Quantum Chemistry of Atoms and Molecules
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Lecture-8
Particle in a Box: Part III

So, here we are we are talking about particular 1d box we know what the wave function is we know what the energies are and now we want to ask does it have any practical manifestation? Actually it does. First example we want to discuss is hexatriene a conjugated molecule which is linear I mean of course it is like this but you can draw a line from beginning to end and the length is 7.3 angstrom.

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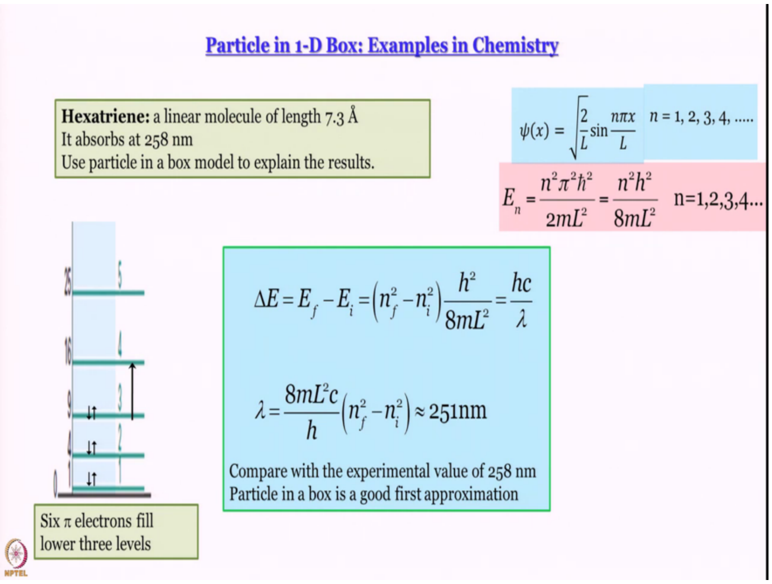

Particle in 1-D Box: Examples in Chemistry

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

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

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

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

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

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

Six π electrons fill lower three levels

Hexatriene absorbs 258 nanometer if you look at the absorption spectrum what we are going to do is we will use particle in a box model to explain the result. To do that what we will do is we will consider that the PI electrons well when we talk about one pi electron in hexatriene we consider that it acts as a particle in a box, is that is that assumption valid, should we even make that assumption. What are we saying here? We are talking about one electron.

So this electron experiences electrostatic attraction by all these nuclei it also experiences electrostatic repulsion by your other electrons. So, what we are trying to say essentially is that the screening that arises out of electrostatic repulsion of this single electron by all the other electrons exactly offsets the electrostatic attraction of this electron by the nucleus, is this a valid approximation? We do not know yet, we will know when we look at the results of the calculation and the experimental result that we have already shared that it absorbs 258 nanometer.

Then only we can comment on the validity of the model right now we are just trying to test it out and see whether it works. So, this is what it is we are saying that these are the molecular orbitals, let us say the molecular orbital energy levels are approximated by 1D box energy levels in hexatriene. How many PI electrons are there? There are 6 and we know that each molecular orbital can accommodate 2, so we have 2, 4 and 6.

So n equal to 3, n equal to 3 is the level of origin of any upward transition and we know that the lowest energy transition will take it to level 4 because we said that odd to even; even to odd transitions are only allowed, great. Now what remains to be done is that we have to work out the energy difference Delta E nf square minus ni square multiplied by h square by a time mL square that will be equal to hc by lambda we want wavelength because in the problem we have stated the wavelength.

So lambda is going to be 8 mL square c by h multiplied by nf square minus ni square so here L is equal to 7.3 angstrom m mass of an electron is known speed of light is known Planck's constant is known we put ni equal to 3 nf equal to 4 and the value of lambda that we get is 251 nanometer. What is the result 258 nanometer are they exactly the same? No they are not; are the close? Yes they are. So, what we can see is that particle in a box upon comparison with the experimental value yields a an okay result.

So, you can see it is a good first approximation but it is definitely not the last word. If you want an estimate for a quick estimate then maybe it will work but for a serious calculation in systems like this the assumptions that we have made are a bit too stringent. The repulsion by the other electrons and consequent screening is in the repulsion does not exactly offset the electro; the nuclear charge that the attraction by the nucleus nuclear than are present.

So it may be a good starting point it is definitely not the end. So, and also if you look at the energies of the MOs of exit trying by a more rigorous quantum mechanical calculation the energy gaps are not going to really increase as you go higher up. So, even though there may be some agreement at lower energy levels at higher energy levels this will definitely not work. But it gives us a starting point. So, it may not be such a bad model after all.

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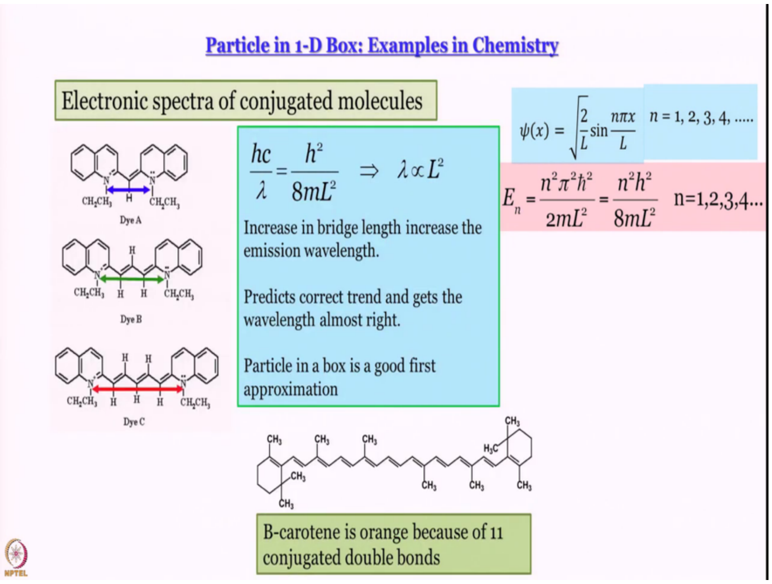

Particle in 1-D Box: Examples in Chemistry

Electronic spectra of conjugated molecules

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

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

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

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

And then if you get more ambitious and start talking about other conjugated molecules things like this in fact one can go to conjugated polymer the guiding principle is lambda is proportional to else L square hc by lambda equal to h square by 8 mL square from there lambda is proportional to L square. So, if you keep on increasing the length of this conjugated bridge between the ring systems one expects the absorption to get more and more and more red shifted.

To the extent when the bridge is really long for example in beta carotene there are 11 conjugated double bonds. There the absorption is expected to be at a much longer energy and it is that is why carrots have that beautiful orange color because carrots contain carotene and this extended conjugation leads to absorption in the visible range. However there is a problem if one tries to work out the expected absorption wavelength of beta carotene using particle in a box model.

Then there is not a good agreement, so this trend is alright that lambda more or less changes along with L square but it is not really quantitative and longer the chain more is a problem because number of nuclei of electrons everything goes up greater is the disagreement. So, what we saw in the last slide the agreement between 251 to 258 that is almost as good as it gets; as we keep increasing the length of the chain the agreement becomes unsatisfactory to bad to very bad.

But it still gives us the right trend so particle box model you given its simplicity is not a bad starting point.

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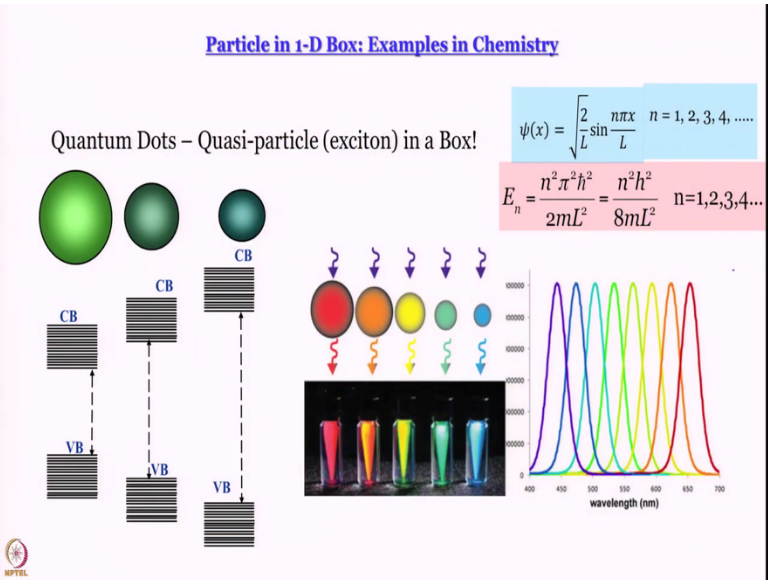

Particle in 1-D Box: Examples in Chemistry

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

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

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

Moreover if one goes to other systems like semiconductor and nano crystals their particle in a box model holds fairly nicely. Now one might get confused because we are saying quantum dot spherical nano particles. So, what is particle what is box in this nano particle? Well the particle is an exciton. An exciton is a couple electron hole pair that excite on of course has to remain inside the nano particle it cannot go out so the diameter of the nano particle defines L.

So we are not really plotting the shape of the nano particle we are plotting if I go from left to right what happens outside the nano particle potential energy is infinite. Inside the nano particle we are saying potential energy is zero why we are saying potential energy is 0 because we consider a single exciton it does not interact with there is no other exciton it can interact with that is the consideration may be correct may not be correct.

But we are considering v equal to 0 when x increases from 0 to L where L is the diameter of the nano particle. Then the moment we reach L once again potential energy becomes infinitely high because exciton has to remain inside nano particle as we said so particle in a box model with a little bit of modification holds quite nicely and this is a diagram that everybody has seen by this stage it is there in NCERT class 11 to 12 level textbook.

As well the size of the particle increases the color of the same substance remember same substance cadmium selenide or cadmium telluride something keeping the substance same. If you just increase the size of the nano particle color changes from or can actually go from even blue to red the entire visible spectrum or beyond. This gives us a handle two nice solid-state material that one can use as pigment or marker and these are usually photo luminescent and there are many applications where that one has you off these quantum dots or semiconductor nano crystals.

And interestingly its optical properties are defined fairly nicely by this simplistic particle in a 1D box model that we have discussed over these last 3 modules. Now we move on to something else and here we will keep this discussion pending we will come back and complete it when we have that module about operators and uncertainty principle.

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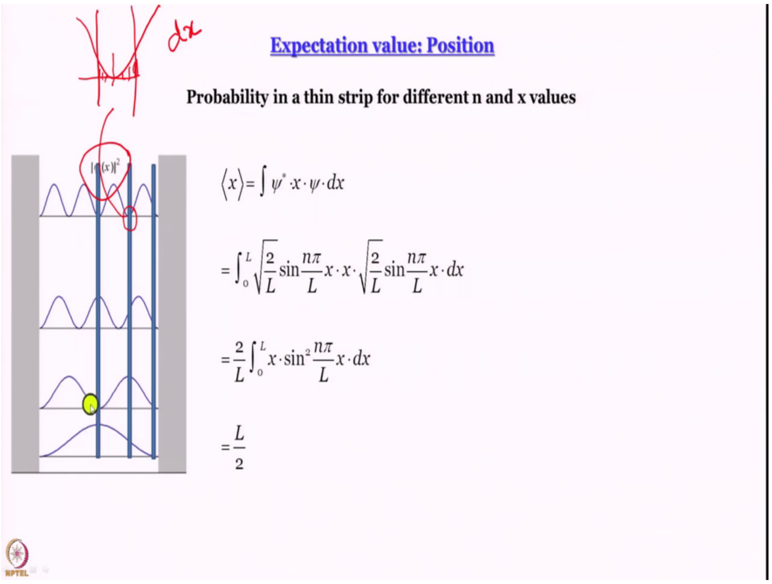

Expectation value: Position

Probability in a thin strip for different n and x values

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

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

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

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

Let us see what the expectation value of position would be for a particle in a box in may be different in different values of quantum numbers. We have said already that the expectation value is integral Psi star x Psi dx in the present case Psi star is simply Psi so we plug in the value and this is what we get integral 0 to L root 2 by L sine n PI x by L multiplied by x multiplied by root over 2 by L sine n PI x by L dx that turns out to be 2 by L integral 0 to L x sine square n PI x by L dx.

Now I am not going to work out the steps of this integration but it is not very difficult to figure out that this definite integral turns out to be L by 2 is there a dependence of n? there is not, expectation value of position is L by 2 that is what it turns out which means that if you perform a large number of measurements then we expect that the average value of the position of the particle will be at the middle okay it does not depend on n.

Next we can think of what happens if you go from left to right or right to left what is the probability and this is a tutorial problem that we are going to work out. Probability are in a thin strip for different n and x values. There some independents will actually come let us think of a thin strip that is towards one of the edges x equal to 0 x equal to L does not matter. Then what will happen first of all the value of Psi Psi star in this position is going to be very small in all the cases.

But not equally small in all cases that is what we will understand when we work out this problem. And dx in any case we are taking a we are taking strips of the same thickness so dx is same in throughout the present discussion we are doing. Now suppose we take this thin same thin strip here now what happens for n equal to 1 Psi is nonzero, so you will have some probability for n equal to 2 probability will be maximum because we are already at maximum the way we have drawn it.

So this we have placed at L by well 3 L by 4 actually x equal to 3 L by 4. If you go from L equal to 2 into n equal L equal to sorry n equal to 2 to n equal to 3 we see a decrease if you go to n equal to 4 that is where the node is. So, Psi Psi star is equal to 0. Is Psi Psi star at d tau equal to

0? Not really, because no matter how thin a strip we might take, we are talking about say this one what does the wave function look like, I am now zooming in, something like this.

So only at this point not at that point, let us see if I can get the right point here only at this point well better Psi is equal to 0 but the strip has a certain width right we always remember when we talk about probability we always have to consider dx as well. So, let us say this is the strip, so the Psi that we consider is some well, well sorry these are plots of Psi square right so the Psi square that we consider remember these are plots of Psi square.

So, we have some non-zero very small but nonzero area so when we talk about the probability of finding a particle at the node we cannot really talk about a point that makes no sense because a point has no dimension. We have to talk about a small volume element dx in this case about that point and no matter how thin a strip of dx we might take we will also always have some small nonzero value of Psi Psi star at d tau, this answers a question that students often asked in this part of the course that they said that the probability they say that the probability of finding the particle here is 0.

So how does the particle even go from this side to that side the answer is first of all when you talk about probability is not 0 probability density is 0 when you talk about probability is not 0 and how it goes from here to there we cannot say because in quantum mechanics we cannot really talk about trajectories. But even at the nodal point well I should say about the noble nodal point there is a nonzero probability of finding the particle that is the argument that we always provide.

Next if you take the strip to L by 2 now we see that probability of finding the particle for n equal to 4 n equal to 1 is maximum very small for n equal to 2 and it varies like this.

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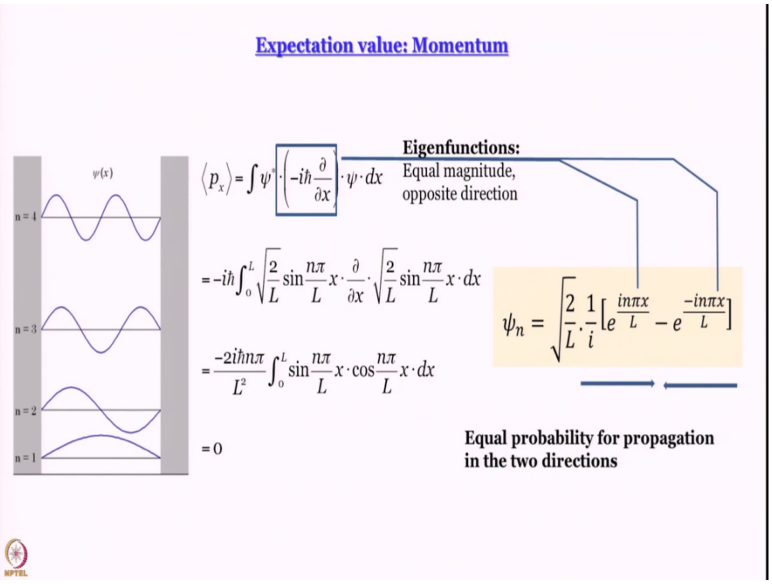

Expectation value: Momentum

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

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

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

$$= 0$$

Eigenfunctions:
Equal magnitude,
opposite direction

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

Equal probability for propagation in the two directions

Now let us talk about momentum and that will lead to some interesting observation that will make use of extensively in later parts of our discussion. For momentum remember the operator is minus ih cross del del x and again there is no need of writing del Del x here I should write d dx because we are working in a one dimensional space. We do not even have y or z so d dx. And once again we get some integral you work it out it turns out to be 0 average value of momentum is 0.

So, it is interesting we said a little while ago that this particle in a box can never be at rest but expectation value of momentum is 0 what does it mean? Why is the expectation value of momentum 0? To understand that let us write the wave function in this form the wave function is a sine function right and we know very well that one can write a sine function as a linear combination of these exponential terms, in a exponential imaginary terms.

And then operate linear momentum operator is minus ih cross del Del x if you take the first term and differentiate it once what do we get we get back the same term multiplied by in pi divided by L that multiplied by minus ih cross u says h cross multiplied by n pi divided by L so you get an eigen value equation. What I am saying is that the first term here is an eigen function of the linear momentum operator.

Second term is also an eigen function of linear momentum operator and if you see carefully their eigenvalues have the same magnitude but in the first case the eigenvalue is positive in the second one eigenvalue is negative. So, they stand for momenta that are equal in magnitude but different in direction. Remember linear momentum is a vector it it does have a magnet when; magnitude what direction is also important.

So what we are saying is that it is equally probable to find the particle moving in this direction and that direction right. So, if you make five lakh measurements 2.5 lakh times you will see the particle moving in this direction 2.5 times you will see the particle moving in that direction same velocity and therefore well sorry same speed therefore where you add them all up you are going to get zero that is the meaning of expectation value it is an average value remember right.

So, what we also learned is that what is a good eigen function for the linear momentum operator e to the power ikx is a good eigenvalue i sorry eigen function for a linear momentum operator and the eigenvalue that you get for e to the power ikx is minus kh cross. This is something that is very important and we will come back to it. So, whenever we have a sine function or a cos function for that matter these are always linear sums of e to the power ikx and e to the power minus ikx kind of terms.

Which means for any sign or any cos functions your contribution from equal momenta moving in this direction in that direction right. So, that has actually some profound implication that we will come back to later on in the course. So, that is what we have learned equal probability for propagation in the two direction right.

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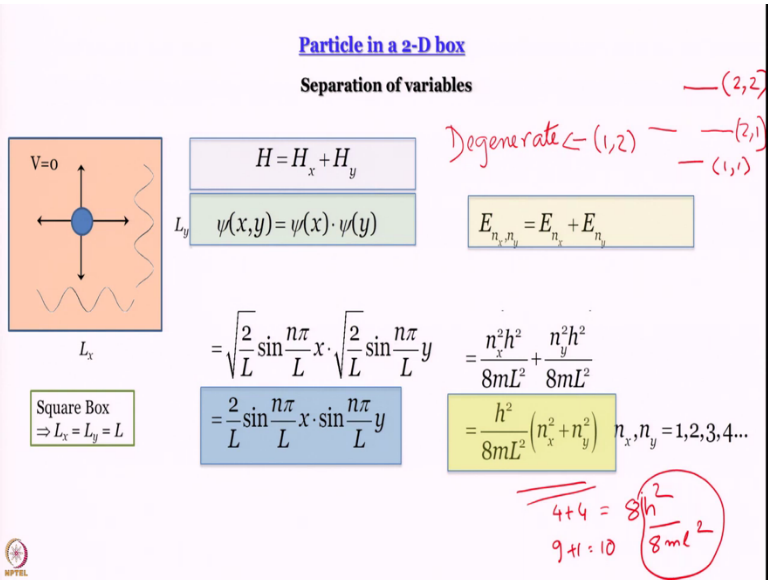

Particle in a 2-D box

Separation of variables

$H = H_x + H_y$

$\psi(x,y) = \psi(x) \cdot \psi(y)$

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

$= \frac{2}{L} \sin\frac{n\pi}{L}x \cdot \sin\frac{n\pi}{L}y$

Square Box
$\Rightarrow L_x = L_y = L$

$E_{n_x,n_y} = E_{n_x} + E_{n_y}$

$= \frac{n_x^2 h^2}{8mL^2} + \frac{n_y^2 h^2}{8mL^2}$

$= \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2\right)$ $n_x, n_y = 1,2,3,4\ldots$

— (2,2)

Degenerate ← (1,2) — — (2,1)

— (1,1)

4+4 = 8 $\frac{h^2}{8ml^2}$

9+1 = 10

Now let us see if we can increase the dimensionality a little bit. Let us talk about a particle not in a 1D box but in a 2D box which means the particle is moving let us say on the surface of a table or something like that. And again to keep things simple let us start talking about a square box. Square box means L x is equal to L y. The; we handle something like this and this is once again a very important thing which you are encountered already when we talked about Schrodinger equation.

We go about this by using separation of variables meaning we say that the x direction and y direction and orthogonal. So, one might as well consider that the Hamiltonian is a simple sum of a Hamiltonian in terms of x and another in terms of y and then energy then would also be sum of kinetic energy for propagation along x and for propagation along y which makes perfect sense. Because we are talking about kinetic energy here right there is no potential energy.

So when we talk about kinetic energy it is a virtue of motion and any motion on a 2D surface can be broken down into a vector sum of motion along x axis and motion along y axis. So, what we are saying is that we look at the normal coordinates of motion great so H is equal to Hx + Hy what about Psi is Psi equal to Psi x + Psi y; no Psi is equal to the product of Psi x and Psi y. You cannot add Psi in x and Psi in y there dimensionally different you can always take a product.

So this is what Psi is root over 2 by L sine n PI x by L multiplied by root over 2 by L sine n pi y by L and I get away writing L here because we are working with the square box L x equal to L y equal to what I have written L ok. So, finally the wave function is 2 by L and product of these two sine terms. Energy as we said earlier is going to be sum of energies for propagation along x and along y. We know the expression is already just have to write them nx square h square by 8 mL square plus ny square a square by 8 mL square equal to h square by 8 mL square multiplied by nx square plus ny square, nx and ny as usual are 1, 2, 3, 4 etcetera.

These are all positive integers what do we have here now we have two quantum numbers. What kind of quantum numbers quantum numbers that are independent of each other they are not like n and L where L is dependent on n, nx and ny are completely independent of each other a particle could have very high kinetic energy along y very little along x right. So, if we think of a particle moving in an arbitrary direction depending on its orientation this distribution of kinetic energies along x and y would differ and that is what and they would differ according to the quantum numbers.

So if nx is small ny is large that means the particle is moving more with a smaller angle with the y axis than with x axis something like that ok so this is what it is nx is a quantum number for x, ny is a quantum number for y obviously. So, now see one quantum number is not enough we need two quantum numbers to depict the energy state of the particle. What would the quantum numbers be rather what would the states look like?

Let me draw here the lowest energy state obviously would be 1,1 nx equal to 1 and ny equal to 1 then what will the next state be 1,2 now I can have two energy states 1, 2 which means nx equal to 1 ny equal to 2 or 2, 1 where nx equal to 2 and ny equal to 1 do they have different energies look at the energy expression. How does it matter whether nx is 2 and ny is 1 or the other way around it does not matter right.

So for the first time we encounter degenerate states. The degenerate states are those that have the same energy for the first time in our discussion in this course we come across and degenerate states great. What is the next one 2,2 and you can go on is it really 2, 2 or is it 1, 3 let us see. For

2, 2 energy will be 4 + 4 equal to 8 h square by 8 mL square. For 3, 1 it will be 9 + 1 equal to 10 8h square by 8 mL square.

So, next one is going to be 2 so this way one can work out the energy levels of a particle in a 2D box but so far we have only talked about a square box. Let us make things even more interesting by moving over to a rectangular box. What have we learned from this square box discussion we have learnt about separation of variables is very important but we knew about it anyway in from our initial discussion about Schrodinger equation and we have encountered degenerate states.

Let us see what happens if we move over to rectangular boxes. Before that I forgot about this sorry what will the wave function look like.

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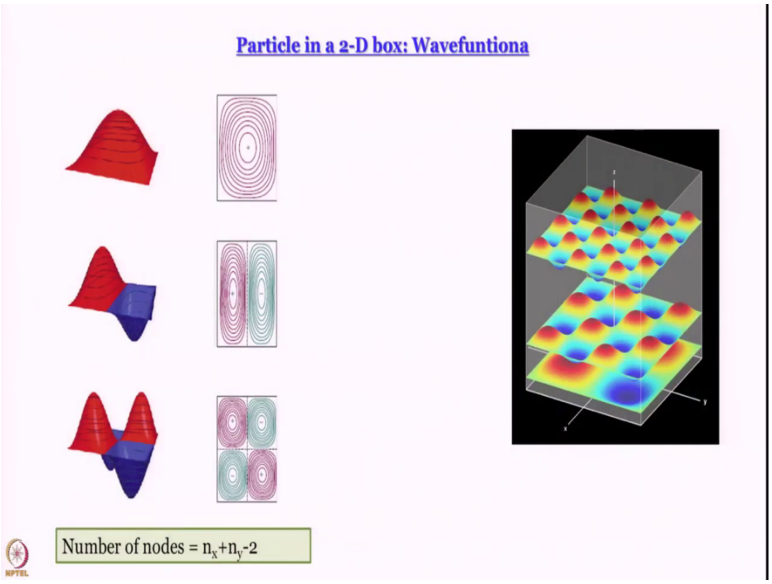

Particle in a 2-D box: Wavefuntiona

Number of nodes = n_x+n_y-2

Remember the wave functions are products of sine functions. So, take the simplest one 1, 1 it will look like a dome if you take a slice you get a sine function along x and a sine function along y and this is a contour diagram contour lines join all the points with the same value of Psi essentially. So, you look down from the top let us say these lines are drawn this is the picture that you see and as we see clearly there is no node in the 1,1 wave function.

What about 1, 2 or 2, 1 wave function there is a node in one direction there is no node in one direction. Suppose it is 1, 2 that means along x direction n equal to 1, nx equal to 1 so no node but along y direction n equal to 2 ny equal to 2 therefore there is a node. So, what we are saying is that we get something like this a node here turns out to be in the contour diagram it is actually a plane you can see the nodal plane here, node remember is where the wave function changes sign.

So, this is the node on this side we have contours we have this side also we have contours but on this side the wave function is positive on this side wave function is negative plus here and minus here. And now for those who have come right after higher secondary this is the meaning of those plus and minus signs in the atomic orbitals that you had drawn. We will come to what are atomic orbitals are? What you have drawn out the atomic orbitals anyway we will come to that later.

What you might remember for p orbital one lobe had a plus sign one row when it had a negative sign it did not mean that the electron has plus sign in one and minus sign in another it is a sign of the wave function that is written in there. So, this is 1, 2 this is 2, 2 so now we have a node along x and you have a node along y so naturally there are 4 lobes. The easiest way to draw any wave function is to draw the nodes first and then draw the contours.

Remembering that the contours are such that the wave function changes sign upon going from one side of the node to the other and here we have a nice depiction of the wave functions for a 2D box n equal to 1, 1 this is I think 2, 2 and then you go to higher values of nx and ny great.

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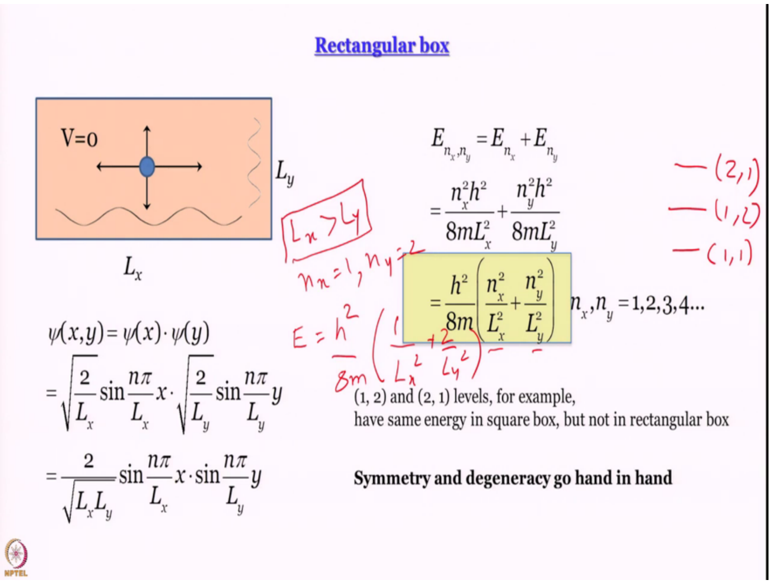

Rectangular box

$$E_{n_x,n_y} = E_{n_x} + E_{n_y}$$

$$= \frac{n_x^2 h^2}{8mL_x^2} + \frac{n_y^2 h^2}{8mL_y^2}$$

$$= \boxed{\frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right)} \quad n_x, n_y = 1,2,3,4\ldots$$

$\boxed{L_x > L_y}$

$n_x = 1, n_y = 2$

$$E = \frac{h^2}{8m}\left(\frac{1}{L_x^2} + \frac{2}{L_y^2}\right)$$

— (2,1)
— (1,2)
— (1,1)

$$\psi(x,y) = \psi(x)\cdot\psi(y)$$

$$= \sqrt{\frac{2}{L_x}}\sin\frac{n\pi}{L_x}x \cdot \sqrt{\frac{2}{L_y}}\sin\frac{n\pi}{L_y}y$$

$$= \frac{2}{\sqrt{L_x L_y}}\sin\frac{n\pi}{L_x}x \cdot \sin\frac{n\pi}{L_y}y$$

(1, 2) and (2, 1) levels, for example,
have same energy in square box, but not in rectangular box

Symmetry and degeneracy go hand in hand

Now we go to rectangular box and having performed all this discussion it should not be very difficult for you to see that once again we do the same separation same kind of wave functions same kind of energy the only difference is that now L x and L y are different so I cannot take L square common. What is the implication that it has? Let us try to draw the energy levels once again the lowest energy level once again is going to be 1, 1.

What is the one that is immediately higher in energy for square box it was 1, 2 and 2, 1 what will be in this case there is not going to be of the same energy we will have something like this 1, 2 and hopefully 2, 1 because this is the thing if this is let us say we are working with the situation where what is the situation here L x is greater than L y right let us say nx equal to 1 and ny equal to 2 then what will it be energy will be h square by 8 m multiplied by 1 by L x square plus 2 by L y square.

If you just interchange 1 and 2 you get 2 by L x square plus 1 by L y square which one will be larger depends on the relative magnitudes of L x and L y but the principle that we embark upon now is that levels that were degenerate in a square box no longer remain degenerate in rectangular box or in other words we learned that symmetry and degeneracy go hand-in-hand. We have more degeneracy in more symmetric system we have less degeneracy in less symmetric systems.

Think of a metal ion free metal ion all the d orbitals are actually degenerate as we learn. When we put them in an octahedral field symmetry is lost to some extent 2p orbitals have the same energy they degenerate 3p orbitals have the same energy they are degenerate of a different energy. Now think of Jahn-Teller distortion. We destroy symmetry even more what happens as a result I think we know this from our inorganic chemistry knowledge degeneracy between these two orbitals in Eg set is lifted.

Degeneracy among the three orbitals in the T 2 G set is also lifted and we get further splitting right that is really a manifestation of this principle that we learn using the very simple particle in a box 2 dimensional box problem that symmetry and degeneracy go hand-in-hand. I hope we have absorbed that and we have understood how beautiful a result we have arrived upon. Now let us quickly increase the dimensionality a little more 3D box.

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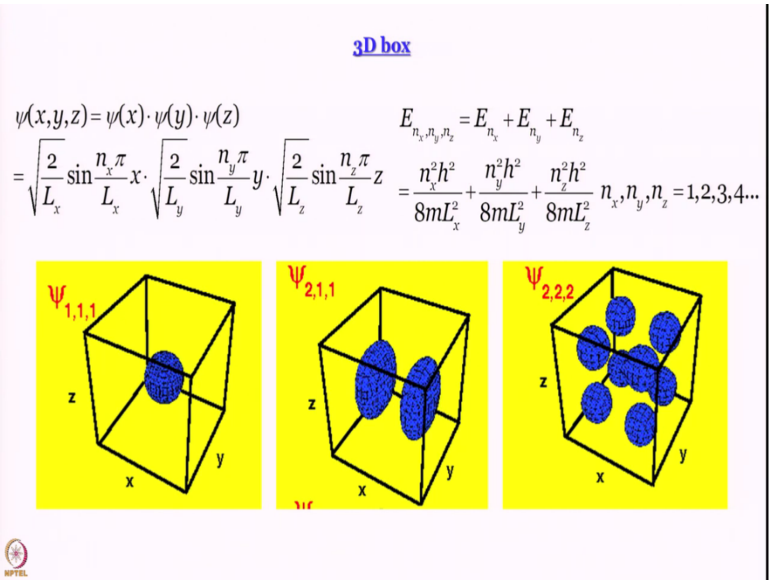

3D box

$$\psi(x,y,z)=\psi(x)\cdot\psi(y)\cdot\psi(z) = \sqrt{\frac{2}{L_x}}\sin\frac{n_x\pi}{L_x}x\cdot\sqrt{\frac{2}{L_y}}\sin\frac{n_y\pi}{L_y}y\cdot\sqrt{\frac{2}{L_z}}\sin\frac{n_z\pi}{L_z}z$$

$$E_{n_x,n_y,n_z}=E_{n_x}+E_{n_y}+E_{n_z} = \frac{n_x^2h^2}{8mL_x^2}+\frac{n_y^2h^2}{8mL_y^2}+\frac{n_z^2h^2}{8mL_z^2} \quad n_x,n_y,n_z=1,2,3,4\ldots$$

Same thing the wave function is now a product of 3 sine functions energy is a sum of 3 terms and you have nx ny nz in the situation can be quite maddening especially if we are talking about a box which is which does not have all same sides. The bigger problem is how am I supposed to draw the wave function because now to draw the wave function I need four dimensions right x y z that is taken up by the box.

Now to draw the wave function I need a fourth dimension. The fourth dimension you can handle in two ways first is you can take section forget about z axis and talk about the wave function or you can use color as a fourth parameter. This comes very handy when we later on talk about orbitals and how to depict them.

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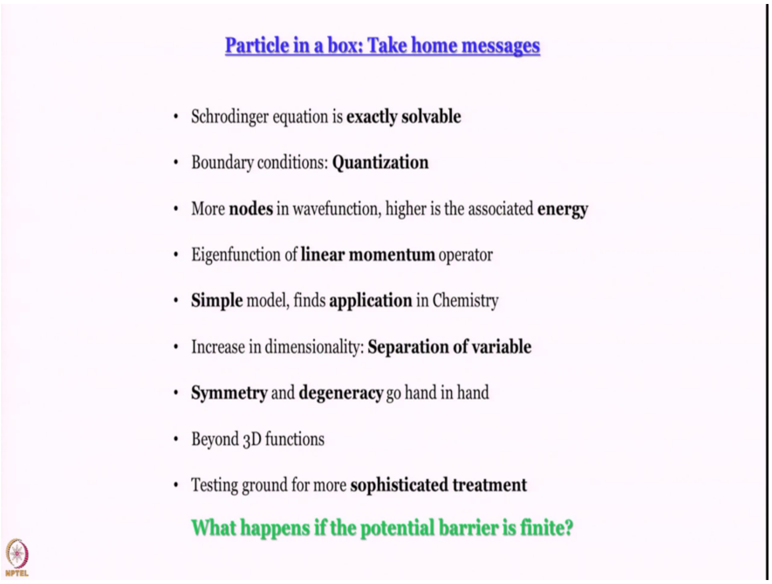

Particle in a box: Take home messages

- Schrodinger equation is **exactly solvable**
- Boundary conditions: **Quantization**
- More **nodes** in wavefunction, higher is the associated **energy**
- Eigenfunction of **linear momentum** operator
- **Simple** model, finds **application** in Chemistry
- Increase in dimensionality: **Separation of variable**
- **Symmetry** and **degeneracy** go hand in hand
- Beyond 3D functions
- Testing ground for more **sophisticated treatment**

What happens if the potential barrier is finite?

But to conclude the discussion of particle in a box that we have talked about over this last 3 modules there are several important things that we have learned. First of all we have demonstrated that Schrodinger equation can be exactly solved for certain systems. Second very important thing that we have learned and this is one of the sort of defining principles of quantum mechanics is that it is boundary conditions that lead to quantization. Next we have learned this thumb rule that if a wave function has more nodes then it is associated with higher energy.

We have got some idea about eigen function of linear momentum operator and the simple model as we have seen thus find applications in chemistry in some cases it is only a guiding principle in some cases it can go beyond that. With increasing dimensionality we have had to use separation of variables which remains a very useful tool in quantum mechanics and another beautiful result with profound implications in chemistry is that symmetry and degeneracy go hand-in-hand that is why it is important to perform a systematic study of symmetry at some later stage not in this course.

Finally we have seen how one can actually go beyond 3D functions as I said is going to be useful when we actually talk about orbitals. So, this is what we have learned when the particle has been confined in a box of infinite potential barrier, the walls are infinitely high. The next question that might come to mind is sorry I forgot to say this it makes ground for sophisticated treatment but the next question that comes to mind is what happens if the potential barrier is finite.

We will discuss it in the next module and we will find that for finite potential energy barriers we see some peculiar behavior that is observable only in quantum world not in classical world. This phenomenon is called tunneling and has profound implications in understanding molecules and also studying materials. There is a technique called tunneling electron microscopy which is entirely based on this principle of tunneling that we will talk about in the next module.