**Electronic Properties of the Materials: Computational Approach**
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Lecture - 14
Quantum Free Electrons: Sommerfeld Theory (Part 4)

Hello friends, in this lecture, we continue our discussion on quantum free electrons and Sommerfeld theory.

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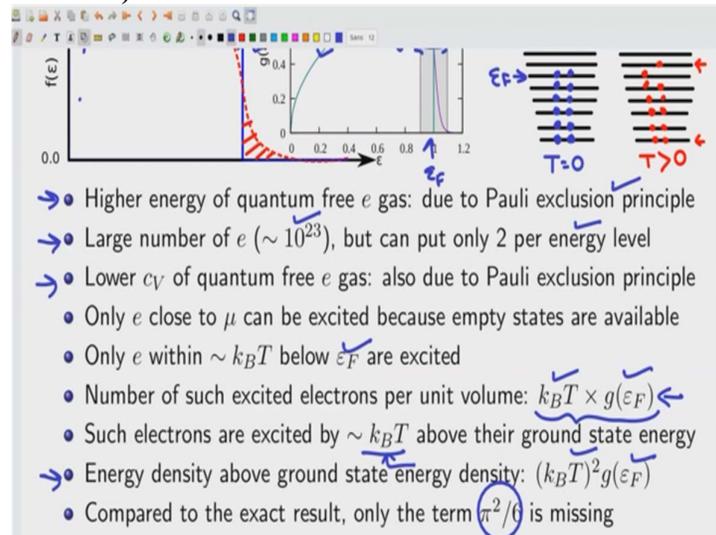
Let us try to understand the difference of c v in case of quantum and classical electron gas. What we have discussed previously is that the higher energy of quantum free electron gas is because of the Pauli's exclusion principle, we need to fill a large number of states which is of the order of 10 power 23, but we can put only 2 electrons per energy level as a result, the electrons occupy the top most energy levels they are energies that are very high.

Now, let us convince ourselves that the lower c v of quantum free electron gas is also due to Pauli's exclusion principle. Now, so, let us assume that these are the energy levels that we need to fill and let us try to do it that t = 0 and t greater than 0. So, at t = 0 we just put 2 electrons per energy level and let us assume that this is the Fermi energy all the states about the Fermi energy they are empty.

Now, let us go to some higher temperature then let us see that how do we fill the states at some temperature which is greater than 0. So, this was already there in case of T greater than 0 now, what happens is that I have put 1 electron in the excited state known that I cannot put say this

electron which is lying at the bottom I cannot excite it to the next energy level because the next energy level is already full.

So, that means only the electrons which is close to the Fermi energy only they can be excited not all electrons, so, electrons close to the ground state energy they cannot be excited because there are no empty states available to put them. So, less energetic electrons cannot be excited to the next energy level because the next level already has 2 electrons and cannot accommodate 1 more as a result of this only electrons within $k_B T$ below the Fermi energy they can be excited.

For example, if you look at this figure, we cannot excite electrons from this region we can only excite electrons from some region which is close to the Fermi energy and they will be excited to this levels. If we consider the plot of energy versus this density of states times Fermi function, we have already seen this plot before, the number of electrons is given by the area under the curve thus number of such excited electrons is approximately that area under that shaded region.

So, if you look at this shaded region this is where this plot differs from the ground state curve. And everywhere else you see in most of the regions the ground state and the excited state curve they just coincide with each other and on only in this region they are different. So, that means, if we can find out the number of electrons within this shaded region, which has an energy weight of $k_B T$ the width of the energy is $k_B T$ then we know that how many electrons are getting excited.

And then how can we find we can just approximate it we know that density of states at the Fermi level, the Fermi level is here we can just excite we can just find the area under the shaded region by calculating the area of this thing, and then that is given by $k_B T$ times g of E_f. Now, know that so this is the number of electrons getting excited at some finite temperature.

Now, what is the amount of excess energy that these electrons are having since the energy at some temperature we can just write it as $k_B T$ So, this is the amount of excess energy that these many electrons are having at finite temperature. So, that means, if we want to calculate the excess energy or the energy density above the ground state energy then what we can then this is just the number of electrons.

So, this is the number of electrons which has been excited and this is the excess energy that those number of electrons are having. So, if we just multiply these 2, we get a term like k B T square times g of E f. Now, you can compare this number to the exact result and you see that they differ by this factor only. So, the exact result has this factor pi square / 6, which is some number which is of the order of 1.

So, that means, if we saw what this qualitative argument that we have presented here is really good because, if we just match with the exact result they are of the same order of magnitude.
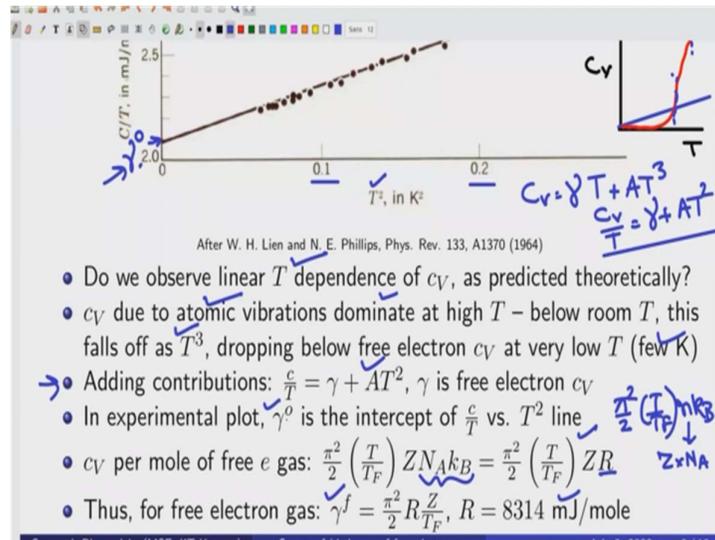
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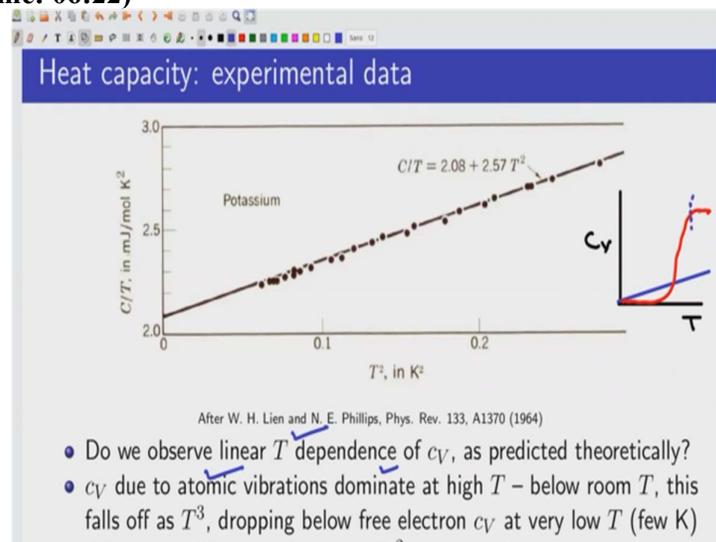
Now, let us try to compare with experiments do we observe the linear T dependence of c v as predicted theoretically? Now, if you take a solid then there are other sources contributing to c v for example, atomic vibrations and at room temperature the atomic vibration will dominate for example, this is how the so, for example, if you look at the red curve, this is how the c v for the atomic vibration changes as a function of temperature.

So, you see that so, this is approximately this is the room temperature and you will see that room temperature the c v because of these atomic vibration they are dominating.

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$c_V = \gamma T + AT^3$

$\dfrac{c_V}{T} = \gamma + AT^2$

After W. H. Lien and N. E. Phillips, Phys. Rev. 133, A1370 (1964)

- Do we observe linear T dependence of c_V, as predicted theoretically?
- c_V due to atomic vibrations dominate at high T – below room T, this falls off as T^3, dropping below free electron c_V at very low T (few K)
- Adding contributions: $\frac{c}{T} = \gamma + AT^2$, γ is free electron c_V
- In experimental plot, γ^o is the intercept of $\frac{c}{T}$ vs. T^2 line $\frac{\pi^2}{2}\left(\frac{T}{T_F}\right) n k_B$
- c_V per mole of free e gas: $\frac{\pi^2}{2}\left(\frac{T}{T_F}\right) Z N_A k_B = \frac{\pi^2}{2}\left(\frac{T}{T_F}\right) ZR$ $Z \times N_A$
- Thus, for free electron gas: $\gamma^f = \frac{\pi^2}{2} R \frac{Z}{T_F}$, $R = 8314$ mJ/mole

But as you go to lower temperature, what happens is that this c v this falls off as a function of T cube like this falls off as the cube as you go to some temperature which is below long temperature. And now, you will see this blue curve for this is the c v for the free electron gas and you will see that this has a linear temperature dependence. So, as the temperature drops down, this also decreases but this decreases linearly.

Since the vibrational part the atomic vibrational part since it decreases or since it falls off as T cube then at very low temperatures, what will happen is that the electronic part will become dominant and this happens only at maybe like few Kelvin. So, now, what we do is that let us just add the 2 parts. So, the total c v the c v, so, we have the electronic part, which has a linear temperature dependence and then we have the atomic vibration part and at low temperature it has like cubic temperature dependence.

So, now if we just we can just rewrite this equation we can just write like c v / T this is equal to gamma + A t square. So, this is what is written here and then let us look at some experimental plot. So, this plot is shown for potassium and if you plot C / T as a function of chi square then this is what you get. So, this is the equation and then you see that it will intersect this axis at some point and in the experimental plot, so, where it intersects.

So, that is that let us call it as gamma observed. So, in fact this gamma observed the intercept at T = 0 that is the experimentally observed value of the free electron specific heat or free electron heat capacity. Now, this implies that if we do the experiment and you look at the temperature range where it has been plotted. So, this is like 0.1 Kelvin square so, this is like

really, really low temperature. So, if we can experimentally measure these and plot this, then from the experimental observation, we can find out that free electron heat capacity.

Now, from our theory we know that free electron heat capacity is given by pi square / 2 T / T f and n times k B so, what we do is that in place of n we just take one more mole so, Z is the number of valence electrons per atom and we multiply it with N A the Avogadro number and then then data we can write it in this form pi square / 2 T / T F Z is the number of valence electrons and r is this constant and r = N times the Avogadro number times the Boltzmann constant.

Thus, for free electron gas, we can define gamma as gamma f is equals to this. So, now, what we are going to do is that we are going to compare gamma 0 and gamma sorry gamma o that is the gamma observed from the experiment and gamma f this is the theoretical prediction.

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- Thus, for free electron gas: $\gamma^f = \frac{\pi^2}{2} R \frac{Z}{T_F}$, $R = 8314$ mJ/mole

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Compare theory and experiment

Since $T_F \propto 1/m$, $\gamma \propto m$. Let us define: $\frac{m^o}{m^f} = \frac{\gamma_{observed}}{\gamma_{free}}$, ideally $\frac{m^o}{m^f} \to 1$

$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m}$
$k_B T_F =$

Valency	Element	$\gamma_{observed}$	γ_{free}	m^o/m^f
1	Li	1.63	0.75	2.18
	Na	1.38	1.09	1.26
	K	2.08	1.67	1.25
	Cu	0.70	0.51	1.38
	Ag	0.65	0.65	1.00
2	Be	0.17	0.50	0.34

Let us compare gamma f and gamma o the theoretical and experimental value, now, we know that E F is equals to we can convert it to some temperature scale k B T F which is equal to h cross square k F square by 2 m this implies that T F is proportional to 1 over m and if you look at the form of gamma f, then gamma f is inversely proportional to T F. So, that means, we can write that gamma is proportional to the mass of the electron.

Now, we define this term m o by m f, which is the ratio of the observed value of gamma and theoretical value of the gamma and ideally this should be equal to 1. So, now, let us see, how does the number look like if we compare gamma observed and gamma free electron.

The handwritten notes show:
$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m}$$
$$k_B T_F = \frac{\hbar^2 k_F^2}{2m}$$

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2	Be	0.17	0.50	0.34
	Mg	1.30	0.99	1.30
	Ca	2.90	1.51	1.90
	Zn	0.64	0.75	0.85
3	Al	1.35	0.91	1.48
	Ga	0.60	1.03	0.58
	In	1.69	1.23	1.37
4	Sn	1.78	1.41	1.26
	Pb	2.08	1.51	1.07

So, you look at this table and then you see that these numbers they are not exactly equal to 1, but the order of magnitude is matching thus, the metals are shown in this table they are reasonably well described by quantum free electron gas model.

The handwritten notes show:
$$\hbar \frac{d\vec{k}}{dt} = \vec{F}$$
$$\hbar \frac{d\vec{k}}{dt} = -e\vec{E}$$
$$d\vec{k} = -e\frac{\vec{E}}{\hbar} dt$$
$$\vec{k}(t) - \vec{k}(0) = -\frac{e\vec{E}t}{\hbar}$$
$$\vec{k}(t) = \vec{k}(0)$$

- We are going to use Newton's second law of motion!!
- $\vec{F} = \frac{d\vec{p}}{dt} = \hbar \frac{d\vec{k}}{dt} = -e\left(\vec{E} + \frac{1}{c}\vec{v} \times \vec{B}\right)$
- Solution for $B = 0$ is: $\vec{k}(t) - \vec{k}(0) = -\frac{e\vec{E}t}{\hbar}$
- $E = 0$, Fermi sphere centered at origin of k-space & net momentum 0
- $E \neq 0$, center of Fermi sphere shifts by $\delta\vec{k} = -e\vec{E}t/\hbar$
- Displaced Fermi sphere remains in a steady state because of scattering

Let us now talk about the electrical conductivity of quantum free electrons, we are going to use Newton's second law of motion, we shall justify the use of classical approach later, instead of d we are going to use the Eigen value of the momentum operator. So, this is that form of second law of motion so, this like dp dt and what we are going to use is you know that the momentum of the momentum operator this is the eigenvalue h bar k.

And we are going to use that in this equation that means, h bar to dk dt = force so, that equation remains as before. So, this force in this case is given by that Lorentz force. Now, let us consider

only the electric field such that the magnetic fields is 0 then what we have to solve this case what the dk dt forces minus e charge of the electrons times E the electric field and then we just rewrite this as the dk = - eE by h bar dt and then we can write the solution as k of t - k of 0 = - eEt by h bar. So, this is what is written assume that E = 0.

So, in that case, so, if I take E = 0 here in that case what will happen is k of t = k of 0. If we draw a Fermi sphere in the case space the Fermi sphere will be centered at the origin so, you look at this diagram. So, when E = 0 then the Fermi sphere, we know that this is the ground state of the free electrons and in case of E = 0, the Fermi sphere will be centered at the origin of the k space, this is equivalent to the statement that if you do not apply any field you do not get any current.

Note that if the Fermi surface is centered at the origin sum of all the E vectors inside the sphere is equal to 0. That is because, we have like 4 quadrants 1, 2, 3, 4. And then if you just sum over all the key points within the sphere, because of the spherical symmetry, in this case, this is like a circular symmetry because we are showing it in 2D because of the circular symmetry the sum of the k vectors inside the Fermi sphere will be equal to 0.

And that implies that net momentum is equals 0, that is, when E equals to 0, then the Fermi sphere will be centered at the origin the moment Fermi sphere shifts from the center of the k space the net momentum will be non 0. So, if you look at this diagram now, the Fermi sphere has shifted from the center of the Fermi's sphere shifted from the origin and now if you just sum over all the k points, it will not give you 0, but there will be some net momentum along this k's and we know that the net momentum implies that there is some net current.

Thus, for E not equal to 0 in this case the center of the Fermi sphere has shifted from this point from the origin to this point and that is given by delta k = - eEt / h bar. Now, the question is does the Fermi sphere keep shifting forever? Because if you look at this equation, then you see that as time is increasing the center will keep shifting from the origin does it happen in that way?

The answer is no, because if that happens that will imply the momentum will increase forever with time as we apply that electric field by what we know that it does not happen in that way similar to the Drude model, we have to assume some scattering and that scattering will keep

the distance Fermi sphere in a steady state. So, you see this is the Fermi sphere will reach some steady state where the center is not at the origin but then it will not keep shifting forever it will remain there and that is because of the scattering.

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Similar to the Drude model will introduce the relaxation time tau. So, in this equation we just replace T with tau T will be replaced with tau we can now find out the velocity at the steady state. So, what we do is h bar k is the momentum. So, if we divide that with mass then that will be the velocity and then this is the velocity when we reach the steady state and remember that the steady state is reached because of scattering.

And now we have the steady state velocity and then we can write that j = - nev and in place of v if we replace this then j = - ne square tau by m electric field and then we know that this term is electrical conductivity sigma = ne square tau by m.

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Free electrons: quantum vs. classical

- How can we justify use of classical equations for transport?
- Momentum uncertainty of free electrons: $\Delta p \sim \hbar k_F$
- Position uncertainly: $\Delta x \sim \frac{\hbar}{\Delta p} \sim \frac{1}{k_F} \sim 1\,\text{Å}$
- Classical description not possible if localized within few Å
- Try to understand **length scales** related to conduction electrons
  - Mean free path at room $T \sim 100\,\text{Å}$
  - Electric field/ temperature gradient 1000 Å or more
  - Thus, classical equations ok to understand electronic transport
- What properties are going to change if we use quantum theory?
  - Properties related to velocity/energy change – FD vs. MB statistics
    - Example: c_V, Q (thermo power), l (mean free path)
  - Properties not related to velocity/energy does not change

(Handwritten: $\hbar k_F$, $k_F \sim 1\,\text{Å}^{-1}$)

Now, let us try to justify the use of a classical equation for transport in a quantum model know that the momentum of the highest occupied energy levels that is given by h cross times k. So, that is we can just take this as the value of momentum uncertainty. So, this is the value of momentum uncertainty. And now we can using the Heisenberg uncertainty principle we can find out the position uncertainty and that will turn out to be del x is h bar by delta p.

Delta p if we just put these values then we see that this number turns out to be 1 by k F remember that k F is of the order of 1 angstrom inverse. So, that means 1 by k F give the position uncertainty that will be of the order of 1 angstrom. Now, this implies that the classical description is not possible if the electron is localized within some region which is of the order of one angstrom.

In that case we have to actually use the quantum description, but let us understand the length scales related to conduction electrons that mean free path at room temperature that is of the order of 100 angstrom which is much greater than is 1 angstrom and the electric field or temperature gradient which we apply that is of the order of like 1000 angstrom that is like maybe like 1 volt per 1000 instruments, so, or like it can be even higher.

So, that means, the length scale that you are talking about in for this transport problem that is much higher than 1 angstrom. Thus, we can actually use classical equations to understand the electronic transport.

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- Try to understand **length scales** related to conduction electrons
  - ▸ Mean free path at room $T \sim 100$ Å ←
  - ▸ Electric field/ temperature gradient 1000 Å or more
  - ▸ Thus, classical equations ok to understand electronic transport ←
- What properties are going to change if we use quantum theory?
  - ↗ Properties related to velocity/energy change – FD vs. MB statistics
    - ★ Example: c_V, Q (thermo power), l (mean free path) $v_F \tau$]→
  - ↗ Properties not related to velocity/energy does not change
    - ★ Example: σ, R_H (Hall coefficient), τ }→ $\frac{1}{100} \times 100$
- → Exception: $\kappa = \frac{1}{3} c_V v^2 \tau$ same for classical and quantum electrons
  - ▸ Error of c_V and v^2 cancel each other - leading to remarkable success of Drude model to predict Wiedemann-Franz law correctly

Now, let us just see that what properties are going to change if we use like quantum theory and what properties are not going to change, let us try to understand that know that all the properties related to the velocity or energy are going to change. So, this is what we have seen the velocity of the quantum electron gas is much higher and also the energy of the quantum electron gas is much higher because we are using Fermi Dirac statistics.

And we are not using the classical Maxwell Boltzmann statistics for example, we have seen that the c v is going to change and then we did not discuss this; what is thermal power, but then thermal power is something that depends on c v, so, that will change the mean free path. So, this is like Fermi velocity times tau. So, since this is a function of velocity this will also change and so on.

And now, let us see that what are the properties which are not going to change whatever is not related to velocity or energy is not going to change for example, the electrical conductivity sigma which is like n square tau / m it does not it is not a function of velocity or energy. So, it is not going to be changed and if we; do the hall coefficients that will also not change.

And of course, the relaxation time is not going to change and so, on not going to change the in the sense that if we take the for example, these properties they do not depend whether we are going to use the classical model or quantum model and these properties they will depend on whether we are going to use the classical model or quantum model. Now, there is only 1 exception and it is the thermal conductivity kappa = 1 by 3 c v v square tau you see that it depends on the heat capacity and it also depends on the velocity.

So, you may expect that kappa should depend on whether we are going to use like quantum model or classical model, but, you see that this in quantum model the c v is the actual c v is 1 by 100 of the classical model and in quantum model, so, that means that the actual c v that is like 1 by 100. So, that is the difference between classical and quantum. And if you look at the velocity in quantum model is 10 times, so, we have a term v square.

So, that means, this will be the actual value of v the quantum value of v that is like 100 times more and then you see that this factor of 100, 100 they will cancel out each other. And then as a result, although kappa depends on c v and velocity, the value of kappa, it will not matter whether we are using the classical or quantum model, because the errors that we are making they are getting cancelled out.

And that is what led to the remarkable success of the Drude model to predict the Wiedemann Franz law correctly.

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- $\rho \sim \mu$-ohm cm at room $T \Rightarrow \tau \sim 10^{-14}$ s
- $T_F \sim 10^4$ K $\Rightarrow T/T_F \sim 0.01$ at room T

Porperty	Classical	Quantum
Velocity	$v = \sqrt{\frac{3k_BT}{m}} \sim 10^5$ m/s	$v_F = \sqrt{\frac{2k_BT_F}{m}} \sim 10^6$ m/s
l	$v\tau \sim 10$ Å, at ~ 300 K	$v_F\tau \sim 100$ Å, at ~ 300 K
E/N	$\frac{3}{2}k_BT = 37.5$ meV	$\frac{3}{5}\varepsilon_F \sim 10^3$ meV
c_V	$\frac{3}{2}nk_B$	$\frac{\pi^2}{2}\left(\frac{T}{T_F}\right)nk_B \sim 0.01nk_B$
$Q = -\frac{c_V}{3ne}$	$-\left(\frac{k_B}{2e}\right)$ $=-0.43 \times 10^{-4}$ volt/K	$-\left(\frac{k_B}{2e}\right)\left(\frac{\pi^2}{3}\right)\left(\frac{T}{T_F}\right)$ $\sim -10^{-6}$ volt/K
κ	$\frac{1}{3}c_Vv^2\tau$	$\frac{1}{3}c_Vv_F^2\tau$
σ	$ne^2\tau/m$	$ne^2\tau/m$

Finally, let me conclude by listing out the differences and similarities between the quantum and classical electronic tests. So, if we calculate the velocity, then we see that the quantum electron gas they have 10 times the velocity than the classical free electron gas. And then the mean free path, since this is a function of velocity, naturally, this is also 10 times higher in case of quantum more in the energy of the quantum electron gas that is 100 times more than the classical model.

So, I have compared the energy at like 300 Kelvin, that turns out to be 37.5 meV whereas, even at 0 Kelvin the energy of the quantum electron gas is of the order of 1000 milli electron Volt. Now, if we calculate the heat capacity, then the quantum model the heat capacity is 1 / 100 of the classical model and then there is something called thermal power which is a function of heat capacity and naturally that is also 1 by 100 in the quantum model.

And note that if you for example, this thermal power you can actually experimentally measure and the experimentally measured value is actually matching with the quantum model and even for c v you can measure it experimentally and that also matches very well with the quantum model. So, that means, quantum theory is actually able to solve certain anomalies that we observed in classical theory.

Now, the next time is the thermal conductivity and thermal conductivity in case of quantum and classical model they are same, but, this happens because, the error in calculating the factor of c v and error in calculating the factor V square they cancel out and that is why kappa is same in the classical and quantum model, electrical conductivity sigma they are also same in the classical and quantum model, because it does not depend on either velocity or the energy.

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And as a result, if we calculate the ratio of kappa by sigma d, they are surprisingly they are like very close to each other in case of quantum as well as classical model and keep in mind that this is because the error that we made in the classical model error in calculating c v and error in calculating v square they are canceling out each other. And then the hall coefficient they are also same in case of quantum and classical model.

Thus what we found is that the quantum model managed to correct these numbers the correct to the value of heat capacity. Now, we have a value which is matching very well with experimental values, it managed to correct the value of the thermal power it is also now matching very well with the experimental value, but then the anomaly that we observed for the hall coefficient the sine anomaly that we cannot just correct by using the quantum free electron.

So, we still have the sine anomaly that we know the hall coefficient that we found for certain metals in hall coefficient that persists and this implies that we the free electron model is not capable of explaining this sine anomaly of the hall coefficient, thus we need to go beyond free electron model and take into account the electron ion interaction. Thank you.