Introduction to Quantum Mechanics

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Lecture – 01

Solution of the Schrodinger equation for free particles and periodic boundary conditions

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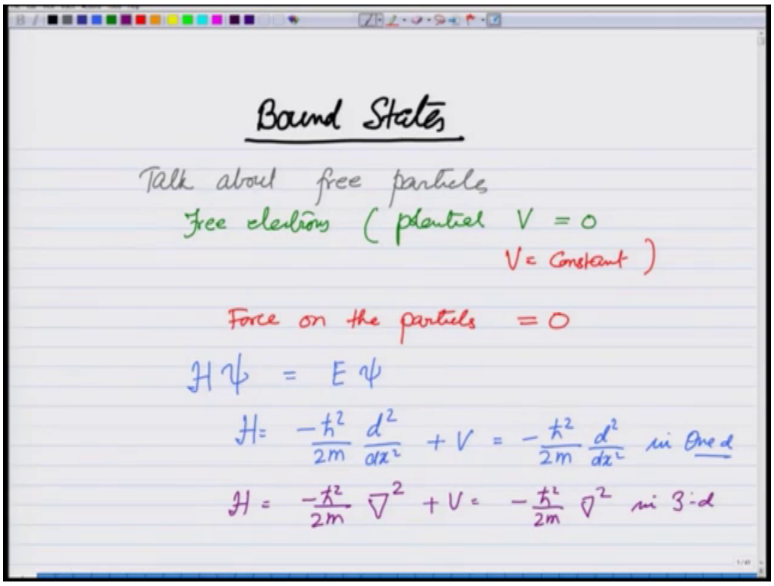

Bound States

Talk about free particle

Free electrons (potential $V = 0$
$V =$ Constant)

Force on the particles $= 0$

$$\mathcal{H}\psi = E\psi$$

$$\mathcal{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \text{ in One d}$$

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2 + V = -\frac{\hbar^2}{2m}\nabla^2 \text{ in 3-d}$$

So, far we have been talking about bound states as obtained by solving the Schrödinger equation. We are going to now change and talk about free particles. And in particular I am going to talk about free electrons, and when I say free electrons; that means, the potential energy v is equal to 0 or equivalently v equals constant. And what that means, is that the force on the particles is equal to 0. And therefore, the Hamiltonian H recall this Hamiltonian is an operator for energy where H psi equals E psi and H is going to be minus h cross square over 2 m d 2 over d x square plus, some constant potential which have taken to be 0.

So, this comes out to be minus h cross square over 2 m d 2 by d x square in 1 dimension. And it is going to be H equals minus h cross square over 2 m. Del square the laplacian plus v which is minus h cross square over 2 m del square in 3 d. So, we want to solve the Schrödinger equation for this particular Hamiltonian and where is it useful.

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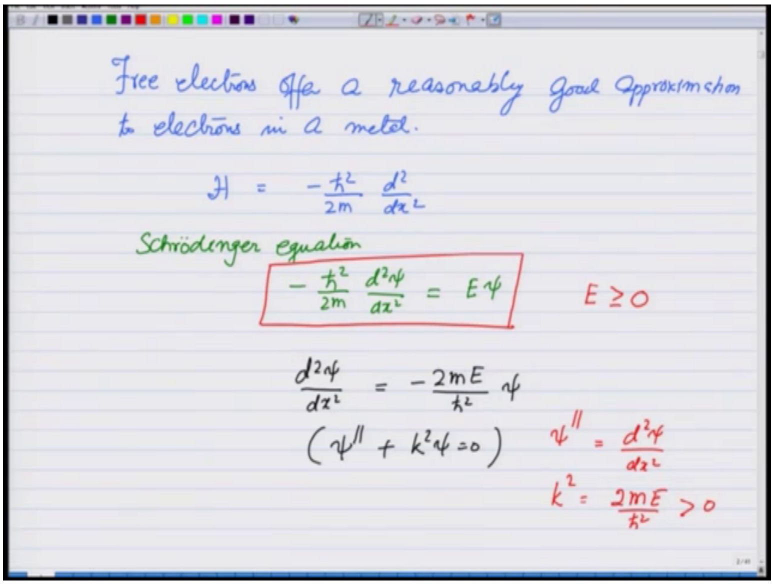

Free electrons offer a reasonably good approximation to electrons in a metal.

$$\mathcal{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

Schrödinger equation

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi} \qquad E \geq 0$$

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi$$

$$(\psi'' + k^2\psi = 0) \qquad \psi'' = \frac{d^2\psi}{dx^2}$$

$$k^2 = \frac{2mE}{\hbar^2} > 0$$

So, free electrons offer a reasonably good approximation to electrons in a metal. And I will talk about it more later. For the time being the Hamiltonian in 1 d is minus h cross square over 2 m d 2 by d x square. Let me focus on 1 dimension first and therefore, the Schrödinger equation is minus h cross square over 2 m d 2 psi over d x square equals E psi. That is my Schrödinger equation. And necessarily v 0 e is going to be greater than or equal to 0. This we have talked about earlier and you have also seen this as a problem in the book.

So, to solve this what I am now going to do is write d 2 psi over d x square is equal to minus 2 m E over h cross psi and therefore, psi double prime plus k square psi is equal to 0 where psi double prime is d 2 psi over d x square and k square is 2 m E over h cross square which is greater than 0.

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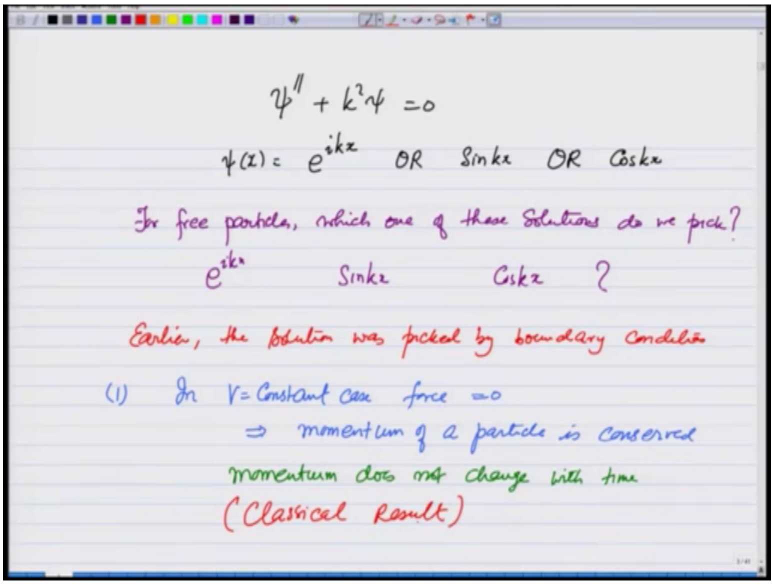

$$\psi'' + k^2\psi = 0$$

$$\psi(x) = e^{ikx} \quad \text{OR} \quad \sin kx \quad \text{OR} \quad \cos kx$$

For free particles, which one of these Solutions do we pick?

e^{ikx} Sinkx Coskx ?

Earlier, the Solution was picked by boundary condition

(1) In $V = \text{Constant}$ case force $= 0$

$\Rightarrow$ momentum of a particle is conserved

momentum does not change with time

(Classical Result)

So, the Schrödinger equation Now, comes out to be psi double prime plus k square psi equal 0. And the possible solutions are you can check it easily, psi x equals e raise to i k x or sin k x or cosine k x or any linear combination. The question is for free particles which one is the correct solution. So, for free particles which one of these solutions do we pick that is the question. Do I pick e raise to i k x do I pick sin k x do I cosine k x. Remember earlier when we where solving the Schrödinger equation a particular form of the solution was decided by the boundary condition. So, recall that earlier the solution was picked by boundary condition.

We are going to take some other consideration is time. And what we are going to do is first anticipate that in v equals constant case a force is 0. And therefore, momentum of a particle is conserved; that means, what is it mean? It means that momentum does not change with time. And this happens classical, this is a classical result. Should we expect the same thing in quantum mechanics?

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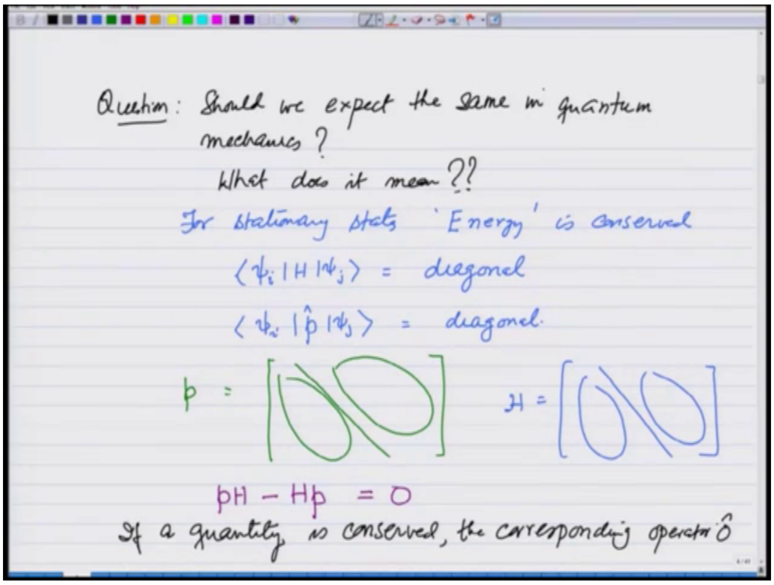

Question: Should we expect the same in quantum mechanics?

What does it mean??

For stationary states 'Energy' is conserved

$\langle \psi_i | H | \psi_j \rangle$ = diagonal

$\langle \psi_i | \hat{p} | \psi_j \rangle$ = diagonal.

$p =$ $\quad$ $H =$

$pH - Hp = 0$

If a quantity is conserved, the corresponding operator $\hat{O}$

So, let the question I ask now is question, should we expect the same in quantum mechanics. Number 1, should we expect that momentum is conserved? And if it is conserved, what does it mean? Recall now to answer this questions that for stationary states E the energy is conserved right. Or the metrics element psi i H psi j is diagonal in terms of Heisenberg's matrix mechanics. Recall that whenever there is a matrix which is diagonal; that means, the corresponding quantity does not change with time and is conserved.

So, here also if momentum is conserved I should expect that psi i momentum operator psi j matrix will be diagonal right. So, this is diagonal what; that means, is that if I write p matrix. It would have all of diagonal term 0 there will be terms here which will be nonzero along the diagonal and everything else would be 0. Now the matrix for the Hamiltonian is also diagonal right. So that means, if I take the product pH matrix and subtract hp this would be 0 right. So, what; that means, is if a quantity is conserved pH minus other that or corresponding operator satisfies if a quantity is conserved the corresponding operator, the corresponding operator O satisfies let me write this in the next page.

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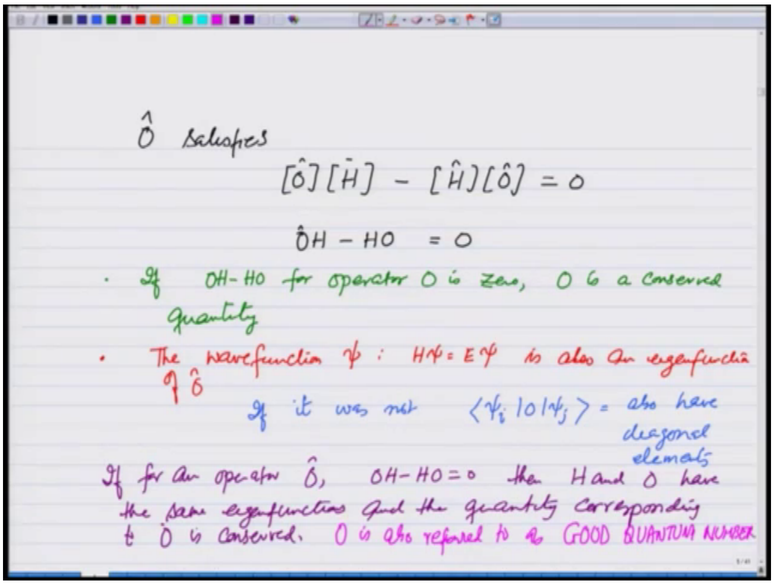

$\hat{O}$ satisfies

$$[\hat{O}][\hat{H}] - [\hat{H}][\hat{O}] = 0$$

$$\hat{O}H - HO = 0$$

- If OH - HO for operator O is zero, O is a conserved quantity
- The wavefunction ψ : $H\psi = E\psi$ is also an eigenfunction of $\hat{O}$

If it was not $\langle \psi_i | O | \psi_j \rangle$ = also have diagonal elements

If for an operator $\hat{O}$, OH - HO = 0 then H and O have the same eigenfunctions and the quantity corresponding to $\hat{O}$ is conserved. O is also referred to as GOOD QUANTUM NUMBER

So, O satisfies that matrix of O time's matrix of H and if I change the order and subtract it is 0. In the operator formalism what it means is that O operator H operator minus H operator O operator would be 0. So, let me now state what I want to say I turn the whole argument around and say. If O H minus H O is 0; that means, O would be a conserved quantity. So, if let us write (Refer Time: 10:57) if O H minus H O for operator O is 0 O is a conserved quantity. And what does that mean? That means, the wave function psi such that H psi equals E psi is also and I can function of O. If it was not, So let us show this if it was not.

Then psi i O psi j will also have diagonal elements. So, let us just summaries this by saying that if for an operator O, O H minus H O is 0 then H and O have the same Eigen functions. And the quantity corresponding to O is conserved and O is also referred to as O is also referred to as not O, but it is Eigen values are referred to as good quantum number.

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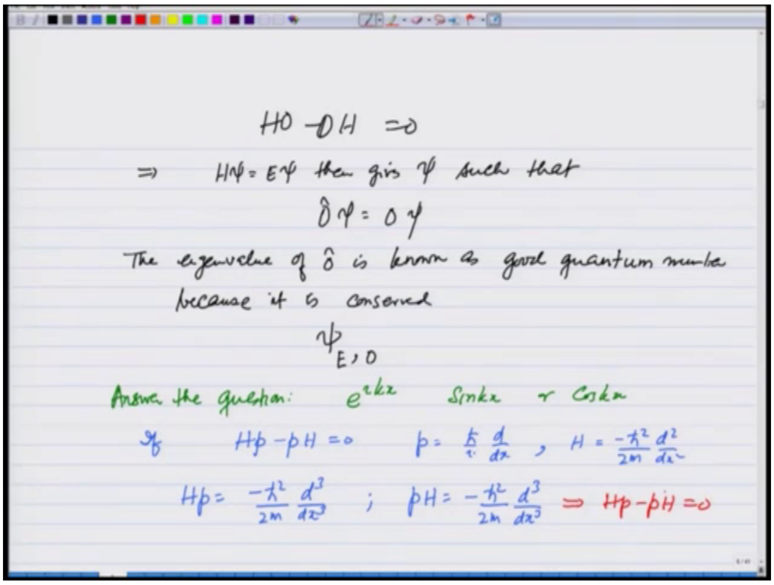

$$HO - OH = 0$$

$\Rightarrow$ $H\psi = E\psi$ then gives ψ such that

$$\hat{O}\psi = O\psi$$

The eigenvalue of $\hat{O}$ is known as good quantum number because it is conserved

$$\psi_{E,O}$$

Answer the question: e^{ikx} $\sin kx$ or $\cos kx$

If $Hp - pH = 0$ $\quad p = \frac{\hbar}{i}\frac{d}{dx}$, $H = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$

$Hp = \frac{-\hbar^2}{2m}\frac{d^3}{dx^3}$; $pH = -\frac{\hbar^2}{2m}\frac{d^3}{dx^3} \Rightarrow Hp - pH = 0$

So, let us write it again that H O minus O H is equal to 0 implies that H psi equals E psi then gives psi such that O psi is also sum O psi, and the Eigen value of O is known as a good quantum number. Why? Because it is conserved. And the wave function psi is not only labeled by Eigen function Eigen value of energy e, but also the Eigen value of that quantity O. With this background let us now try to answer. The question answer the question e arise to i k x sin k x or cosine k x. Now to anticipate the answer again I go back to the classical result that in the case when the potential is constant or potential is 0 momentum is conserved.

So, let us now see if H p minus p H is 0. Remember what is p? P is h cross over i d y d x and what is H? H is minus h cross square over 2 m d 2 by d x square. So, H p would be minus h cross square over 2 m, d 3 by d x cube the third derivative and pH will also be h cross square over 2 m d 3 over d x cubed, the third derivative implying there by that H p minus p H is 0.

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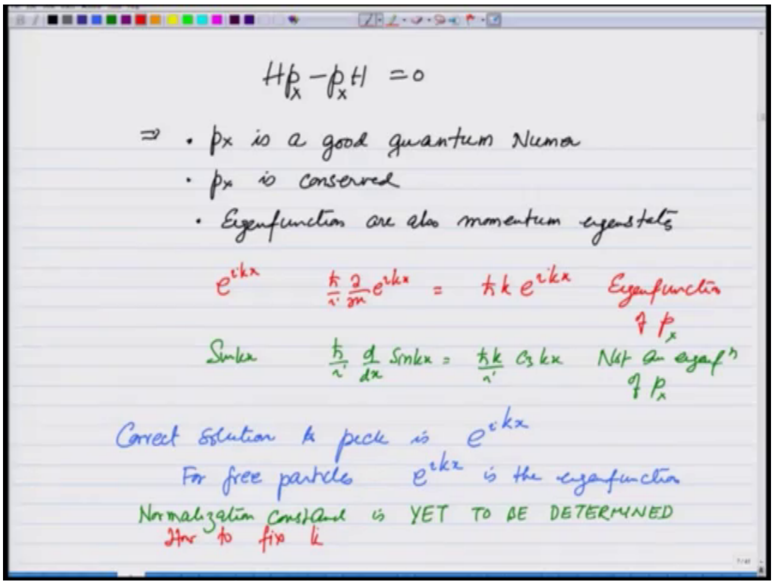

$H p_x - p_x H = 0$

$\Rightarrow$
- p_x is a good quantum Numer
- p_x is conserved
- Eigenfunction are also momentum eigenstates

e^{ikx} $\quad \frac{\hbar}{i}\frac{\partial}{\partial x}e^{ikx} = \hbar k e^{ikx}$ Eigenfunction of p_x

$\sin kx$ $\quad \frac{\hbar}{i}\frac{d}{dx}\sin kx = \frac{\hbar k}{i}\cos kx$ Not an eigenfn of p_x

Correct solution to pick is e^{ikx}

For free particles e^{ikx} is the eigenfunction

Normalization Constant is YET TO BE DETERMINED

How to fix k

So, if I find that H p minus p H is 0 and by the way when I write p here this is the x component of the momentum p x. This means p x is a good quantum number p x is conserved and third Eigen function let me say Eigen function is the stationary state Schrödinger equation solutions are also momentum Eigen states. So, of the 3 e raise to i k x h cross over i d by d x of e raise to i k x gives me h cross k e raise to i k x is an Eigen function of p. Sin k x gives me h cross over i d by d x of sin k x equals h cross k over i cosine k x not an Eigen c function of p let us write this p x. And similarly cosine k x is also not an Eigen function. So, if I want to satisfy the symmetry property that the momentum is conserved that p be a good quantum number and therefore, H and p have the same Eigen function the correct solution to pick is e raise to i k x.

So, for free particles this is the Eigen functions. So, for free particles with all the symmetry satisfy and all that e raise to i k x is the Eigen function. Notice that I have not written the normalization constant. So, normalization constant is yet to be determined. And also we want to find how to fix k. That means, is it continuous does it change discontinuously or what happens recall that for particle in a box problem k was one pi over L here how do we fix k. So, these 2 problems are related and that is what we have going to address now.

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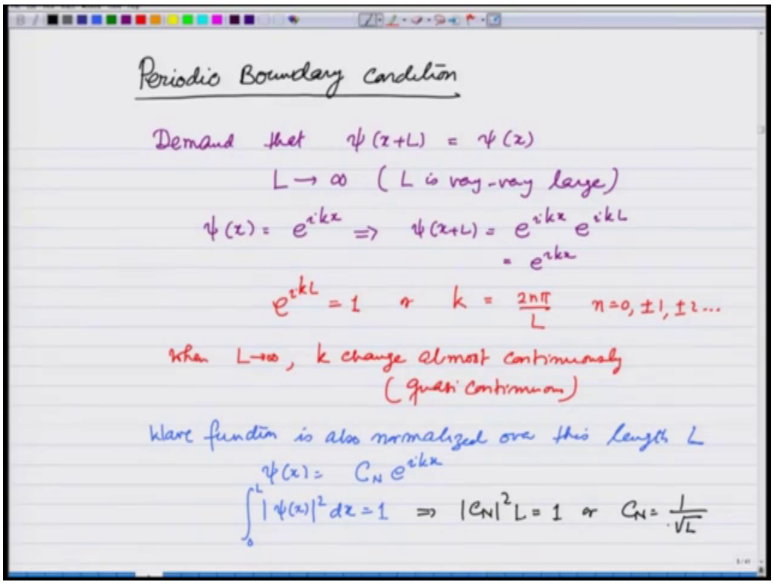

Periodic Boundary condition

Demand that $\psi(x+L) = \psi(x)$

$L \to \infty$ (L is very-very large)

$$\psi(x) = e^{ikx} \Rightarrow \psi(x+L) = e^{ikx} e^{ikL}$$
$$= e^{ikx}$$

$$e^{ikL} = 1 \quad \text{or} \quad k = \frac{2n\pi}{L} \qquad n = 0, \pm 1, \pm 2 \ldots$$

When $L \to \infty$, k change almost continuously (quasi continuous)

Wave function is also normalized over this length L

$$\psi(x) = C_N e^{ikx}$$

$$\int_0^L |\psi(x)|^2 dx = 1 \Rightarrow |C_N|^2 L = 1 \quad \text{or} \quad C_N = \frac{1}{\sqrt{L}}$$

And the way it is address is through something all the periodic boundary condition. This is a trick through which we count case we can enumerate k and we can also fix the normalization constant.

So, what periodic boundary condition does is demand that psi x plus L be same as psi x; that means, make the wave function periodic over a length L and in the limit thermodynamic limit will at L go to infinity. What it means is L is very, very large. It is made. So, large that all the counting can be done through integration and you will see in a minute. So, when we demand this now psi x is equal to e raise to i k x and this implies that psi x plus L is equal to e raise to i k e raise to i k L. And this we want to be equal to e raise to i k x, and what this means is that we have e raise to i k L equals 1.

Or k equals 2 n pi over L, where n equals 0 plus minus 1 plus minus 2 and so on. This is how we fix the value of k and when L goes to infinity k changes almost continuously. What I will call is quasi continuous. So, this is the trick of making k change continuously I will be able to change the summation over k to integral over k which also in a few minutes. And now how do we normalize the wave function. So, the wave function is also normalized over this length L. So, what do we do is suppose the wave function is taken to be c normalization e raise to i k x what I am going to demand is mod psi x square integral from 0 to L d x be 1 and this immediately gives me mod C n square times L equals 1 or C n equals 1 over root l.

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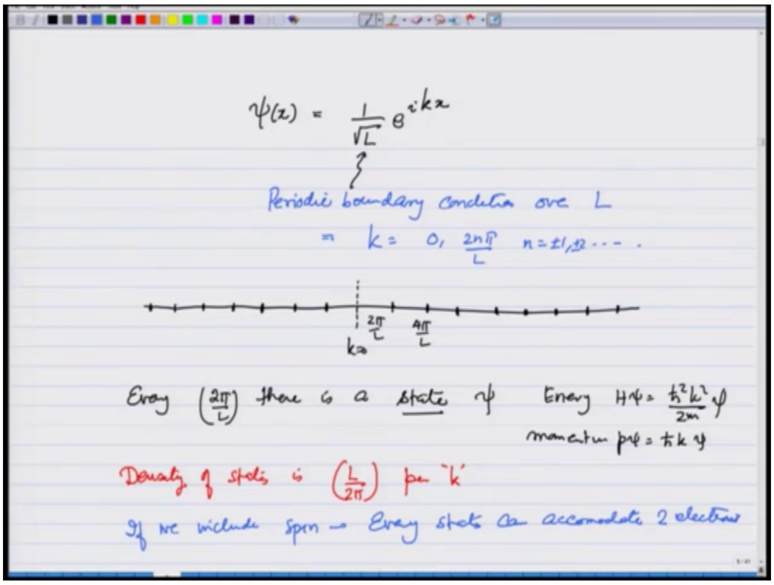

$\psi(x) = \frac{1}{\sqrt{L}} e^{ikx}$

Periodic boundary condition ove L

$\Rightarrow k = 0, \frac{2n\pi}{L} \quad n = \pm 1, \pm 2 \dots .$

$k=0 \quad \frac{2\pi}{L} \quad \frac{4\pi}{L}$

Every $\left(\frac{2\pi}{L}\right)$ there is a state ψ Energy $H\psi = \frac{\hbar^2 k^2}{2m}\psi$

momentum $p\psi = \hbar k \psi$

Density of states is $\left(\frac{L}{2\pi}\right)$ per 'k'

If we include spin → Every state can accomodate 2 electrons

And therefore, we are going to write wave function psi x with periodic boundary conditions and box normalized over this length L as 1 over root L e raise to i k x. The moment arrived this L here; that means, I also imply periodic boundary condition over L and this means k equals 0 2 n pi over L n equals 1 2 3 and so on plus minus 1 plus minus 2 and so on.

So, this is how we count k, and this is how we normalize the wave function. So, if I want to picturize this suppose I draw it on a line this is k equal to 0 every 2 pi over L there is 1 k value 4 pi over L and so on. All these points show one particular k value on the negative side of k also. So, what I am going to say is every 2 pi over L there is a state psi, which has energy H psi which gives me h cross square k square over 2 m psi. And momentum p psi equals h cross k psi.

So, it as the Eigen state of both the Hamiltonian and the momentum with the Eigen values being here and every 2 pi by L there is a state. Or this is also written in another words is that the density of states is L over 2 pi per k. We change k by unity and even allow 2 pi states. If you include spin if include spin then every state can accommodate 2 electrons.

So, this is what we do in 1 dimension what about 3 dimensions.

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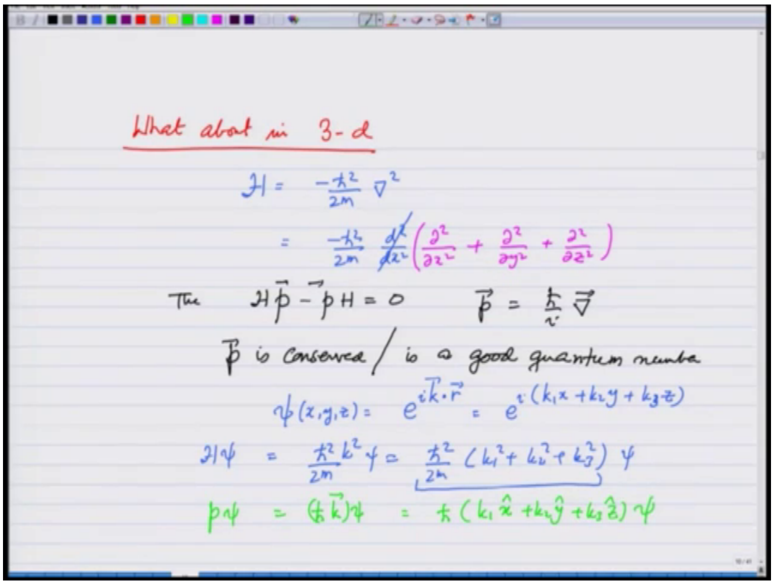

What about in 3-d

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2$$

$$= \frac{-\hbar^2}{2m}\cancel{\frac{d^2}{dx^2}}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

The $\mathcal{H}\vec{p} - \vec{p}H = 0 \qquad \vec{p} = \frac{\hbar}{i}\vec{\nabla}$

$\vec{p}$ is conserved / is a good quantum number

$$\psi(x,y,z) = e^{i\vec{k}\cdot\vec{r}} = e^{i(k_1x + k_2y + k_3z)}$$

$$\mathcal{H}\psi = \frac{\hbar^2k^2}{2m}\psi = \underbrace{\frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2)}\psi$$

$$p\psi = (\hbar\vec{k})\psi = \hbar(k_1\hat{x} + k_2\hat{y} + k_3\hat{z})\psi$$

So, next question we ask is what about in 3 d the Hamiltonian in 3 d is going to be minus h cross square over 2 m del square, which is minus h cross square over 2 m d 2 by d x square. Now I am going to change this d 2 by d x by partial del to by del x square because now I am going to have all 3 derivatives plus del to by dell y square plus del 2 by del z square. We can do separation of variables and solve the problem now again the Hamiltonian satisfies this equal to 0 because p, vector let me write this is a vector is nothing but h cross over i times the gradient operator any can satisfy yourself that this satisfies hp minus p H equal 0.

And therefore, p is conserved one and the same thing is a good quantum number. And therefore, the solution should be the Eigen function of both H and p and without going through details I can just now tell you that psi as a function of x y and z is nothing but e raise to i k dot r which I am going to write that as e raise to i k 1 x plus k 2 y plus k 2 k 3 z. This is a wave function there will be a constant (Refer Time: 26:59) which will discuss in a few moments and H psi is now going to give me h cross square over 2 m k square which is h cross square over 2 m k 1 square plus k 2 square plus k 3 square psi which is the energy. So, this is the energy, h cross square k square over 2 m or p O square over 2 m. And p psi is nothing but h cross k vector time psi which is h cross k 1 x unit vector plus k 2 y unit vector plus k 3 z unit vector psi. And energy is p square over 2 m, So in 3 d this is what happens?

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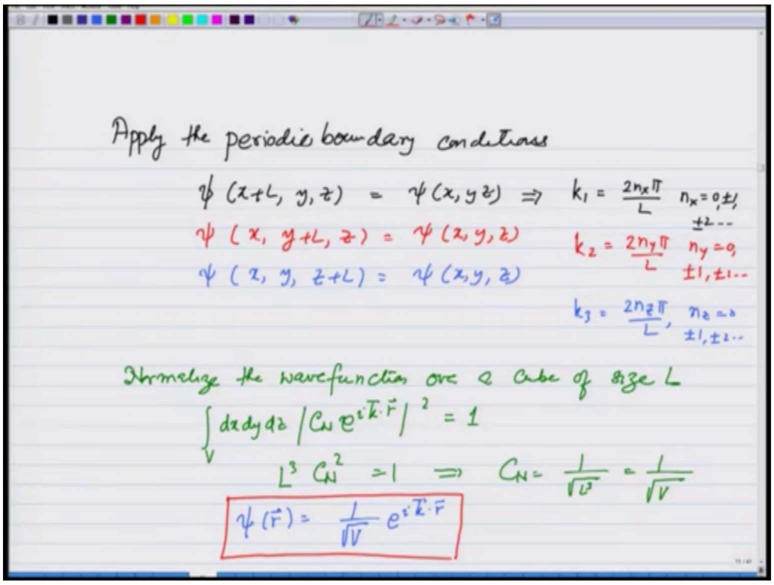

Apply the periodic boundary conditions

$\psi(x+L, y, z) = \psi(x, y, z) \Rightarrow k_1 = \frac{2n_x\pi}{L}$ $n_x = 0, \pm 1, \pm 2 \ldots$

$\psi(x, y+L, z) = \psi(x, y, z)$ $k_2 = \frac{2n_y\pi}{L}$ $n_y = 0, \pm 1, \pm 2 \ldots$

$\psi(x, y, z+L) = \psi(x, y, z)$ $k_3 = \frac{2n_z\pi}{L}$, $n_z = 0, \pm 1, \pm 2 \ldots$

Normalize the wavefunction over a cube of size L

$$\int_V dx\,dy\,dz \left| C_N e^{i\vec{k}\cdot\vec{r}} \right|^2 = 1$$

$$L^3 C_N^2 = 1 \Rightarrow C_N = \frac{1}{\sqrt{L^3}} = \frac{1}{\sqrt{V}}$$

$$\boxed{\psi(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}}$$

Now, if I applied the periodic boundary conditions here. We get psi x plus L y z equals I want psi x y z. Similarly I want psi x y plus L z equals psi x y and z, and I want psi x y z plus L equals psi x y and z. And this immediately implies just as I did in the case of 1 dimension, this implies that k 1 is 2 n let me call it now n x pi over L n x equal 0 plus minus 1 plus minus 2 and so on. Similarly k 2 is going to be 2 n y pi over L n y is 0 plus minus 1 plus minus 2 and so on.

And k 3 is going to be 2 n z pi over L n z 0 plus minus 1 plus minus 2 and so on. And now I am going to normalize the wave function over a cube of size L. So, I am going to have integration over the volume, d x d y d z C n e raise to i k dot r mod square equals 1. And that gives me the volume L cubed times C n square equals 1 or C n equals 1 over square root of L cubed. Which is also I can try it as 1 over square root of v. And therefore, my wave functions now are going to be psi r is going to be 1 over square root of a v e raise to i k dot r. This is the wave function in 3 dimensions with periodic boundary conditions and box normalized.

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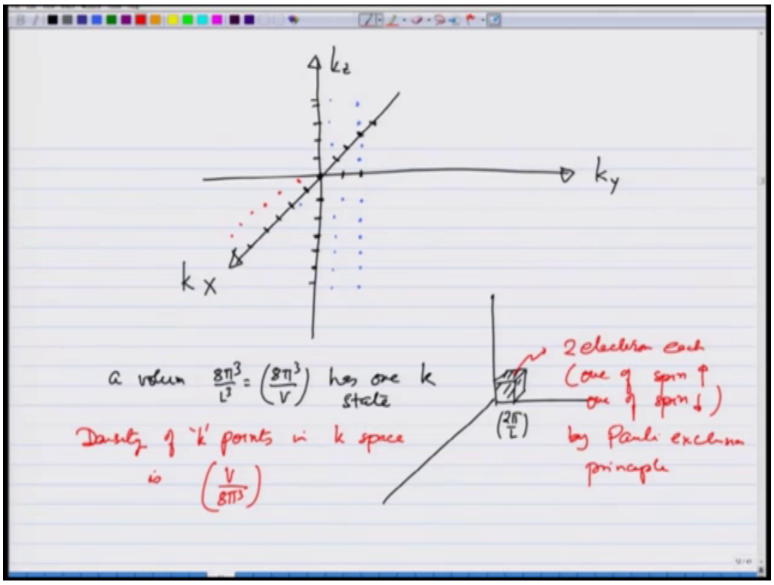

a volume $\frac{8\pi^3}{L^3} = \left(\frac{8\pi^3}{V}\right)$ has one k state

Density of 'k' points in k space is $\left(\frac{V}{8\pi^3}\right)$

2 electrons each (one of spin ↑ one of spin ↓) by Pauli exclusion principle

Again if I want to now represent this wave function in 3 d this is what I am going to do this is my x axis or k x axis, this is my k y axis and this is my k z axis.

And by the way this is usually referred to as the k space. So, 0 k is going to be here again every 2 pi by L there is one state on each axis. And then everywhere else wherever there is an interior matching there is going to be one state. So, these states are represented by these dots where I just keep increasing everything by an integer let me make this dots on this sides also. In other words if I take this space and make a box of size 2 pi by L in the k space there is one state in it.

So, a volume of 8 pi cube over L cubed which is 8 pi cubed over v has 1 k state. Or we can say the density of k points in k space is v over 8 pi cubed. So, if I have a some volume k space v k if I multiply that by v over 8 pi cubed I am going to get the number of k points in that k space volume, how about the number of electrons? Each of these k state can take 2 electrons each one of spin up one of spin down by pauli exclusion principle.

So, by now I have set up pretty much for you what all be require to do a very simple approximation for metals.

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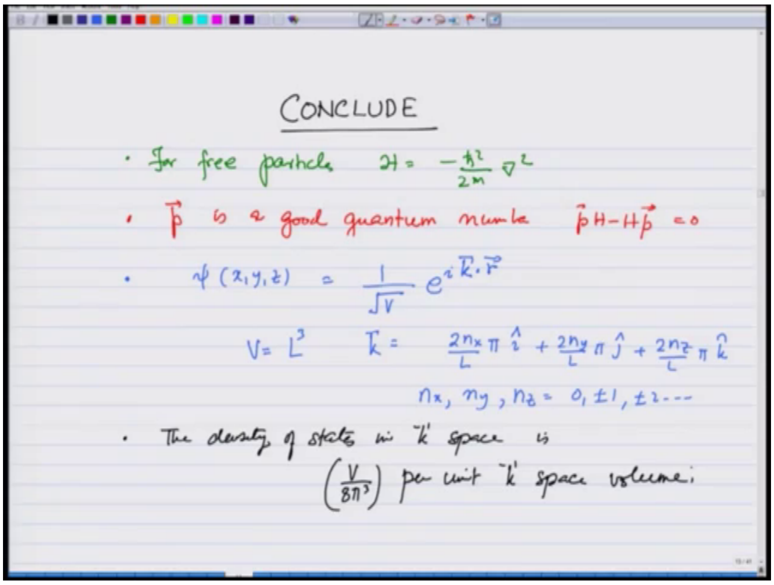

CONCLUDE

- For free particle $\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2$
- $\vec{p}$ is a good quantum number $\vec{p}H - H\vec{p} = 0$
- $\psi(x,y,z) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$

$V = L^3$ $\vec{k} = \frac{2n_x}{L}\pi\hat{i} + \frac{2n_y}{L}\pi\hat{j} + \frac{2n_z}{L}\pi\hat{k}$

$n_x, n_y, n_z = 0, \pm 1, \pm 2 \ldots$

- The density of states in 'k' space is $\left(\frac{V}{8\pi^3}\right)$ per unit 'k' space volume.

So, let me conclude now this lecture by saying that for free particles H equals minus h cross square over 2 m del square, then momentum p is a good quantum number; that means, p H minus H sorry p H minus H p vector is 0. The wave functions psi x y z is 1 over square root of v e raise to i k dot r v equals L cubed I am box normalizing over a cube of L and k vector equals 2 n x over L pi x direction plus 2 and y over L pi, j direction plus 2 n z over L over L pi k direction n x and y and n z are all 0 plus minus 1 plus minus 2 and so on and finally, the density of states in k space, because k or p is about quantum number.

So, I can measure density in k space is v over 8 pi cubed per unit k space volume. With this we will now apply these ideas to metals in a very simple way in the next lecture, where we learn about Fermi energy Fermi momentum and things like this.