**Electronic Properties of the Materials Computational Approach**
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Lecture – 11
Quantum Free Electrons - Sommerfeld Theory(Part 1)

Hello friends, in this lecture, we are going to learn about quantum free electron model proposed by Sommerfeld.

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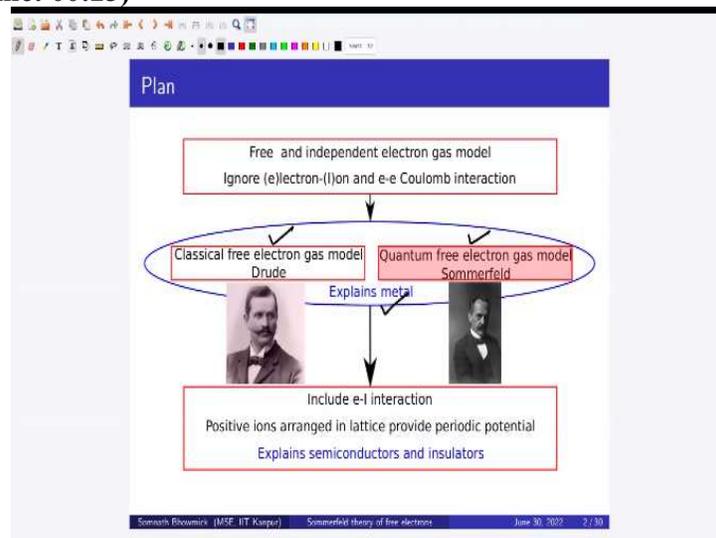
Before we start the lecture, let us revise the plan of the course. So, we are doing free and independent electron gas model by ignoring electron ion and electron-electron Coulomb interaction, this can explain the properties of the metals to some extent, we already have done classical free electron gas model proposed by Drude. Now, we are going to do quantum free electron gas model proposed by Sommerfeld.

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Boundary condition	$\psi(0) = \psi(L) = 0$ Fixed ✓	$\psi(x) = \psi(x+L)$ Periodic ✓
At boundary	Particle reflected, momentum (p) changes ✓	Particle exit, re-enter opposite end, p-conserved ✓
Eigen function	$\psi_n(x) = \sqrt{\frac{2}{L}} \sin(kx)$	$\psi_k(x) = \frac{1}{\sqrt{L}} \exp(\imath kx)$ ✓
✓ $\hat{p} \equiv -\imath\hbar\frac{d}{dx}$	$\psi_n(x) \neq$ eigenfn	$\psi_k(x)$ eigenfn (eigenval: $\hbar k$) ✓
Allowd k-values	$\frac{n\pi}{L}, n = 1, 2, ..$ ✓	$\frac{2n\pi}{L}, n = .. -1, 0, 1..$ ✓
Energy ✓	$\varepsilon_n = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2mL^2}$ $\varepsilon > 0$ ✓	$\varepsilon(k) = \frac{\hbar^2 k^2}{2m}$ $\varepsilon \geq 0$ ✓
Physical meaning	Standing wave ✓ k not momentum	Traveling wave k momentum

Plane waves are normalizable only within a box. They have definite p, but any confinement makes p uncertain (uncertainty principle). PBC is a smart

Schrodinger equation for free particles is given by this now, the time independent Schrodinger equation for free particles can be solved using 2 different types of boundary conditions, fixed boundary condition and periodic boundary condition. In case of fixed boundary condition the Eigen functions must vanish at the boundary as a result Eigen functions are standing wave solutions.

However, charge and energy transport by electrons is more conveniently described by travelling waves this can be achieved by using a periodic boundary condition. In case of fixed boundary condition particles get reflected from the boundary causing momentum to change sign. In case of periodic boundary condition particles leaves the box from one end and simultaneously renders from the other end conserving the momentum note that psi n x are not Eigen functions of the momentum operator in case of fixed boundary condition.

So, this is the Eigen function and this is the momentum operator and now, you will see that if you take a derivative of this then this becomes cosine correct. So, that means that Eigen functions are not the Eigen function of momentum operator however, if you take the solution for the Eigen function for the periodic boundary condition then if you take a derivative of this then this psi of kx this is actually an Eigen function of the momentum operator with Eigen value h bar k.

Now, the other things are the following the allowed values of k for the fixed boundary condition or even by this whereas, the allowed values for kr for the periodic boundary condition are given by this and then we have the energy Eigen values for fixed boundary condition and we have

the energy Eigen values for the periodic boundary conditions. And then in case of fixed boundary condition we get like standing wave solutions, where k is not momentum in case of periodic boundary condition, we have travelling wave solution where h bar k is momentum.

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So, far we have been discussing in 1 dimension, let us make a transition from 1D to 3D we can see that a cubic box of volume V. So, the electrons are confined in this cubic box of volume V all the sides of length equal to L. The time independent Schrodinger equation for free electron in case of 3D box is given by this. Now, this is the divergence operator so, we are going to work in Cartesian coordinates the divergence operator is given.

$$\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$$

Now, what we do is that, we can do a separation of variables and we can just write the wave function as $\psi(x, y, z) = X(x)Y(y)Z(z)$ Now, if we put these 2 terms like we take the divergence operator in Cartesian coordinates and we just replace this wave function in this equation then after separation of the variables we can write the 3 equations

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} = \varepsilon_x X$$

$$-\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2} = \varepsilon_y Y$$

$$-\frac{\hbar^2}{2m}\frac{d^2Z}{dz^2} = \varepsilon_z Z$$

and then of course $\varepsilon_x + \varepsilon_y + \varepsilon_z = \varepsilon$. Now, you will see we got like 3 time independent Schrodinger equations in 1 dimension.

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Now, let us try to solve one of them and then this is again like as we did before we just write this equation say

$$\frac{d^2 X}{dx^2} = -k_x^2 X$$

Where $k_x^2 = \frac{2m\varepsilon_x}{\hbar^2}$

then the solution for this equation is since we are using now periodic boundary condition the solution is given by

$X(x) = \frac{1}{\sqrt{L}} e^{ik_x x}$, $Y(y) = \frac{1}{\sqrt{L}} e^{ik_y y}$ and $Z(z) = \frac{1}{\sqrt{L}} e^{ik_z z}$

Now, we can combine these 3

$$\psi(x, y, z) = \frac{1}{V} e^{i\vec{k}.\vec{r}}$$

So, if we are using periodic boundary condition, then this is the Eigen function.

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So, we have solved for the Eigen functions for free particles in a cubic box of volume V. Now, let us focus on the periodic boundary condition. If this is 1D problem, we will write the periodic boundary condition as $X(x + L) = X(x)$, $Y(y + L) = Y(y)$ and $Z(z + L) = Z(z)$. Note that difference in case a fixed boundary condition with the wave function must go to 0 at the box changes, but that is not required if we are using periodic boundary condition then these are the boundary conditions in case we are using the periodic boundary.

In case of 3D we can combine and then write the boundary conditions like this. So, psi x + L, y, z = psi x, y, z. So, this is along x, the boundary condition along y can be written as psi x, y + L, z = psi x, y, z and boundary conditions allows Z can be written as psi x, y, z + L = psi x, y, z. Now, let us apply and see what we get.

$$\psi(x + L, y, z) = \frac{1}{V} e^{i(k_x(x+L))} e^{ik_y y} e^{ik_z z} = \frac{1}{V} e^{ik_x x} e^{ik_y y} e^{ik_z z}$$

if you cancel terms, we are left with

$$e^{ik_x x L} = e^{ik_y y L} = e^{ik_z z L} = 1 = e^{i2\pi n}$$

Similarly, if we take the boundary condition along y and along z, then we will get e power iK y times L = 1 and e power iK z times L = 1 and we know that one in the exponential form we can just exponential 1 as this e power i 2 pi n where n is an integer.

So, that implies that we have K x times L this must be equal to 2 pi n x and so on. And n that case, the allowed values of

$$k_x = \frac{2\pi n_x}{L}, \; k_y = \frac{2\pi n_y}{L} \text{ and } k_z = \frac{2\pi n_z}{L}$$

where n_x n_y and n_z are integers that means, these can be like positive integers negative integers as well as 0 we can also get the Eigen values like

$$\varepsilon(\vec{k}) = \frac{\hbar^2 \vec{k}}{2m} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

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What is the physical significance of this vector K? There are 2 points the first one is h bar k momentum for example, if we take the Eigen functions, then we see that these Eigen functions are also the Eigen functions of the momentum operator with the Eigen value is h bar k. So, that means electrons in state this has a definite momentum equal to h bar k and we get to find the corresponding velocity $\vec{v} = \hbar \vec{k}/m$. Then we get the velocity and then the energy can be expressed in a familiar classical form $\varepsilon = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}$. And once we identify h cross k as momentum, then we can hide that energy = p square by 2m is the classical form of kinetic energy.

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Now, K can also be related to the de Broglie wavelength. So, we have this wave particle duality and then, if lambda is the de Broglie wavelength, then we know that, then we can actually show that this K and lambda they are related by this equation.

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Before I go to the next part, let us summarize what we have done so far. So, we have taken free electron in a cubic box of volume V and then this is the time independent Schrodinger equation. And since we are doing it in 3D, so del square, this is the divergence operator and then the Eigen functions for this time independent Schrodinger equation can be found to be this, and then the energy Eigen values are h cross square k square divided by 2m and now, if we apply periodic boundary condition in all the 3 directions.

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- Eigenfunctions: $\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} \exp(i\vec{k} \cdot \vec{r})$
- Energy eigenvalues: $\varepsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}$
- Periodic boundary condition:
  - $\psi(x + L, y, z) = \psi(x, y, z)$
  - $\psi(x, y + L, z) = \psi(x, y, z)$
  - $\psi(x, y, z + L) = \psi(x, y, z)$
- Allowed values of $\vec{k}$: $k_x = \frac{2\pi n_x}{L}, k_y = \frac{2\pi n_y}{L}, k_z = \frac{2\pi n_z}{L}$
- n_x, n_y, n_z are integers $\cdots, -2, -1, 0, 1, 2, \cdots$
- Physical significance of $\vec{k}$
  - $\exp(i\vec{k} \cdot \vec{r})$ eigenfunction of momentum operator with eigenvalue $\hbar\vec{k}$
  - Wave-particle duality: de Broglie wavelength $\lambda = \frac{2\pi}{k}$

Then the allowed values of K are given by this so we have like K x, K y, K z and here n x, n y, n z are integers so, that means they can take values like this all the positive and negative values as well as 0 and what is the physical significance of K? So, e power i K dot r is the Eigen function of momentum operator with Eigen value h bar k and like wave particle duality, the de Broglie wavelength is related to K by this equation.

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- Construct k-space using allowed values:
  $k_x = \frac{2\pi n_x}{L}, k_y = \frac{2\pi n_y}{L}, k_z = \frac{2\pi n_z}{L}$

  $n_x = 0, n_y = 0 \rightarrow (0,0)$ \quad $(0,0)$
  $n_x = 1, n_y = 0 \rightarrow (1,0)$ \quad $(\frac{2\pi}{L}, 0)$
  $n_x = 1, n_y = 1 \rightarrow (1,1)$ \quad $(\frac{2\pi}{L}, \frac{2\pi}{L})$

- Volume occupied by a point in k-space$=$
  $\triangle k = \left(\frac{2\pi}{L}\right)^3 = \frac{8\pi^3}{V}$
- Each point in k-space represent a stationary state
- Each point in k-space corresponds to one energy level:
  $\varepsilon(k_x, k_y, k_z) = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$
- Energy levels can be degenerate: $(\pm\frac{2\pi}{L}, 0, 0), (0, \pm\frac{2\pi}{L}, 0), (0, 0, \pm\frac{2\pi}{L})$

Let us now construct space with the allowed values of K x, K y and K z and using like K x, K y and K z as 3 mutually perpendicular axes this is known as K-space for the purpose of illustration, I am going to use 2D. So, you see that we can take this K x and K y these are 2 axes and then we have these allowed values. So, for example, we can take a point where n x = 0, n y = 0. So, that is my 0, 0 point in K-space this one.

Then we can take n x = 1, n y = 0 that means is my 1, 0 point so, this is the 1, 0 point in that K-space and similarly, we can do n x = 1, n y = 1 and that will become the 1, 1 point and so on. Note that each point in the K-space represent a stationary state for example, 0, 0 this represents the ground state 1, 0 represents the first excited state and so on. Now, we can also say that each point in K-space corresponds to 1 energy level.

So, for example that 0, 0 represents the ground state energy 1, 0 represents left first excited state energy and so on. So, now what we notice here is that each K-point occupies some volume in the K-space which is shown by this blue shaded region this is very simple, we just join this point 0, 0 and 1, 0 and then just join this perpendicular this is the perpendicular bisector. And similarly, we join this point 0, 0 and 0, 1 and this is the perpendicular bisector and so on.

So, that means the blue shaded region this is some volume or some area which is unique to this point. So, for example, the first point is say this is like 0, 0 and the second point if I put n x = 1. The second point is 2 pi by L, 0 and the third point is 2 pi by L, 2 pi by L and so on. So, that means, the area right each side of the square has a length occupy by L. So, that means, the area occupied by each point is 4 pi by L square and if we consider 3D the volume of occupy 2 pi by L whole cube that is equal to 8 pi cube by V. So, this is the volume occupied by a point in space.

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Now, let us come back to this interpretation. So, now, each point in the K-space will corresponds to 1 energy level and energy values are given by this and then you see that the energy levels can be degenerate. Degenerate means they can have same energy, for example,

energy will be same for different allowed K-values. So, this is what allowed K-values plus minus say 2 pi by L 0, 0. So, this is 1 allowed K-values, the energy for this will be same as energy for some other set of allowed K-values like 0, 2 pi by L, 0, 0 or like 0, 0, 2 pi by L.

So, that means, you see that there are like if I just consider this plus and minus sign separately there are like 6 allowed K-values and all of them have same energies. Now, we already have found the volume occupied by a point in K-space. Now, if we invert the volume occupied by a point in - space, we get the K-space density of energy level that is the number of energy levels permitted per unit volume of the K-space, we will see that this is the most useful information we get as a consequence of quantization of K-values.

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- Let us populate the energy levels: must obey Pauli exclusion principle
- Filling energy levels with e is same as filling the k-space with e
- Any connection between *occupied* volume in k-space and # electrons?
- Let us calculate number of k-points in a given volume in k-space
- Consider volume within a sphere of radius k_F (Fermi wave vector)

Now, let us fill the energy levels with electrons. Since electrons are fermions they must obey Pauli exclusion principle, remember that each point in K-space corresponds to an energy level thus filling up energy level is same as filling of K-space with electrons. So, let us see some example. So, let us fill the ground state with electrons. So, we will put like 2 electrons in the ground state and this is same as putting 2 electrons in this box in K-space.

Similarly, the first excited states there are 4 of them because we have like 1, 0 and then we have -1, 0 we have 0, 1 and 0, -1. So, now, if we feel the first excited states we take electrons that is same as filling these boxes with 2 electrons since, each K-point occupies a fixed volume certain amount of volume in K-space is related to the number of electrons. Now, let us take a sphere with origin and 0, 0, 0. So, you see this is the origin and then calculate the number of K-points inside this sphere you see this red circle.

Since, we I am showing the sphere in 2D this looks like a circle. So, this is the sphere with some radius and then we have to calculate the number of K-points inside the sphere. Now, the radius of the sphere is called K F for Fermi wave vector and the reason behind the name will become clear in next couple of slides.

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- Fermi sphere: within the sphere (radius k_F) states are filled
- Fermi surface: surface separating occupied and unoccupied states
- Fermi surface spherical for free electrons: $k_x^2 + k_y^2 + k_z^2 = \frac{2m\varepsilon}{\hbar^2}$
- In general, Fermi surface need not be spherical (to be discussed later)
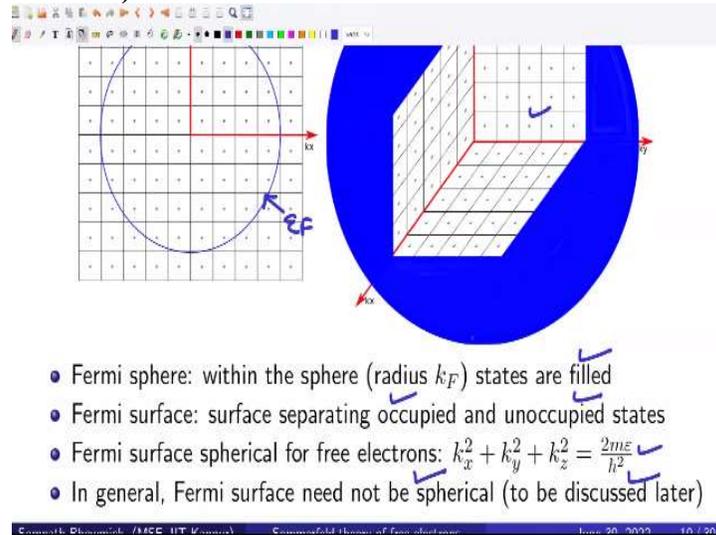
So, far I have only shown a 2D figure the circle of radius K F so, far I have shown this circle, this circle will become a sphere of radius K F in case of 3D all the states inside the sphere of radius K F or feet and all the states outside the radius K F their unoccupied. Thus Fermi surface, is the surface separating them occupied and unoccupied states. Fermi surface is spherical for free electrons this is because that energy is given by this equation.

The energy the Eigen values are given by this equation and this is an equation of a sphere in K-space for given energy F so, we can just call this energy. So, this line corresponds to some constant energy and we can call this E F energy. In general Fermi surface need not be spherical this point will be discussed in detail later.

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So, far we have chosen Fermi wave vector in ad hoc manner. Now, the question is, Is Fermi wave vector K F related to some measurable quantity? To find this out let us calculate the number of states or number of energy levels within the Fermi sphere with radius K F. So, if the radius is K F then volume of K-space within radius K F is 4 third pi K F cube. Now volume occupied by 1 K-point. So, this is given by 8 pi cube divided by V.

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Thus, we can find out that number of K-points correct number of K-points within the sphere this is given by 4 third pi K F cube into so, 1 by delta V by 8 pi cube. So, this is the number of K-points within the Fermi sphere of radius K F this is given by this according to Pauli's exclusion principle, each state can hold up 2 electrons. So, thus the total number of electrons in the sample according to the metal if it is equal to N then N must be equal to 2 times this number the number of states correct.

So, 2 times number of states and then this number is equal to this. Now, what we do is that we just turn the done and note that N by V correct. So, if I just bring this V to the denominator then N by V this is equals to K F cube divided by 3 pi square correct, but what is N by V? N by V is that number of electrons per unit volume correct. So that is n = electron density. So, that means the Fermi wave vector K F this is equal to 3 pi square to the power 1 by 3.

And we can also express this with this expression 3.63 divided by r s divided by a naught this number r s by a naught, this is a number which is like between 2 and 3 for most of the metals. So, if we just put this number then we see that this K F the magnitude of K F turns out to be of the order of 1 angstrom inverse. So, what we have achieved here is that we have finally related the wave vector or rather the Fermi wave vector to a measurable quantity and which is the free electron density.

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- Fermi energy: energy of the highest occupied energy level
- $\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} = \left(\frac{e^2}{2a_0}\right)(k_F a_0)^2 = \frac{50.1}{(r_s/a_0)^2}\text{eV} \approx 1 - 10 \text{ eV}$
- Classically, kinetic energy should be zero at $T = 0$ K !!
- Fermi temperature: $T_F = \frac{\varepsilon_F}{k_B} = \frac{58.2}{(r_s/a_0)^2} \times 10^4 \text{K}$
- To match kinetic energy of quantum gas at $T = 0$ K, temperature of classical gas should be 10^4K!!
- Fermi velocity: velocity of the most energetic electrons
- $v_F = p_F/m = \left(\frac{\hbar}{m}\right)k_F = \left(\frac{4.20}{r_s/a_0}\right)10^8\text{cm/s}$
- At 0K, v_F 10x velocity of classical electrons at room temperature!!
- Quantum electrons more energetic (100x) than classical electrons!!
- Remember: all these are consequences of Pauli exclusion principle

We can relate several quantities to the Fermi surface for example, we can define something called a Fermi energy which is the energy of the highest occupied energy level and then this Fermi energy turns out to be a number which is of this magnitude 1 to 10 electron volt for most of the metals remember that we are still at T = 0 Kelvin. So, classically the kinetic energy should be 0, but, we see that quantum mechanically this turns out to be a number which is lying between 1 to 10 electron volt.

Now, if we take the Fermi energy and divide it by Boltzmann constant, we can define some temperature and that we call as Fermi temperature. And this turns out to be a number which is huge, which is like 10 power 4 Kelvin. So, to match the kinetic energy of quantum gas that T

= 0, the temperature of classical gas should be of the order of 10 power 4 Kelvin. Now, we can also define Fermi velocity, which is the velocity of the most energetic electrons. How do we do that?

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- Classically, kinetic energy should be zero at $T = 0$ K !!
- Fermi temperature: $T_F = \frac{\varepsilon_F}{k_B} = \frac{58.2}{(r_s/a_0)^2} \times 10^4 \text{K}$
- To match kinetic energy of quantum gas at $T = 0$ K, temperature of classical gas should be 10^4 K!!
- Fermi velocity: velocity of the most energetic electrons
- $v_F = p_F/m = \left(\frac{\hbar}{m}\right)k_F = \left(\frac{4.20}{r_s/a_0}\right)10^8 \text{cm/s}$ $\sim 10^7 \text{cm/s}$
- At 0K, v_F 10x velocity of classical electrons at room temperature!!
- Quantum electrons more energetic (100x) than classical electrons!!
- Remember: all these are consequences of Pauli exclusion principle
- Since we can put only 2 e per energy level and a solid has typically $\sim 10^{23}$ of them, electrons close to ε_F have very high energy

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So, we just V F is equals to this we just define something called Fermi momentum. And then Fermi momentum h cross time K F divided by mass that will be the V F and then that turns out to be a number which is of the order of 10 power 8 centimetre per second. Now, that 0 Kelvin Of course, the velocity will be 0, but if you measure at room temperature, then for classical electrons, this turns out to be a number which is of the order of 10 power 7 centimetre per second.

But in case of quantum free electron gas, even at 0 Kelvin, this is 10 times higher than the classical electrons at room temperature. So, this implies that so if we try to calculate the kinetic energy, which is the square of the velocity, this implies that quantum electrons are 100 times energetic than classical electrons. Remember that all these are the consequences of Pauli's exclusion principle. Since, we can put only 2 electrons per energy level and a solid has typically 10 power 23 of them, electrons close to the Fermi level have very high energy.

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	n (cm^{-3})	k_F (cm^{-1})	v_F (cm s^{-1})	ε_F (eV)	T_F (K)
Li	4.70×10^{22}	1.11×10^8	1.29×10^8	4.72	5.48×10^4
Na	2.65	0.92	1.07	3.23	3.75
Cu	8.45	1.36	1.57	7.00	8.12
Ag	5.85	1.20	1.38	5.48	6.36
Be	24.2	1.93	2.23	14.14	16.41
Mg	8.60	1.37	1.58	7.13	8.27
Al	18.06	1.75	2.02	11.63	13.49
Ga	15.30	1.65	1.91	10.35	12.01
Sn	14.48	1.62	1.88	10.03	11.64
Pb	13.20	1.57	1.82	9.37	10.87

Before I finished the lecture, let me show some Fermi surface related parameters for selected metals. For example, the electron density turns out to be a number which is like 10 power 22 per centimetre cube, the Fermi wave vector turns out to be a number which is of the order of 10 power 8 centimetre inverse the Fermi velocity turns out to be a number which is of the order of 10 power 8 centimetre per second and then the Fermi energy this lies between like 1 and 10 electron volts roughly.

And Fermi temperature lights or Fermi temperature is of the order of 10 power 4 Kelvin. In the next lecture, we shall derive various thermodynamics properties of metals. Thank you