Spectroscopic Technique for Pharmaceutical and Biopharmaceutical Industries

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Lecture 19

UV Visible Spectroscopy of Conjugated Molecules

Hello students, welcome to the lecture on UV visible spectroscopy, in the last lectures I have discussed about electronic spectroscopy of metals or elements and diatomic molecules, in this lecture I will discuss about electronics spectroscopy of conjugated systems, I will also discussed about how your particle in a box concept, which we studied in quantum chemistry will be apply to understand spectroscopy of conjugated system and the spectroscopy of Nano systems.

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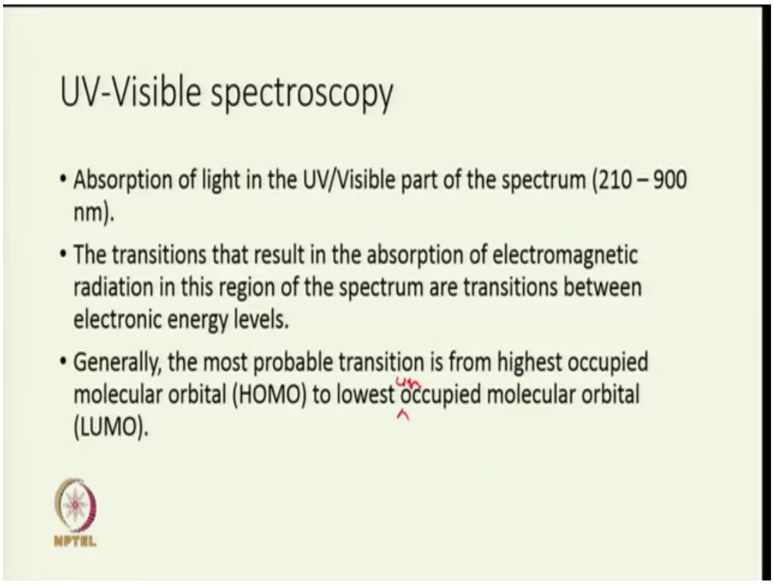

UV-Visible spectroscopy

- Absorption of light in the UV/Visible part of the spectrum (210 – 900 nm).
- The transitions that result in the absorption of electromagnetic radiation in this region of the spectrum are transitions between electronic energy levels.
- Generally, the most probable transition is from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO).

So, let us go ahead and discuss the electronics spectroscopy of conjugated system is generally known as UV visible spectroscopy, UV visible spectroscopy is quite often used in organic chemistry in organic chemistry physical chemistry and bio chemistry, so in UV visible spectroscopy we deal with absorption of light in UV visible part of the spectrum, which is basically extends from 210 Nano meter to 900 Nano meter.

As I discussed earlier the transitions that results in the absorption of electromagnetic radiation in this region of the spectrum are basically transitions between electronic energy level and generally we are concerned about the most probable transition and the most probable transition is from highest occupied molecular orbital HOMO lowest unoccupied molecular orbital LUMO. So, please change this to unoccupied so most probable transition is from

HOMO to highest HOMO means highest occupied molecular orbital to LUMO which is lowest unoccupied molecular orbital.

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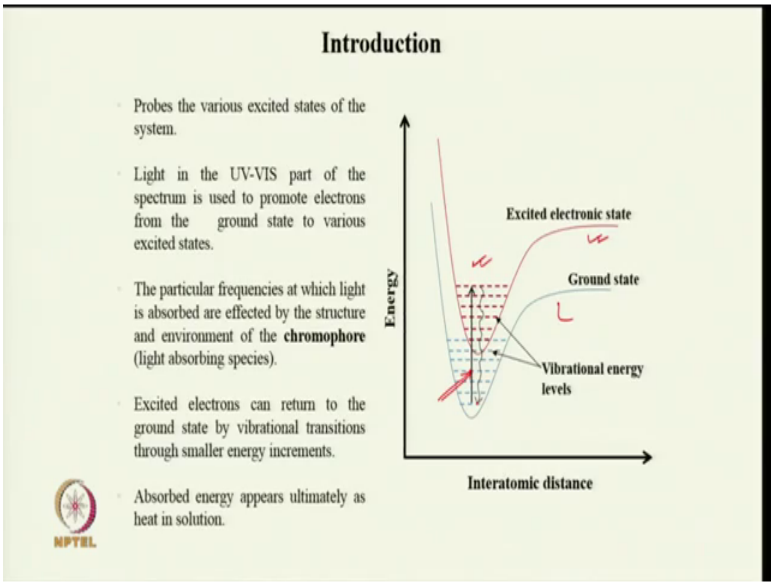

Introduction

- Probes the various excited states of the system.
- Light in the UV-VIS part of the spectrum is used to promote electrons from the ground state to various excited states.
- The particular frequencies at which light is absorbed are effected by the structure and environment of the **chromophore** (light absorbing species).
- Excited electrons can return to the ground state by vibrational transitions through smaller energy increments.
- Absorbed energy appears ultimately as heat in solution.

In UV visible spectroscopy we prove the various excited states of the system, so here is your ground state this is exited electronics state so we prove in this spectroscopy we prove the various excited states of the system. Here light in UV visible region used to promote your electrons from the electrons from the one electronic level to another electronic level one electronic level to other electronic level.

Basically we are going from ground electronic state to various excited electronic stats. The particular frequency at which light is absorb are affected by structure environment of the chromophore, so here we are going to discuss about conjugated double bond system as chromophore and structure and environment of the chromophore well decidable the frequency of the transitions frequency of the transition your electrons an exited state can return to ground state by vibrational transitions through small energy increment.

So, we will first come to here and then it can also come back to your ground state absorbed energy appears ultimately as heat in solution when the exited electron returns to ground state by vibrational transitions in that case absorb energy appears as heat in the solution. So this is called non radiative transition this is known as non radiative transition, I will also discuss the radiative transition from exited electronic state to ground state when I will discuss floresence.

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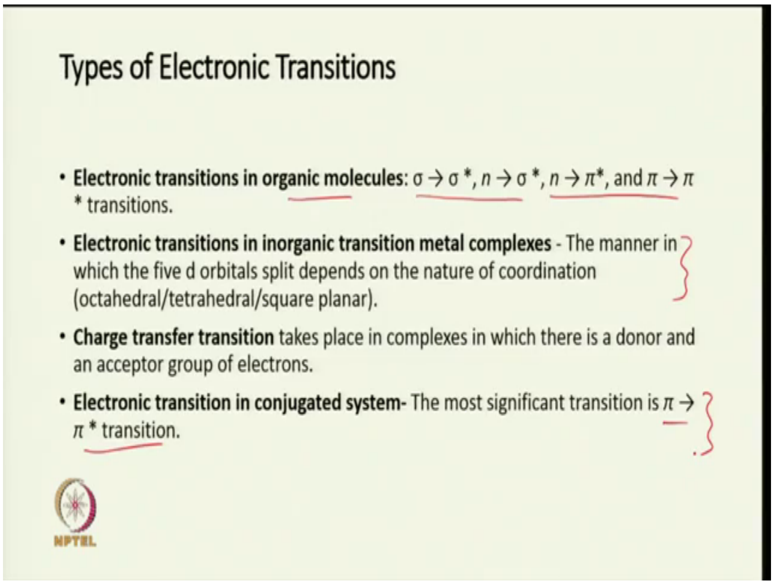

Types of Electronic Transitions

- **Electronic transitions in organic molecules:** $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$, and $\pi \rightarrow \pi^*$ transitions.
- **Electronic transitions in inorganic transition metal complexes** - The manner in which the five d orbitals split depends on the nature of coordination (octahedral/tetrahedral/square planar).
- **Charge transfer transition** takes place in complexes in which there is a donor and an acceptor group of electrons.
- **Electronic transition in conjugated system-** The most significant transition is $\pi \rightarrow \pi^*$ transition.

The type of electronics transition are, in organic molecule basically we deal with sigma to sigma star, n to sigma star, n to pie star and pie to pie star transition, in inorganic transition metal complexes we again come across electronic transition and that is basically our dd transition and in that dd transition will be governed by the manner in which 5 d orbital splits on the nature of or when ligands comes to metal the 5 degenerate d orbital of metals splits into two different groups or three different groups depending on the nature of coordination nature of coordination can be of three types octahedral, tetrahedral, or square planner.

Charge transfer transition are also electronic transitions they happen in UV (())(6:52) region and it take place in complexes and which there is a donor and acceptor group of electrons, I will discuss it later then we have electronic transition in conjugated systems and most significant transition is pie to pie star transition. So in this lecture I will focus on electronic transition in conjugated system some of them I have already discussed few of them I will disused after this lecture.

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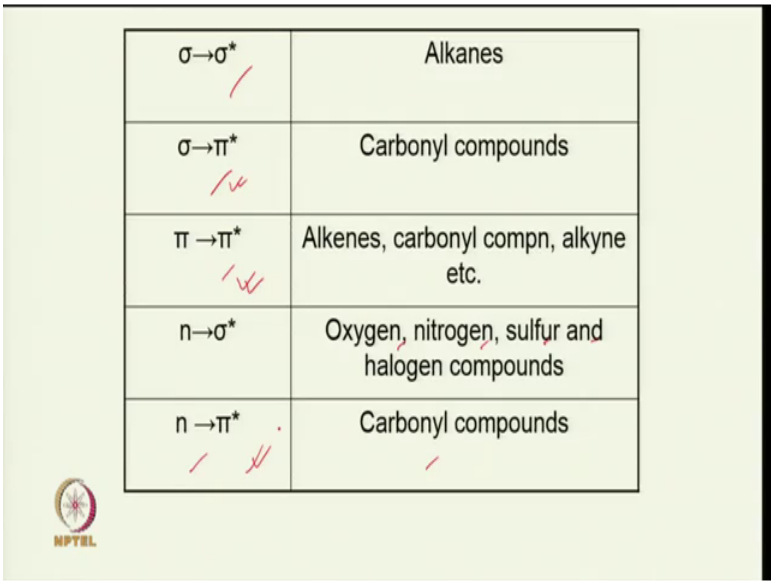

σ→σ*	Alkanes
σ→π*	Carbonyl compounds
π →π*	Alkenes, carbonyl compn, alkyne etc.
n→σ*	Oxygen, nitrogen, sulfur and halogen compounds
n →π*	Carbonyl compounds

So, if you go and look at the compounds there are the few transitions which happens in alkanes and that is your sigma to sigma star transitions common transitions in carbonyl compound is sigma to pie star and your pie to pie star happens in alkenes, carbonyl compound, alkyne etc, n to sigma star generally takes place in compounds containing oxygen nitrogen sulfur and halogen compounds and your n to pie star transition takes place in carbonyl compounds. So, in carbonyl compounds there are three different kinds of transition which can happen sigma to pie star, pie to pie star and n to pie star, whereas alkene and alkyne have pie to pie star transition.

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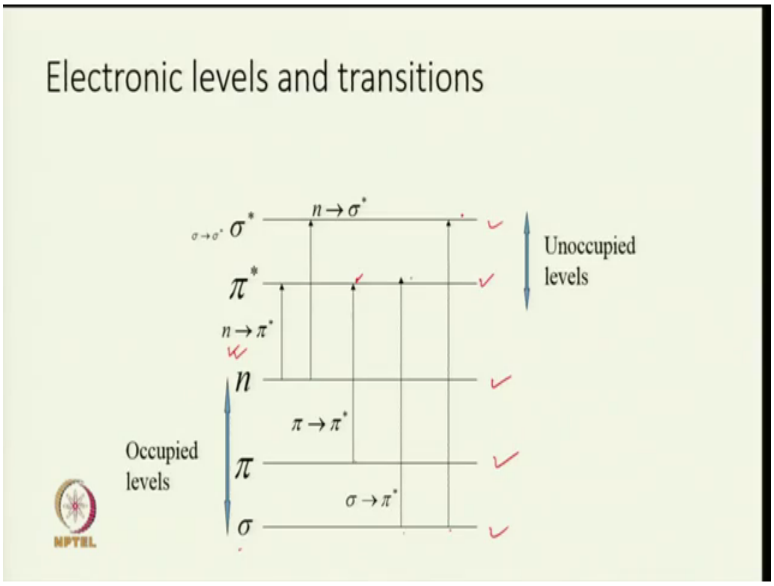

Electronic levels and transitions

And here is the different occupied level and unoccupied level, so here sigma is occupied level pie n this are the occupied levels and pie star and sigma star are unoccupied levels, so you can see that when electron is in the n level and it goes to pie star that is known as n to pie star transition when electron are in pie outer most electrons are in the pie level then it goes to pie star it can go to pie star and when it is in sigma it can have sigma to pie star it can have sigma to your sigma. So, all these different kind of transition are possible in this lecture we will discuss mostly the effect of conjugation particularly in alkenes kind of system.

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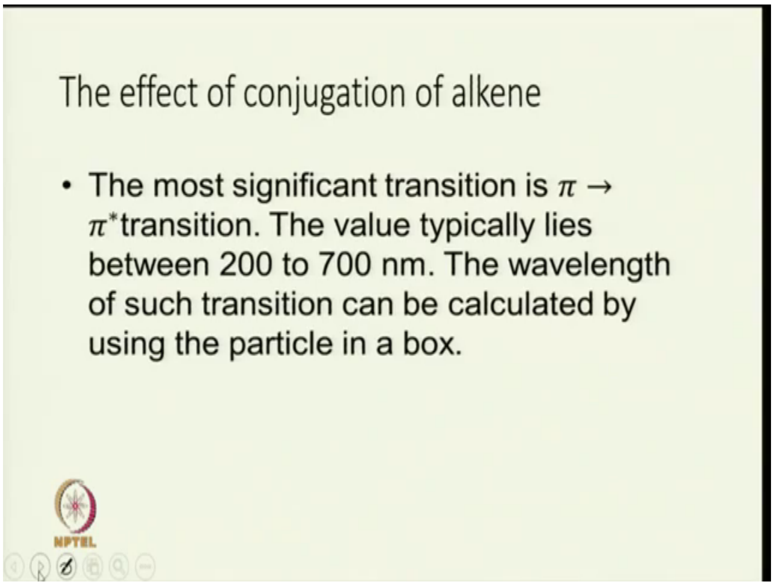

The effect of conjugation of alkene

- The most significant transition is $\pi \rightarrow \pi^*$transition. The value typically lies between 200 to 700 nm. The wavelength of such transition can be calculated by using the particle in a box.

The most significant transition is pie to pie star transition in alkene and the value typically lies between 200 to 700 Nano meter, we can actually calculate the value of lambda and the way we do is by using the particle in a box kind of system. Using a particular in a box system, we can write the Schrodinger equation and we can solve to get the energy of different electronic levels and the delta E between two levels where transition is taking place will give you the value of lambda and as I told you the value of lambda lies between 200 to 700 Nano meter.

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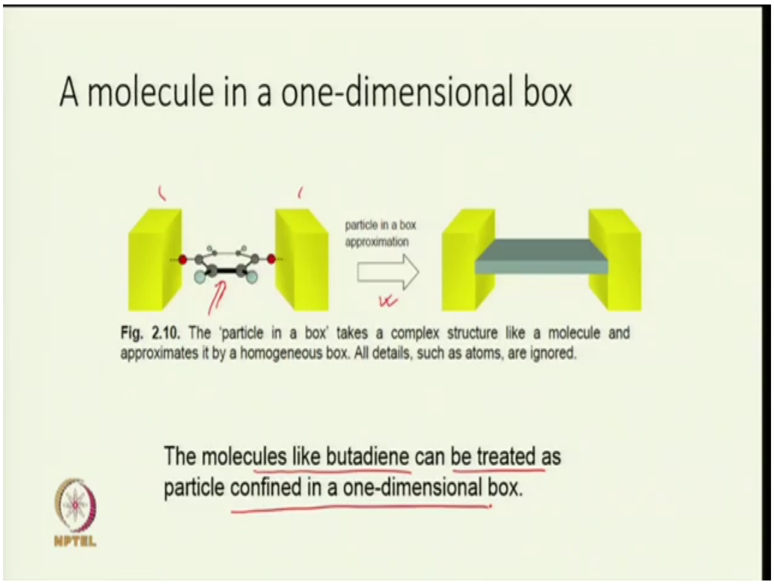

A molecule in a one-dimensional box

Fig. 2.10. The 'particle in a box' takes a complex structure like a molecule and approximates it by a homogeneous box. All details, such as atoms, are ignored.

The molecules like butadiene can be treated as particle confined in a one-dimensional box.

So, basically what you do is you take your molecule conjugated system as a particle and you confined between two walls and then you can apply particle in a box approximation, so molecules like butadiene which is an alkene can be treated as particle confined in one dimensional box, so if you take butadiene or you can think of hexatriene these can be treated as particle confined in one dimensional box, and when we apply Schrodinger equation for particle in one dimensional box and we can get the energy of butadiene kind of system.

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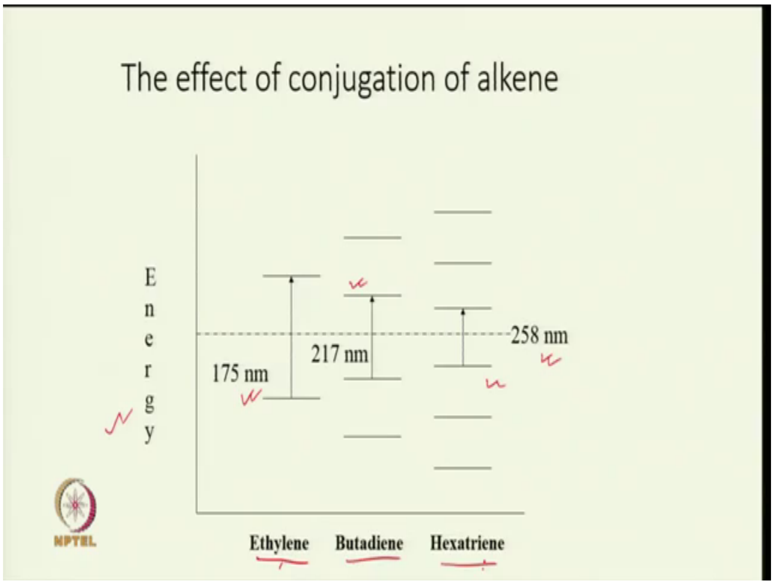

The effect of conjugation of alkene

Now, what is the effect of conjugation of alkene, if you go from ethylene to butadiene to hexatriene and if you look at the energy then the energy gap between HOMO to LUMO decreases and so the lambda of transition between HOMO to LUMO increases since energy gap decreases. So it goes from 175 Nano meter in ethylene to 258 Nano meter in Hexatriene. Now we like to see how we can explain this decreased in delta E and increase in your lambda value.

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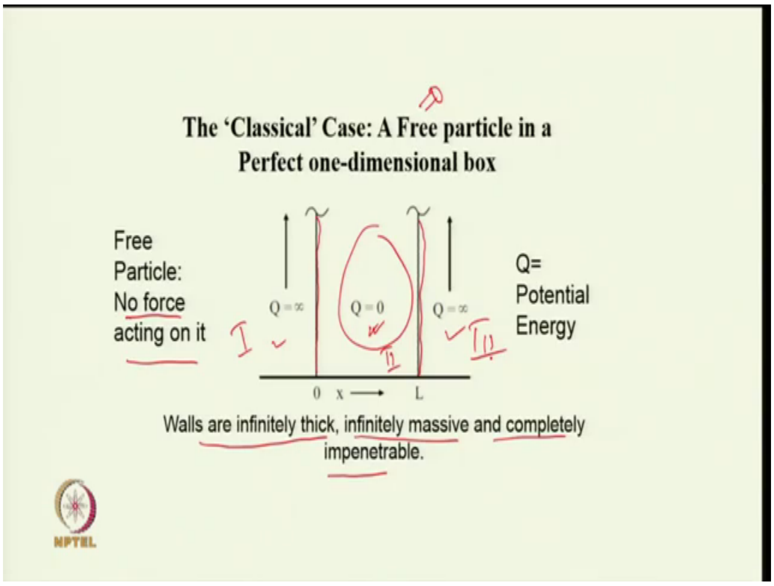

The 'Classical' Case: A Free particle in a Perfect one-dimensional box

Free Particle: No force acting on it

Q= Potential Energy

Walls are infinitely thick, infinitely massive and completely impenetrable.

So, for that we need to understand the concept of the particle in a box. So let first think of a classical case of free particle in a perfect one dimensional box, so you are talking about big system for example racket ball and now you are trying to see you are trying to look at its behavior in one dimensional box so one dimensional box is basically a space confined by two walls, walls are infinitely thick infinitely massive and completely impenetrable.

So, if you have this kind of system then you are basically dealing with a perfect one dimensional box, now I told it is a free particle what I mean by free particle that no force acting on it, so there is no force acting on it, when there is no force it means potential energy is 0 here potential energy is 0 and since the no way particle will be in this region or this region, so in this region let say this region 1 and this is region 3 and this is region 2, so in region 1 and 3 potential energy is infinite because there is no way this free particle will exist in this region.

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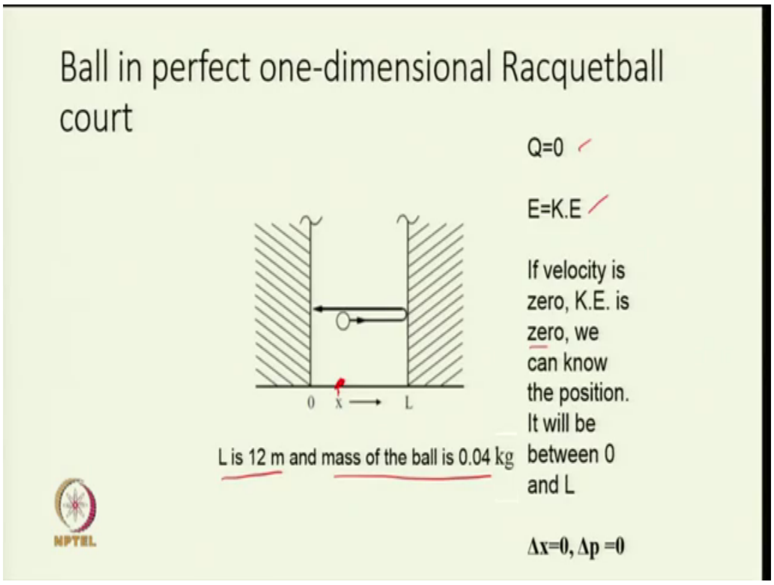

Ball in perfect one-dimensional Racquetball court

Q=0

E=K.E

If velocity is zero, K.E. is zero, we can know the position. It will be between 0 and L

L is 12 m and mass of the ball is 0.04 kg

$\Delta x=0, \Delta p=0$

So, now let us think of the behavior of free particle here, so suppose free particle here and (()) (14:31) so it will rebound at this wall it will go back again it will come here it will go back and since there is no force acting on it, it will keep on doing this, it will keep on doing this and since it is free particle so Q is equal to 0 it means energy is equal to kinetic energy.

So, energy will depend on velocity energy will depend on velocity and suppose if velocity is 0, it means kinetic energy is 0 and when it is 0 it will be somewhere on the surface somewhere on the surface line step and so I know the position it will be in between 0 and L and if it is here then it is at position x. So I know the position of the particle I also know momentum since I know velocity, velocity is 0 means momentum is 0 and the position is at x and so uncertainty in position is 0 and uncertainty in momentum is 0. So this is for ball imperfect one dimensional racquet ball court where the length is 12 meter and mass of the ball is 0.04 kg, so this is for ball imperfect one dimensional racquet ball court.

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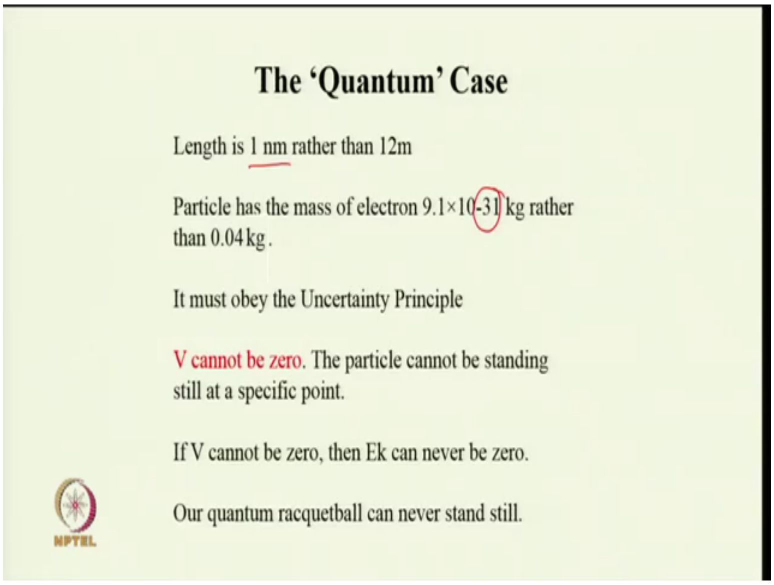

The 'Quantum' Case

Length is 1 nm rather than 12m

Particle has the mass of electron 9.1×10-31 kg rather than 0.04 kg.

It must obey the Uncertainty Principle

V cannot be zero. The particle cannot be standing still at a specific point.

If V cannot be zero, then Ek can never be zero.

Our quantum racquetball can never stand still.

Now, let us think of the quantum case. In the quantum case length is not 12 meter, length of the box is 1 Nano meter and particle has the mass of the electron which is very small 9.1 into 10 to the power minus 31 kg rather than 0.04 kg. So it must obey the uncertainty principle it must obey the uncertainty principle, here V cannot be 0 the particle cannot be standing at a specific point, why V cannot be 0 V is 0 then you know it will violet uncertainty principle because you know V and you also know the position which is simply not allowed by uncertainty principle.

So, if V cannot be 0 which is velocity cannot be 0 then kinetic energy can also not be 0, kinetic energy can also not be 0, so one quantum racquet ball can never stand still, and the energy of ball can never be 0.

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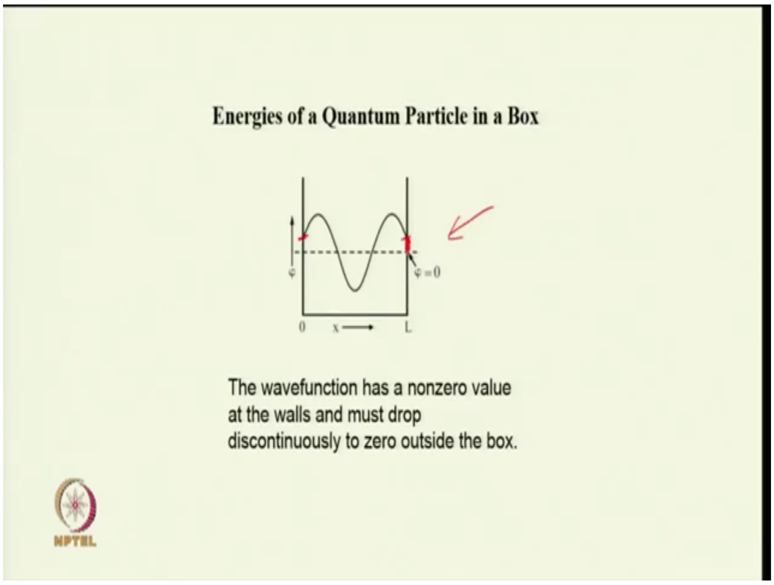

Energies of a Quantum Particle in a Box

The wavefunction has a nonzero value at the walls and must drop discontinuously to zero outside the box.

So, how to calculate the energy of a quantum particle in a box, so if we simply allow the concept of or simply take the concept of wave function which is allowed due to quantum postulate being may be able to get the energy of a quantum particle in a box without doing much calculation. So what I mean by that is please look at this picture if you look at this wave function this does not go to 0, and this wave function is not allowed because if this function is allowed then or this wave function should go to 0 quite rapidly or you can say that it will drop discontinuously to 0 outside the box outside the box and so this kind of wave functions are not allowed.

If you remember when I discussed about a postulates of quantum mechanics I told you that wave function must be continuous and here what you are seeing is that wave function is chopping discontinuously to 0 outside the box.

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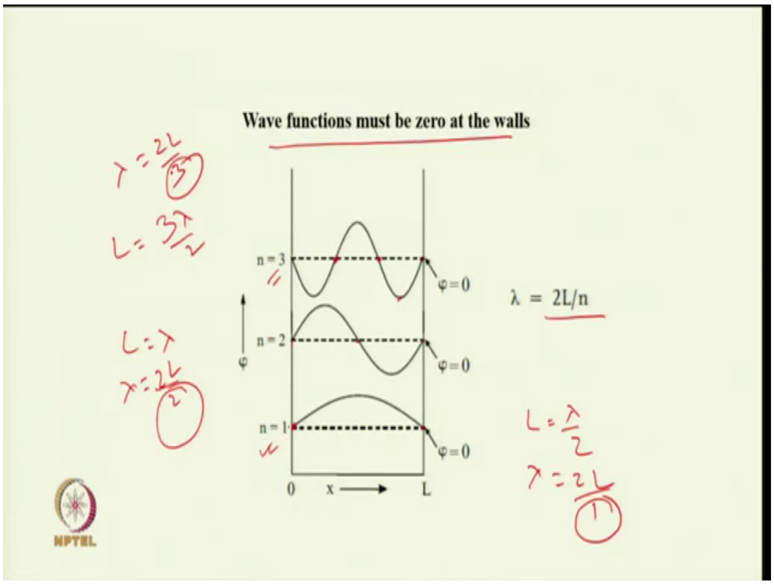

Wave functions must be zero at the walls

$\lambda = 2L/n$

So, what kind of wave function is allowed the wave function is allowed which is 0 at the x is equal to the 0 position and x is equal to L position, so now you can think of how a wave function will look like in a box, so wave function must be 0 at the walls that is the very important criteria.

Now, you see the first wave function you can think of which is 0 at the wall is when you know it is start from here from 0 position it goes back to 0 at this position, so this is when n is equal to 1 now second thing will be you starts here you go down to 0 you go back you go like this and your at end of at 0 at x is equal to L, this has to be like this because your light behaves as a way.

Now, the third thing which you can think of is first it decreases goes up becomes 0 here goes up then it starts decreasing towards to 0 goes to minima and then again back to the phi is equal to 0 phi is equal to 0 amplitude becomes 0, so this are allowed wave function and if you look at the wave function then what you will be able to get is lambda of the wave should be equal to 2L divided by n, so if n is equal to 1 then lambda is 2L.

So you see here this is L is equal to lambda by 2 in this case, so lambda is equal to 2L. In this case L is equal to lambda or lambda is equal to 2L by 2 here you can say 2L by 1. Now, let us look at here and this is L is equal to 3 lambda by 2, so lambda will be 2L by 3 so for n is equal to 1 there is 1 here for n is equal to 2 there is 2 here and for n is equal to 3 there is 3 here, so lambda is equal to 2L by n.

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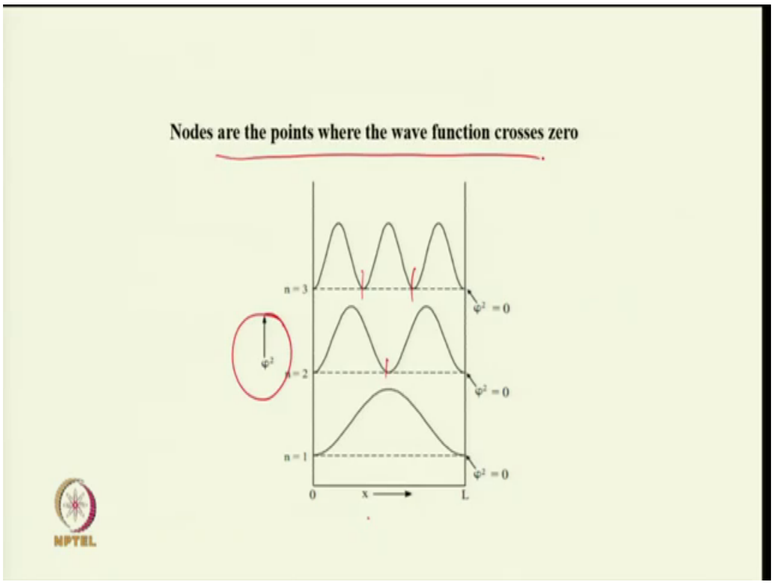

Nodes are the points where the wave function crosses zero

And again if you look at the wave function square verses x (())(21:53) it will look like this, so now you have everything as positive and the amplitude tells you about probability phi square tells you about the probability, so can know what is the probability at the particular point in the one dimensional box and this are the position which are known as nodes, so nodes are the points where the wave function crosses 0.

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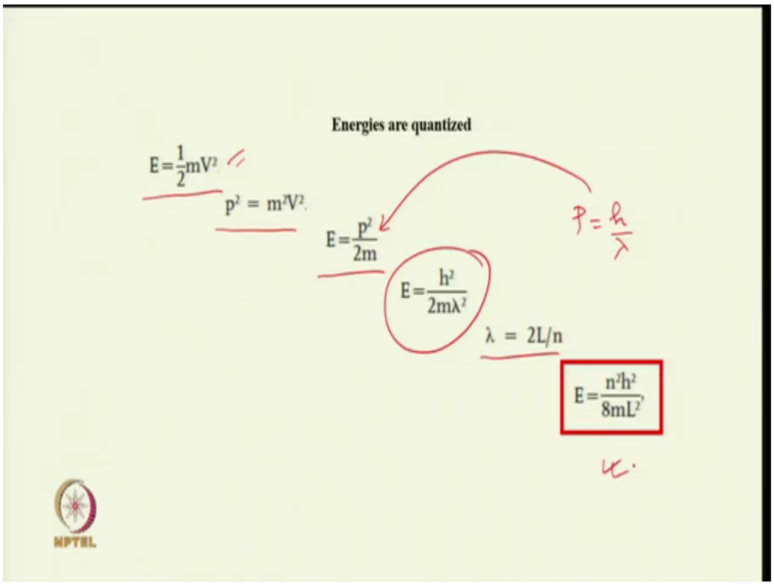

Energies are quantized

$E=\frac{1}{2}mV^2$

$p^2 = m^2V^2$

$E=\frac{p^2}{2m}$

$p=\frac{h}{\lambda}$

$E=\frac{h^2}{2m\lambda^2}$

$\lambda = 2L/n$

$\boxed{E=\frac{n^2h^2}{8mL^2}}$

Now, we know what is the value of lambda, lambda is a function of n which is a, which is known as principle quantum number, now let us calculate energy. We know that E is equal to half mV square and using this let us calculate the momentum, so p square will be a p we know that p is equal to m square V square so what I am trying to do is, I am trying to relate E with p and I know the relationship between p and lambda so I can calculate the energy as a function of n, so energy is half mV square and now I am trying to first express energy in terms of momentum.

So, we know that p is equal to mV so p square is equal to m square V square so energy is p square by 2 m and p is equal to h by lambda from De Broglie hypothesis, so I am replacing p by h by lambda and I plug in value of p to this equation what we get is E is equal to h square by 2 m lambda square and just I showed you hat lambda is equal to 2L by n so you can put it here and what you get is E is equal to n square h square by 8 mL square and this is the way you can know the value of energy of different electronic levels where n is equal to 1, 2, 3, 4.

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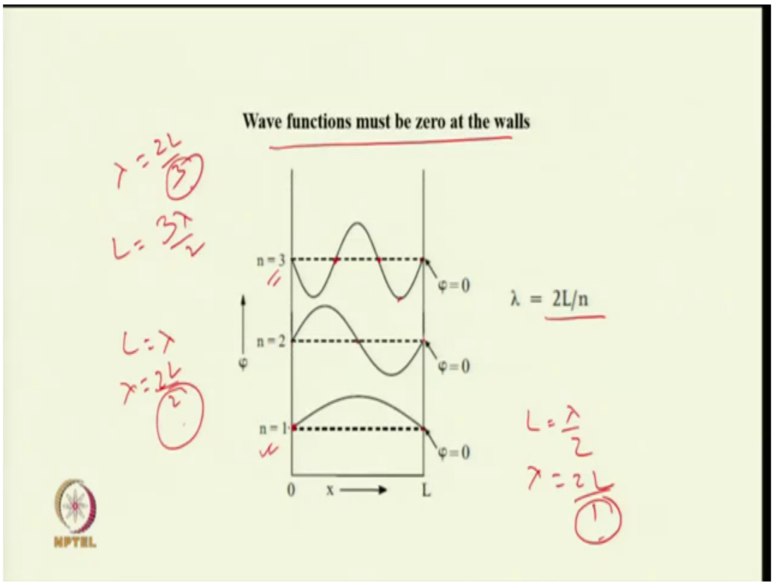

Wave functions must be zero at the walls

In can only take if you look at the previous particle in a box it can only take integer value it can take 1, 2, 3 it can not take a fraction value because in that case the wave function will not be 0 at x is equal to L, x is equal to L.

So, please keep that think in mind and here comes the concept of confinement concept of confinement when a particle is confined in a one dimensional box then its energy can only take discreet values, energy can take only discreet values

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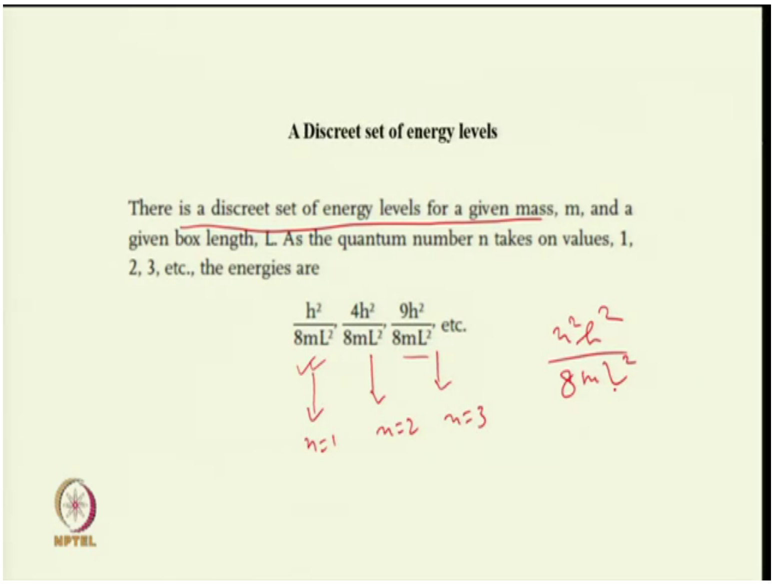

A Discreet set of energy levels

There is a discreet set of energy levels for a given mass, m, and a given box length, L. As the quantum number n takes on values, 1, 2, 3, etc., the energies are

$$\frac{h^2}{8mL^2}, \frac{4h^2}{8mL^2}, \frac{9h^2}{8mL^2}, \text{etc.}$$

$n=1$ $n=2$ $n=3$

$$\frac{n^2h^2}{8mL^2}$$

So, there is a discreet set of energy level for a given mass m and given box length L, in can take values 1, 2, 3 and so energy is h square by 8 mL square, 4h square by 8 mL square, 9h square by 8 mL square this is when n is equal to 1 this will be when n is equal to 2 this is when n is equal to 3 as we know that the energy is given by n square l square by 8mL square. So, if n is equal to 1 then you have h square by 8 mL square and n is equal to 2 you have 4h square by 8 mL square and when n is equal to 3 and you have a 9h square by 8 mL square.

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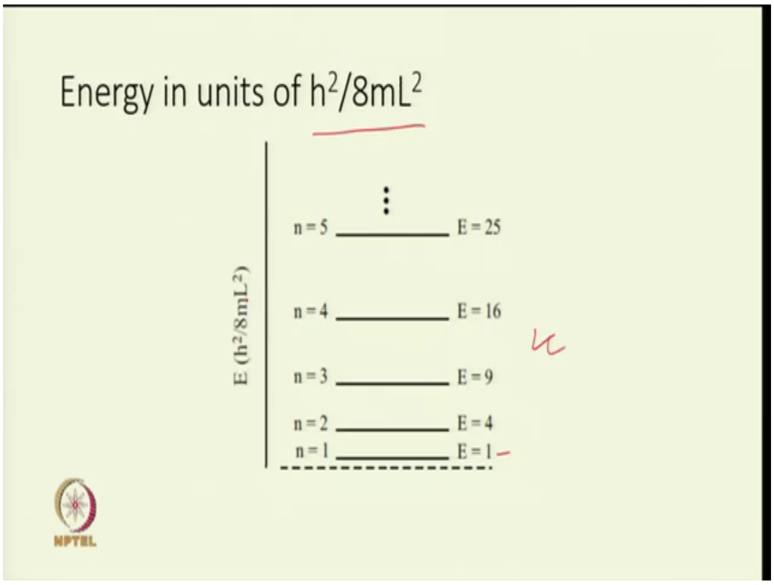

Energy in units of $h^2/8mL^2$

So, here your energy expressed in unit of h square by 8 mL square, so n is equal to 1 it means energy is 1 into h square by 8mL square, so n is equal to 2 then energy is 4 into h square divided 8mL square. So now we know the energy of different levels now we can discuss why are cherries is red and blue where is blue this kind of question we can now, we will now be able to answer.

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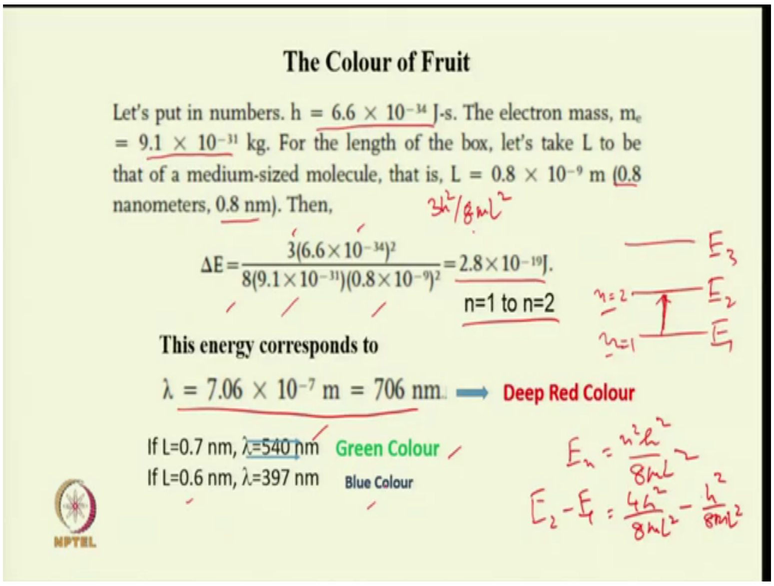
Why are Cherries Red and Blueberries blue ?



The Colour of Fruit

Let's put in numbers. h = 6.6×10^{-34} J-s. The electron mass, m_e = 9.1×10^{-31} kg. For the length of the box, let's take L to be that of a medium-sized molecule, that is, L = 0.8×10^{-9} m (0.8 nanometers, 0.8 nm). Then,

$3h^2/8mL^2$

$$\Delta E = \frac{3(6.6\times10^{-34})^2}{8(9.1\times10^{-31})(0.8\times10^{-9})^2} = 2.8\times10^{-19}\text{J}.$$

n=1 to n=2

$n=2$ — E_2

$n=1$ — E_1

E_3

This energy corresponds to

$\lambda = 7.06 \times 10^{-7}$ m = 706 nm → Deep Red Colour

If L=0.7 nm, λ=540 nm Green Colour

If L=0.6 nm, λ=397 nm Blue Colour

$$E_n = \frac{n^2h^2}{8mL^2}$$

$$E_2 - E_1 = \frac{4h^2}{8mL^2} - \frac{h^2}{8mL^2}$$

So let discuss why certain fruit colour is red and certain fruit colour is blue, so we know now the energy of different levels E1, E2, E3 and suppose the transition takes place between E1 to E2 what does that mean is am going from n is equal to 1 to n is equal to 2 and we know that En is equal to n square h square by 8 mL square and so E2 minus E1 will be equal to 4h square by 8 mL square minus h square by 8 mL square, so here n square is 4 and n is equal to

2 and n square is 1 when n is equal to 1. So E2 minus E1 will be equal to 3h square 4h square minus 1h square 3h square by 8 mL square.

Now, we know the value of h which is this we know the mass of electron which is 9.1 into 10 to the power minus 31 kg and suppose the length is 0.8 Nano meter length of the molecule is 0.8 Nano meter. Now we want to calculate what will the value of delta E and corresponding lambda, so delta E is 3h square by 8 mL square so 3 this is h square into 8 this is mass of electron and this is your length which is 0.8 Nano meter square and this is for transition between n is equal to 1 to n is equal to 2.

The delta will in this case will be 2.8 into 10 to the power minus 19 joule and this energy corresponds to lambda is equal to 706 Nano meter which means that the fruit is going to have deep red colour, fruit is going to have deep red colour, so all these fruits have conjugated system or conjugated molecule and when the fruit has conjugated molecule we can take this molecule and consider it to be placed in a one dimensional box in that way we will be able to calculate energy of different electronic levels of that molecule and once we know the energy it is easy to calculate delta E and corresponding lambda.

So, lambda for transition between n is equal to 1 to n is equal to 2 when the length is 0.8 Nano meter 0.8 Nano meter is your 706 Nano meter which corresponds to deep red colour. Now you can think of same molecule but with smaller length for example L is equal to 0.7 Nano meter in that case your lambda will be equal to 540 Nano meter which will corresponds to green colour and if L is equal to 0.6 Nano meter then it will have blue colour.

So, when for n is equal to L to n is equal to 2 transition the colour of a particular compound will be governed by its length and if length is 0.8 Nano meter then it will corresponds to deep red colour, if L is equal to 0.7 Nano meter it will corresponds to green colour and if L is equal to 0.6 then it will corresponds to blue colour.

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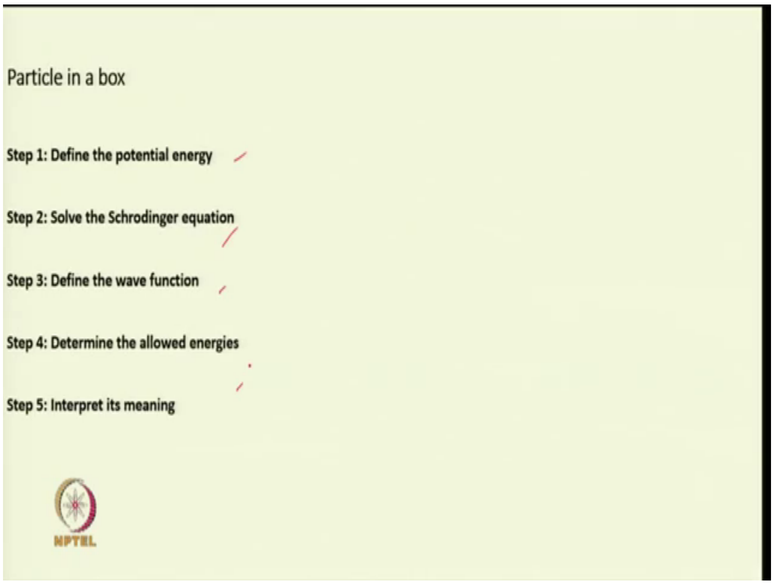

Particle in a box

Step 1: Define the potential energy

Step 2: Solve the Schrodinger equation

Step 3: Define the wave function

Step 4: Determine the allowed energies

Step 5: Interpret its meaning

Now, let us discuss particle in a box in a detail, so first thing we need to write is Schrodinger equation for that we need to know what is the potential energy and when we write Schrodinger equation and solve it we will get wave function we will get the allowed energy and once we have we have allowed energy then we can interpret the transition between different energy levels and lambda corresponding to those transitions.

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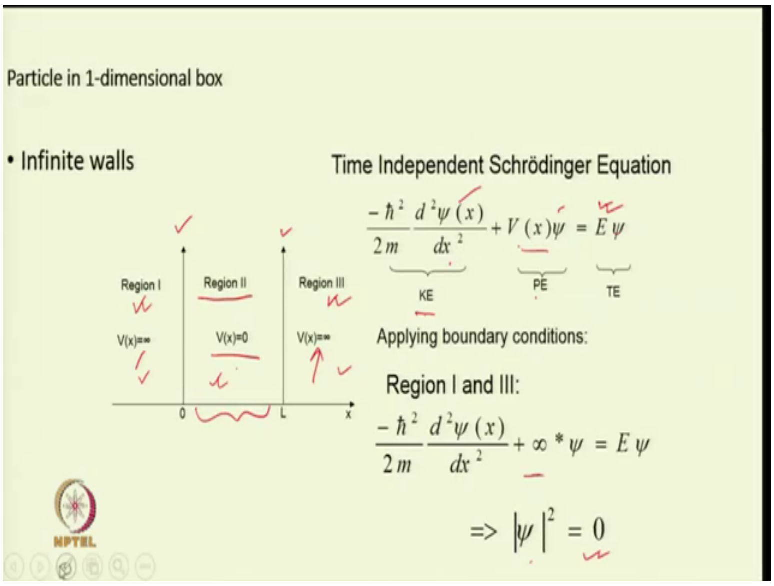

Particle in 1-dimensional box

- Infinite walls

Time Independent Schrödinger Equation

$$\underbrace{\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}}_{KE} + \underbrace{V(x)\psi}_{PE} = \underbrace{E\psi}_{TE}$$

Applying boundary conditions:

Region I and III:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \infty * \psi = E\psi$$

$$\Rightarrow |\psi|^2 = 0$$

So, let us think about particle in one dimensional box as we discuss this space is confined by two infinite walls and let us tells this space to be region 2 where your potential energy is equal to 0 there are two other regions region 1, region 2 and this we Vx is infinity here Vx is equal to infinity again since it is a free particle so potential energy will be 0 in this region and there is no scope to be for a particle to be region 1 or region 3, so Vx is equal to infinity.

Now let us write Schrodinger equation this time independent Schrodinger equation will be minus h cross by 2 m d 2 psi x by dx square this is your kinetic energy term this is potential energy term and when we apply kinetic energy operator plus potential energy operator on the wave function wave function we will get energy as I n value energy at I n value. So, now let us go and apply the boundary conditions in region 1 and 3, this potential is infinity and so wave function must be equal to 0, so psi square must be 0, so wave function must be 0 in this 2 regions.

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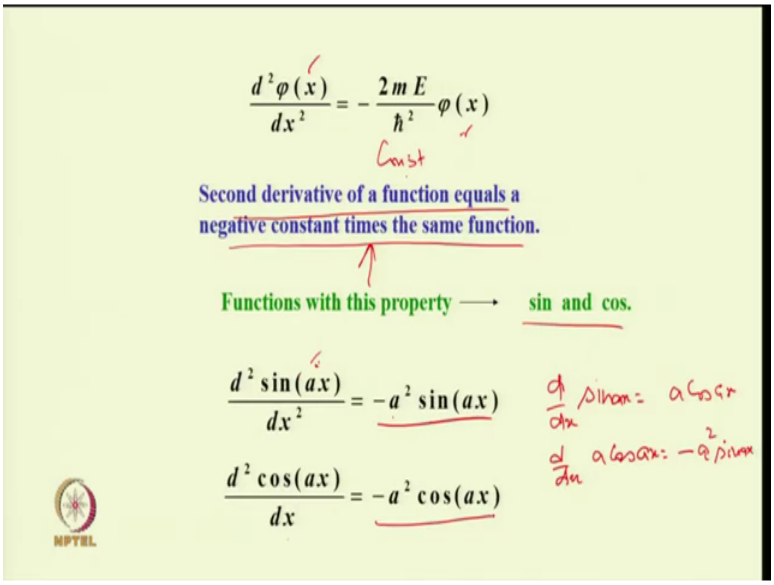


$$\frac{d^2\varphi(x)}{dx^2} = -\underbrace{\frac{2mE}{\hbar^2}}_{\text{Const}}\varphi(x)$$

Second derivative of a function equals a negative constant times the same function.

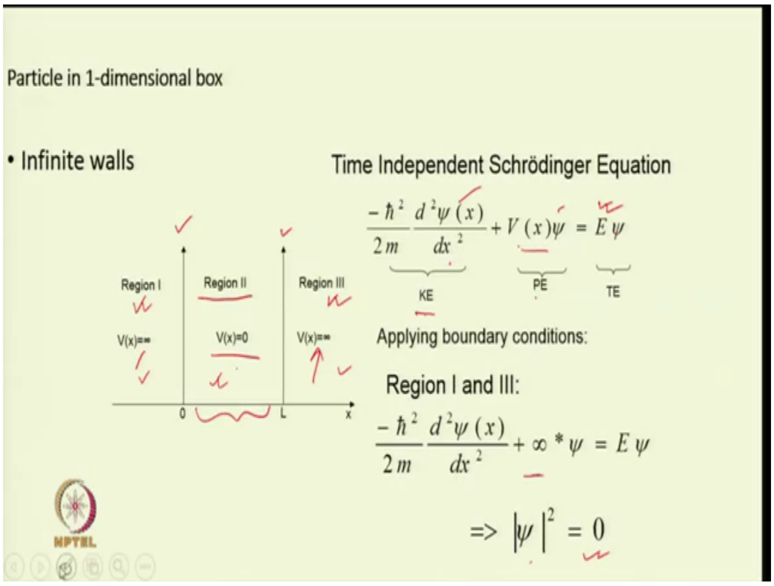
Functions with this property ⟶ sin and cos.

$$\frac{d^2\sin(ax)}{dx^2} = -a^2\sin(ax)$$

$$\frac{d^2\cos(ax)}{dx} = -a^2\cos(ax)$$

$$\frac{d}{dx}\sin ax = a\cos ax$$

$$\frac{d}{dx}a\cos ax = -a^2\sin ax$$



Particle in 1-dimensional box

- Infinite walls

Time Independent Schrödinger Equation

$$\underbrace{\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}}_{\text{KE}} + \underbrace{V(x)\psi}_{\text{PE}} = \underbrace{E\psi}_{\text{TE}}$$

Applying boundary conditions:

Region I and III:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \infty * \psi = E\psi$$

$$\Rightarrow |\psi|^2 = 0$$

Now, let us go back and see what is the equation this equation here and this, suppose this V is 0 which is in this region and so what equation left is this is equal to E psi and this basically get the formulaic this d 2 phi x by dx square is equal to minus 2 m E divided by h cross square into phi x, second derivative of a function equals a negative constant times the same function, so this is basically a constant multiplied by phi, the second derivative of a function equals a negative constant times this the same function, if you have a this kind of differential equation it is quite easy to guess what will be the solution.

Now let us think of this the function with this property can be represented by sin or cosine function, so function with this property is sin and cosine function, function with this property is sin and cosine function now let us think of if I take second differential what will happen, so let us take second differential of sin ax we know that first differential is d by dx sin ax is equal to a cos ax and when we take d by dx of a cos ax is equal to minus a square sin ax.

So that is what I have written here and now you can see that the second differential of this function is minus a square multiplied by sin function similarly you can do for cos ax by d square by dx of cos ax and that will be minus a square cos ax similar way you can prove it. So what that means is solution of this differential equation is either sin function or cosine function.

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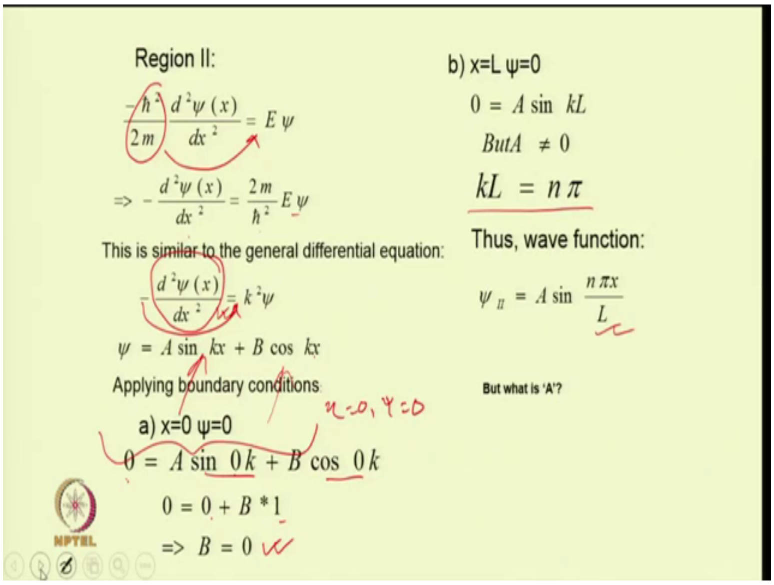

Region II:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi$$

$$\Rightarrow -\frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar^2}E\psi$$

This is similar to the general differential equation:

$$-\frac{d^2\psi(x)}{dx^2} = k^2\psi$$

$$\psi = A\sin kx + B\cos kx$$

Applying boundary conditions

x=0, ψ=0

a) x=0 ψ=0

$$0 = A\sin 0k + B\cos 0k$$

$$0 = 0 + B*1$$

$$\Rightarrow B = 0$$

b) x=L ψ=0

$$0 = A\sin kL$$

$$But A \neq 0$$

$$kL = n\pi$$

Thus, wave function:

$$\psi_{II} = A\sin\frac{n\pi x}{L}$$

But what is 'A'?

So, let us again go back to region 2 and try to solve this so minus h cross square by 2m d2 psi x by dx square is equal to E psi and if I take this 2 to this side what I will get is minus d2 psi x by dx square is equal to 2 m in the numerator divided by h cross square into E psi and then you get there is differential equation which is the second derivative is equal to if you take minus this side second derivative is equal to minus k square psi and for that your solution can be a sin wave function or cosine wave function and general way to denote this is psi is equal to A sin kx plus b cos kx.

Now, what we will do is will try boundary conditions we will apply boundary conditions to get the value of k, so if I apply boundary condition what we know that wave function is your 0 at the boundary, so we know that at x is equal to 0 wave function is 0 so if we apply that condition so at x is equal to 0 wave function is 0 if we apply this condition what I am going to get is b is equal to 0, since sin 0 is 0 cos 0 is 1 and so B is equal to 0 So, now we got the value of B,

Now second condition is at x is equal to L psi is equal to 0 so at L also wave function must be 0 and if we apply that condition what we are going to get is this 0 is equal to A sin k into L and since A is not equal to 0 which means kL is equal to n pie and your and thus the wave function is your A sin in place of k you can put n pie by L so n pie x by L, this is your solution of the wave function, solution of the wave function from the Schrodinger equation, but what is A we have already calculated B we know what is the value of A, now we need to know the value of A once we know that everything is known and you know what will be the wave function.

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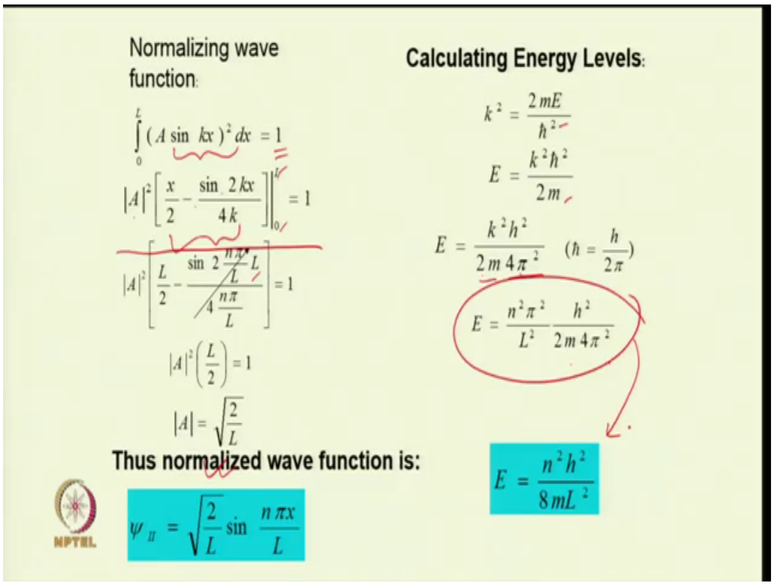

Normalizing wave function:

$$\int_0^L (A\sin kx)^2\,dx = 1$$

$$|A|^2\left[\frac{x}{2}-\frac{\sin 2kx}{4k}\right]_0^L = 1$$

$$|A|^2\left[\frac{L}{2}-\frac{\sin 2\frac{n\pi}{L}L}{4\frac{n\pi}{L}}\right] = 1$$

$$|A|^2\left(\frac{L}{2}\right) = 1$$

$$|A| = \sqrt{\frac{2}{L}}$$

Thus normalized wave function is:

$$\psi_n = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$$

Calculating Energy Levels:

$$k^2 = \frac{2mE}{\hbar^2}$$

$$E = \frac{k^2\hbar^2}{2m}$$

$$E = \frac{k^2h^2}{2m4\pi^2} \quad \left(\hbar = \frac{h}{2\pi}\right)$$

$$E = \frac{n^2\pi^2}{L^2}\frac{h^2}{2m4\pi^2}$$

$$E = \frac{n^2h^2}{8mL^2}$$

So, for that you need to do normalization and we know that in the normalization your psi star psi dx when it’s a vindicator between to L it should be 1 because somewhere in between your particle is present, so probability of finding the particle in the box is 1, now if you do this what you are going to get is A square x by 2 minus sin 2 kx by 4k and 0 to L, so this is your this part is basically integration of sin square Ax dx sin square Ax dx.

So, you do this integration and you do this integration you will get this value, now you put this conditions when you put this conditions what you are going to get is when x is equal to L then it will be L by 2 minus sin 2, 2kx so 2k put the value of k also you will get this value and for 0 you are going to get 0 here and again here it will be 0.

So, using this you will be able to get value of A which is square root of 2 divided by L which is a square root of 2 divided L and thus the normalized wave function for a particle in a box is equal to square root of 2 by L multiplied by sin n pie x by L, sin n pie x by L.

Now, let us calculate energy levels we know that k square is equal to 2m E by h cross square so E is equal to k square h cross square by 2m where h cross is h by 2 pie then E will be k square h square by 2m into 4 pie square and k we know k will be n pie by L, so k square is n square pie square by L square multiplied by h square 2m 4 pie square from here and so energy is will be given by energy will be given by is equal to n square h square by 8mL square and that is what we got when we applied this simple concept of wave becoming 0 at 2 walls.

But now we have energy term and as you can see it E is dependent on n value and n can take only values integer values, so 1, 2, 3, 4 n can take values 1, 2, 3, 4 and once I know what is the energy level now I can go and calculate what will be the value of energy of different levels of a conjugated system conjugated system.

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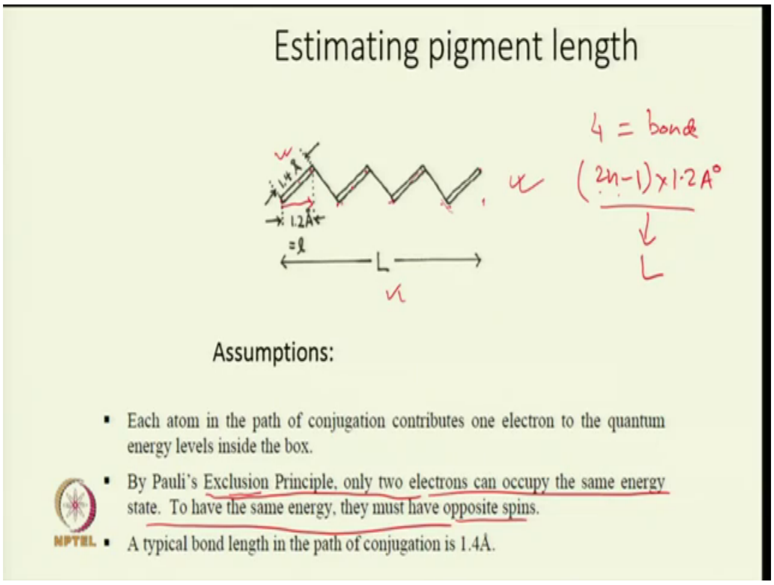

Estimating pigment length

Assumptions:

- Each atom in the path of conjugation contributes one electron to the quantum energy levels inside the box.
- By Pauli's Exclusion Principle, only two electrons can occupy the same energy state. To have the same energy, they must have opposite spins.
- A typical bond length in the path of conjugation is 1.4Å.

So, this is your conjugated system double bond followed by a single bond double bond followed by a single bond, so first thing is that what will be the value of L what will be the value of this L or you can say that your size of one dimensional box generally this bond is double bond is equal to 1.4 angstrom and if you take in this direction this length is equal to 1.2 angstrom and so you can know what is the length of this box, so for example if it is four double bond system now you see here 1.2, 1.2.

So this is your 2.4 this is 2.4 this is 2.4 and this is 1.2 so 1, 2, 3, 4, 5, 6, 7 and so what you can do is you can write this as your 2n minus 1 multiplied by 1.2 angstrom so if there is a four number of double bond then you have a 2 into 4 minus 1 that is 7 multiplied by 1.2 angstrom length.

Now, each atom in the path of conjugation contribute to 1 electron to the quantum energy level inside the box, so how many atom is here 1, 2, 3, 4, 5, 6, 7, 8 and each one of them is contributing 1 electron, so total number of electron in the conjugated system is 8 from Pauli Exclusion principle only two electron can occupied the same energy state to have to same energy they must have opposite spins and a typical bond length in the path of conjugation is 1.4 angstrom.

One thing you must keep in mind is, this is larger than a bond length of carbon double bond carbon it is not basically double bond corrector since it is in conjugation with another double bond and so it is between a single bond and double bond.

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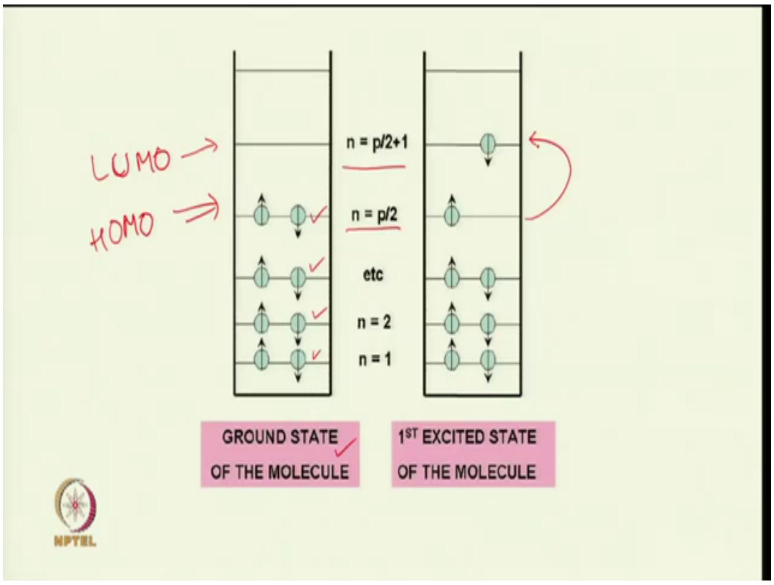

Now, lets us talk about your last system where there are four double bonds in conjugation, so the number of electron in conjugation is 8 and so if I try to fill in the electronic states the different molecular levels how we are going to do is to is in this ground state to is in this state to is in this state and to is in this state and this is your highest occupied molecular orbital and this will be lowest unoccupied LUMO lowest unoccupied molecular orbital and this will be equal to p by 2 where p is total number of electron and so 8 by 2 is 4 and n is going to be 4 plus 1 5, so this is your ground state of the molecule and first exited state when 1 from HOMO goes to 1 electron from HOMO goes to LUMO.

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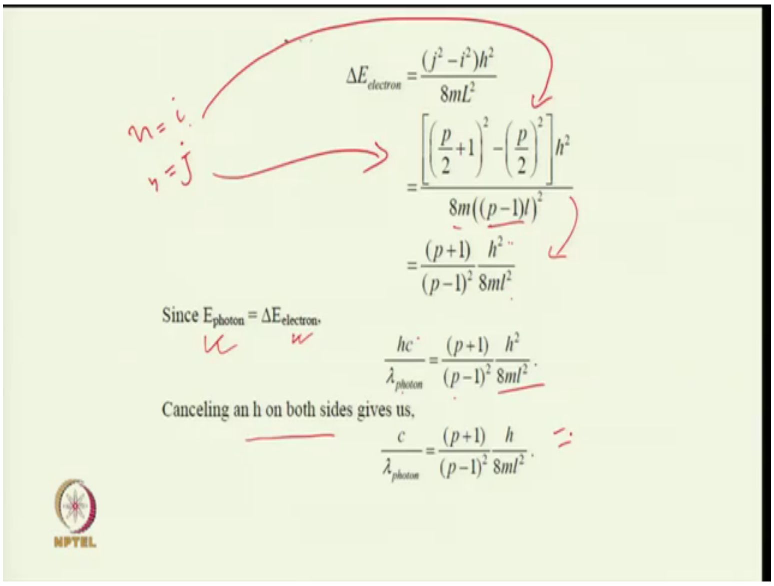

n = i

n = j

$$\Delta E_{electron} = \frac{(j^2 - i^2)h^2}{8mL^2}$$

$$= \frac{\left[\left(\frac{p}{2}+1\right)^2 - \left(\frac{p}{2}\right)^2\right]h^2}{8m((p-1)l)^2}$$

$$= \frac{(p+1)}{(p-1)^2}\frac{h^2}{8ml^2}$$

Since $E_{photon} = \Delta E_{electron}$,

$$\frac{hc}{\lambda_{photon}} = \frac{(p+1)}{(p-1)^2}\frac{h^2}{8ml^2}.$$

Canceling an h on both sides gives us,

$$\frac{c}{\lambda_{photon}} = \frac{(p+1)}{(p-1)^2}\frac{h}{8ml^2}.$$

And now we can calculate delta E, so delta E is equal to j square minus i square h square by 8mL square so what I am giving is when I go from n is equal to I to n is equal to j this will be the delta E for electron and just we saw that j will be given by p by 2 plus 1 whereas I will be given by p divided by 2.

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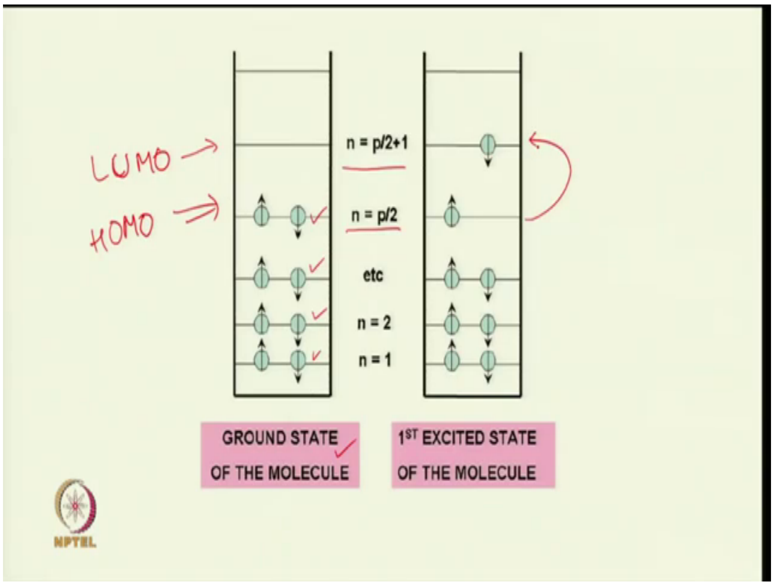
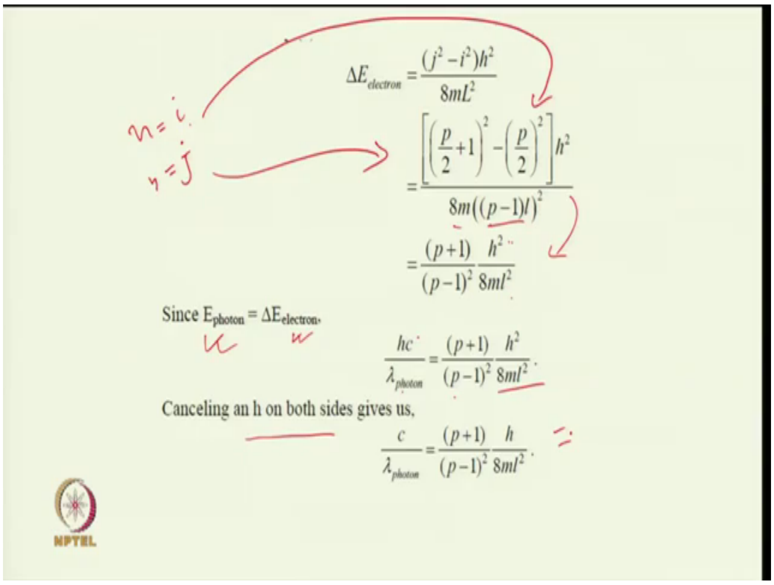


GROUND STATE OF THE MOLECULE

1ST EXCITED STATE OF THE MOLECULE



$$\Delta E_{electron} = \frac{(j^2 - i^2)h^2}{8mL^2}$$

$$= \frac{\left[\left(\frac{p}{2}+1\right)^2 - \left(\frac{p}{2}\right)^2\right]h^2}{8m((p-1)l)^2}$$

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Canceling an h on both sides gives us,

$$\frac{c}{\lambda_{photon}} = \frac{(p+1)}{(p-1)^2}\frac{h}{8ml^2}.$$

If you remember that in this case n is equal to p by 2 and this n will be equal to p by 2 plus 1, so HOMO for HOMO n is equal to p by 2 for LUMO your n is equal to p by 2 plus 1, so I is HOMO and this is your p by 2 and j is LUMO which is p by 2 plus 1, and 8m p minus 1 into L square let me explain this here.

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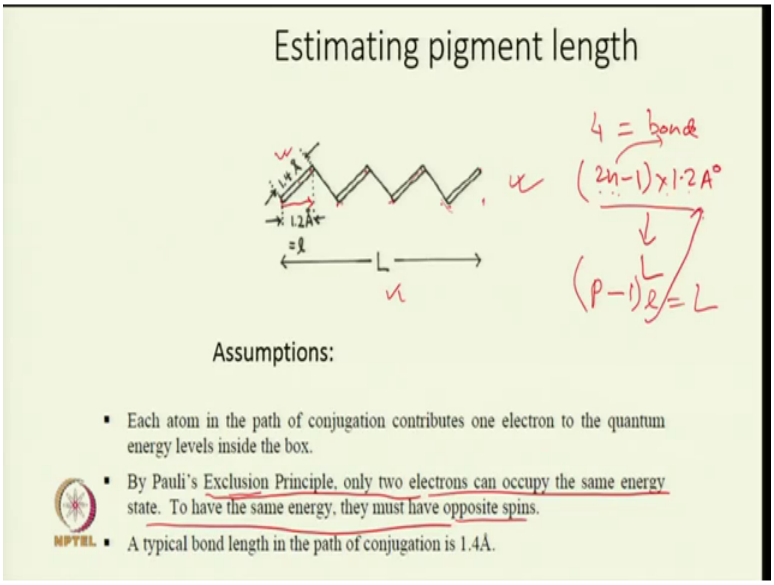

Estimating pigment length

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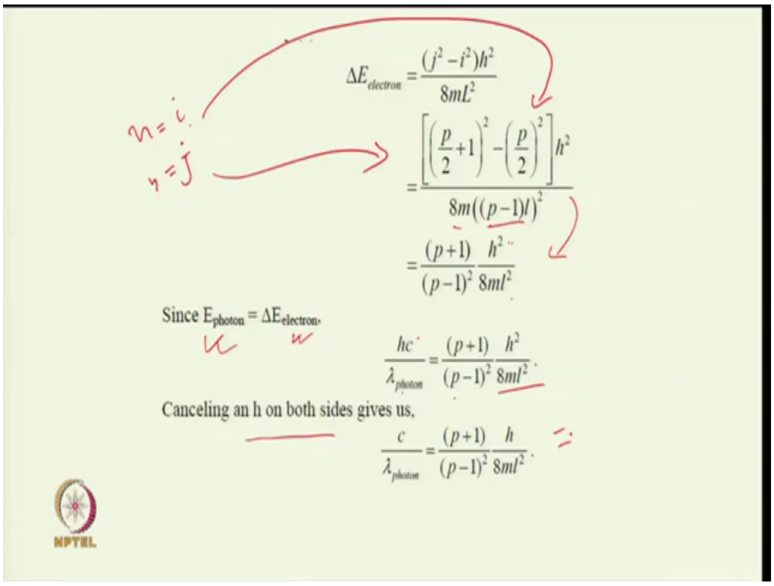

$$\Delta E_{electron} = \frac{(j^2-i^2)h^2}{8mL^2}$$

$$= \frac{\left[\left(\frac{p}{2}+1\right)^2-\left(\frac{p}{2}\right)^2\right]h^2}{8m((p-1)l)^2}$$

$$= \frac{(p+1)}{(p-1)^2}\frac{h^2}{8ml^2}$$

Since $E_{photon} = \Delta E_{electron}$,

$$\frac{hc}{\lambda_{photon}} = \frac{(p+1)}{(p-1)^2}\frac{h^2}{8ml^2}.$$

Canceling an h on both sides gives us,

$$\frac{c}{\lambda_{photon}} = \frac{(p+1)}{(p-1)^2}\frac{h}{8ml^2}.$$

We just calculated 2n minus 1 multiplied by 1.2 angstrom where n is number of bond and 2n will be number of electrons conjugated electrons, so p minus 1 into small l will be equal to L where small l is 1.2 angstrom and so if I put it here it will be p minus 1 into L square and if you simplify it what you are going to get is p plus 1 divided by p minus 1 square multiplied by h square by 8mL square and E photon will be equal to delta E electron and so hc by lambda of photon will be equal to p plus 1 h square divided by p minus 1 square 8mL square. Canceling h on both side gives you C by lambda is equal to this and so you can know what is the value of lambda.

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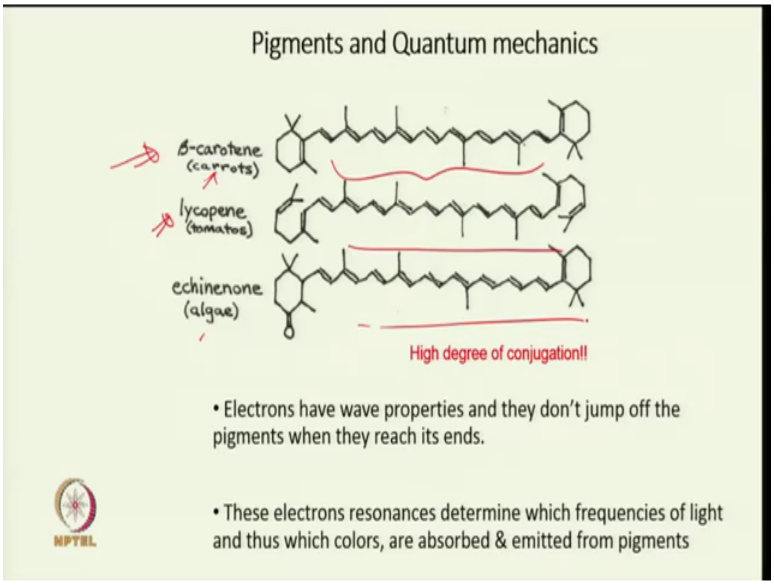
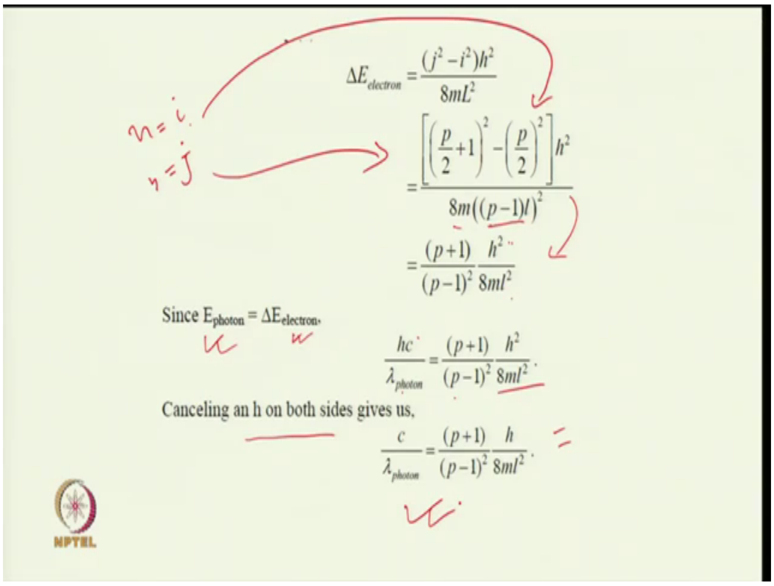


Pigments and Quantum mechanics

- Electrons have wave properties and they don't jump off the pigments when they reach its ends.
- These electrons resonances determine which frequencies of light and thus which colors, are absorbed & emitted from pigments



n = i

n = j

$$\Delta E_{electron} = \frac{(j^2 - i^2)h^2}{8mL^2}$$

$$= \frac{\left[\left(\frac{p}{2}+1\right)^2 - \left(\frac{p}{2}\right)^2\right]h^2}{8m((p-1)l)^2}$$

$$= \frac{(p+1)}{(p-1)^2}\frac{h^2}{8ml^2}$$

Since $E_{photon} = \Delta E_{electron}$,

$$\frac{hc}{\lambda_{photon}} = \frac{(p+1)}{(p-1)^2}\frac{h^2}{8ml^2}.$$

Canceling an h on both sides gives us,

$$\frac{c}{\lambda_{photon}} = \frac{(p+1)}{(p-1)^2}\frac{h}{8ml^2}.$$

Now once you have this concept now you can go ahead and calculate the lambda value for different fruits, now let me give three examples of fruits for example carrot, tomato and algae there colour is due to different conjugated molecules for example in carrots there is beta carotene and its structure is given here. In tomatoes you have a lycopene and its structure is given here, and in algae there is echinenone and here is the conjugation, and you can now see that there is high degree of conjugation in this compound and that basically results into colour.

Electrons here electrons you can think of electrons have wave property and they do not jump of the pigment when they reach its ends, the electrons resonance is determines which frequency of light and thus which colour are absorbed or emitted from the pigment, so it is not very difficult to calculate the I have already told you that if there is if there is E electron in conjugating then this is the formula which can be used to calculate the value of lambda, an same thing you can do it here you see here conjugation 2 to 4, 6, 8, 10, 12, 14, 16, 18, 20 and 22 these are the number of electrons in conjugation and now you know the value of p you can calculate what will be the lambda.

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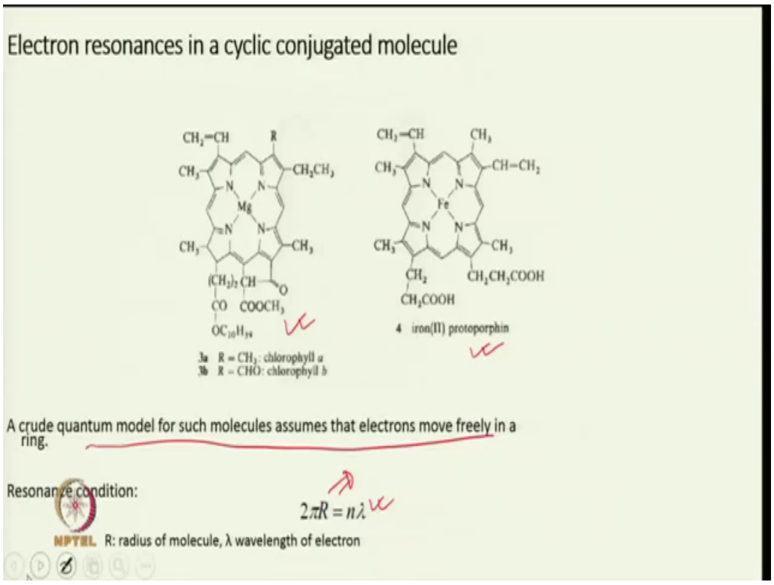

Electron resonances in a cyclic conjugated molecule

A crude quantum model for such molecules assumes that electrons move freely in a ring.

Resonance condition:

$$2\pi R = n\lambda$$

R: radius of molecule, λ wavelength of electron

Now, can we calculate the lambda value for cyclic conjugated molecule because there are lot of molecules in the nature which is a cyclic conjugated molecule, for example your chlorophyll or protoporphis they have a cyclic structure and they are cyclic conjugated system. Here again we can apply the crude quantum model, crude quantum model now you can think of this as a ring and a ring the resonance condition is 2 pie R is equal to n lambda, if you remember we have discussed this when we were discussing rotation, rotation.

So, the resonance condition is 2 pie R is equal to n lambda so now I know the lambda value and since lambda is related to momentum p and so I can know what is the value of p and now p is related to energy and so energy can be calculate.

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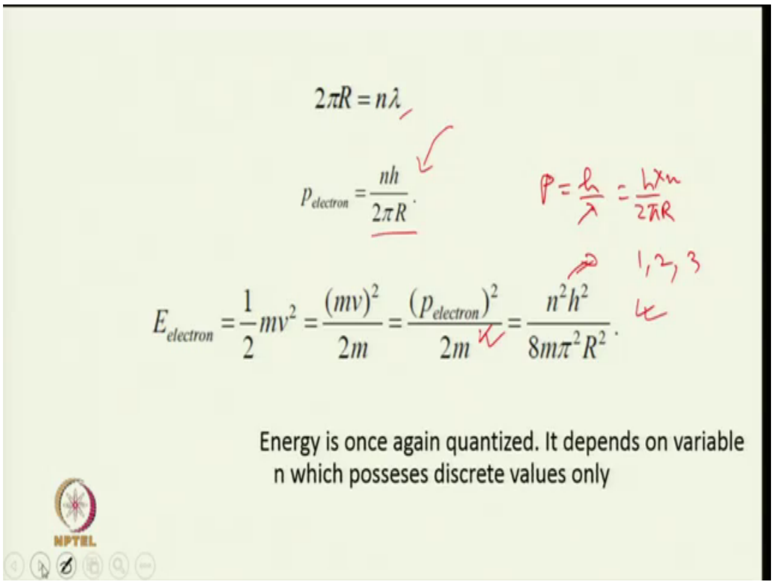

$$2\pi R = n\lambda$$

$$p_{electron} = \frac{nh}{2\pi R}$$

$$p = \frac{h}{\lambda} = \frac{h \times n}{2\pi R}$$

1, 2, 3

$$E_{electron} = \frac{1}{2}mv^2 = \frac{(mv)^2}{2m} = \frac{(p_{electron})^2}{2m} = \frac{n^2h^2}{8m\pi^2R^2}$$

Energy is once again quantized. It depends on variable n which posseses discrete values only

So, 2 pie R is equal to n lambda and we know that p is equal to h by lambda and so your p will be nh by 2 pie R, so you can simply put h by lambda will be equal to 2 pie R and that is all and now once we know the value of p we can calculate energy of the electron and that will be given by p square by 2m, so p is equal to nh by 2 pie R so take the square of this and divide by 2m you can get the energy of electron and now you can see energy is once again quantized because n can only take value 1, 2, 3 so it depends on variable n which is which possesses discrete value and so we have only discreet energy levels, discrete energy levels.

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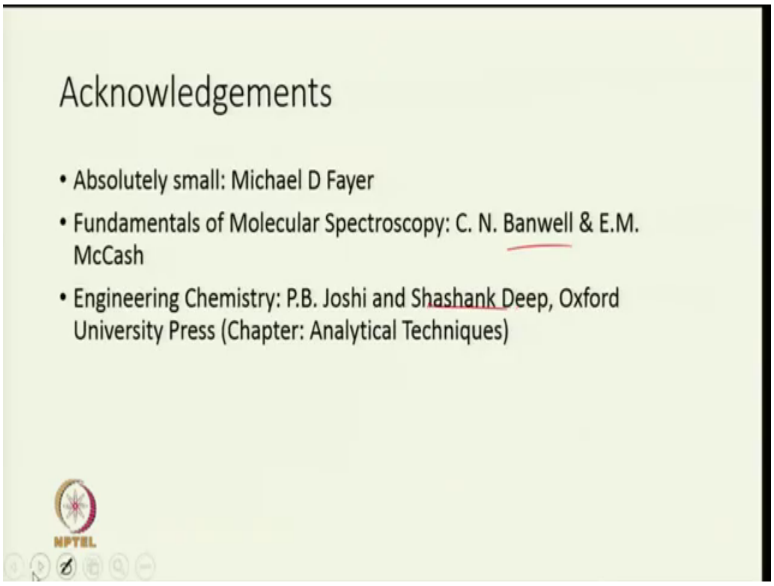

Acknowledgements

- Absolutely small: Michael D Fayer
- Fundamentals of Molecular Spectroscopy: C. N. Banwell & E.M. McCash
- Engineering Chemistry: P.B. Joshi and Shashank Deep, Oxford University Press (Chapter: Analytical Techniques)

Time is up so I will discuss about this electronic material thing in the next lecture thank you very much for listening, I will directly go to acknowledgement section and I will recommend you to read the book called absolutely small by Michael D Fayer very well written book and certainly you can also look at Banwell book and the book written by me lot of figures has been taken from these books or waves and I have tried to acknowledge all of them.