Concepts of Chemistry for Engineering

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Lecture No. 06
Particle in 1D box

We have discussed free particle and we have seen that for free particle energy is not quantized. Now, what we are going to do is that we are going to put a particle in a box. What does that mean, we will see that shortly. But let me tell you that, this model that we are going to study now not only does it teach us a little bit about quantum mechanics but also this very simple model that we are going to talk about now is applicable in many many chemical systems as a first approximation at least.

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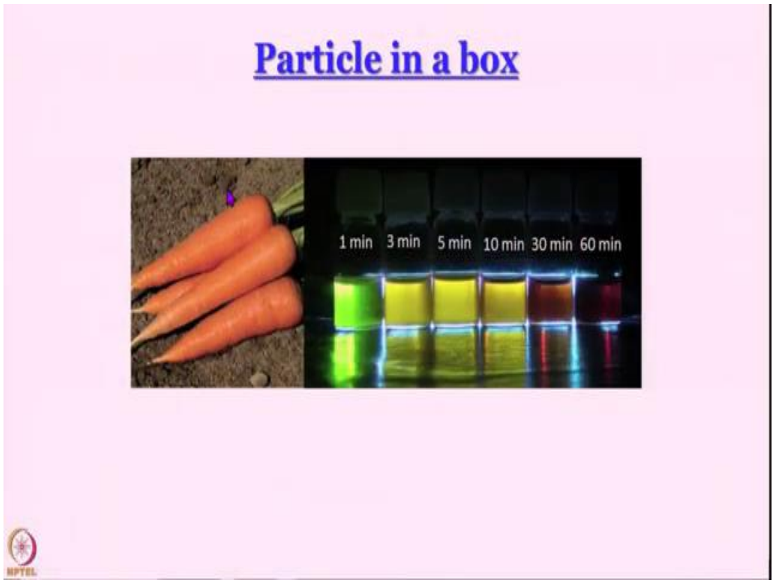
Particle in a box

It is this model that can be used to tell us why carrots have this beautiful color, it is this model that can be modified a little bit and tell us why quantum dots many of you might have heard about quantum dots, now we here are things like quantum dot television and all. So, why quantum dots have different color depending on their size, but more about that when we come to it.

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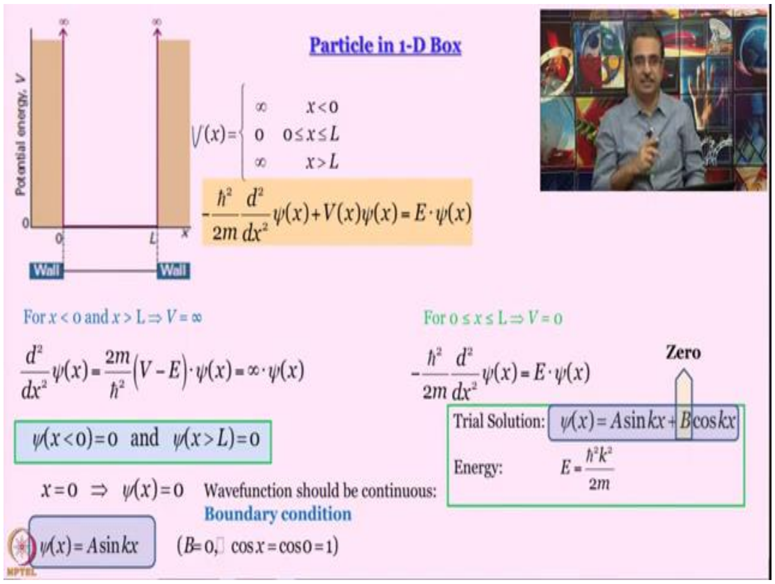

Particle in 1-D Box

$$V(x)=\begin{cases}\infty & x<0\\ 0 & 0\le x\le L\\ \infty & x>L\end{cases}$$

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

For $x<0$ and $x>L \Rightarrow V=\infty$

$$\frac{d^2}{dx^2}\psi(x)=\frac{2m}{\hbar^2}\left(V-E\right)\cdot\psi(x)=\infty\cdot\psi(x)$$

$$\boxed{\psi(x<0)=0 \text{ and } \psi(x>L)=0}$$

$x=0 \Rightarrow \psi(x)=0$ Wavefunction should be continuous: **Boundary condition**

$\boxed{\psi(x)=A\sin kx}$ $(B=0,□ \cos x=\cos 0=1)$

For $0\le x\le L \Rightarrow V=0$

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

Trial Solution: $\psi(x)=A\sin kx+B\cos kx$

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

Let us say we put this particle in a box defined by two walls where there is an infinite potential barrier, where the potential $V(x)$ is 0 between x=0 and x=L. If you go below 0, $x<0$ or if you go more than L, $x>L$ then the potential is infinite. So, the box essentially is a plot of the potential, there is a discontinuity.

So, at x=0 and x=L all of a sudden potential becomes infinity and it remains infinity everywhere else. So, this is called a particle in a box. So, let us see what the equation will be for the particle inside the box and outside the box. This here is the most general Schrodinger equation you can write for a particle in one dimension.

First term remember $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)$, this tells us about kinetic energy and second term $V(x)\psi(x)$ that gives us information about potential energy, right hand side is total energy value E multiplied by $\psi(x)$, this is an Eigen value equation. Outside the box what happens? For $x<0$ and $x>L$, V equal to infinity.

So, if V equal to infinity you just write it like this it is a very strange situation, , what will this become, $\frac{2m}{\hbar}\,(V-E)\,\psi(x)$, well operating on $\psi(x)$ you can say whatever, multiplying $\psi(x)$. That is going to be $\infty\psi(x)$. So, this can only be correct if $\psi(x)$ is 0, so right away we learn that for x less than 0 and x greater than L, the wave function is equal to 0.

Now, we say that for x between 0 and L, we have said that the potential is 0, so as long as x is between 0 and L the particle behaves as a free particle and we know what the Schrodinger equation for free particle is going to be, this is what it is. What is the trial solution? We have discussed this already, trial solution is going to be $\psi(x) = (A\ sinkx + B\ coskx)$ and energy is going to be $E = \frac{\hbar^2 k^2}{2m}$, this is what we know already from our previous discussion of particle in for of free particle, great.

Now see, now let us look at what happens at the boundaries. For x less than 0 wave function equal to 0, let us work with that first. Remember Born interpretation, $\Psi\Psi^*$ is probability density and one of the conditions that Ψ must satisfy is that Ψ must be continuous. So, since at any point very very close to x equal to 0 but less than 0, since wave function has to be 0, it is implied that at x equal to 0 also, $\psi(x)$ must be equal to 0.

Why? Because the wave function should be continuous, this is what is called a boundary condition, a boundary condition is a condition that puts a restriction on the wave function. Now, if we put 0 in the expression of the wave function, what do we get? $(A\ sink0 + B\ cosk0)$, what is $sink0$? $sink0$ is equal to 0 and what is $cosk0$? That is equal to 1. So, we actually obtain the expression for $\psi(0)$, $\psi(0)$ turns out to be B.

So, what we get then is, B is equal to 0 and B equal to 0 for everything. It is not as if B equal to 0 only for x, A and B remember are independent of x, they are constants. So, we find that when we apply the condition that $\psi(x)$ must be 0 for x equal to 0, it implies that B has to be equal to 0. So, the wave function becomes a little simpler than what it was for particle, for free particle. The wave function for particle in a box now becomes $\psi(x) = A\ sinkx$.

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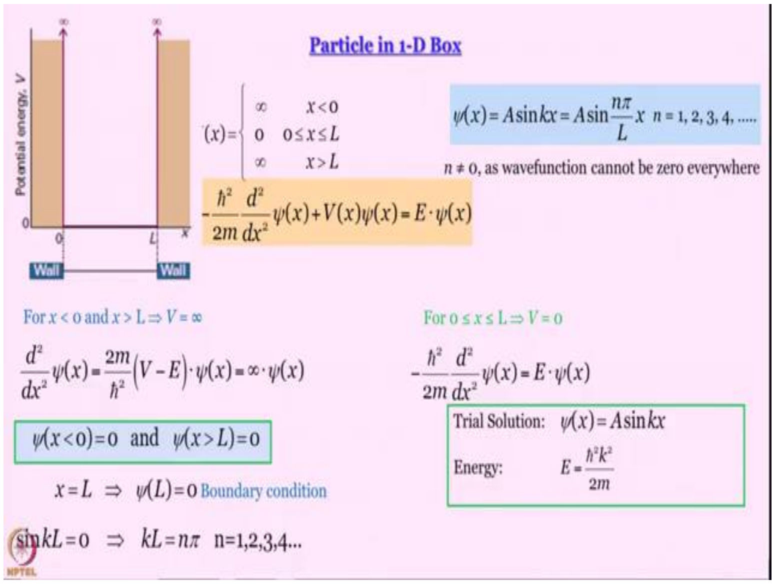

Particle in 1-D Box

$$(x)=\begin{cases}\infty & x<0\\ 0 & 0\le x\le L\\ \infty & x>L\end{cases}$$

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

$$\psi(x)=A\sin kx=A\sin\frac{n\pi}{L}x \quad n=1,2,3,4,\ldots..$$

$n\neq 0$, as wavefunction cannot be zero everywhere

For $x<0$ and $x>L \Rightarrow V=\infty$

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

$$\psi(x<0)=0 \text{ and } \psi(x>L)=0$$

$x=L \Rightarrow \psi(L)=0$ Boundary condition

$\sin kL=0 \Rightarrow kL=n\pi$ n=1,2,3,4...

For $0\le x\le L \Rightarrow V=0$

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

Trial Solution: $\psi(x)=A\sin kx$

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

We have a simple solution now $A\ sinkx$. Now, let us look at the other side of the boundary, the other boundary. Remember that even for x equal to L Ψ must be equal to 0, because wave function has to be continuous boundary condition. So, when we apply that, we get that sign $\sin kL$ must be equal to 0, when will $\sin kL$ be equal to 0? When kL is equal to nπ, where n can be 1, 2, 3, 4, so on and so forth, integral multiple of n.

What about minus 1, minus 2, minus 3, minus 4? That also, but we do not take the minus sign because it does not add any value to the problem, you only take plus sign, n equal to 1, 2, 3, 4. So, this is the solution we have so far, $\psi(x) = A\ sin\frac{n\pi}{L}\ x$, where n is some discrete positive integer 1, 2, 3, 4.

I will be surprised if you are not wondering why is n not equal to 0, n is not equal to 0 because in this expression here if you put n equal to 0, then what happens? Then the entire wave function becomes 0 for all values of x. Here, when we put $\frac{nx}{L}$ equal to 0, well when I put n equal to 1 then the expression of wave function becomes $A\ sin\frac{\pi}{L}\ x$. So, when L equal to 0 that will be equal to 0 that is a different issue altogether.

But for other values of x between 0 and L it is not necessarily 0, but if I put L equal to 0, then what is the wave function $\psi(x) = A\ sin0$, discrete wave function and that is 0. So, if the wave function is 0 everywhere inside the box, then that means probability of finding the particle inside the box is 0, we have already established that probability of finding the particle outside the box is 0.

So, if n equal to 0 then the particle is not there anywhere in the universe. So, that is why n cannot be equal to 0 and the only values we can get are n equal to 1, 2, 3, 4 follows nicely from a simple mathematical treatment that we have performed so far. The only thing that is left now as far as the wave function is concerned is to determine what is the value of A.

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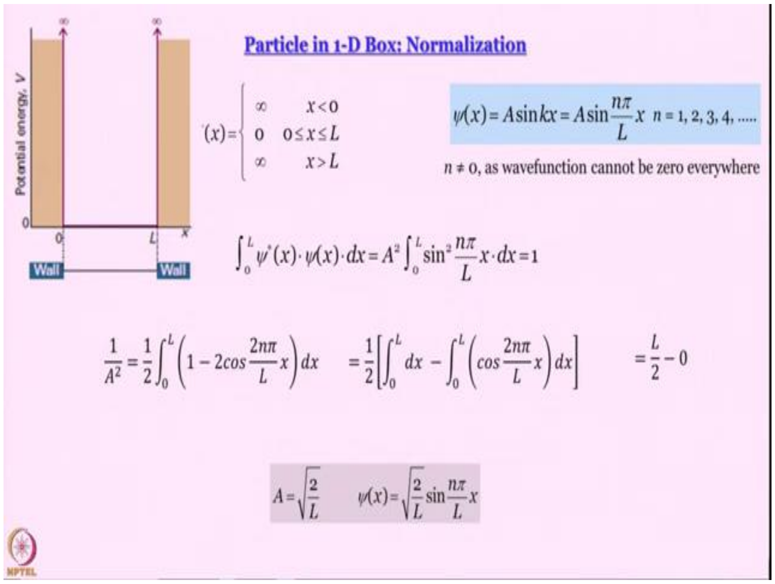

Particle in 1-D Box: Normalization

$$(x)=\begin{cases}\infty & x<0\\ 0 & 0\le x\le L\\ \infty & x>L\end{cases}$$

$$\psi(x)=A\sin kx=A\sin\frac{n\pi}{L}x \quad n=1,2,3,4,.....$$

$n\neq 0$, as wavefunction cannot be zero everywhere

$$\int_0^L\psi^*(x)\cdot\psi(x)\cdot dx=A^2\int_0^L\sin^2\frac{n\pi}{L}x\cdot dx=1$$

$$\frac{1}{A^2}=\frac{1}{2}\int_0^L\left(1-2cos\frac{2n\pi}{L}x\right)dx \quad =\frac{1}{2}\left[\int_0^L dx-\int_0^L\left(cos\frac{2n\pi}{L}x\right)dx\right] \quad =\frac{L}{2}-0$$

$$A=\sqrt{\frac{2}{L}} \qquad \psi(x)=\sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x$$

But before that, well to determine value of A what we do is we normalize, we know that when we integrate and now, I want to draw your attention to something, we integrate between limits of x equal to 0 and x equal to L, I do not have to integrate from minus infinity to plus infinity. Why? Because in any case the particle we have said is confined within this space it is not there, outside so, I do not have to consider the part that is outside, so integration does not have to be always from minus infinity to plus infinity, please remember that.

So, when I integrate it is very straight forward $\int_0^L \psi^*(x)\psi(x)dx = A^2\int_0^L sin^2\frac{n\pi}{L}x\,dx = 1$

. Now, this is what you get, this is the standard way of proceeding whenever you try to integrate sin^2x, you use the trigonometric relationship and in place of sin^2x express it in terms of $cos\frac{2n\pi}{L}x$, instead of $sin^2\frac{n\pi}{L}x$ in terms of $cos\frac{2n\pi}{L}x$, very simple trigonometric relationship.

And then proceed you get two terms, in the integration $\frac{1}{2}[\int_0^L dx - \int_0^L (cos\frac{2n\pi}{L}x)dx]$, second term turns out to be equal to 0. Why? Because this integration, what will it give you? It will give you some sin term, $sin\ \frac{2n\pi}{L}x$ multiplied by some constant. But remember, that at x equal to 0 and at x equal to L that sign term has to be equal to 0, it is same as wave function. So, the second term becomes 0 because of that boundary condition that we have used.

The first term is very simple you are integrating between 0 to L, integrating dx you get L and you have 1/2 outsides, you get L/2. So, $\frac{1}{A^2}$ turns out to be $\frac{L}{2}$, so A turns out to be $A = \sqrt{\frac{2}{L}}, \psi(x) = \sqrt{\frac{2}{L}}\ sin\frac{n\pi}{L}x$, we have found an expression for the wave function of particle in a 1D box completely, this is a normalized wave function.

What would happen if I use the exponential form e^{ikx} $, e^{-ikx}$, I encourage you to work that out, you will find out that even after normalization and everything you still have e^{ikx} and e^{-ikx}. So, the same system can actually be described by different wave functions which are interrelated with each other, it is important to understand that. We have got the energies and we have understood that we have some kind of a quantum number already because n equal to 1, 2, 3 and 4 and so on and so forth all the way up to infinity.

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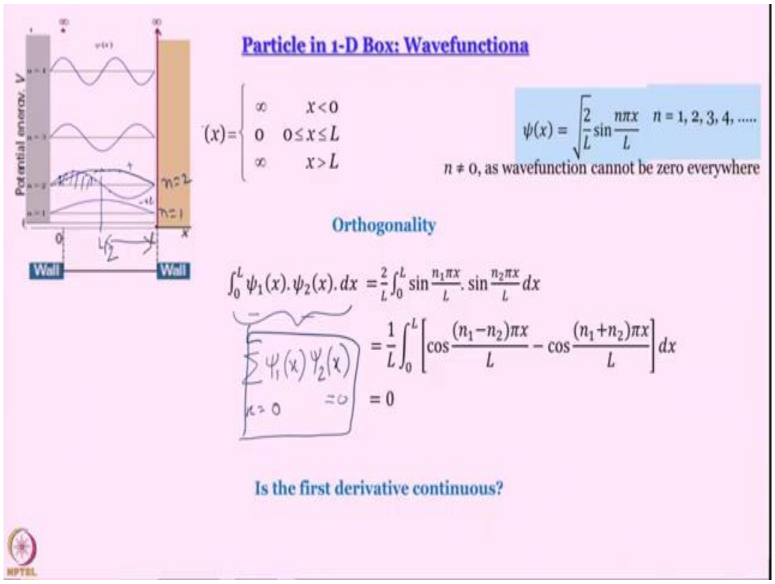

Particle in 1-D Box: Wavefunctiona

$$(x)=\begin{cases} \infty & x<0 \\ 0 & 0\le x\le L \\ \infty & x>L \end{cases}$$

$$\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \quad n = 1, 2, 3, 4, ...$$

$n \neq 0$, as wavefunction cannot be zero everywhere

Orthogonality

$$\int_0^L \psi_1(x).\psi_2(x).dx = \frac{2}{L}\int_0^L \sin\frac{n_1\pi x}{L}.\sin\frac{n_2\pi x}{L}dx$$

$$= \frac{1}{L}\int_0^L\left[\cos\frac{(n_1-n_2)\pi x}{L} - \cos\frac{(n_1+n_2)\pi x}{L}\right]dx$$

$$= 0$$

$\sum_{x=0} \psi_1(x)\psi_2(x) = 0$

Is the first derivative continuous?

Now, let us think a little more about the wave functions, wave functions not wave functiona, sorry about that typo once again. Are these wave functions orthogonal? You can do the integration and you can work it out that it is orthogonal, I like to do it in a little different way. What is the meaning of this integration?

For every value of x, I have to multiply the value of ψ_1 and ψ_2 and then I have to add it up. So, this integration I can also write as $\sum_{x=0}^{x=l} \psi_1(x)\, \psi_2(x)$, that is essentially a numerical way of doing the integration. So, let me see whether I can understand what this would mean. I am going to work with say these two, n =1 wave function and n =2 wave function, it is written on the other side anyway.

Let me try to draw this n =1 wave function on top of the n =2 wave function, it is roughly like this. So, when I try to do this summation, what do I do? Multiply the value of ψ_1 here by the value of ψ_2 at the same x, add it to the product of $\psi_2,\ \psi_1$ value of this value of x and this x and repeat for all values of x.

I hope it is not very difficult to see that, as long as I am between x equal to 0 and x equal to L/2 this product will always be positive. What happens between x equal to L/2 and x equal to L? $\psi_1$is negative, ψ_2 is positive and when I multiply this by this, I get a negative quantity, multiply this by this I get a negative quantity.

However, magnitudes are all the same, so this sum is going to be equal to 0, I can see it pictorially as well. You take any pair of wave functions, you can satisfy yourself that is what is going to happen. So, this is how we establish that the wave functions are indeed orthogonal. Is the first derivative continuous?

Yes except for x equal to 0 and x equal to L. What is the derivative of $sinkx$? Well, it is $cos\ kx$. At x=0, what is the value of $cos\ kx$, it is going to be 1, but we have already established that just outside x = 0 it is a flat line, so it is 0, so there is a discontinuity in the first derivative here, so that is what I was saying that even if it is discontinuous at boundaries one can accept that wave function.

There is another way of solving the particle in a box problem in which this continuity, this violation of continuity is not there, but there is a more sophisticated treatment, we are not going to go there. For our purpose, for this course let us just understand that, it is okay to have a discontinuous first derivative at boundaries, as long as it is continuous inside it is fine.

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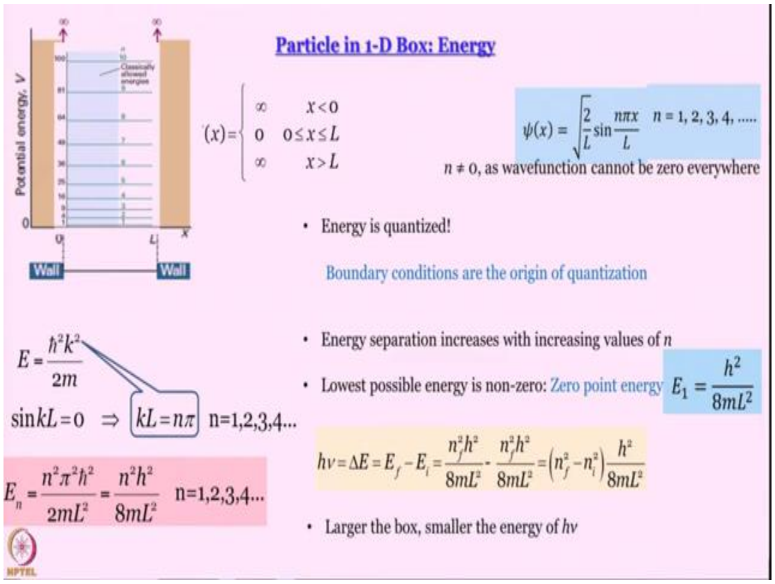

Particle in 1-D Box: Energy

$$(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 \le x \le L \\ \infty & x > L \end{cases}$$

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L} \quad n = 1, 2, 3, 4, \ldots$$

$n \neq 0$, as wavefunction cannot be zero everywhere

- Energy is quantized!

Boundary conditions are the origin of quantization

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

$$\sin kL = 0 \Rightarrow \boxed{kL = n\pi} \quad n=1,2,3,4\ldots$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2} \quad n=1,2,3,4\ldots$$

- Energy separation increases with increasing values of n
- Lowest possible energy is non-zero: Zero point energy $E_1 = \frac{h^2}{8mL^2}$

$$h\nu = \Delta E = E_f - E_i = \frac{n_f^2h^2}{8mL^2} - \frac{n_i^2h^2}{8mL^2} = (n_f^2 - n_i^2)\frac{h^2}{8mL^2}$$

- Larger the box, smaller the energy of $h\nu$

NPTEL

Next, we want to talk about energies. Remember what the expression of energy would be, we have solved this Schrodinger equation for a free particle and we know that E is going to be $\frac{\hbar^2k^2}{2m}$ for a free particle there was no restriction on the values of k, so we had a continuous spectrum of energies, not so for a particle in a box.

Remember for a particle in a box, $kL = n\pi$, where n is equal to 1, 2, 3, 4 so on and so forth. So, I can write the expression of k from here, k will be $= \frac{n\pi}{L}$, so take that value and plug it into the value of, into the expression of energy, you get energy for any given number n is, $\frac{n^2h^2}{8mL^2}$, where n as we have established earlier has to be 1, 2, 3 and 4, and that is why we do not care about the negative sign.

See, square of minus n is equal to square of plus n anyway, and this wave function, the way we write it $sinkL$, this is in any case not an eigen function of the momentum operator. So, if you want to talk about momentum this way or that you will work with e^{ikx}, e^{-ikx} there the minus sign exists in the linear sum anyway, so that negative value of n does not add value to the problem that is why we do not take it.

So, we have got quantized energies, $E = \frac{n^2h^2}{8mL^2}$ where n equal to 1, 2, 3, 4 so on and so forth. So, what happens with increase in energy is that energy gap keeps increasing, energy is proportional to square of n, so in this energy ladder you see the spacing keeps increasing as you go higher and higher and higher.

Another very important thing is what happens when you increase the size, but before that let us just summarize what we have learnt so far. Very important concept that we have learnt is that quantization originates in boundary conditions and boundary conditions come from the requirement of the wave function to satisfy bond condition $\Psi\Psi^*$ has to be your energy density.

Energy separation increases with increasing values of n we have established that. Lowest possible energy is non-zero we talked about that n cannot be equal to 0, so this energy which has n square in the numerator that also cannot be 0 so that means the free particle is always in motion, it has to move this way or that way, so some minimum what is called Zero-point energy is there and that Zero-point energy for particle in a box is $\frac{h^2}{8mL^2}$.

Now, what is the $h\nu$? Suppose there is a transition from some initial level i to some final level f, $\Delta E = (n_f^2 - n_i^2)\frac{h^2}{8mL^2}$. Now, let us say that f is equal to i +1, let us talk about energy gap between two successive levels. Then what will I get?

That is going to be proportional to $\frac{1}{L^2}$, so this energy gap increases as, well, energy gap decreases as L increases, this is something that has profound implication in chemical systems as we are going to see. Just remember this energy gap decreases as L increases, because L^2 appears in the denominator for the expression of energy gap. Larger box, smaller is the energy of $h\nu$ you can say, energy corresponding to $h\nu$.

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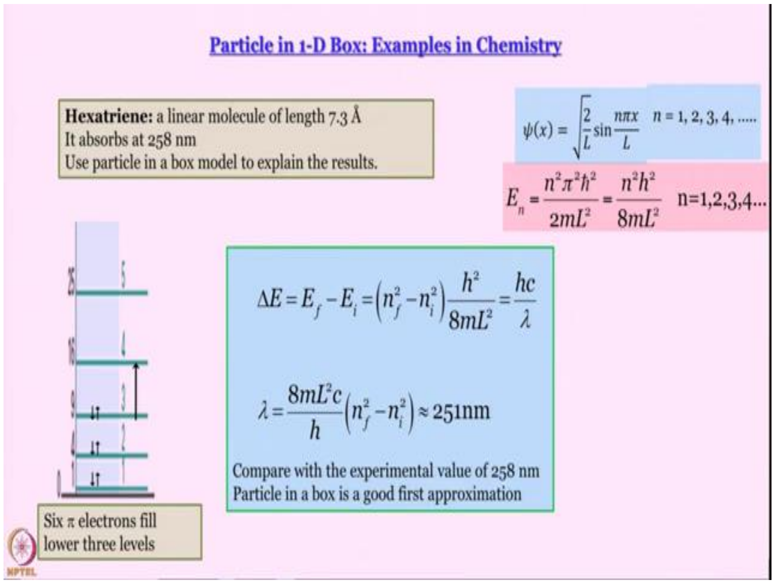

Particle in 1-D Box: Examples in Chemistry

Hexatriene: a linear molecule of length 7.3 Å
It absorbs at 258 nm
Use particle in a box model to explain the results.

$$\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \quad n = 1, 2, 3, 4, \ldots$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2} \quad \text{n=1,2,3,4...}$$

$$\Delta E = E_f - E_i = \left(n_f^2 - n_i^2\right)\frac{h^2}{8mL^2} = \frac{hc}{\lambda}$$

$$\lambda = \frac{8mL^2c}{h}\left(n_f^2 - n_i^2\right) \approx 251\text{nm}$$

Compare with the experimental value of 258 nm
Particle in a box is a good first approximation

Six π electrons fill
lower three levels

Chemical examples that we can think where particle in a box model might apply is conjugated molecule say hexatriene. Well, hexatriene of course is not really a linear molecule, we have bond angles of 120 degrees approximately but if we just join the tips, the first carbon atom and the last carbon atom, that is the line we are talking about, that length is say 7.3 angstrom or you can just add up the bond lengths that are there.

It is known that it absorbs 258 nanometers, so what we can do is that we can say that these molecular orbitals, now here we are jumping the kernel a little bit because but then you have studied molecular orbitals qualitatively earlier, anyway. So, let us say that the energies of molecular orbitals are given by a particle in a box model.

So, how many electrons are there, π electrons? There are 6, so this is how you fill in using that rule that each orbital cannot accommodate more than 2 electrons, what will be the highest occupied molecular orbital n equal to 3. So, the lowest energy transition that can take place will be from n=3 to n=4.

Why should the particle in a box model apply here? What we are saying is that we have these 6 electrons, 6 π electrons, fine. And we have these 6 carbon atoms, let us even not talk about the hydrogen atoms now. If you talk of any particular electron, any particular pi electron it experiences the electrostatic attraction due to the nuclei and it experiences electrostatic repulsion but due to the other electrons.

What we are saying is that the nucleus electron attraction for that electron is exactly offset by the repulsion of all the other electrons, that is the condition in which this will be actually a free electron. So, this phenomenon as you know I think is called shielding or screening. So, each electron is shielded effectively from the nuclear charge by the other electrons that are there in the molecule.

This is an absolutely valid model of course not; it is an approximate model. But let us see what we get. So, using this model we can find out what is the energy of n=3, what is the energy of n=4, considering the capital L value to be 7.3 angstrom. When we do that, we find that this λ turns out to be 251 nanometer, experimental result is 258 nanometer and theoretically predicted result is 251 nanometer, not exactly but the same, but not very different either.

So, for something like hexatriene this particle in a box model is not too bad a first approximation. Of course, it is not the last word, you need much better more sophisticated quantum mechanical treatment but to start with particle in a box model is not too bad.

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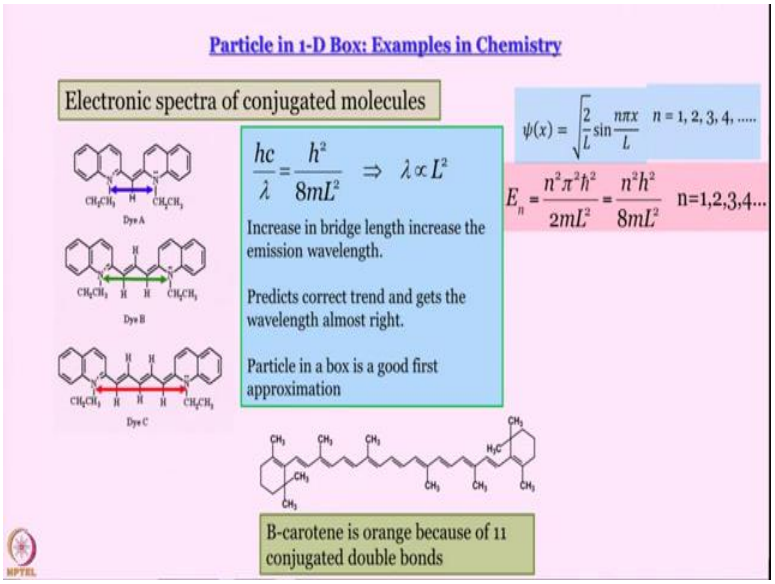

Particle in 1-D Box: Examples in Chemistry

Electronic spectra of conjugated molecules

$$\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \quad n = 1, 2, 3, 4, \ldots..$$

$$\frac{hc}{\lambda} = \frac{h^2}{8mL^2} \Rightarrow \lambda \propto L^2$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2} \quad \text{n=1,2,3,4...}$$

Increase in bridge length increase the emission wavelength.

Predicts correct trend and gets the wavelength almost right.

Particle in a box is a good first approximation

B-carotene is orange because of 11 conjugated double bonds

What it can tell us quantitatively is that as you increase this length of the chain, this lambda of light that is absorbed is going to go towards the red. So, see when it absorbs 258 nanometer that is UV, so the molecule is going to be colorless, if you keep on increasing the chain length then this absorption is going to go into blue at least, it is still called a red shift because it goes to lower energy but from ultraviolet the wavelength that is absorbed would go into blue.

So, the color that you would see would be the complementary color that is red, so that is what you see, in beta carotene the pigment that is there in orange or in carrots and so on and so forth it is orange because it has 11 conjugated double bonds. So, for this, the absorption is in blue, if the absorption was in ultraviolet it would have been colorless because the absorption is in blue, you see the color red of oranges and carrots and all these things.

But if you try to calculate what is the actual absorption wavelength you will get a very bad agreement for beta carotene because there are too many electrons, too many nuclei so this free electron model does not really work all that well. So, this is one example in chemistry.

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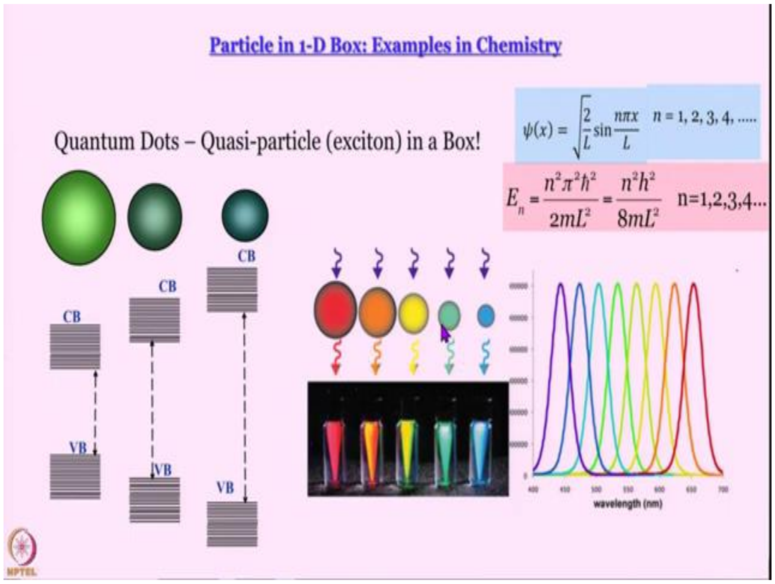

Particle in 1-D Box: Examples in Chemistry

Quantum Dots – Quasi-particle (exciton) in a Box!

$$\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \quad n = 1, 2, 3, 4, \ldots$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2} \quad n=1,2,3,4\ldots$$

The other example is for quantum dots. Now, what is the meaning of a quantum dot? See in solids you have bands and perhaps we will talk about that a little later also. When you go down to nanometer regime if you keep on breaking down say take a semiconductor, keep on breaking it down then what happens is that the gap becomes smaller and smaller. So, if the gap becomes smaller absorption will also going to become of comparable energies.

So, if you think in the other way, if you take a very small particle say a sphere that is of 1 nanometer radius and you keep on increasing it from 1 nanometer to 10 nanometer, the box size increases from 1 to 10. What is the particle here? The particle is an exciton, exciton means you have promoted an electron from valence band to conduction band, the electron is in conduction band what is called a hole is there in valence band.

So, this electron and hole pair move together that is called an exciton, that is the particle, well it is called a quasiparticle. This particle moves in a box whose diameter, whose length is equal to the diameter of the nano particle. So, now for this exciton, as the size of the nanoparticle increases you can think capital L increases as well, so absorption spectrum also will move from blue to red and color is going to change accordingly. So, absorption as you see has moved from blue to red and color has changed accordingly.

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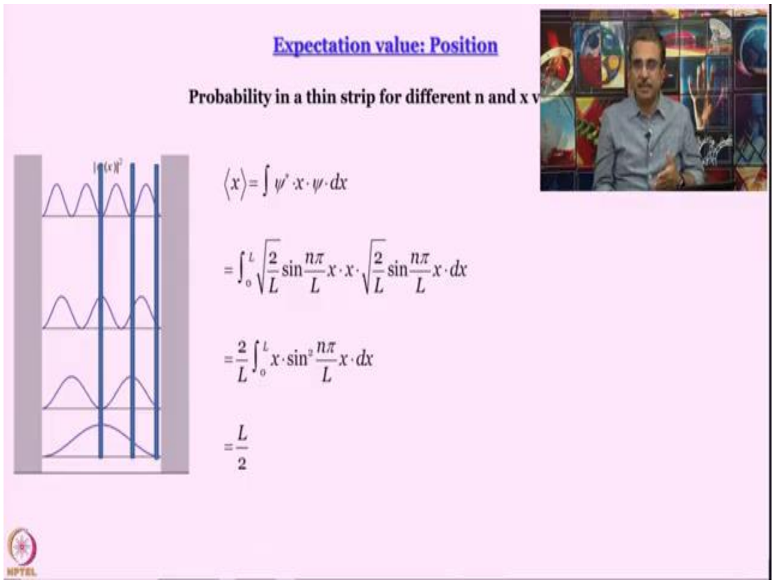

Expectation value: Position

Probability in a thin strip for different n and x v

$$\langle x \rangle = \int \psi^* \cdot x \cdot \psi \cdot dx$$

$$= \int_0^L \sqrt{\frac{2}{L}} \sin\frac{n\pi}{L} x \cdot x \cdot \sqrt{\frac{2}{L}} \sin\frac{n\pi}{L} x \cdot dx$$

$$= \frac{2}{L} \int_0^L x \cdot \sin^2\frac{n\pi}{L} x \cdot dx$$

$$= \frac{L}{2}$$

You can calculate the expectation value of position and you can calculate the expectation value of momentum here, one thing that you can do and this should be a part of our tutorial that you should try to find out the expectation value in different positions, take the same thin strip but place it at x equal to L, x equal to maybe L/4, x equal to L/2 and calculate what are the probabilities, you will get different values, please do it and you will see what you get. But the average value is going to be L/2, that means expectation value of position for the particle is at the center of the box. I am skipping the mathematics here, please do it yourself.

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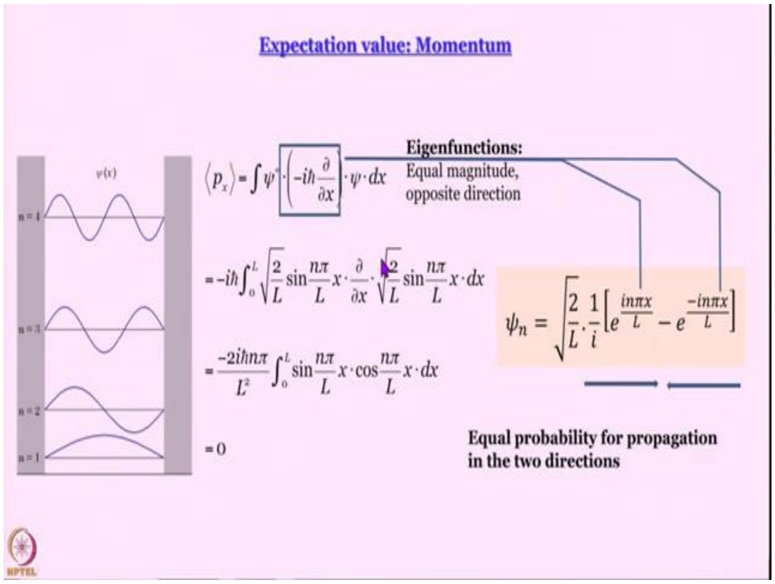

Expectation value: Momentum

$$\langle p_x \rangle = \int \psi^* \cdot \boxed{\left(-i\hbar \frac{\partial}{\partial x}\right)} \cdot \psi \cdot dx$$

Eigenfunctions:
Equal magnitude,
opposite direction

$$= -i\hbar \int_0^L \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \cdot \frac{\partial}{\partial x} \cdot \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \cdot dx$$

$$\psi_n = \sqrt{\frac{2}{L}} \cdot \frac{1}{i} \left[e^{\frac{in\pi x}{L}} - e^{\frac{-in\pi x}{L}} \right]$$

$$= \frac{-2i\hbar n\pi}{L^2} \int_0^L \sin \frac{n\pi}{L} x \cdot \cos \frac{n\pi}{L} x \cdot dx$$

$$= 0$$

Equal probability for propagation in the two directions

What is the expectation value of momentum, we do not even have to do the math we know already, there is equal probability of the particle moving this way and that. Remember we can write the expression of the wave function as a linear sum of two exponential terms and that this one, the first one is for movement in positive direction, the second one is for movement in negative direction, expectation value of momentum has to be equal to 0, but you can work it out more formally in this manner.

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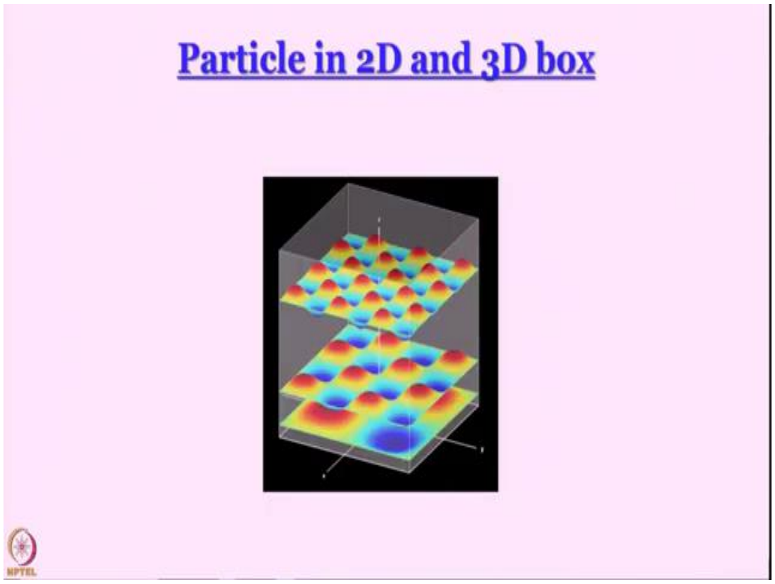

Particle in 2D and 3D box

So, this discussion that were performed is for particle in 1D box. What happens if the box is 2 dimensional or 3 dimensional that is the discussion that we are going to perform next.