Electronic Properties of the Materials: Computational Approach

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Lecture: 2

Drude Model and Failure of the Classical Theory

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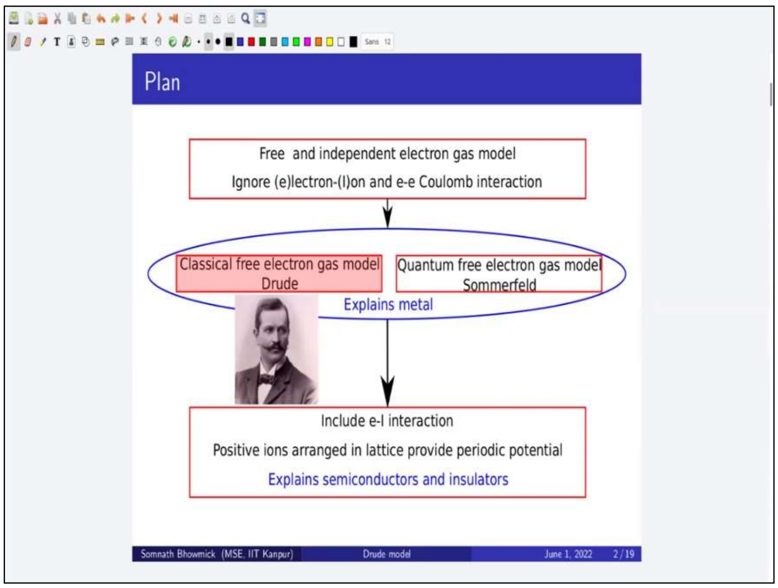

Hello friends in this lecture we talk about druid model and failure of classical theory first.. Let us revise the plan of the course we would like to understand electronic properties of metals, semiconductors and insulators. Metals can be understood to some extent by using free and independent electron gas model. Free electron model ignores electron ion interaction and independent electron model ignores electron-electron interaction.

Free and independent electrons can be discussed at two different levels classical and quantum. In this lecture we shall focus on classical free electron gas model proposed by Drude around 1900 before the development of the quantum mechanics.

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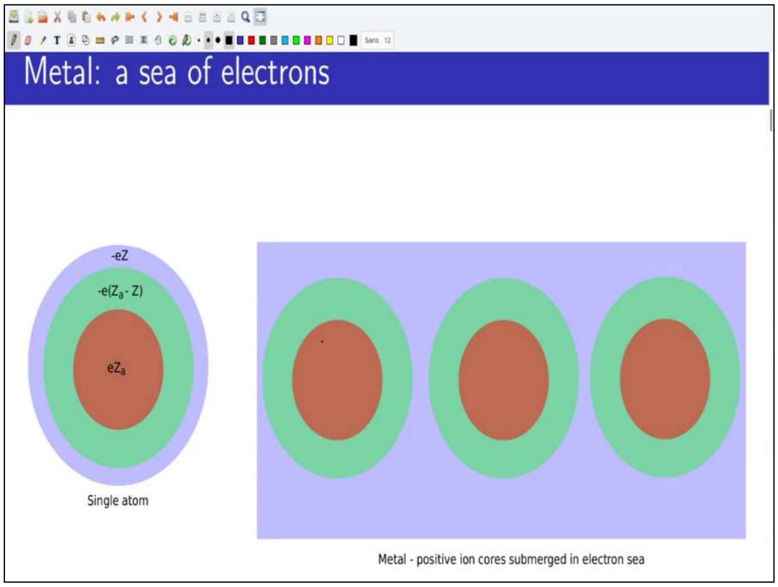

Drude applied kinetic theory of gases to a metal considered to be a gas of electrons. First. Let us understand how does the electron gas form. Let us consider sodium. Sodium has 11 electrons the electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^1\ 1s^2\ 2s^2\ 2p^6\ 3s^1$a metal is formed when approximately 10^{23} atoms come together. So, this is the Avogadro's number. In a metal the nucleus and the core electrons retains their free electron configuration.

So, I have a nucleus shown here and then I have cold electrons 10 of them ah occupying this region. So, this is the case of a single atom when a single atom comes together and forms the solid then what happens is the nucleus and the core electron they roughly retain their atomic configuration. Nucleus and core electrons they together form the positive ions okay. And these positive ions they are very heavy and immobile than compared to the single electron. The valence electrons which is $3s^1$ in case of sodium gets detached and moves freely forming the electron gas.

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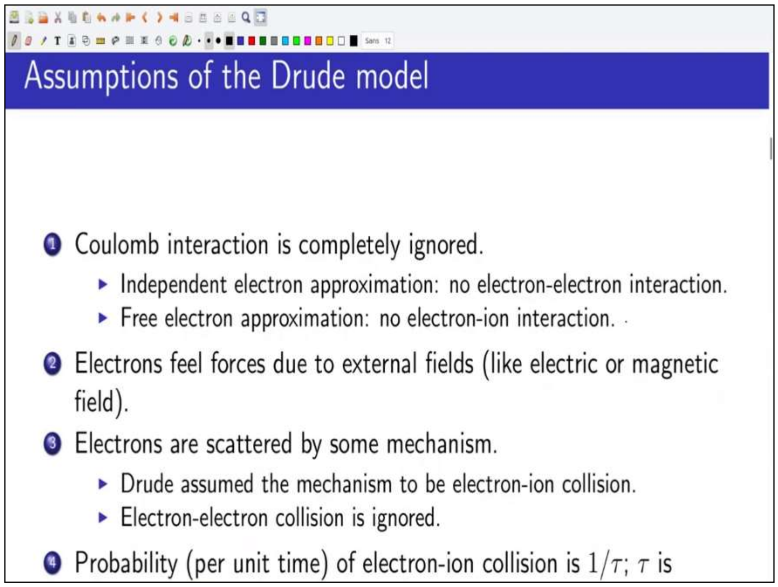

Let us understand the assumptions of the Drude model. It is assumed that the coulomb interaction is absent that means there is no electron-electron interaction and there is no electron ion interaction. The first one is known as the independent electron approximation and the second one is known as the free electron approximation. Although electrons are not experiencing any force due to the ions and due to other electrons however electrons feel force due to the external fields like electric or magnetic field. Next electrons are scattered by some mechanism rude assume the mechanism to be electron ion collision and electron-electron collisions are ignored. Probability per unit time of electron ion collision is $\frac{1}{\tau}$ where τ is the relaxation time. Note that free electron density is 1000 times higher than the classical gas at room temperature despite this and despite strong electron ion and electron-electron interaction Drude very boldly applied kinetic theory of dilute gas to the gas of electrons. Let us try to understand what happens between two collisions in the absence of any external electric field or magnetic field electrons move in a straight line until the next collision taking place approximately every τ second. If external field is applied motion of electron is determined by the Newton's second law of motion. Let us try to understand this using a schematic diagram.

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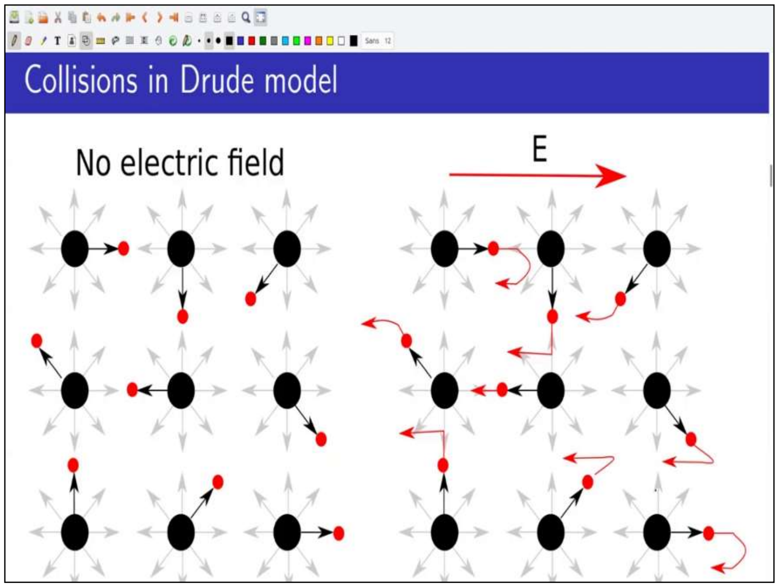

In this diagram the gray arrows are showing all the possible directions in which the electrons can be scattered after a collision. Black arrows are showing the actual direction along which the electrons are getting scattered. Clearly if there is no external field the electrons will get scattered randomly leading to 0 current. However if there is some external field for example electric field in this direction then the electrons are experiencing some force in this direction.

In this case the electrons move according to the force acting on them despite scattering in random directions for example you see electrons are still getting scattered in random directions. In this case it is getting scattered in this direction however since there is some force in this direction it will initially start moving in this direction and then gradually it will turn out. Similarly in this case it will start moving in this direction initially after the collision but gradually it will turn around. As a result of this coordinated motion we expect to see some current in this case.

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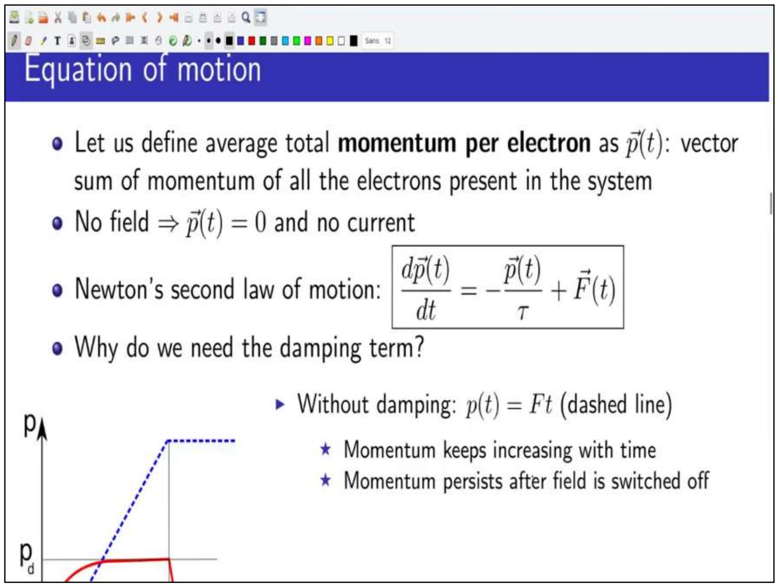

Let us define average total momentum per electron as $\vec{p}(t)$ this is the vector sum of momentum of all the electrons present in the system. So, that means I sum over all the electrons present in the system and then divided by number of electrons presented in the system and define that as $\vec{p}(t)$. Note that in the absence of field p i's they are completely random and as a result $\vec{p}(t) = 0$ and there is no current.

Now in the presence of the applied fleet we can write the Newton's second law of motion as dp dt rate of change of momentum is equals to force and then there is some additional term okay this is like the damping okay. Now let us try to understand why do, we need the damping target note that the damping term arises from the electron ion collision. Now let us consider that if we do not have the damping term what would happen?

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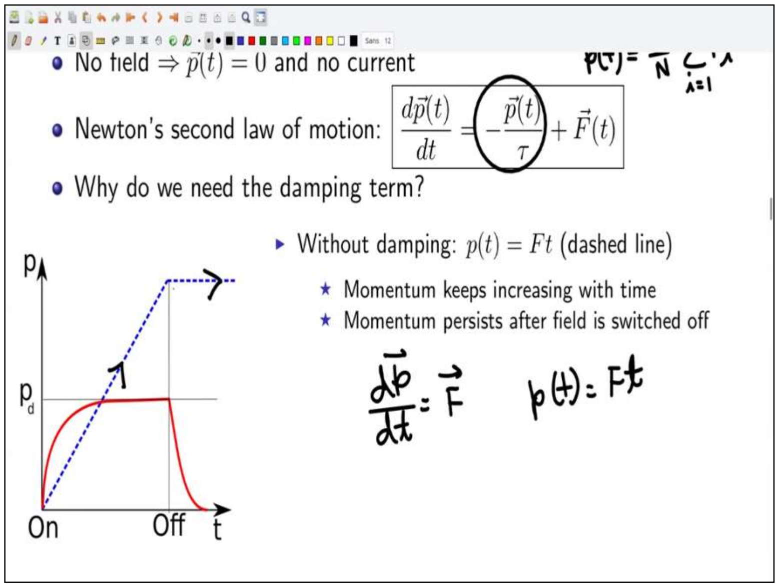

In this case the equation just turns out to be $\frac{dp}{dt}$ is equals to f there is no damping term okay and the solution is $\vec{p}(t)$ is equals to force times time. So, in this case what happens the momentum keeps increasing like this along this dashed line and once the field is switched off electrons keep moving. So, at this point we switch off the field and then the electrons keep moving with constant momentum. However, this clearly contradicts with what we know from our experience we know that current does not keep increasing with time like this as we apply an electric field moreover once the electric field is switched off the current becomes 0 instead of maintaining some constant value. Let us see whether the damping term helps us to remove the inconsistency with damping the solution of this equation looks like this. So, now you see in this equation as t increases this term becomes insignificant thus momentum and current does not keep increasing with time but saturates to some constant value e d is equals to f times tau this you can see here. Moreover, once the field is switched off at this point the momentum as well as current becomes 0.

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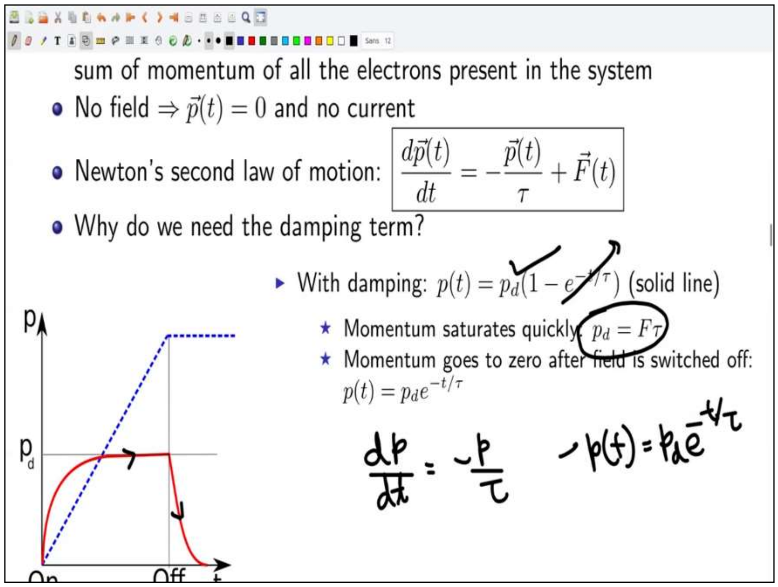

So, let us see that how does that happen. So, $\frac{dp}{dt} = -\frac{p}{\tau}$ after I switch off the field and then you can solve this $\vec{p}(t) = p_d e^{-t/\tau}$ and as time increases the current becomes 0 exponentially.

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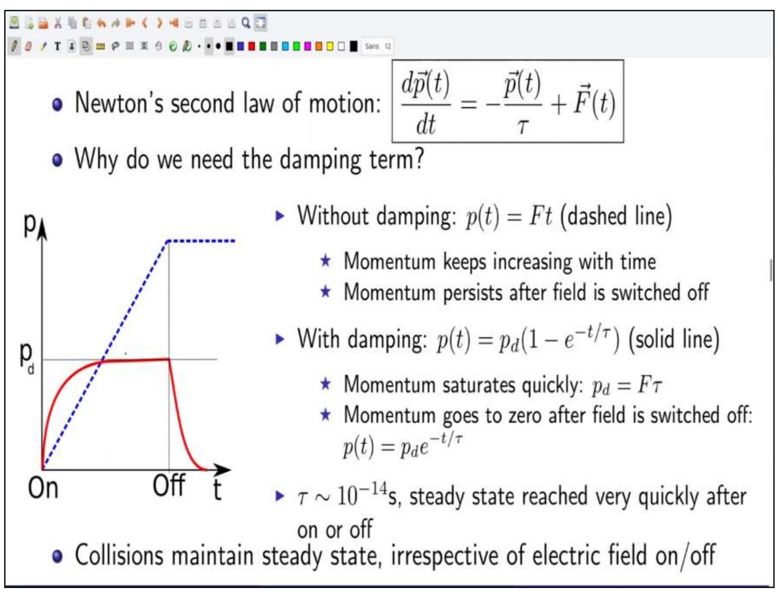

Finally, we can ask the question that how long does, it take for the current to saturate. So, you see the current will reach the saturation level at this point and after you switch off the field it will move to 0 in this fashion. The question is how long does it take to reach the saturation level or once after you switch off the field how long does it take to become 0. The answer is very small time because tau is of the order of 10^{-14}second. Thus, the saturation should take less than even a nanosecond remember that tau originates om the electron higher collisions and it helps to maintain the steady state that is what we must state $\frac{dp}{dt} = 0$ the rate of change of momentum is 0. So, it helps to maintain the steady state both in the presence or absence of the electric field.

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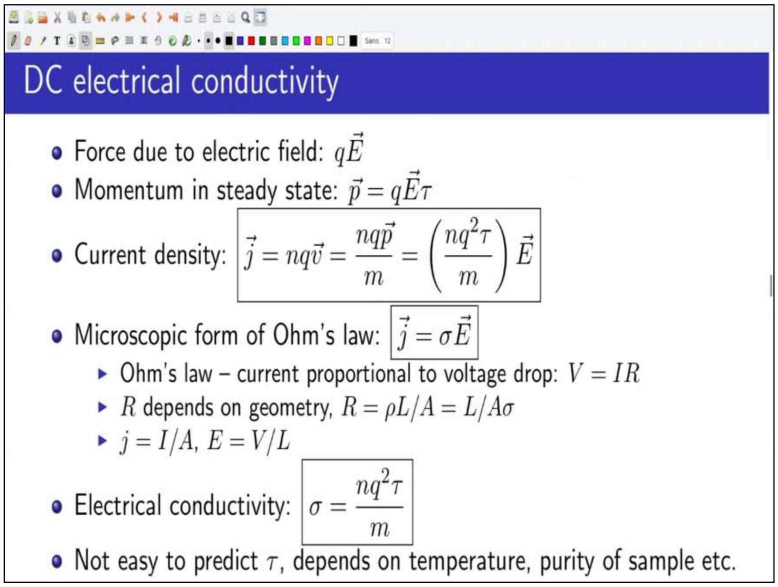

Let us now discuss DC electrical conductivity. We know that if we apply some electric field this is the force on the electrons where q is the charge of the electron. Momentum in steady state is given by force times tau where tau is the relaxation time. Now we can define current density $\vec{j} = nq\vec{p}$. For example if the wire looks like this and then this is the V velocity and then we can define current density j as this square n is the carrier density and q is the charge of the electron.

And ultimately using this equation we can get j in this form. We can write the microscopic forms of ohm's law like this j is equals to sigma times e where sigma is the conductivity. The derivation is very simple and even here. So, comparing these two equations what we can say is that sigma the electrical conductivity is equal to n q square tau by m. So, in this equation and the carrier density it can be estimated q is a fundamental constant because this is the charge of the electron m is the mass of the electron another fundamental constant.

The only term that remains here which is very difficult to predict is tau because tau will depend on temperature tau will depend on pure if you have sample etcetera. Drude model will be put to test in different experiments however we shall always look to have quantities independent of τ because τ is not so, easy to predict.

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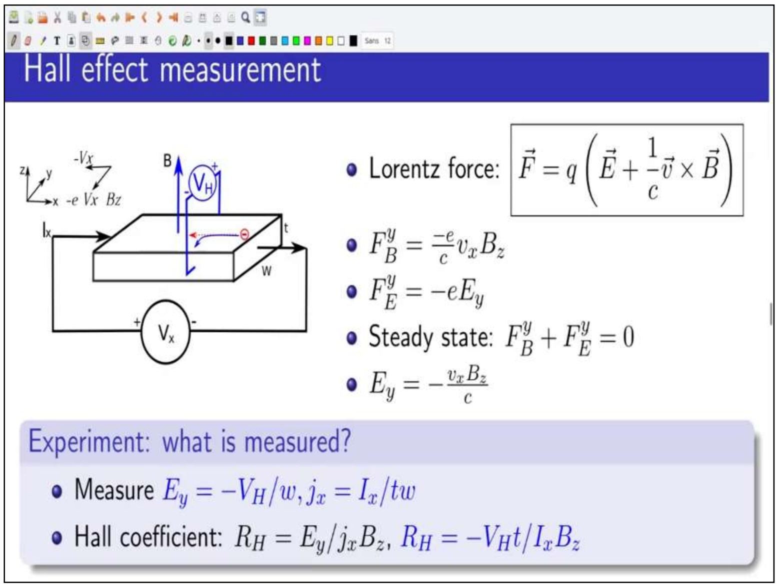

Hall effect is one of the experiments which we are going to use to test the Drude model. In this experiment we apply an electric field in the positive *x* direction and the magnetic field in the positive *z* direction. In the absence of the magnetic field electrons would move in a straight line shown by this dotted line. However, because of the magnetic field electrons feel a force in this direction shown by the blue arrow.

So, in presence of both electric and magnetic field the electrons will feel a force which is known as the Lorentz force and the movement along the blue line will happen because of the magnetic part of the Lorentz force. So, as a result positive and negative charges will build up. So, electrons are experiencing a force in this direction they will move in this direction and the negative charge will build up along this end and a positive charge will build up along this end. As a result some electric field will build up along this. Now this electric field is going to oppose the motion of the electrons that was happening due to the magnetic field. In steady state the forces are going to balance out each other. We can experimentally measure something called a Hall voltage V of H. Now we can define a term called the hall coefficient which can be calculated from the experimentally measured value of hall voltage I of x the current index direction and B of z the field applied in the set direction.

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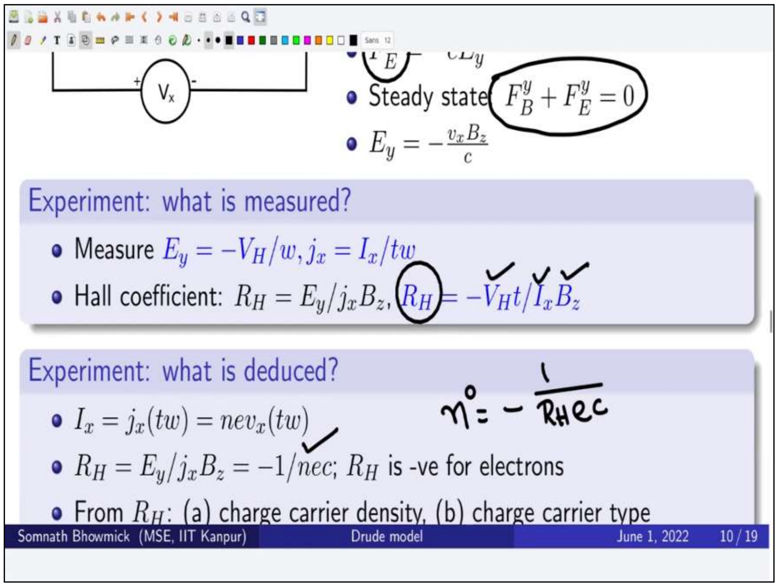

In the next slide we shall find that Drude model predicts $R_H = -1/nec$ thus if we can measure R_H from the experiment which we definitely can do we can calculate the charge carrier density $n^o = \frac{1}{R_H ec}$ because e and c these are two fundamental constants charge of electron and speed of light and R_H we have measured from the experiment plus we can calculate the value of n and I note it as n^o . Now we can easily estimate the charge carrier density n from the crystal structure data. So, what we are going to do is that we will see that what are the values of n naught or n^o we get from the experiment and what are the values we calculate from crystal structure data and we will try to compare them but before that let us derive this term from Drude model.

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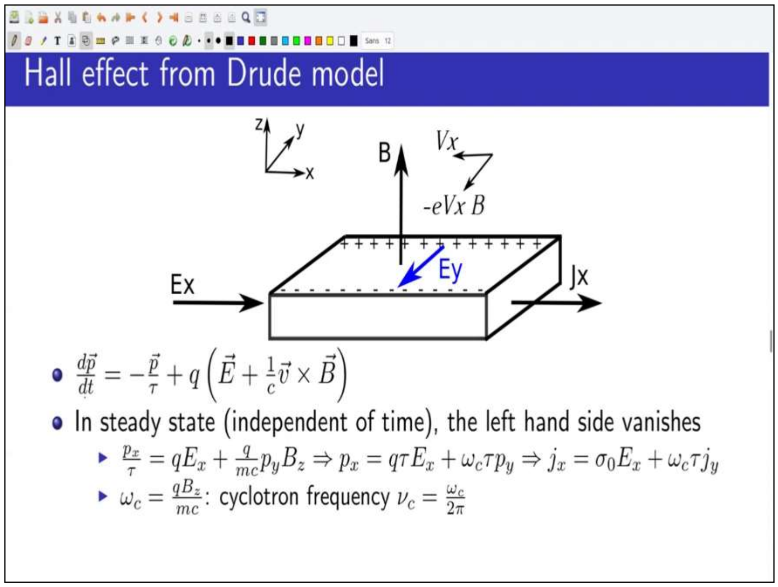

This is the equation of motion $\frac{dp}{dt}$ rate of change of momentum is equal to this is the Lorentz force part and this is the damping term. In steady state $\frac{dp}{dt}$ goes to 0.

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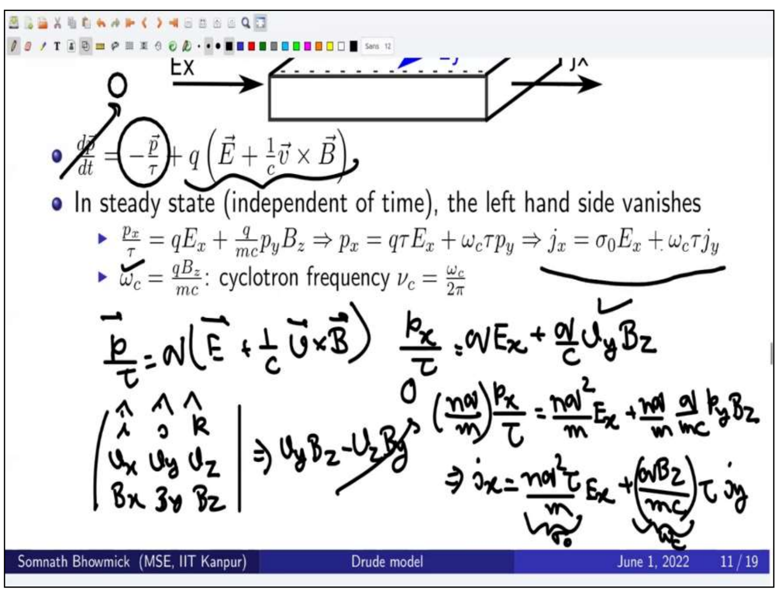

So, now then the equation can be written as

$$\frac{dp}{dt} = \frac{\vec{p}}{\tau} + q\left(\vec{E} + \frac{1}{c}\vec{v} \times \vec{B}\right)$$

is the charge of the electron τ is the relaxation time this is the electric field v is the velocity b is the magnetic field and c is the speed of light . Now let us write this equation term by done. So, let us write the *x* component. So, this is

$$\frac{p_x}{\tau} = qE_x + \frac{q}{c} v_y B_z$$

this term you can easily get by calculating cross product.

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$$\begin{matrix} \hat{\imath} & \hat{\jmath} & \hat{k} \\ v_x & v_y & v_z \\ B_x & B_y & B_z \end{matrix}$$

And if we write the x component, this turns out to be $v_y B_z - v_z B_y$. Now if we take this equation and multiply both the sides

$$\frac{nq}{m}\frac{p_x}{\tau} = \frac{nq^2}{m}E_x + \frac{nq}{m}\frac{q}{mc}p_y$$

And then you see that this is like $\frac{nqp_x}{m}$ that turns out to be

$$j_x = \frac{nq^2\tau}{m}E_x + \frac{qB_z}{mc}\tau j_y$$

So, now if we just write $\omega_c = \frac{qB_z}{mc}$ then what equation do we have and then you know that this is equal to σ_o and this is equal to ω_c.

So, if we know that then we can just write this equation as

$$j_x = \sigma_o E_x + \omega_c \tau j_y$$

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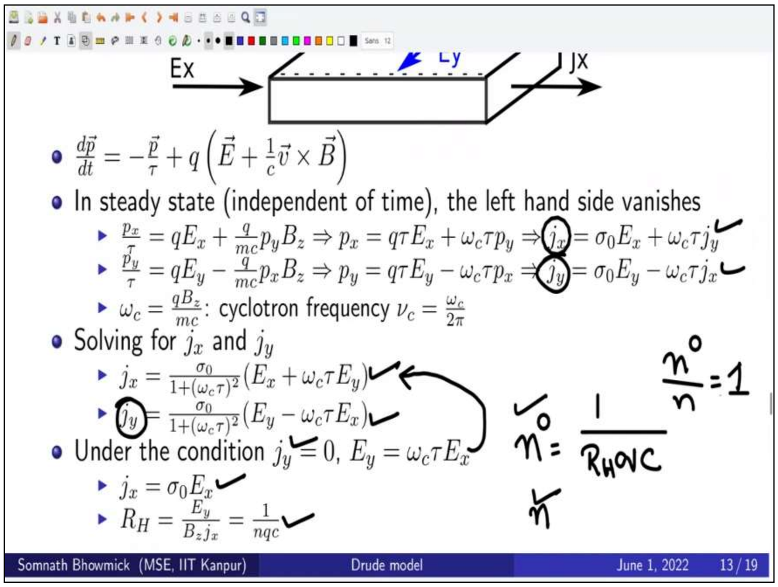

Similarly, we can write the y component and get this equation

$$j_y = \sigma_o E_y + \omega_c \tau j_x$$

Now we have two equations this and this and two unknowns j_x and j_y. If we solve the two equations then these are the values of j_x and j_y. Now in steady state we know that there is no current in this direction the current is only in the *x* direction. So, that means in steady state $j_y = 0$. So, if we put $j_y = 0$ in this equation then we get $E_y = \omega_c \tau E_x$ and now if we replace $E_x$in this equation right then we get these two equations

$j_x = \sigma_o E_x$ and $R_H = \frac{E_y}{B_z j_x} = \frac{1}{nqc}$

. Now look at this equation *q* is a fundamental constant charge of electrons c is another fundamental constant speed of light. So, thus what we can do is that we can find out n^o and observe in hall experiment if we can measure R_H from the experiment. So,$n^o = \frac{1}{R_H qc}$.

Now, as I said that we can calculate n the charge carrier density if we know the crystal structure data. Now ratio of experimentally measured value n^o and the calculated value *n* so, this $\frac{n^o}{n}$ ideally this should give me a number equal to 1. So, if we get $\frac{n^o}{n} = 1$ that will validate the correctness of the Drude model.

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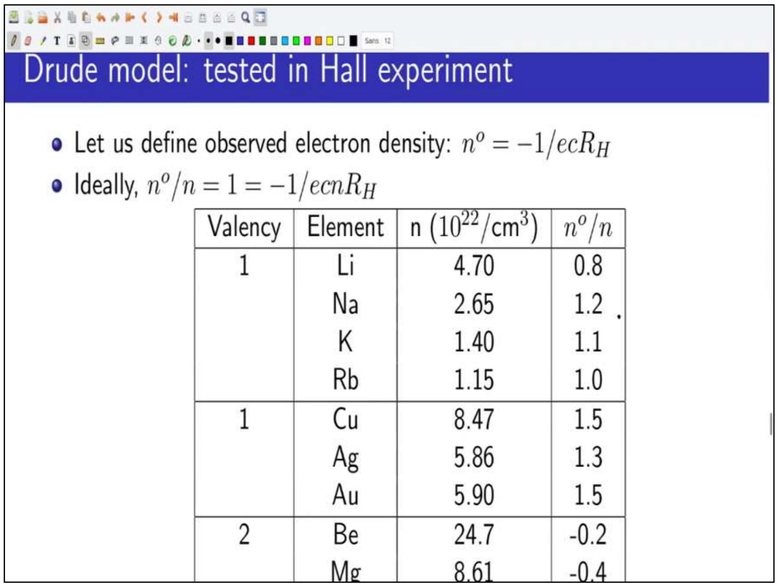

Let us see what are the values of n^o divided by n for different metals. So, if you look at the alkali metals like lithium sodium potassium rubidium the match is very good because the number that we get is very close to one.

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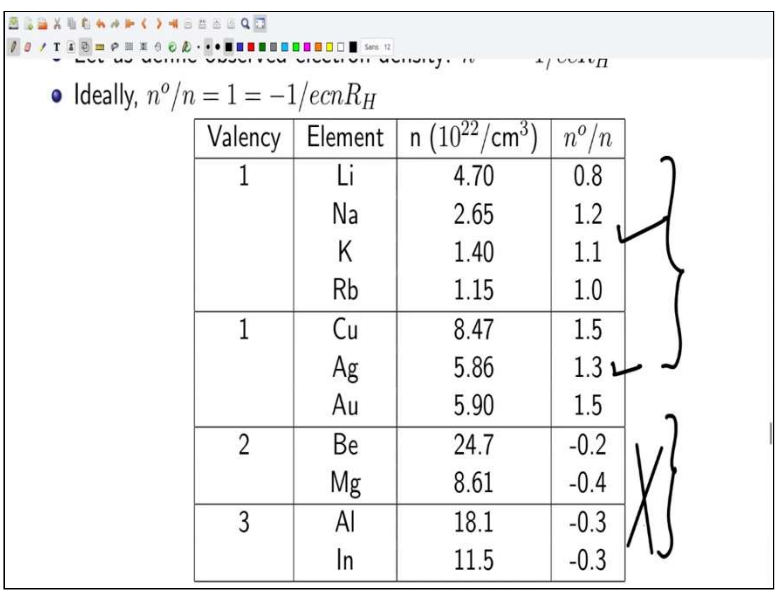

If you look at noble metals like copper silver gold then the match is not that good because the numbers are slightly away from one okay. However now if you look at like divalent and trivalent metals like beryllium magnesium aluminum etcetera in that case the Drude model fails completely because not only the number is far from one the sign is also different you see the minus sign here where we have plus sign over here okay. So, this implies that if the electrons are charged negatively in these cases right in case of monovalent metals the electrons are charged positively in case of divalent and trivalent metals. But this does not make any sense.

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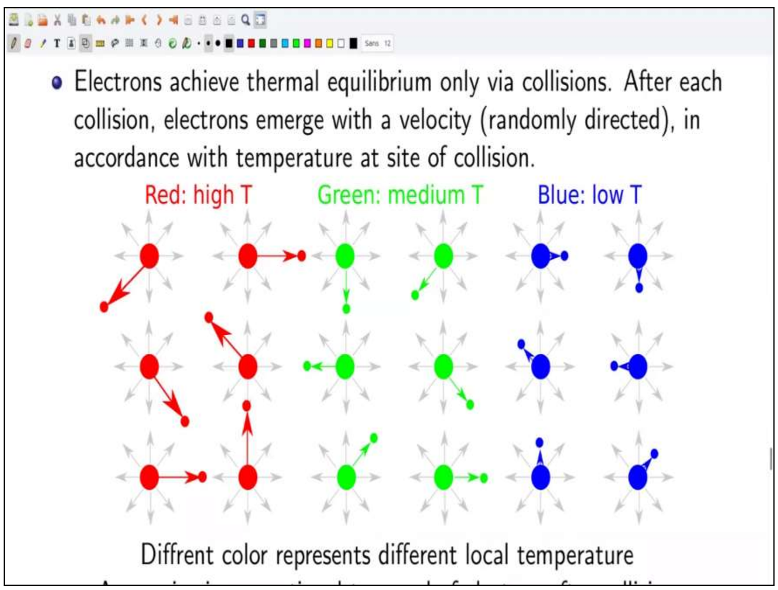

Let us test one more thing using Drude model before we do that, we have to know one more postulate of the Drude model. Electrons achieve thermal equilibrium only by a collision. After each collision electrons emerge with a velocity which is randomly directed in accordance with the temperature at the side of the collision. So, let us look at the figure and try to understand this statement. So, as you see in this diagram this gray arrow all possible directions in which the electrons can be scattered and then you see these red arrows and green arrows and blue arrows these are the actual directions in which the electron is getting scattered. Now you see electrons are still getting scattered in different directions and the size of the arrow this is proportional to the speed with which the electron emerges after the collision.

So, for example sizes of these red arrows which we assume to be at high temperature these are very large. So, that means electrons is emerging with a large velocity after this collision whereas the size of the blue arrows they are very small which implies that the electrons are emerging with relatively small velocity after collision from a region which is at low temperature.

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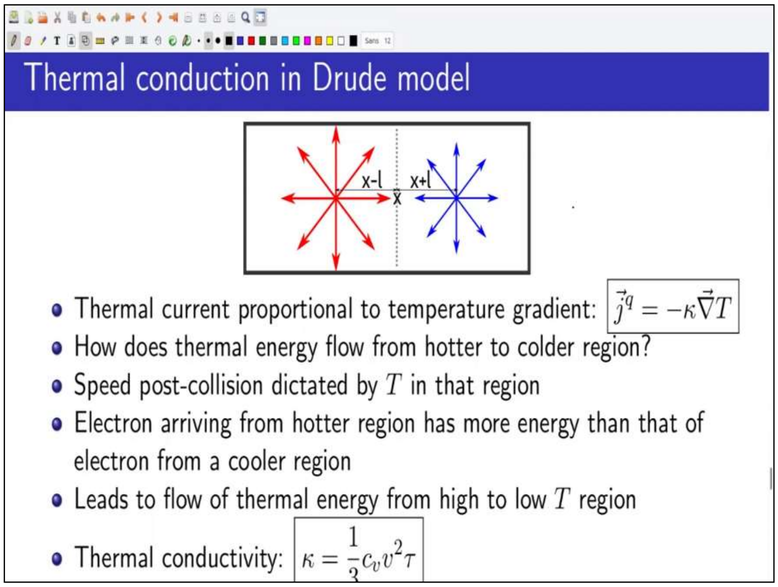

Let us try to understand thermal conduction in the Drude model. So, we know that thermal current is proportional to the temperature gradient this is the Fourier law. Now let us consider how does thermal energy flows from hotter to the colder region. So, let us assume that this region is hotter and this region is cooler and let us assume some imaginary plane separating the two regions. In this region in this is a hotter region electrons will emerge with higher velocity after each collision.

And in this region which is a cooler region electrons will emerge with a lower velocity or smaller velocity after every collision. So, that means electrons crossing this plane from the hotter region will have more kinetic energy than compared to the electrons crossing from the cooler to the hotter region. As a result there will be a net flow of thermal energy from the water to the cooler region.

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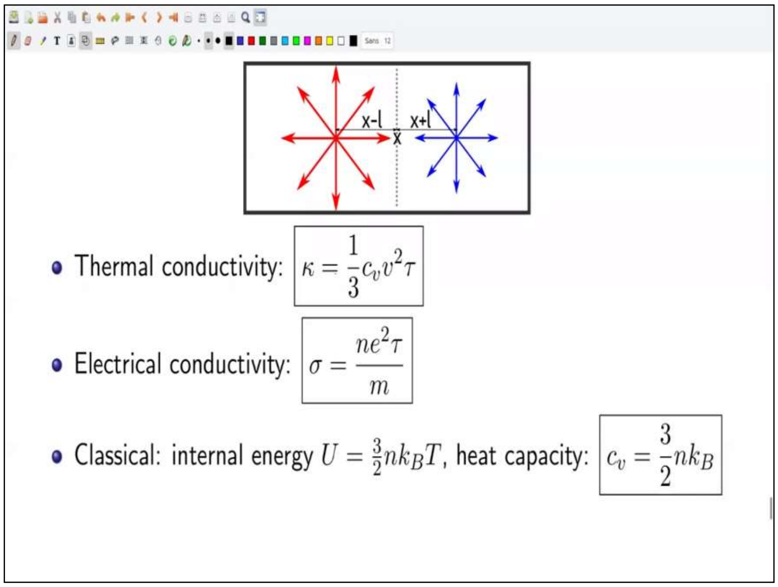

Now let us try to estimate thermal conductivity by using this formula

$$\kappa = \frac{1}{3}c_v v^2$$

where c_v is the heat capacity v is the speed of electrons and τ is the relaxation time. Now we can also estimate electrical conductivity using this formula. Now you see that both these equations contain this term τ which is difficult to measure however we can get rid of this τ if we take the ratio of $\frac{\kappa}{\sigma}$. So, let us do that.

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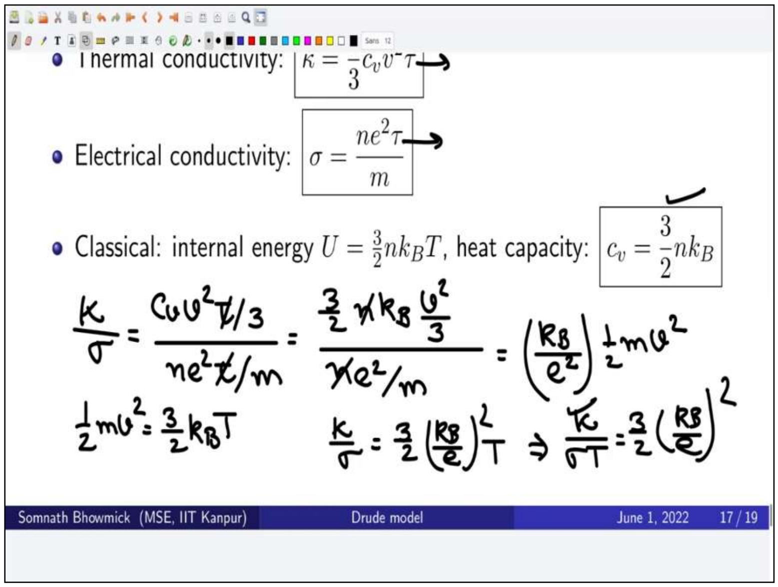

$$\frac{\kappa}{\sigma} = \frac{c_v v^2 \tau/3}{ne^2\tau/m} = \frac{3/2 n k_B v^2/3}{ne^2/m} = \frac{k_B}{e^2}\frac{1}{2}mv^2$$

Now we know that $\frac{1}{2}mv^2 = \frac{3}{2}k_BT$ that is kinetic energy is related to the temperature in this way. So, this implies that we can write

$$\frac{\kappa}{\sigma} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2 T \textit{ and this implies that } \frac{\kappa}{\sigma T} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2$$

So, this is known as the Weidman France law. You see that the number in the right-hand side it just depends on two fundamental constants k_B the Boltzmann constant and *e* the charge of the electron. So, this number is known as the Lorentz number. So, that means in an experiment I would just calculate or I would just measure the thermal conductivity of the metal. I would just measure the electrical conductivity of metal at some given temperature and that number should match with this okay.

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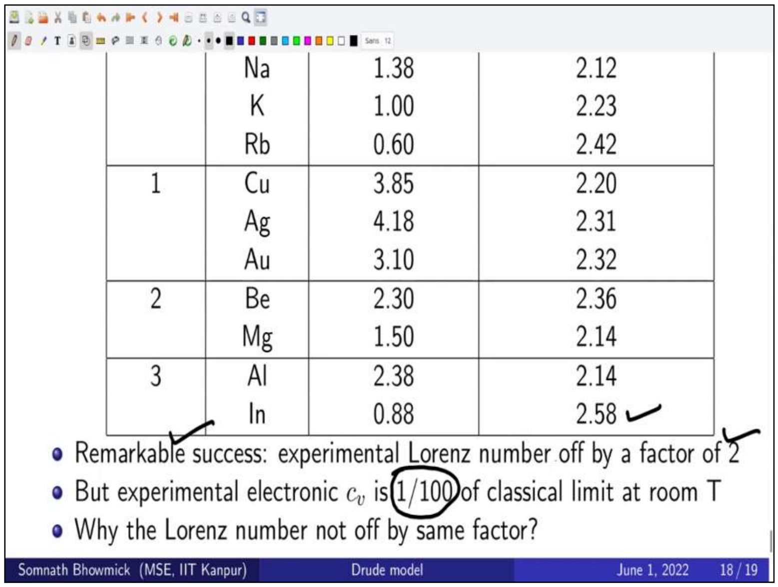

Now if you calculate this Lorentz number ideally the Lorentz number from the dodo model this appears to be this turns out to be 1.11 into 10 power -8 watt ohm per Kelvin square and now if you calculate kappa and sigma in experiment then that ratio uh turns out to be 2.22 into 10 power -8 and then if you look at different metals it varies slightly but still it is within a range of like 2 to 2.6 correct. So, that means the Lorenz number according to the Drude model it differs from the experimentally calculated value only by a factor of 2 which is a remarkable success of the Drude model.

However there is a small problem we can also experimentally calculate the electronic c v and this turns out to be 1 by 100 of the classical limit at room temperature which has been used by Drude. So, then there is a question that if the experimentally observed heat capacity is off by a factor of 100 then why the loadings number is not off by the same factor.

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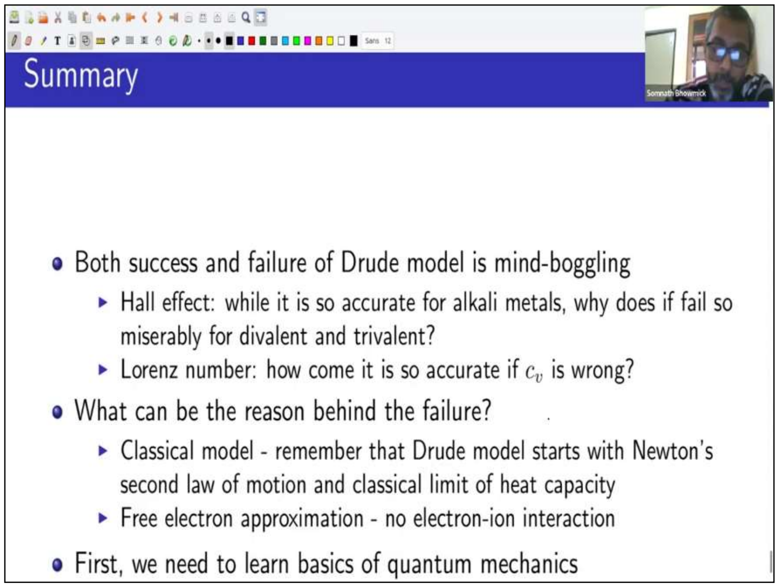

Finally let us summarize whatever we have learned in this chapter. So, both the success and failure of road model is mind-boggling. So, if we consider Hall effect then it is very accurate for alkali metals but it fails very badly for divalent and trivalent metals. Lorenz's number the prediction of Drude model is very close to what is observed experimentally however the experimentally observed c v is off by a factor of 100. So, in that case how come the load is number is. So, accurate if c v is wrong. So, in this course we will try to see what additionally we need to do to overcome these difficulties but let us try to guess the reason behind the failure. There can be two sources the first one is classical model remember that Drude model starts with Newton second law of motion and classical limit of heat capacity.

So, we have to check whether if we apply quantum model whether we can overcome these difficulties. Next one is free electron approximation we assume that there is no electron ion interaction. So, this can be another source of error. So, before we discuss further we need to learn the basics of quantum mechanics, thank you.