superposition state and or it has to be a wave packet. And the wave packet more general mathematical form is going to be this is expansion coefficient, it is time independent part and the time dependent phase factor.

We are adding them infinite number of states if the states are discrete, like this, we can start from n equals 1 to infinite number of states, we can add them together and form this wave packet. This kind of mathematical expression, what is the origin of such superposition that we have described without superposition will not be able to see the change in density. So, anything in relevant in quantum dynamics which is practically relevant or which can be used for to observe experimental quantities, that is related to this kind of wave packet.

And if the states are continuous, like I cannot distinguish all the states are available kind of continuous states, then I can use this integration directly. This is called continuous state in some kind of continuum let us say. So, in that case, I will be able to integrate from 0 to infinite over this dE states.

So, these are the two more mathematically rigorous definition of the superposition states or wave packet. We will use this kind of expression later for the mathematical derivation, but the origin of such equation comes from those two state superposition states we have discussed in the earlier session.

(Refer Slide Time: 05:34)



Module 1: Introduction

Example 1: Electronic Superposition State

$^2\Sigma_u^+$ $\quad \psi_u(r;R_0) = \frac{1}{\sqrt{2}}(\varphi_{1s,A} - \varphi_{1s,B})$

$^2\Sigma_g^+$ $\quad \psi_g(r;R_0) = \frac{1}{\sqrt{2}}(\varphi_{1s,A} + \varphi_{1s,B})$

Electronic wavefunctions of the ground $^2\Sigma_g^+$ and first electronically excited $^2\Sigma_u^+$ states of H_2^+

Time dependent Quantum Chemistry

The real test of understanding what is going on is to solve some of the problems and in next two examples will be given one is electronic superposition state how do we create electronic superposition state and another one will be given vibrational superposition states. So, we will start with electronics superposition state we will start with this example of H_2^+, when H_2 makes bond it actually coming from A and B we have given to visit to designate the particular hydrogen atom.

So, two 1s orbitals, they linearly combined together this is called LCAO method linear combination of atomic orbital this linear combination of atomic orbitals when they combine positively they form this sigma bond and this sigma state is because it is an one electron system, this ground state can be represented by this where R_0 is the distance between this two atoms is two atoms hydrogen atoms.

We have fixed it at a particular fixed R_0 we have linearly combine two atomic orbitals one is from each orbital and we get the ground state wave function of that H_2^+ system. And the ground state wave function has a symmetric symmetry notation and that is given by ${}^2\sum_g^+$. Group theory is related and using group theory one can find out how to give the symmetry nomenclature of a particular electronic state.

This is not the scope of this course. So, we will not go over that part, we will assume that we understand how to give the name the symmetry notation for a particular electronic state. So, ground state has this symmetry and excited state. So, basically what is going on I have 1 electron so, electron can stay here, if electron is staying here I get ground state if electronic staying in the is here, then I get 1 excited state.

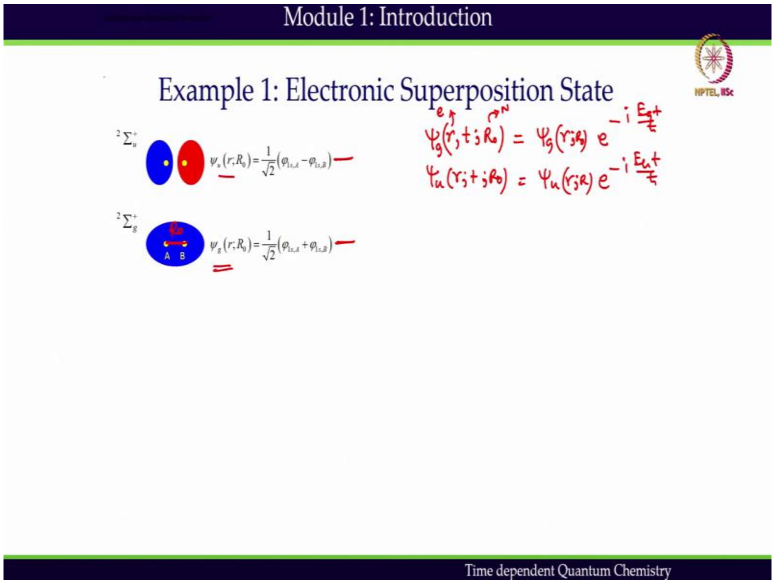
And that excited state is nothing but the anti-bonding, sigma anti-bonding orbital which is given by negative combination of these 2, 1 is orbitals again and this is given by this wave function. So, there are two wave functions I have right now, to electronic states I have one here one here, both states and H_2^+, can stay here H_2^+ can stay here also.

If H_2^+ is staying only in this state that is called stationary state. If H_2^+ is staying only in the excited state excited electronic state that is also stationary state. But somehow, if I managed to create a superposition state linearly combining both states what will happen? Interesting thing will show up.

Now, how do we create such a superposition state, that is a different question we can use some kind of laser photoexcitation which can simultaneously excite these two states together that is possible, but that is not the discussion point of discussion here. The point of discussion here is we create the superposition state by linearly combining these two electronic states. So, if we linearly combine these two electronic states, then what will happen?

Here I will mention that LCAO is also linear combination of two atomic orbitals. But, there is a difference between superposition state and LCAO scheme. LCAO scheme does not include the temporal phase factors of individual atom. So, superposition state, the superposition scheme is different from LCAO scheme in supervision scheme we have two states we will linearly combine these two states with its characteristic phase factor, phase factor is going to be $e^{-\frac{iE_g t}{\hbar}}$ and this one is going to be $e^{-\frac{iE_u t}{\hbar}}$ its corresponding energy is E_g here is E_g and E_g and this is E_u. So, we will consider those corresponding phase factor and then linearly combine it.

(Refer Slide Time: 10:26)



Module 1: Introduction

Example 1: Electronic Superposition State

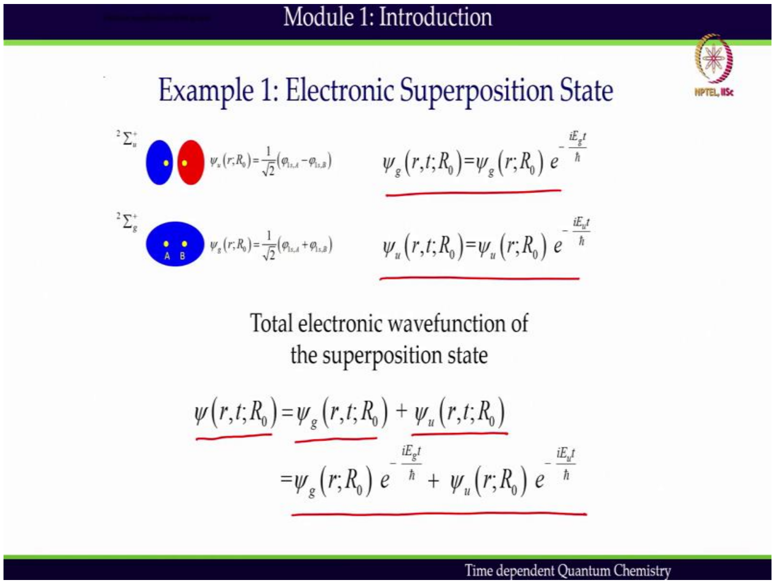
$^2\Sigma_u^+$ $\psi_u(r;R_0)=\frac{1}{\sqrt{2}}(\varphi_{1s,A}-\varphi_{1s,B})$

$^2\Sigma_g^+$ $\psi_g(r;R_0)=\frac{1}{\sqrt{2}}(\varphi_{1s,A}+\varphi_{1s,B})$

$$\psi_g(\overset{e}{r},t;\overset{N}{R_0}) = \psi_g(r;R_0)\, e^{-i\frac{E_g t}{\hbar}}$$

$$\psi_u(r;t;R_0) = \psi_u(r;R)\, e^{-i\frac{E_u t}{\hbar}}$$

Time dependent Quantum Chemistry



Module 1: Introduction

Example 1: Electronic Superposition State

$^2\Sigma_u^+$ $\psi_u(r;R_0)=\frac{1}{\sqrt{2}}(\varphi_{1s,A}-\varphi_{1s,B})$

$^2\Sigma_g^+$ $\psi_g(r;R_0)=\frac{1}{\sqrt{2}}(\varphi_{1s,A}+\varphi_{1s,B})$

$$\psi_g(r,t;R_0)=\psi_g(r;R_0)\, e^{-\frac{iE_g t}{\hbar}}$$

$$\psi_u(r,t;R_0)=\psi_u(r;R_0)\, e^{-\frac{iE_u t}{\hbar}}$$

Total electronic wavefunction of the superposition state

$$\psi(r,t;R_0)=\psi_g(r,t;R_0)+\psi_u(r,t;R_0)$$

$$=\psi_g(r;R_0)\, e^{-\frac{iE_g t}{\hbar}}+\psi_u(r;R_0)\, e^{-\frac{iE_u t}{\hbar}}$$

Time dependent Quantum Chemistry

What we will have is following I have this two states and I can write down because these two states are stationary states, I can write down it is time dependent states as $\psi_g(r,t;R_0)$, then semicolon R_0 when I say semicolon, it means that $R_0$is constant internuclear distance has been kept constant and r is the is representing the electronic coordinate and R_0 is representing nuclear coordinate which is kept to be fixed.

So, that time dependent wave functions can be written as

$$\psi_g(r,t;R_0) = \psi_g(r;R_0)e^{-\frac{iE_g t}{\hbar}}$$

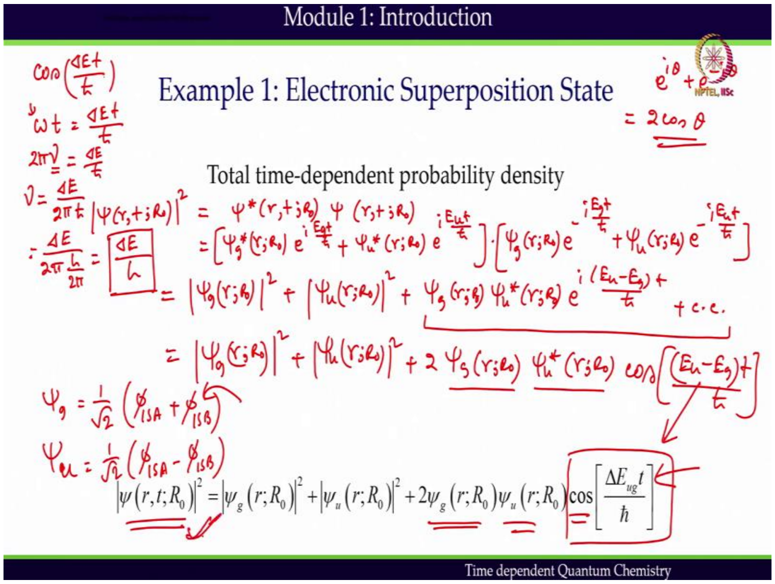
Similarly, the excited state time dependent wave function can be written as with its corresponding phase factor.

$$\psi_u(r,t;R_0) = \psi_u(r;R_0)e^{-\frac{iE_u t}{\hbar}}$$

So, we have assumed that this inter nuclear distance does not change it is kept to be constant, the equilibrium geometry R_0, we have kept it constant.

And so, what we will do is that we will create the superposition state right now, and the superposition state we will create by taking the total electronic wave function of the solution state is given by linearly combining these two states. These two states we have already written and if we linearly combine them, we get this wave function we create this wave function. Now, all we need to do is that this wave function is not an important thing we have to find out the density because in the end we have to check how the density is changing.

(Refer Slide Time: 12:39)



Module 1: Introduction

Example 1: Electronic Superposition State

$$\cos\left(\frac{\Delta E t}{\hbar}\right)$$

$$\omega t = \frac{\Delta E t}{\hbar}$$

$$2\pi\nu = \frac{\Delta E}{\hbar}$$

$$\nu = \frac{\Delta E}{2\pi\hbar} = \frac{\Delta E}{2\pi\frac{h}{2\pi}} = \boxed{\frac{\Delta E}{h}}$$

$$e^{i\theta}+e^{-i\theta} = 2\cos\theta$$

Total time-dependent probability density

$$|\psi(r,t;R_0)|^2 = \psi^*(r,t;R_0)\,\psi(r,t;R_0)$$

$$= \left[\psi_g^*(r;R_0)e^{i\frac{E_g t}{\hbar}} + \psi_u^*(r;R_0)e^{i\frac{E_u t}{\hbar}}\right]\cdot\left[\psi_g(r;R_0)e^{-i\frac{E_g t}{\hbar}} + \psi_u(r;R_0)e^{-i\frac{E_u t}{\hbar}}\right]$$

$$= |\psi_g(r;R_0)|^2 + |\psi_u(r;R_0)|^2 + \underbrace{\psi_g(r;R_0)\,\psi_u^*(r;R_0)\,e^{i\frac{(E_u-E_g)t}{\hbar}} + c.c.}$$

$$= |\psi_g(r;R_0)|^2 + |\psi_u(r;R_0)|^2 + 2\,\underline{\psi_g(r;R_0)}\;\underline{\psi_u^*(r;R_0)}\cos\left[\frac{(E_u-E_g)t}{\hbar}\right]$$

$$\psi_g = \frac{1}{\sqrt{2}}(\phi_{1SA}+\phi_{1SB})$$

$$\psi_u = \frac{1}{\sqrt{2}}(\phi_{1SA}-\phi_{1SB})$$

$$|\psi(r,t;R_0)|^2 = |\psi_g(r;R_0)|^2 + |\psi_u(r;R_0)|^2 + 2\psi_g(r;R_0)\psi_u(r;R_0)\boxed{\cos\left[\frac{\Delta E_{ug}t}{\hbar}\right]}$$

Time dependent Quantum Chemistry

So, I will write down the density expression here

$$|\psi(r,t;R_0)|^2 = \psi^*(r,t;R_0)\psi(r,t;R_0)$$

which is nothing but

$$= \left[\psi_g^*(r;R_0)e^{-\frac{iE_g t}{\hbar}} + \psi_u^*(r;R_0)e^{-\frac{iE_u t}{\hbar}}\right]\cdot\left[\psi_g(r;R_0)e^{\frac{iE_g t}{\hbar}} + \psi_u(r;R_0)e^{\frac{iE_u t}{\hbar}}\right]$$

$$= |\psi_g(r;R_0)|^2 + |\psi_u(r;R_0)|^2 + 2\psi_g(r;R_0)\psi_u^*(r;R_0)e^{-i\frac{(E_u-E_g)t}{\hbar}} + c.c.$$

$$= |\psi_g(r;R_0)|^2 + |\psi_u(r;R_0)|^2 + 2\psi_g(r;R_0)\psi_u^*(r;R_0)\cos\left(\frac{(E_u-E_g)t}{\hbar}\right)$$

Whenever I have $e^{i\theta}$ and $e^{-i\theta}$ we basically get $2\cos\theta$.

$$|\psi(r,t;R_0)|^2 = |\psi_g(r;R_0)|^2 + |\psi_u(r;R_0)|^2 + 2\psi_g(r;R_0)\psi_u^*(r;R_0)\cos\left(\frac{\Delta E_{ug}t}{\hbar}\right)$$

So, we multiply this is just tedious multiplication that is all but it is very simple. So, if we multiply, then we get its individual components that is $\psi_g(r;R_0)$ ground state plus $\psi_u(r;R_0)$

excited state plus cross term which is $\psi_g(r;R_0) \quad \psi_u(r;R_0)\ e^{-i\frac{(E_u-E_g)t}{\hbar}}$ plus is complex conjugate, the other part of this wave function.

So, this is the equation we get which is nothing but this delta energy difference E_u-E_g is going to be the energy difference of these two states.

And because, this is as I mentioned before, this is going to be the real part these are all real part. So, this can be considered as real because,

$$\psi_g = \frac{1}{\sqrt{2}}\left(\phi_{1sA} + \phi_{1sB}\right)$$

$$\psi_u = \frac{1}{\sqrt{2}}\left(\phi_{1sA} - \phi_{1sB}\right)$$

So, both are real atomic orbitals s orbitals are real that is why these are becoming real part and what we get is from this is that density will depend on time and it is oscillatory oscillation controlled by this cos function it is oscillatory with a period the period of the oscillation is going to be $\cos\left(\frac{\Delta E_{ug} t}{\hbar}\right)$. So,

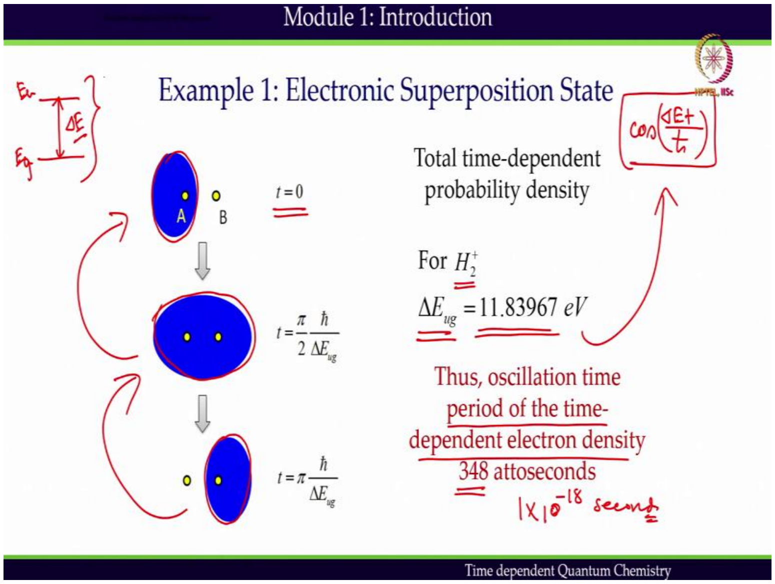
$$\omega t = \frac{\Delta E t}{\hbar}$$

$$2\pi\nu = \frac{\Delta E}{\hbar}$$

$$\nu = \frac{\Delta E}{\hbar} = \frac{\Delta E}{2\pi \times \frac{h}{2\pi}} = \frac{\Delta E}{h}$$

So, this is the frequency with which density this density of this system will change. And that is exactly we have shown.

(Refer Slide Time: 18:57)



Module 1: Introduction

Example 1: Electronic Superposition State

Total time-dependent probability density

For H_2^+

$\Delta E_{ug} = 11.83967\ eV$

Thus, oscillation time period of the time-dependent electron density 348 attoseconds

1×10^{-18} seconds

$\cos\left(\frac{\Delta E t}{\hbar}\right)$

Time dependent Quantum Chemistry

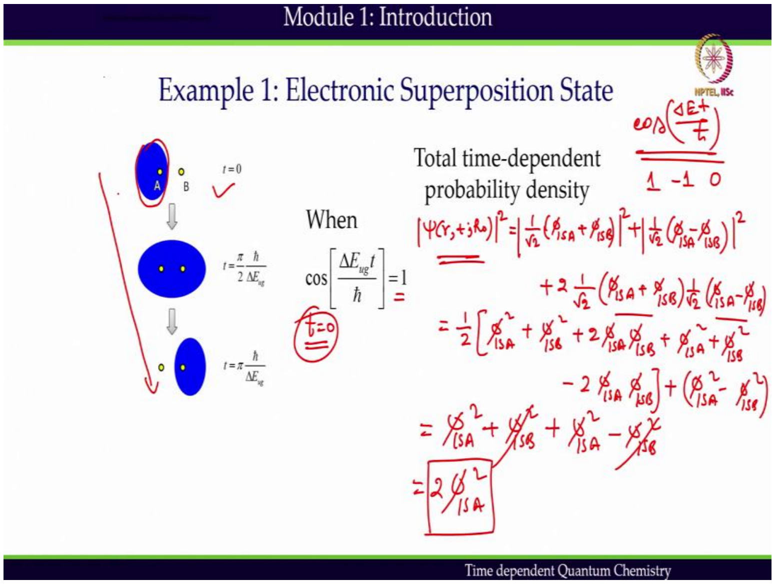
The probability density depends on $\cos\left(\frac{\Delta E_{ug} t}{\hbar}\right)$. This is the term which is going to control the change in density as a function of time. So, the moment I create the superposition at t = 0, we will see that the electron density is localized in a particular atom, it is not delocalized. After a certain time, the electron density will be delocalized over the 2 atoms and then after a certain time again electron density will be localized in the other part of the molecule and this will keep coming back like this way and it will keep oscillating.

So, electron density if I have hydrogen atom, then electron density in the superposition state electron density is localized here, delocalized, then again localized here delocalized again, localized here delocalized. And this is the way, it is more like an electronic wave, the wave which we see in a sea beach or the waves coming to you. And going back is something like that electron density is now oscillating as a function of time. And that is exactly the simplest representation of the quantum dynamics, that electron density is moving.

And when this electron density in the end moving, it depends on the period, or how fast is moving, it depends on the energy difference, because we have taken two different states and then linearly combine them. This was E_g and this was E_u, this two electronic states were linearly combined, when we linearly combine them, then the density will depend on this energy difference. For H_2^+ the energy difference is 11.83 eV almost.

And because of that, if we plug that in here, then we will be able to get the period of the time dependent electron density is 248 as attosecond is 1×10^{-18} s, extremely fast, this kind of oscillation can happen extremely fast. It is going to be 10^{-18} s, within this timescale is oscillating. But this oscillation will be controlled by this energy gap. And that is very important to understand in a superposition state.

(Refer Slide Time: 21:57)



Module 1: Introduction

Example 1: Electronic Superposition State

When

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

$$\boxed{t=0}$$

$$\cos\left(\frac{\Delta E t}{\hbar}\right)$$

1 -1 0

Total time-dependent probability density

$$|\Psi(r,t;R_0)|^2=\left|\frac{1}{\sqrt{2}}(\phi_{1SA}+\phi_{1SB})\right|^2+\left|\frac{1}{\sqrt{2}}(\phi_{1SA}-\phi_{1SB})\right|^2$$

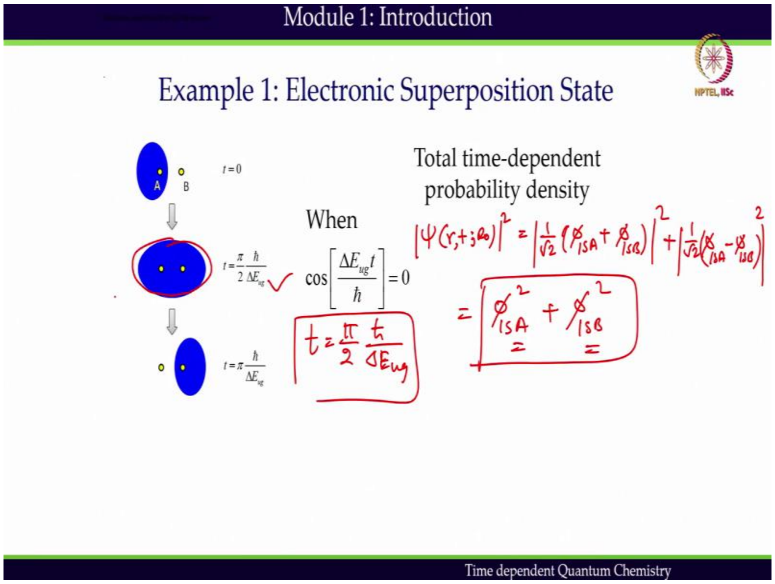
$$+2\frac{1}{\sqrt{2}}(\phi_{1SA}+\phi_{1SB})\frac{1}{\sqrt{2}}(\phi_{1SA}-\phi_{1SB})$$

$$=\frac{1}{2}\left[\phi_{1SA}^2+\phi_{1SB}^2+2\phi_{1SA}\phi_{1SB}+\phi_{1SA}^2+\phi_{1SB}^2-2\phi_{1SA}\phi_{1SB}\right]+(\phi_{1SA}^2-\phi_{1SB}^2)$$

$$=\phi_{1SA}^2+\cancel{\phi_{1SB}^2}+\phi_{1SA}^2-\cancel{\phi_{1SB}^2}$$

$$=\boxed{2\phi_{1SA}^2}$$

Time dependent Quantum Chemistry



Module 1: Introduction

Example 1: Electronic Superposition State

When

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

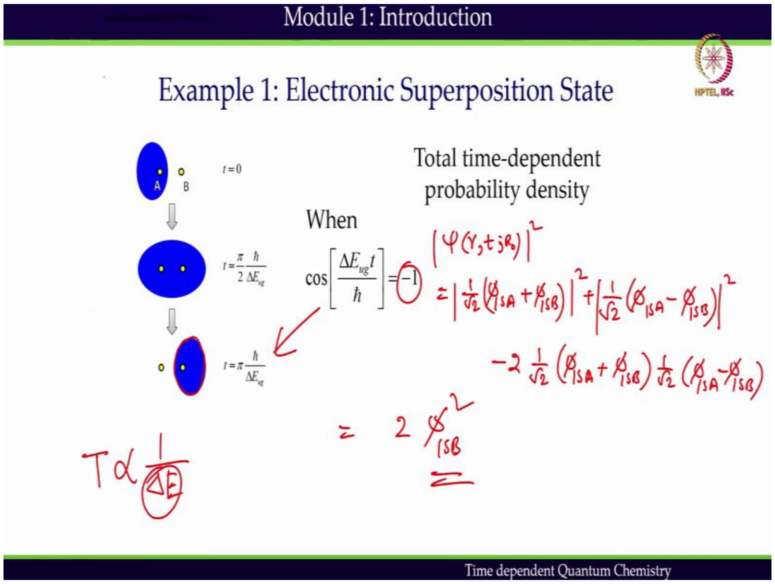
$$\boxed{t=\frac{\pi}{2}\frac{\hbar}{\Delta E_{ug}}}$$

Total time-dependent probability density

$$|\Psi(r,t;R_0)|^2=\left|\frac{1}{\sqrt{2}}(\phi_{1SA}+\phi_{1SB})\right|^2+\left|\frac{1}{\sqrt{2}}(\phi_{1SA}-\phi_{1SB})\right|^2$$

$$=\boxed{\phi_{1SA}^2+\phi_{1SB}^2}$$

Time dependent Quantum Chemistry


Module 1: Introduction

Example 1: Electronic Superposition State

Total time-dependent probability density

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

$$|\Psi(r,t;R_0)|^2$$

$$=\left|\frac{1}{\sqrt{2}}(\phi_{1sA}+\phi_{1sB})\right|^2+\left|\frac{1}{\sqrt{2}}(\phi_{1sA}-\phi_{1sB})\right|^2$$

$$-2\frac{1}{\sqrt{2}}(\phi_{1sA}+\phi_{1sB})\frac{1}{\sqrt{2}}(\phi_{1sA}-\phi_{1sB})$$

$$=2\phi_{1sB}^2$$

$$T\propto\frac{1}{\boxed{\Delta E}}$$

Time dependent Quantum Chemistry

We will be able to confirm that what kind of oscillation we get is that by the fact that because in the end, my density will be controlled by this simple equation, which is $\cos\left(\frac{\Delta E_{ug}t}{\hbar}\right)$. By this expression, we know that cos can take different values, cos can take 1 cos can take - 1 cos can take 0 values, and we will consider all these values to find out to prove that this kind of change in density will be going on in space as a function of time for this for the superposition state.

So what we will do first, we will use cos equals 1 and that is, when we get cos equals 1, it means that I am at t equals 0, because cos 0 is actually 1. So, at t equals 0 time this is the time what will happen the total density is now can be written as-

$$|\psi(r,t;R_0)|^2=\left|\frac{1}{\sqrt{2}}(\phi_{1sA}+\phi_{1sB})\right|^2+\left|\frac{1}{\sqrt{2}}(\phi_{1sA}-\phi_{1sB})\right|^2+2.\frac{1}{\sqrt{2}}(\phi_{1sA}+\phi_{1sB})\frac{1}{\sqrt{2}}(\phi_{1sA}-\phi_{1sB})$$

$$=\frac{1}{2}\left[\phi^2{}_{1sA}+\phi^2{}_{1sB}+2\phi_{1sA}\phi_{1sB}+\phi^2{}_{1sA}+\phi^2{}_{1sB}-2\phi_{1sA}\phi_{1sB}\right]+\left(\phi^2{}_{1sA}-\phi^2{}_{1sB}\right)$$

$$=\phi^2{}_{1sA}+\phi^2{}_{1sB}+\phi^2{}_{1sA}-\phi^2{}_{1sB}$$

So, it suggests that at t = 0 time, the density, total density will be localized only on the A part and that is exactly shown here. On the A side, what will happen if the, if we get cos equals 0, if I get this cos equals 0 term, then total wave function now, I will be writing like this way.

$$\left|\psi(r,t;R_0)\right|^2 = \left|\frac{1}{\sqrt{2}}\left(\phi_{1sA}+\phi_{1sB}\right)\right|^2 + \left|\frac{1}{\sqrt{2}}\left(\phi_{1sA}-\phi_{1sB}\right)\right|^2$$

Which gives me finally, if we simplify it, I am skipping one step. You can check it by rigorously doing this math is just tedious.

$$= \phi^2{}_{1sA} + \phi^2{}_{1sB}$$

So, what it suggests that when $t = \frac{\pi}{2} \times \frac{\hbar}{\Delta E}$ when this time, that is this time, the density will be delocalized over A and B and that is exactly what is shown here density is delocalized.

Now, another part where cos term is taken to be minus 1 if we take cos to b minus 1, then t is going to be, $t = \pi \frac{\hbar}{\Delta E_{ug}}$ and one can write down,

$$\left|\psi(r,t;R_0)\right|^2 = \left|\frac{1}{\sqrt{2}}\left(\phi_{1sA}+\phi_{1sB}\right)\right|^2 + \left|\frac{1}{\sqrt{2}}\left(\phi_{1sA}-\phi_{1sB}\right)\right|^2 - 2.\frac{1}{\sqrt{2}}\left(\phi_{1sA}+\phi_{1sB}\right)\frac{1}{\sqrt{2}}\left(\phi_{1sA}-\phi_{1sB}\right)$$

So, if we simplify it finally,

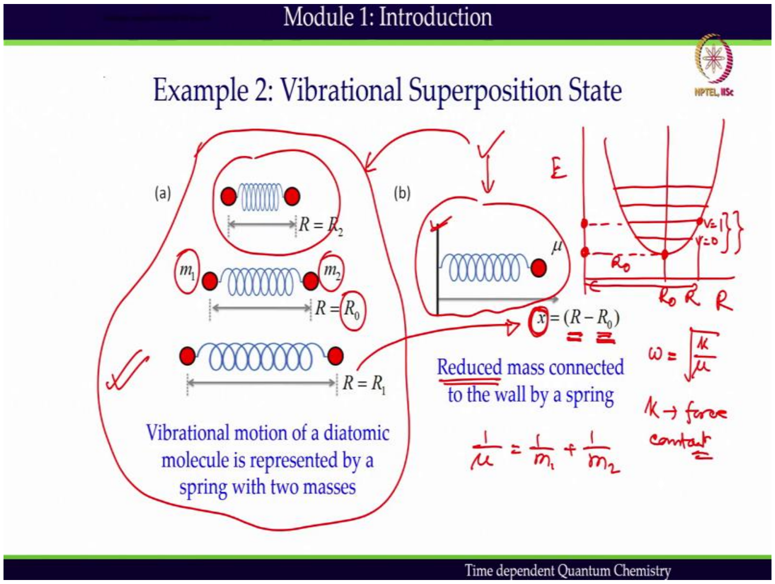
$$= 2\phi^2{}_{1sB}$$

it means that the density at this time will be localized only on B this is where it is localized.

So, this demonstration shows that this exercise shows that how the densities are changing as a function of time and different time. And what this periodic change in density is controlled by inversely controlled by the, this time period will be inversely proportional to this energy difference between the states which are involved in the superposition creating the superposition.

So, this is a demonstration for electronic superposition state electronic supervision can be as fast as attosecond and how to observe that that is a different question. But, we can create electronic superposition state by linearly combining two electronic states. Next, we will go over quickly go over vibrational superposition state.

(Refer Slide Time: 29:11)



Module 1: Introduction

Example 2: Vibrational Superposition State

Vibrational motion of a diatomic molecule is represented by a spring with two masses

$x = (R - R_0)$

Reduced mass connected to the wall by a spring

$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$

$\omega = \sqrt{\frac{k}{\mu}}$

$k \rightarrow$ force contant

Time dependent Quantum Chemistry

When you think about vibrational superposition state, we will again these are the vibrational state generally under harmonic oscillator approximation, we get different vibrational states like this and one can think about, what about if we consider V equals these two states if we linearly combine with this characteristic phase factor, what will happen to those states? But, before we get into these states, first we will remind few things and that will help one understand what is all about this diatomic vibration.

One of the simplest examples of vibrational superposition state can be realized from a superposition of the ground and the first excited state of the diatomic quantum harmonic oscillator which we have shown here, we can linearly combine these 2 states. A quantum harmonic oscillator is a good model for a vibrating diatomic molecule.

Under this model diatomic molecule can be represented by a spring, just like the one I have shown here, like a spring and this is vibrating when this is vibrating, it is vibrating like two balls are connected by a spring and spring is compressed, sometimes stretched, then compressed stretch and that is a good model for the harmonic oscillator. So, harmonic oscillator is a good model for the quantum vibration.

And when we have that, we say that two atoms having mass m_1 and m_2 its equilibrium distance is R_0 , which is here at the R_0 distance this is your E and this is your R. So, this is called R_0, when I say R_0 it means that one atom is anchored here and another atom is here and that is why this is called R_0. R_0 is the equilibrium bond distance, but it can have different bond distances it can have I can have my I can have vibration like this way. So, this can be one distance that is that is the R distance I can have R distance.

So, different it can be stretched it can be compressed, depending on what time of the vibration we are in. Equilibrium bond distances R_0 and R represents the instantaneous bond length during the vibration. Now, when we do that, when we think about this one, this two body vibration like this way which we have presented, the mathematics gets little tedious and difficult to deal with so often for mathematical convenience, what do we do?

We define another to express the same vibration, we define another physical quantity called x, x is the difference between the instantaneous bond distance and the equilibrium bond distance. That is the difference. So, we are defining x and we are defining so, we have defined an x coordinate which is represented by $R- R_0$, which means that if x is positive, it means I have stretched it R is greater than R_0 and if x is negative, it means that I have compressed it.

So, that is the way we can think about it. And in this picture, this when we have changed the coordinate from R coordinate to x coordinate, we can also another change we can make we can make a reduce mass. So, we can say that,

$$\frac{1}{\mu}=\frac{1}{m_1}+\frac{1}{m_2}$$

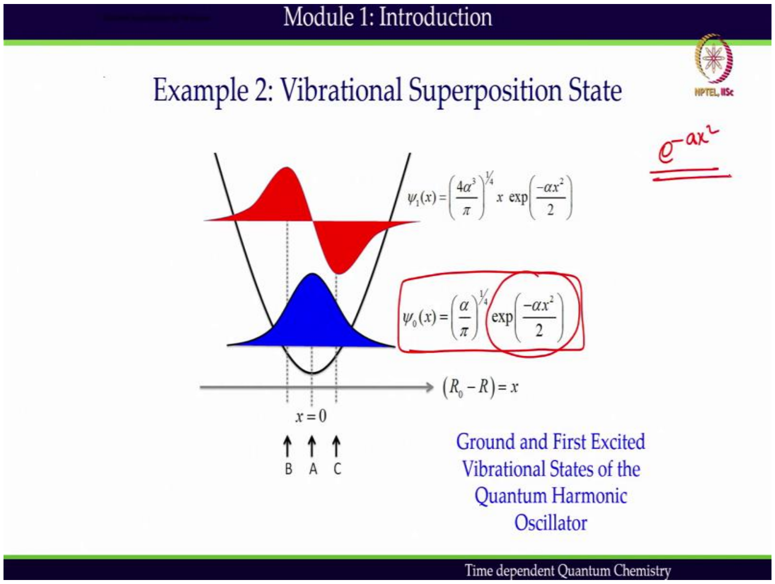
If we do that, then this whole two body problem becomes a one body problem given here.

And if we perform the math with the help of one body problem, we can easily translate the information to the two body problem and that is what we do very often in dealing with two body or diatomic species in spectroscopy or quantum mechanics. Where in the one body if we consider the one body system, then the angular frequency which is governing this vibration in the x coordinate is given by $\omega=\sqrt{\frac{k}{\mu}}$, k is the force constant.

So, just to remind ourselves that, we basically we have a diatomic molecule, but to deal with diatomic molecule I have to deal with this R coordinate and also two body instead of dealing with two body there is a mathematical convenience or mathematically you can convert this two body system to one body problem. And if we use this one body problem that I have only one body with reduced mass vibrating with respect to this wall in x coordinate, if we solve it, then we will be able to translate the information to the two body problem.

So, it is basically seeing simplifying one complicated problem in one dimension and then solving it and discussing the diatomic vibration.

(Refer Slide Time: 34:52)



Module 1: Introduction

Example 2: Vibrational Superposition State

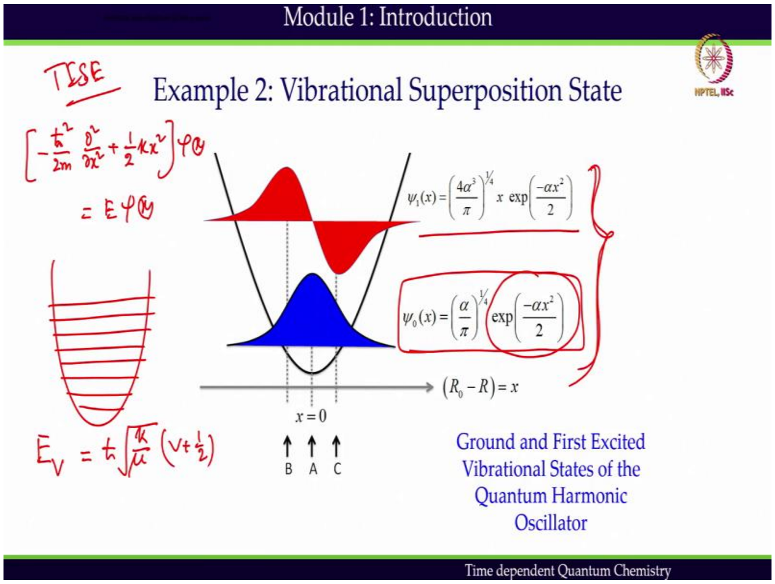
e^{-ax^2}

$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x \exp\left(\frac{-\alpha x^2}{2}\right)$

$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(\frac{-\alpha x^2}{2}\right)$

Ground and First Excited Vibrational States of the Quantum Harmonic Oscillator

Time dependent Quantum Chemistry



Module 1: Introduction

Example 2: Vibrational Superposition State

TISE

$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2\right]\psi(x) = E\psi(x)$

$E_v = \hbar\sqrt{\frac{k}{\mu}}\left(v+\frac{1}{2}\right)$

$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x \exp\left(\frac{-\alpha x^2}{2}\right)$

$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(\frac{-\alpha x^2}{2}\right)$

Ground and First Excited Vibrational States of the Quantum Harmonic Oscillator

Time dependent Quantum Chemistry

When you do that, we get the wave functions for the ground and the first excited, state vibrational state, where I have shown this wave function interesting thing to note that the ground vibrational state in simple harmonic oscillator is actually look like a Gaussian wave function e^{-ax^2} it is a Gaussian function. So, similar functions we are getting here also.

A Gaussian function and the first excited state wave function looks like this, this wave functions we get from TISE Time Independence Schrödinger Equation which can be written as

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\frac{1}{2}kx^2\right]\psi(x)=E\psi(x)$$

We get a set of solutions, we get set of solutions just like this any TDT, TISE we solve, we get a set of solution.

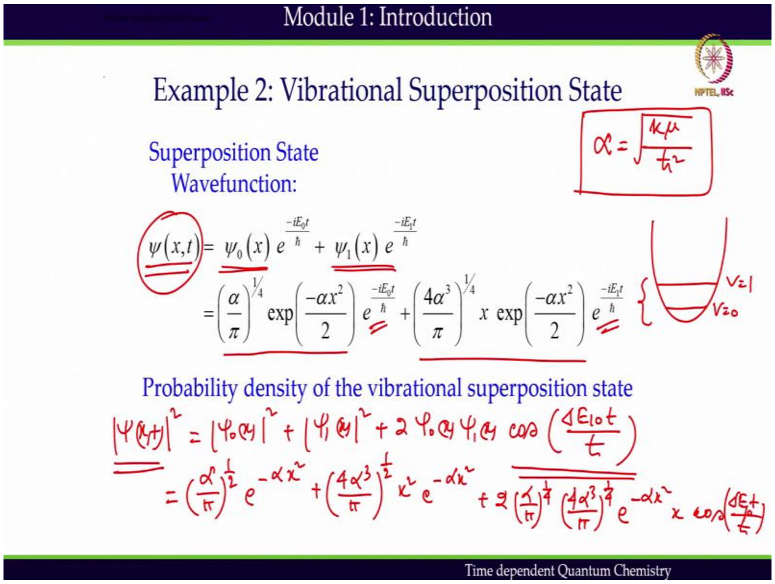
And each state is defined by this quantum number v where energy of that state is given by

$$E_v=\hbar\sqrt{\frac{k}{\mu}}(v+\frac{1}{2})$$

which is nothing but yeah, this is the this is each state is given by this and they are non degenerate state in the simple harmonic oscillator and these are the two wave functions we get. So, it is giving an idea to approach a quantum dynamics fast at t equals 0 before the time evolution, we have to find out it is such as that we have to find out the stationary states.

Once we find out the stationary states, then we have to create the superposition and then let it evolve through this TDSE, that is the basic approach. And that is exactly reflected here also. We have we are trying to find out with the help of TISE, we have found its possible energy states and then we are linearly combining these two states to find out its superposition the behavior of the superposition state.

(Refer Slide Time: 37:24)



Module 1: Introduction

Example 2: Vibrational Superposition State

$$\boxed{\alpha = \sqrt{\frac{k\mu}{\hbar^2}}}$$

Superposition State Wavefunction:

$$\underline{\psi(x,t)} = \underline{\psi_0(x)}\, e^{\frac{-iE_0 t}{\hbar}} + \underline{\psi_1(x)}\, e^{\frac{-iE_1 t}{\hbar}}$$

$$= \underline{\left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(\frac{-\alpha x^2}{2}\right)} e^{\frac{-iE_0 t}{\hbar}} + \underline{\left(\frac{4\alpha^3}{\pi}\right)^{1/4} x \exp\left(\frac{-\alpha x^2}{2}\right)} e^{\frac{-iE_1 t}{\hbar}}$$

Probability density of the vibrational superposition state

$$\underline{|\psi(x,t)|^2} = |\psi_0(x)|^2 + |\psi_1(x)|^2 + 2\psi_0(x)\psi_1(x) \cos\left(\frac{\Delta E_{10} t}{\hbar}\right)$$

$$= \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} e^{-\alpha x^2} + \left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{2}} x^2 e^{-\alpha x^2} + 2\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{4}} e^{-\alpha x^2} x \cos\left(\frac{\Delta E t}{\hbar}\right)$$

Time dependent Quantum Chemistry

So, what we do, what we will do here is that the superposition state will be expressed as this is the ground state ground vibrational state this is the first excited vibrational states explicitly written like this way where alpha we have already defined alpha,

$$\alpha = \sqrt{\frac{k\mu}{\hbar^2}}$$

system characteristic of the system is a constant for a particular vibrating diatomic species.

So, this probability if we know the wave-function superposition state wave function, then we will be able to find out the probability density how it is changing, it is obviously changing like this way.

$$|\psi(x,t)|^2 = |\psi_0(x)|^2 + |\psi_1(x)|^2 + 2\psi_0(x)\psi_1(x)\cos\left(\frac{\Delta E_{10} t}{\hbar}\right)$$

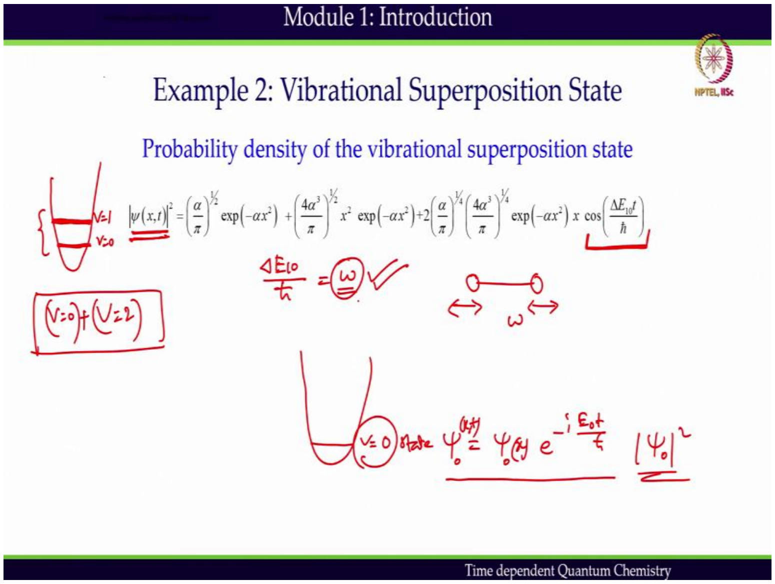
So, basically what we have is that this is the this is v=0, this is v=1, we have linearly combine these 2 states with his own characteristic phase factors, these are the phase vectors we have and the moment we do that, then the total wave function the total density the state, the particle is now in the superposition state created by two vibrational wave functions.

And in that state, the density is changing as a function of time like this way, which can be expressed as explicitly can be expressed as

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

this is between 1 and 0 states.

(Refer Slide Time: 40:26)



Module 1: Introduction

Example 2: Vibrational Superposition State

Probability density of the vibrational superposition state

$$|\psi(x,t)|^2 = \left(\frac{\alpha}{\pi}\right)^{1/2} \exp\left(-\alpha x^2\right) + \left(\frac{4\alpha^3}{\pi}\right)^{1/2} x^2 \exp\left(-\alpha x^2\right) + 2\left(\frac{\alpha}{\pi}\right)^{1/4} \left(\frac{4\alpha^3}{\pi}\right)^{1/4} \exp\left(-\alpha x^2\right) x \cos\left(\frac{\Delta E_{10} t}{\hbar}\right)$$

$\frac{\Delta E_{10}}{\hbar} = \omega$ ✓

(V=0)+(V=2)

V=0 state $\psi_0(x,t) = \psi_0(x) e^{-i\frac{E_0 t}{\hbar}}$ $|\psi_0|^2$

Time dependent Quantum Chemistry

So, we get this expressions and once we get these expressions, then an interesting point here we can notice here that this total wave function this is a density total density will be evolving as a function of this term. And if we look at this term, this $\frac{\Delta E_{10}}{\hbar}$, this is the so, the this is going to be the omega frequency and this omega is the frequency of change in this density, this superposition state density this is created by v = 1 state and v = 0 state these two states so, what it suggest that omega is the frequency of the vibration.

So, this two atoms are vibrating with a frequency omega, question is can I observe that vibration? Let us say the system is in the v = 0 state. If the system is v= 0 state we know that even at V equals 0 state molecules this diatomic species is vibrating all the time. Question is can I observe that vibration? No, if it is staying at V equals 0 state it means that it is wave function is going to be represented by.

$$\psi_0(x,t) = \psi_0(x) e^{-\frac{iE_0 t}{\hbar}}$$

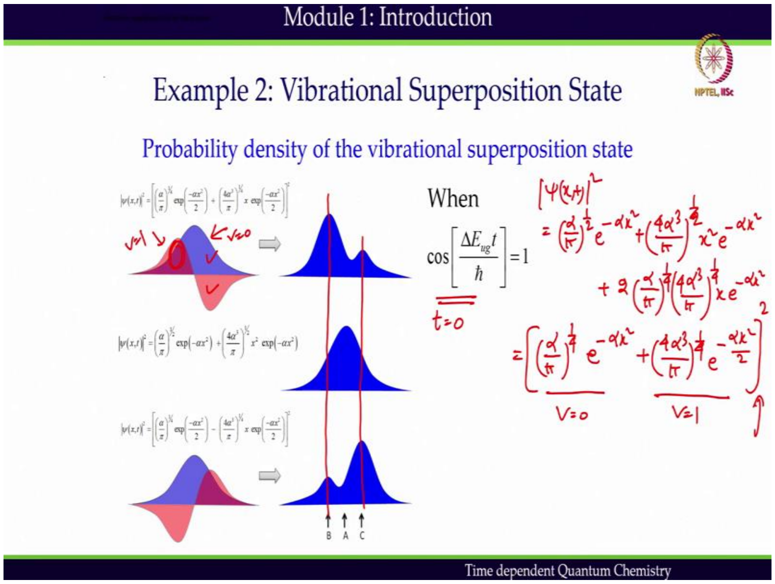
And because it is wave function depends, because we function because the system is at v=0 state even if it is vibrating. There is no way experimentally I can observe this vibration, because in the end, this is a stationary state total density will not be sensitive to the time. Because total density depends on its densities depends on the psi star psi.

So, in order to observe that frequency observe that vibration, what you need to do is that we can create the superposition between v = 0 and v =1 superposition. If we create that, then there is a change in density that change in density will also follow the same frequency. So, coherence the, we are creating superposition state with the help of coherence, this coherence is allowing me to observe vibration in a molecule.

the molecule is staying only at v=0 state, that is a stationary state. I will not although it is vibrating all the time, but I will not be able to observe that vibration. The only way I can observe the vibration with the same frequency is by creating a superposition state between v = 0 and v = 1.

So, coherence is allowing me to observe the inherent vibration in the molecular system. This may not be true if you do a superposition between v = 0 and v = 2 states. Check what is the outcome? Check what kind of frequency you should observe for the density. How does it compare with its own frequency, that can be different. But if we create these v = 0 and v = 1. states proposition, then we will be able to observe the same frequency with which the molecule is vibrating.

(Refer Slide Time: 44:32)



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

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

t=0

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

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

Time dependent Quantum Chemistry

We will now move to similar kind of derivation which we did for the electric superposition state, we will consider different cos values in the expression and we will try to find out what is going to happen to the total density. We will start with cos equals 1 which means that I am at t equals 0 if we add t equals 0, then we can write down explicitly density is going to be

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

Which is nothing but,

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

Which means that I have to add these two functions first and then square it. So, if I want to add these two function, these two functions, what is these two functions? These two functions was v = 0 wave function and v = 1 wave function, that is exactly I have plotted here, ` this one is v = 0 wave function, and then this one is v = 1 wave function.

Now phase becoming an important issue, you see, on this side, this part will be added together, it will be magnified, but this part they are cancelling each other. So, they will be they will be diminished. And that is why finally, the density will be localized more on this part at the B position than this C position that is the effect we have right now. So, we see that there is a localized density in one part of the molecule. So, we will stop here and we will continue this module in the next session.