Concepts of Chemistry for Engineering
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Lecture No. 07
Particle in 2D box

We have discussed the free particle, we have discussed what happens when we put this free particle into confined space in one dimension that is a particle in a box problem. Now, let us see what happens if we increase dimensionality of the problem, what happens if you put this particle in a 2D box, what happens if we put the particle in a 3D box, and when you do that, we will see that to depict the wave functions we will need to draw very good-looking pictures like the one that we see here.

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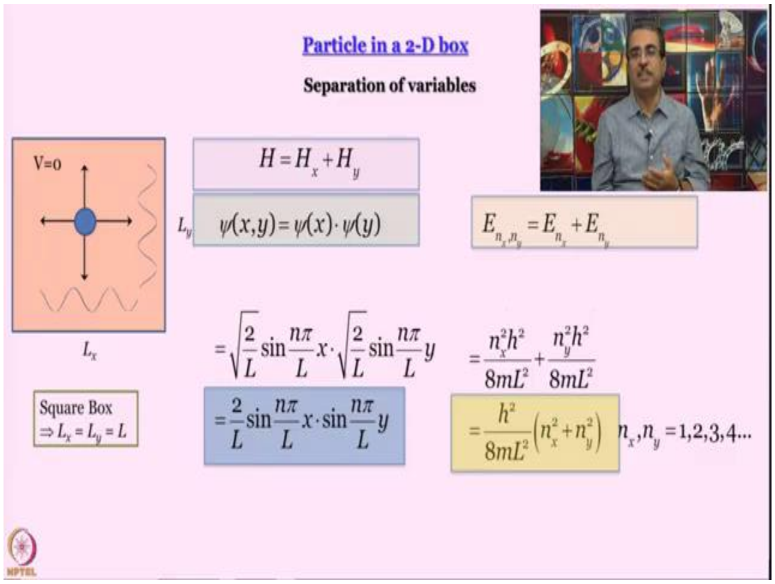

Particle in a 2-D box

Separation of variables

$H = H_x + H_y$

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

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

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

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

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

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

Square Box
$\Rightarrow L_x = L_y = L$

Also, we are going to learn a very very important technique, which we have already used, but this is something that we are going to elaborate a little further upon in this discussion. So, when we say we put particle in a 2D box, what we mean is that it is free to move in say on the surface of a table that kind of a situation or you can think of we had talked about these conjugated polyenes earlier and we said that very approximately, you can treat the and a particular electron in those conjugated molecules using a particle in a 1D box model.

Now, think of something like graphene, graphene is a flat 2-dimensional molecule, think of a free electron in graphene, conduction electron in graphene, it is free to move over the entire surface that would be the chemical application of particle in a 2D box model. To start with, let us talk about square box, which means L_x is equal to L_y. So, from 0 to L_x that is the range in x and from 0 to L_y that is the range in y, this is a space in which the electron can move freely, outside it the wave function is 0, it cannot go there.

What will the wave function be and what will the equation be? We use here the technique of separation of variables that we had also used when we talked about separating the spatial part of Schrödinger equation from the time dependent part. So, we write the Hamiltonian as $H_x + H_y$, here we can do this because x and y are independent of each other and we are talking about kinetic energy only, if potential energy was involved, then we would not have been able to separate it so easily, we would not have been able to write H= $H_x + H_y$, we get away doing it because the only kind of energy that a particle has here is kinetic energy.

Otherwise, it would have been impossible we are going to encounter situations later on where you cannot write things like this. Wave function is a product of $\psi(x)\psi(y)$, this is not difficult to understand. First of all, H contains the Hamiltonian contains second order derivative, that kind of an operation. So, if you take a product, the derivative is the sum, we want the energy to be a sum, that is why it makes perfect sense.

Also, something in x something in y, they are independent, you cannot add them, you can only multiply them because you are talking about displacements along x and displacement along y. There is no way you can just add them, multiplication is fine. So, when we do that, this is the kind of wave function that we get, in fact, we have been, we have written something like this $\sqrt{\frac{2}{L}} sin\frac{n\pi}{L}x \sqrt{\frac{2}{L}} sin\frac{n\pi}{L}y$, two particles in a box wave functions, here one in x and one in y.

Then the constant turns out to be $\frac{2}{L}\ sin\frac{n\pi}{L}x.sin\frac{n\pi}{L}y$. Please check whether this is a normalized wave function or not. But remember when you try to do that, this is going to be a double integral, when you integrate this, it will be an integral with respect to x, integral with respect to y also, so it will turn out to be a normalized wave function. What about energy? Kinetic energy as we said, it arrives $\frac{P^2}{2m}$ and p is essentially a vector sum of p_x and p_y.

So, naturally energy is also going to be sum of E_x and E_y, we have an $E_{n_x}E_{n_y}$. So, this is what is going to be $\frac{n_x^2h^2}{8mL^2}+\frac{n_y^2h^2}{8mL^2}$. Since the length is the same along x and y direction equal to L, we can take it out. So, we get $\frac{h^2}{8mL^2}(n_x^2+n_y^2)$, but n_x and n_y are 1, 2, 3, 4, so on and so forth, independent of each other. So, we have learned separation of variables and we have learned how to tackle the problem when the dimensionality increases a little bit.

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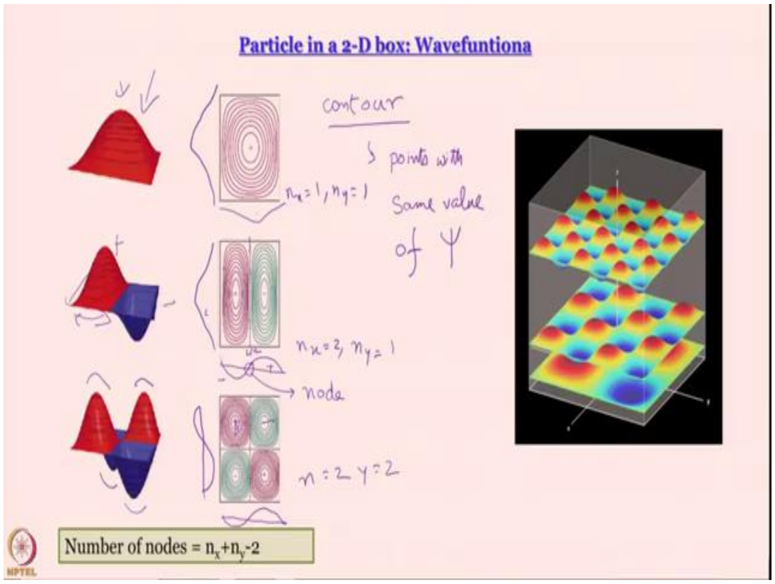

Particle in a 2-D box: Wavefuntiona

Number of nodes = n_x+n_y-2

Now, let us learn how to draw the wave function. How do we draw the wave function? Well, two depictions are shown here. So, along x side let us see, I am talking about 1, 1 wave function. So, what is it? It is a sin wave along x. I will draw here. And it is a sin wave along y, sorry for the distortion, I meant this to be a square box for whatever reason is become distorted.

Now, what happens when I multiply this by that? Do not I get a hill that looks like this? A very symmetric looking hill, 0 at the boundaries, maximum at the center of the box. And the hill rises like this, product of two sin functions. So, this diagram, I think we understand nicely, what is the meaning of color, we will come to that. But what is the meaning of these lines. So, here, what I have done is, these lines are basically joining all points that have the same value of Ψ. So, these are called contour lines, contours join all points.

Here with the same value of Ψ. Those who know how to read survey maps would be familiar with contours in context of those maps. There it is, those contour lines add, join, not all points with the same value Ψ. But all points with the same height from mean sea level, you might have seen maps like this in atlases and geography books. So, these are the contours, so what will the contours look like? You join everything it is a box.

So, it is going to look like squares that are rounded at the ends. And this point at the middle, that is the maximum point. So, this is your $n_x = 1, n_y = 1$. This is $n_x = 2, n_y = 1$. So, $n_x = 2$ means the wave function will be something like this in x direction, wave function will remain what it was in y direction.

Now, when you multiply what will happen? You consider this line here at x= L/2, you are multiplying whatever it is there in the y part of the wave function, y dependent part of the wave function by a 0, this point is called a node, a node is where the wave function goes through 0 and changes sign. Sign of a function is minus here and plus here.

So, well, I have drawn it the other way, because I have written plus here and minus here, but anyway does not matter, so it changes sign. So, what will you get from between 0 and L/2 along the x direction, you will get one hill, and the hill now will not be completely symmetric on both sides, it will be longer on the y side, and it will be half as long on the x side because it is going up to L/2.

What happens beyond x by 2, this sign of your x dependent part of the wave function has become negative. So, we are going to get a trough and that is the meaning of the color. Here red denotes plus sign, blue denotes minus sign, does it mean the wave function is actually red and blue? No, these are pseudo colors. These are colors that we add to help us understand what the shape is, once again if you go back and look up an atlas or a map, you will see colors are used in addition to contour lines to denote height or depth of terrain. Here height and depth is in terms of wave function.

What about this wave function? This is $n_x = 2\ n_y = 2$. So, now I will draw it in the right manner. Change in sign and here also we have a change in sign, my diagram is not good. So, we have four quadrants, a peak, a trough a peak, another trough and this is how you draw the contours. Remember in contours in order to show what is the sign you either use different colors or use explicitly you write the signs or better still you do both.

So, this is how you depict 3 dimensional surfaces. So, here why has it become three-dimension? Because the x and y, these are the two spatial dimensions, third dimension is wave function. Again this will become very, very important when we talk about wave functions of hydrogen atom later on. One more thing we are, this is functiona everywhere, I am very sorry about that.

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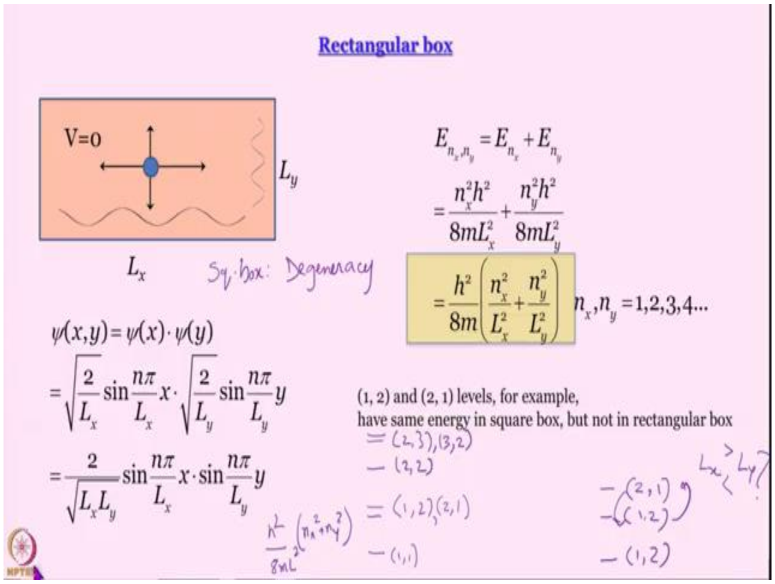

Rectangular box

Sq. box: Degeneracy

$$\psi(x,y)=\psi(x)\cdot\psi(y)$$
$$=\sqrt{\frac{2}{L_x}}\sin\frac{n\pi}{L_x}x\cdot\sqrt{\frac{2}{L_y}}\sin\frac{n\pi}{L_y}y$$
$$=\frac{2}{\sqrt{L_xL_y}}\sin\frac{n\pi}{L_x}x\cdot\sin\frac{n\pi}{L_y}y$$

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

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

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

= (2,3),(3,2)
— (2,2)
= (1,2),(2,1)
— (1,1)

$L_x \gtrless L_y$?

— (2,1)
— (1,2)
— (1,2)

Now, what happens if we have a rectangular box instead of a square box, everything else is same, the only difference is now L_x is not equal to L_y. So, energy expression is $\frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}\right)$, where n_x and n_y again are 1, 2, 3, 4, so on and so forth. So, what is the difference? Let us say I tried to draw the energy levels of a square box and a rectangular box, I will draw both.

For a square box, what is the lowest energy level? 1, 1. What is the next energy level? 1, 2. But what is the energy of 2, 1? Well, 1, 2 means n_x equal to 1, n_y equal to 2. What happens if n_x is equal to 2 and n_y equal to 1, the energy is the same, because remember what the expression is $\frac{h^2}{8mL^2}(n_x^2+n_y^2)$. How does it matter, whether I write n_x first or n_y first, it is the same. So, here for a square box we have degeneracy.

Degeneracy means we have energy levels whose energies are the same. What is the next level? Both can be 2. What is the level after that? Well, it can be 2, 3 or it can be 3, 2, this is 2, 2: 2, 3 and 3, 2. So, what we see is that we have alternate levels that are doubly degenerate and single.

What about a rectangular box? Well, 1, 1 is the lowest energy level, fine. The next level is let us say 1, 2.

What is the level after that? Is 1, 2 and 2, 1 are they the same energy, both they have the same energy? No, 1, 2 and 2, 1 will have different energies and whether 1, 2 will be lower or 2, 1 will be lower will depend on what is the relationship between L_x and L_y. Is L_x greater than L_y or is L_x less than L_y, that is what we will determine, which one is lower, which one is higher. So, degeneracy is not there. I think I have something written here.

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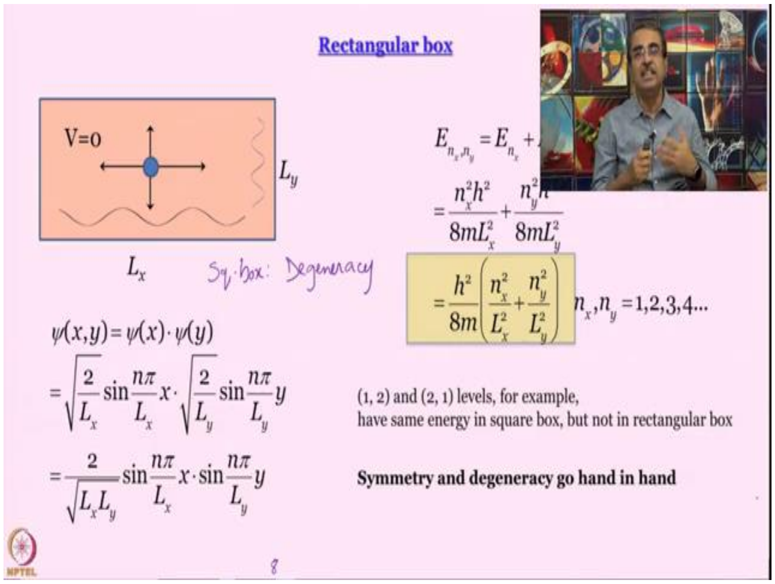

Rectangular box

Sq. box: Degeneracy

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

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

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

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

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

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

(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

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So, I am just going to erase all this. So, what we learned from here is that symmetry and degeneracy go hand in hand, you have more degeneracy when you have more symmetry, if you break symmetry, then degeneracy is lost. And this is something that we encounter in say, metal ion complexes, think of a free metal ion, is a perfectly symmetric object, it is a sphere.

So, all the d orbitals have the same energy, put it in an octahedral field what happens, symmetry is a little less and now you have d orbital splitting, e_g and t_{2g} perform jahn-teller distortion, then what happens? Energy decreases even more and so, the degeneracy even within this t_{2g} and e_g sets is lifted to certain extents.

So, the symmetry and degeneracy going hand in hand is a very important concept in chemistry. And we encountered it for the first time in our discussion from this particle in a 2D box model. Now, let us talk about 3D box.

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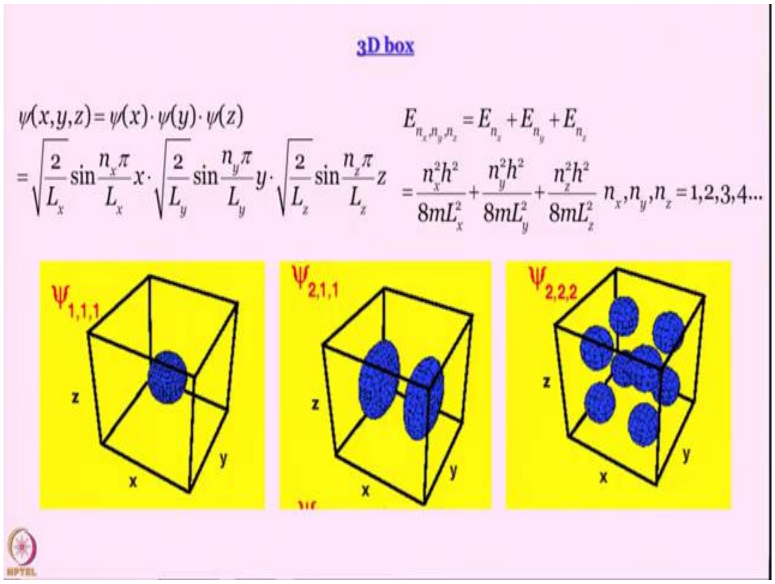

3D box

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

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

Everything else is same, wave function is a product of $\psi(x)$ and $\psi(y)$and $\psi(z)$. Energy is a sum of $E_x + E_y + E_z$, fine. So, these are the expressions. Problem is how do I draw this? Because now, x, y, z, three dimensions are there and ψ is the fourth dimension, I do not know how to draw a four dimensional graph. The way you draw it is that you assign color to the fourth dimension.

The way these are generated is that I have decided that I want particular value of ψ, actually mod ψ, let us say I want value of ψ to be something like 0.2 units. So, wherever value of ψ is 0.2 unit, I put a dot, and then all these dots generate a shape. That is my depiction of wave functions. So, for psi 1, 1, 1, I will get a sphere, not very difficult to understand, what about psi 2, 1, 1?

Now, I am going to get a node and that node is going to show up like this, I will join all the points that have value of say 0.2 and I will join all the points that have value of - 0.2. So, you get something that reminds you of p orbital, does not it? Similarly, for 2 to 2 and so on and so forth. So, this is how we can draw a 4-dimensional picture in 3-dimensional space by using color or by using point for a particular value of the fourth dimension that which is ψ here.

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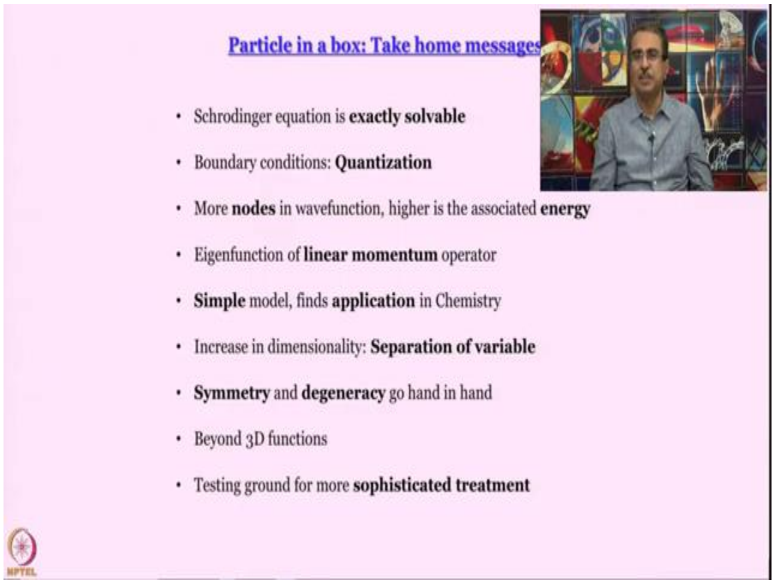

Particle in a box: Take home messages

- 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**

So, in our discussion of particle in a box what have we learned? First of all, we have encountered a situation where Schrödinger equation is exactly solvable in free particle as well as particle in a box. Free particle is less satisfying, because you get a wave function that is not all that great, in particle in a box you get a wave function that is better.

What is more important, for the first time in our discussion, we arrive at quantization that arises automatically from application for imposition of boundary conditions. So, we learned that boundary conditions lead to quantization. Remember, Schrödinger equation is a perfectly classical equation for de Broglie waves, that is where it started from. And then we forgot about de Broglie waves later on that is a different issue.

But there was no quantum number there, quantum numbers arise when we use Born interpretation and apply boundary conditions. One thing that we have seen is that if you have more nodes in wave function, higher is the associated energy, remember particle in a box wave functions, n equal to 1 no node, n equal to 2, 1 node, n equal to 3 more nodes and so on and so forth. So, this is an important thumb rule that we use often in Chemistry that, a function that has more nodes is associated with higher energy.

We learned about Eigen function of linear momentum operators, is this wave function of particle in a box an Eigen function of linear momentum operator? No, it is not. But we showed that we can express it as sums of two Eigen functions of linear momentum operator. So, when we make a measurement, we will see either $+\hbar k$ or $-\hbar k$, average value of linear momentum is going to be 0, because overall wave function is not an Eigen function, it is a linear function, linear sum of two Eigen functions.

The simple model as we have seen, yet it does find application as a starting point for many interesting chemical systems. We have started working on separation of variables, which is going to be a very important tool in our subsequent discussion. And finally, we have learned that symmetry and degeneracy go hand in hand, I absolutely love this, symmetry and degeneracy go hand in hand. So, we get a hint that symmetry is going to be an important parameter in chemistry.

We are not going to dwell too much upon this in this course, but just we advise that there this is an entire subject in itself, symmetry in chemistry. And also, we learned how to plot functions that are more than 3-dimensions. This has proved to be a testing ground for more sophisticated treatment, which we are not going to get into here. With all this background, we are going to talk about hydrogen atom. How do you perform a quantum mechanical treatment for hydrogen atom?

And there one important question that we are going to pose and hopefully learn the right answer too, is what is an orbital? So, that would be the theme of the next maybe 3 or 4 lectures.