Physics of Nanoscale Devices
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Lecture - 58
Thermoelectric Effects, Quantum Dot Devices

Hello everyone, today we will conclude our discussion on Thermoelectric Effects and we will start a new and interesting topic, the topic on Quantum Dot Devices. I am sure you will you will be quite interested in this new topic, but before going into this lets quickly review what we have seen.

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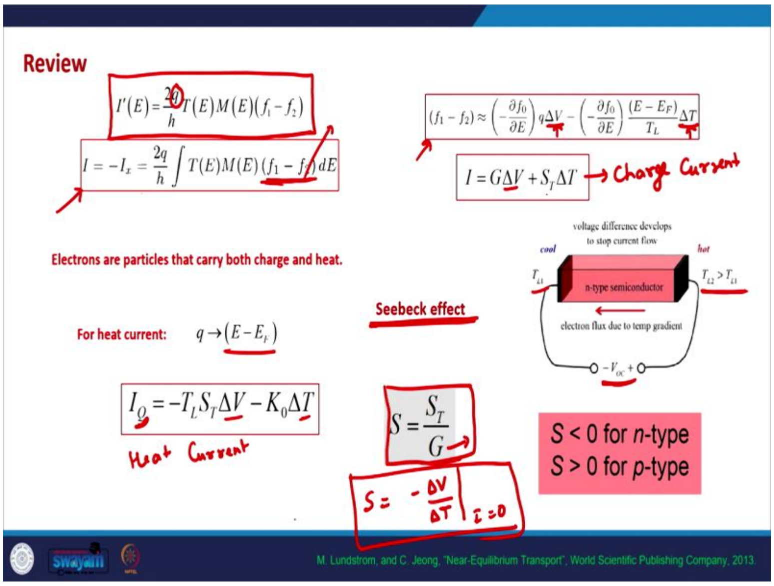

Review

$$\boxed{I'(E) = \frac{2q}{h} T(E) M(E)(f_1 - f_2)}$$

$$\boxed{I = -I_x = \frac{2q}{h} \int T(E) M(E) \underline{(f_1 - f_2)}\, dE}$$

Electrons are particles that carry both charge and heat.

For heat current: $q \rightarrow \underline{(E - E_F)}$

$$\boxed{I_Q = -T_L S_T \Delta V - K_0 \Delta T}$$

Heat Current

$$\boxed{(f_1 - f_2) \approx \left(-\frac{\partial f_0}{\partial E}\right) q\Delta V - \left(-\frac{\partial f_0}{\partial E}\right) \frac{(E - E_F)}{T_L} \Delta T}$$

$$\boxed{I = G\Delta V + S_T \Delta T} \rightarrow \text{Charge Current}$$

Seebeck effect

$$\boxed{S = \frac{S_T}{G}}$$

$$\boxed{S = -\frac{\Delta V}{\Delta T}\bigg|_{I=0}}$$

$S < 0$ for *n*-type
$S > 0$ for *p*-type

M. Lundstrom, and C. Jeong, "Near-Equilibrium Transport", World Scientific Publishing Company, 2013.

So, what we have seen is that that in the expression of the current ($f_1 - f_2$) is the forcing function. And forcing function means that, if this term is non zero in that case the current will be will also be non zero. And ($f_1 - f_2$) depends both on voltage difference across a conductor and temperature difference across a conductor.

So, this lies at the root of the thermoelectric effects. In thermoelectric effects broadly the thermoelectrics is thermoelectric effects are defined as the inter convertibility of heat into electricity and electricity to heat basically.

Which means; by a temperature difference we can produce a voltage difference and vice versa. So, study of this phenomena this inter convertibility of heat and electricity is that comes in thermoelectric effects and in this sequence what we also need to consider is the notion of heat current. Because what we have seen so far in this course is the notion of charge current, which is given by this expression and that comes from the expression of the differential charge current.

In heat current we just need to replace q by $(E-E_F)$ in this expression and that way we will obtain the heat current. And if we have a voltage difference of ΔV and a charge difference of ΔT in that case the charge current, the total charge current in the semiconductor is given by this expression I is $G\ \Delta V + S_T\ \Delta T$.

And the total heat current is given by this expression in which I_Q, Q means now it is the heat current is $-T_L S_T \Delta V - K_0 \Delta T$ and we have discussed about these two forms of current in our previous class. So, that naturally brings us to what is known as Seebeck effect which is the development of a voltage difference across a conductor when we have a temperature difference across its contacts.

So, what Seebeck effect says is that if one of the contacts is hotter as compared to the other one in that case there will be an open circuit voltage if the semiconductor is open circuited we have not connected anything. And if we connect the semiconductor to an external electronic circuit in that case this will supply a current to the external circuit. So, it means that we are converting heat essentially the temperature difference to electricity.

And what we saw was that the Seebeck coefficient can be defined as $-\Delta V$ the voltage produced as a function of ΔT the temperature difference applied when the current is 0 in a semiconductor. And this is given by S_T/G; S_T is this comes from the solid electro thermal diffusion and G comes, G is the electrical conductance of the material ok. So, this is what we have seen so far.

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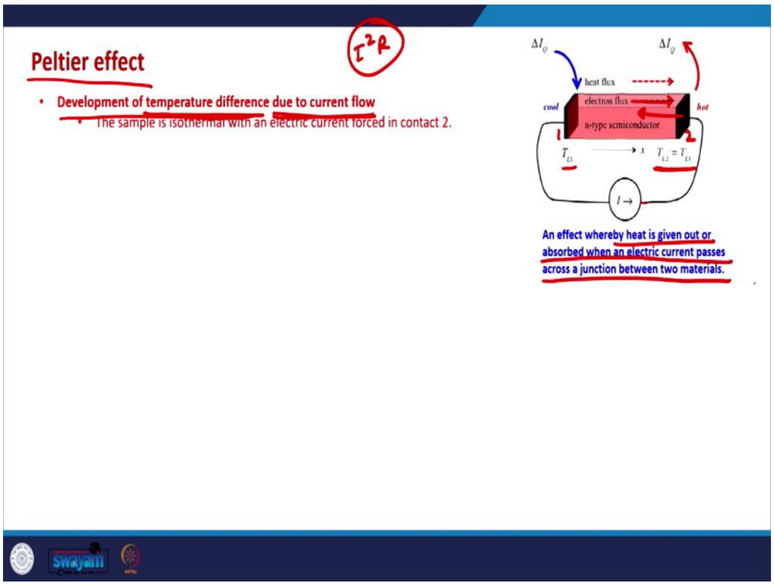

Peltier effect

I^2R

- Development of temperature difference due to current flow
  - The sample is isothermal with an electric current forced in contact 2.

An effect whereby heat is given out or absorbed when an electric current passes across a junction between two materials.

A complementary thermoelectric effect is the Peltier effect. And what is Peltier effect? It is the development of temperature difference due to current flow in a conductor ok. And now we need to be very careful because due to current flow the heat is generated because the joule heating is appears because of the current flow because of the scattering of electrons with the lattice atoms or intra or in electron-electron scattering

But this is something different this is when we force a current. So, for example, if we have a semiconductor and T_{L1} is equal to T_{L2}, which means both of the ends are at same temperature. And in this semiconductor if we force a current from contact 2 to contact 1, this way which means that electrons will flow from 1 to 2 electron flux will be in this direction.

In that case a temperature difference will appear in this semiconductor and this is known as Peltier effect, development of temperature difference due to current flow. And please also keep in mind that this is different from joule heating the I square R heating and this will become clear as well. So, in other words what we can say is that the Peltier effect is an effect, whereby the heat is given out or absorbed when an electrical current passes across a junction of two materials, ok.

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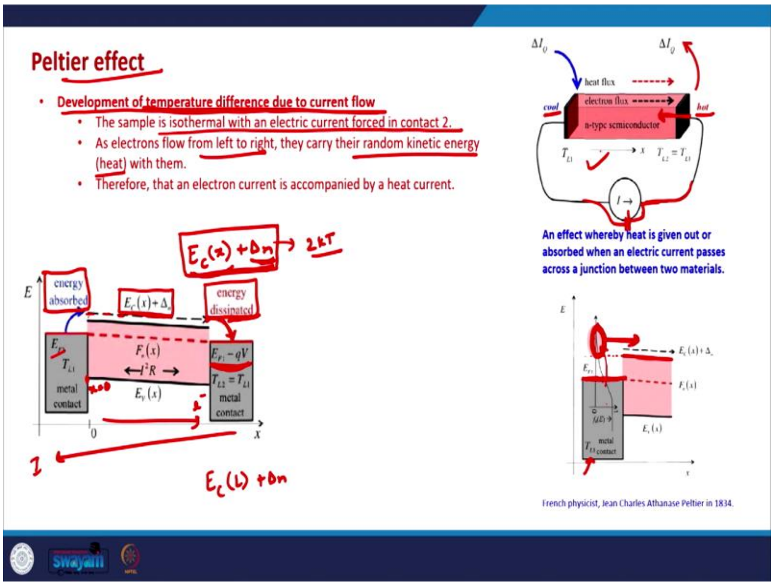

Peltier effect

- **Development of temperature difference due to current flow**
  - The sample is isothermal with an electric current forced in contact 2.
  - As electrons flow from left to right, they carry their random kinetic energy (heat) with them.
  - Therefore, that an electron current is accompanied by a heat current.

An effect whereby heat is given out or absorbed when an electric current passes across a junction between two materials.

French physicist, Jean Charles Athanase Peltier in 1834.

And in this case initially the sample the semiconductor is isothermal, which means the temperature is the same everywhere. And electrons as electrons flow from left to right they essentially carry kinetic energy and what it means is that they carry a certain form of heat or they carry heat in the form of kinetic energy from left contact to the right contact.

What it means is means is, that they absorb heat from the left contact and put it in the right contact. So, the left contact becomes cool and the right contact becomes hot. And that is how this temperature difference is created. So, let us also have a more I would say intuitive picture of this generation of temperature difference as a because of the current flow.

So, we are taking an n-type material this essentially this material and the left contact Fermi level is E_{F1} the right contact Fermi level is now E_{F1}-qV because we are forcing a current from contact 2 to contact 1 and that is done by most of the times that is done by applying a battery of positive terminal on the right contact.

So, forcing a current from contact 2 means that the right contact is on a higher voltage, so which means that the Fermi level on the right contact is now slightly lower as compared to the Fermi level on the left contact, ok.

So, this is how this heat is absorbed from the left contact and given to the right contact. We are assuming that the contacts are bulk materials where most of the times near equilibrium conditions prevail as we assume in most of our discussion.

And that is a fear assumption because generally these contacts are metallic contacts and they have a lot of electrons also they are big in size. And that is why these near equilibrium thing is not or near equilibrium assumption is not an invalid assumption. So, as all of us know that the electrons transport through the semiconductor in the conduction band.

So, what needs to happen is, that electrons when there is a current from right to left it means there is an electron flow from left to right. So, electrons need to jump from left contact into the semiconductor and then to the right contact. And if we take an n type semiconductor electrons essentially need to jump from here to the conduction band of the semiconductor.

So, we are assuming that the current conduction happens at energy level E(x), $E_c(x) + \Delta n$. So, $E_c(x)$ is the bottom of the conduction band, but as all of us know from the modes that generally the number of modes in a bulk semiconductor right at the bottom of the conduction band is very low in number. So, the actual current flow happens slightly above the bottom of the conduction band and this is the average energy at which the current conducts.

So, it is the bottom of the conduction band $E_c(x) + \Delta n$ and this Δn is quite close to is few kT essentially. So, the current conduction in most of the semiconductor happens, few kT above the bottom of the conduction band.

So, essentially we need to or the left contact needs to put electron in the semiconductor at this energy level $E_c(x) + \Delta n$, $E_c(0) + \Delta n$ essentially. Because this is x equal to 0 and similarly the right contact will take electrons from this energy level, $E_c(L) + \Delta n$ to its Fermi level.

So, this is a more I would say a more magnified picture of the current conduction and here we have only shown the left contact also its Fermi function. So, as is clear that the Fermi function is a distribution function across the Fermi level and the bottom of the conduction band of the semiconductor is above the Fermi level of the metal Fermi level of the contact.

So, the electrons that will go from the left contact to the semiconductor will be the electrons that are above this energy level. So, from the Fermi distribution function this the electrons in the tail of the Fermi function will jump to the semiconductor ok, because these electrons will see empty states right in front of them. So, what it means is that now the Fermi function on the metal after these electrons have jumped into the semiconductor this is disturbed from its equilibrium state.

Now, the Fermi function is disturbed and since this is a bulk contact and we always most of the times near equilibrium conditions are ensured very quickly because of electron phonon interaction because of the inelastic scattering in the contact the Fermi function will attain its equilibrium value it will its equilibrium shape essentially. So, what it means is that some electrons will essentially jump from below the Fermi level to above the Fermi level.

So, what it means is, that the semiconductor has taken high energy electrons into it and these high energy electrons need to be replenished from the bulk. So, that way it is as if the semiconductor has extracted energy or the heat from the contact. And similarly, on the right side these electrons will be given to the right contact.

So, these high energy electrons are given to the right contact at a lower Fermi energy at a lower Fermi level and that way this heat excess heat is given to the right contact and energy is dissipated on the right contact.

So, energy is absorbed a net energy is absorbed on the left contact and a net energy is given to the right contact in this way, because in this way this is like evaporation actually that is a good way to understand this. Because in evaporation what happens is that in a liquid for example, in water high energy particles essentially evaporates that leave the rest of the liquid colder.

Similarly, high energy electrons go to the semiconductor to the n-type semiconductor and then to the right contact and this left contact becomes slightly cooler. Now the these high energy electrons dissipate this excess energy to the on the right contact and this right contact becomes slightly hotter. And that way a temperature difference is created across the device from the left contact to the right contact, which means that a net heat current is also there in the semiconductor.

So, because of an applied voltage because of an a current being forced in contact 2 there will be a heat current as well in the system. And that is essentially the underlying mechanism of the Peltier effect, which is the development of temperature difference due to current flow, which means that a net heat current is also produced because of an current flow in the system.

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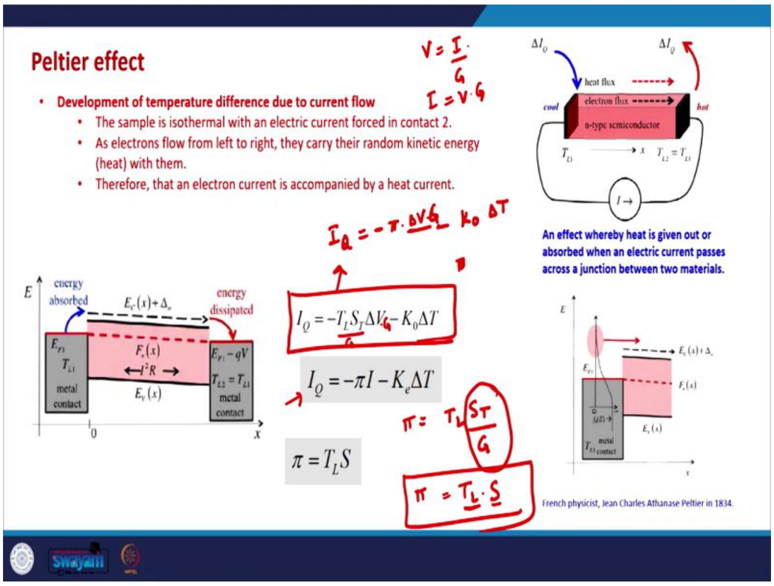

Peltier effect

- Development of temperature difference due to current flow
  - The sample is isothermal with an electric current forced in contact 2.
  - As electrons flow from left to right, they carry their random kinetic energy (heat) with them.
  - Therefore, that an electron current is accompanied by a heat current.

$V = \frac{I}{G}$

$I = V \cdot G$

$I_Q = -\pi \cdot \underline{\Delta V G}\ K_0 \Delta T$

$$\boxed{I_Q = -\underline{T_L S_T} \Delta V G - K_0 \Delta T}$$

$$I_Q = -\pi I - K_e \Delta T$$

$$\pi = T_L S$$

$\pi = T_L \frac{S_T}{G}$

$$\boxed{\pi = \underline{T_L} \cdot \underline{S}}$$

An effect whereby heat is given out or absorbed when an electric current passes across a junction between two materials.

French physicist, Jean Charles Athanase Peltier in 1834.

So, now we need to understand the heat current and the heat current is given by if you remember from the last class is given by this expression I_Q is $-T_L S_T \Delta V - K_0 \Delta T$. And this is rewritten as this term I_Q is $-\pi(\Delta VG) - K_0 \Delta T$, (ΔVG) is the current the charge current in the system because of the applied voltage. So, this becomes I. So, that is why we can write it like this.

And this pi is now. So, V is equal to I times R, I by G. So, I is V times G. So, it should be. So, please correct this should be ΔV times G. So, this becomes. So, we need to divide by G multiply by G and in that case this π essentially is $T_L S_T/G$ and S_T/G is the Seebeck coefficient. So, this is T_L times Seebeck coefficient. So, π is known as the Peltier coefficient. And what is the Peltier coefficient? It is the lattice temperature times the Seebeck coefficient.

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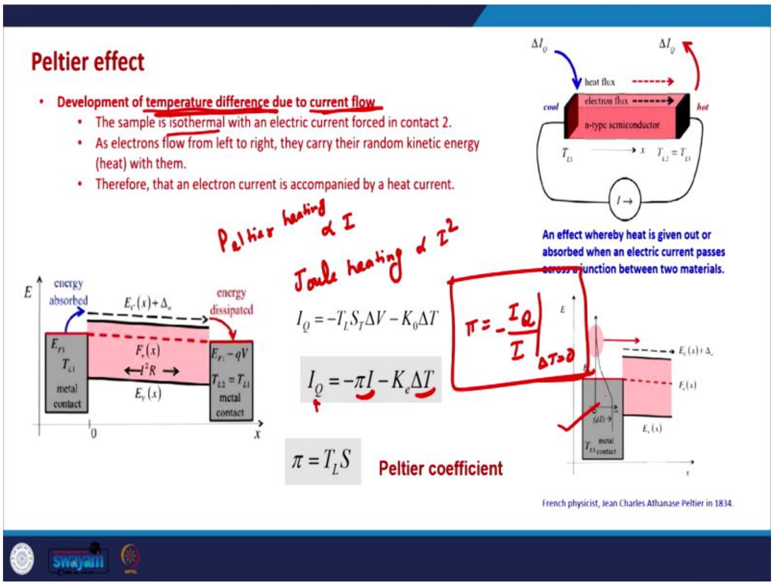

Peltier effect

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Peltier heating $\propto I$

Joule heating $\propto I^2$

$$I_Q = -T_L S_T \Delta V - K_0 \Delta T$$

$$\underset{\uparrow}{I_Q} = -\pi \underset{\smile}{I} - K_e \underset{\smile}{\Delta T}$$

$$\boxed{\pi = -\left.\frac{I_Q}{I}\right|_{\Delta T=0}}$$

$$\pi = T_L S$$ Peltier coefficient

An effect whereby heat is given out or absorbed when an electric current passes across a junction between two materials.

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And in other words what it means is that if there is no temperature difference that we do not apply any temperature difference we take an isothermal conductor. So, if this ΔT is 0, in that case π is or the Peltier coefficient is essentially the ratio of the heat current to the charge current essentially at ΔT equal to 0. So, this is the definition of the Peltier coefficient and as you might have already guessed the Seebeck coefficient or the Seebeck effect.

And Peltier effect are in a way complementary to each other, Seebeck means development of a voltage difference because of a an externally applied temperature difference. And Peltier means development of temperature difference because of the current induced in the system.

So, this is these two are the I would say the building blocks of or these two are the central concepts on thermoelectric effects thermoelectric devices and most of the thermoelectric devices are based on these two principles these two effects. So, I hope you would be able to if you come across any thermoelectric idea you would be able to understand from these basic concepts that we have discussed so far.

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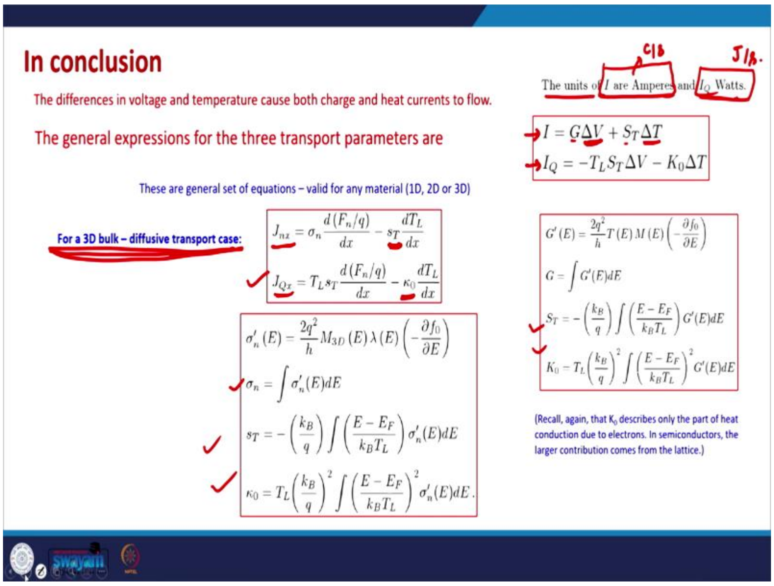

In conclusion

The differences in voltage and temperature cause both charge and heat currents to flow.

The general expressions for the three transport parameters are

These are general set of equations – valid for any material (1D, 2D or 3D)

For a 3D bulk – diffusive transport case:

$$J_{nx} = \sigma_n \frac{d(F_n/q)}{dx} - s_T \frac{dT_L}{dx}$$

$$J_{Qx} = T_L s_T \frac{d(F_n/q)}{dx} - \kappa_0 \frac{dT_L}{dx}$$

$$\sigma'_n(E) = \frac{2q^2}{h} M_{3D}(E) \lambda(E) \left(-\frac{\partial f_0}{\partial E}\right)$$

$$\sigma_n = \int \sigma'_n(E) dE$$

$$s_T = -\left(\frac{k_B}{q}\right) \int \left(\frac{E - E_F}{k_B T_L}\right) \sigma'_n(E) dE$$

$$\kappa_0 = T_L \left(\frac{k_B}{q}\right)^2 \int \left(\frac{E - E_F}{k_B T_L}\right)^2 \sigma'_n(E) dE.$$

C/s J/s.

The units of I are Amperes and I_Q Watts.

$$I = G\Delta V + S_T \Delta T$$

$$I_Q = -T_L S_T \Delta V - K_0 \Delta T$$

$$G'(E) = \frac{2q^2}{h} T(E) M(E) \left(-\frac{\partial f_0}{\partial E}\right)$$

$$G = \int G'(E) dE$$

$$S_T = -\left(\frac{k_B}{q}\right) \int \left(\frac{E - E_F}{k_B T_L}\right) G'(E) dE$$

$$K_0 = T_L \left(\frac{k_B}{q}\right)^2 \int \left(\frac{E - E_F}{k_B T_L}\right)^2 G'(E) dE$$

(Recall, again, that K_0 describes only the part of heat conduction due to electrons. In semiconductors, the larger contribution comes from the lattice.)

So, in conclusion what we can say is that always the electric current the charge current and the heat current are accompanied with each other and both of them depend on the applied voltage and applied temperature gradient in the system. I would also like to say that just to sort of remind you that the Peltier this temperature difference due to current flow this is different from joule heating.

Because now this heat I_Q means heat generated in the system is directly proportional to I. So, the Peltier heating is directly proportional to I and joule heating which comes from the scattering of electrons with the lattice is proportional to I square.

So, that is the central difference that is please keep in mind, but the origin of Peltier heating is from the can be understood from the Fermi distribution on both sides as we understood from this particular diagram, that high energy electrons are taken from the left contact and put into the right contact that is how heat is absorbed from the left contact and given to the right contact.

And as you can see that this kind of heat transfer is reversible as well. So, if we change the direction of the current the direction of heat current will also change the joule heating is not reversible it is irreversible thing.

So, in conclusion there is always we need while considering the charge current and heat current we need to consider the effect of both voltage applied and temperature applied. And these currents these coefficient in these current expressions are given by these expressions, this we have discussed already just put to we have just put them to keep everything at a single place.

And this idea this discussion can be extended to a 3D bulk case as well, which is essentially the diffusive transport case. And a 3D bulk case these equations will get modified in this way this will be the charge current density this will be the heat current density. And the solid coefficients and this K coefficients will change these are the bulk analog of S_T and K_0 and these are the corresponding expressions.

So, I would recommend all of you to go through these expressions these are just the natural generalizations of the derivations that we have already done ok. So, this essentially concludes our discussion this completes our discussion of thermoelectric effects we have not gone into the details of thermoelectric devices.

How do we, how do we convert electricity into heat practically and heat into electricity, but with the understanding of Seebeck effect and Peltier effect, I hope you would be able to understand those kind of devices as well if you encounter them anywhere ok.

So, now, let us begin with an interesting topic that is the quantum dot devices. Before going into that topic let me quickly remind you that the unit of the charge current is ampere and the unit of heat current is watts ok joule per second essentially this is coulomb per second this is joule per second please keep this in mind this is the minor point, but an important ok.

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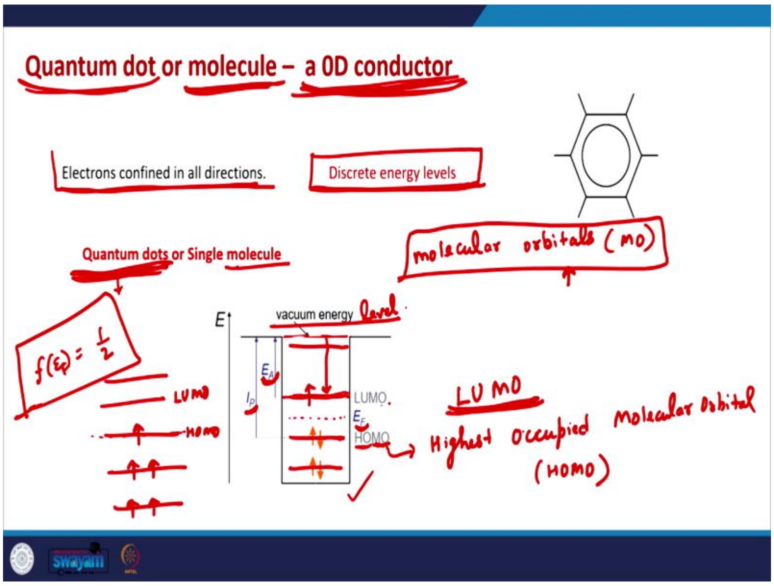

Quantum dot or molecule – a 0D conductor

Electrons confined in all directions.

Discrete energy levels

Quantum dots or Single molecule

molecular orbitals (MO)

$f(E_F) = \frac{1}{2}$

So, now let us begin with the quantum dot devices, a quantum dot device means that the active region of the device now is a quantum dot or a 0D conductor, which means a conductor in which electrons are confined in all the directions ok is. So, it can be a molecule it can be a nanostructure very small nanostructure in which electrons are confined from all the directions.

And it can be anything it is the quantum dot or a 0D material is a very general term and as all of us know that one of the most interesting features I would say of modern semiconductor industry has been scaling. Scaling means making smaller and smaller devices with better and better performance. And I would say that these quantum dot devices are the ultimate limit of that scaling because here in these devices we use almost a single molecule as a device as a channel.

So, we put a single molecule between the 2 contacts and that becomes a quantum dot device, ok. Or we can also make fabricate semiconductor structures in which the size of the semiconductor in all three directions is few nanometers only ok. And that is a quantum dot.

So, quantum dot is also known as an artificial atom it is like an atom because atom is also very small electrons are confined in all the directions. And because of the confinement of electrons we always need to deal with the discrete energy levels in these systems.

So, far we have mostly dealt with 2D channel 1D channel or 3D channel bulk materials as well, we did not do a very thorough analysis of 0D channels and that is what we are going to do now. And in a 0D conductor the characteristics is, that the electrons are confined in all the directions, which means that the electronic energy is discrete. There is no continuum of energies it is like energy of a single atom ok and this is how the energy levels of a quantum dot or a molecule look like ok.

So, if you recall in an atom there are atomic orbitals in which electrons reside, atomic orbitals are electronic allowed electronic wave function in the atom. Similarly, in a molecule or in a quantum dot we have molecular orbitals MOs.

So, electrons in different atoms interfere with each other and because due to this interference due to the interference of various electronic wave functions in a molecule molecular orbitals are formed. So, these molecular orbitals essentially belong to the entire molecule they do not belong to a particular atom in that molecule.

Similarly, in quantum dots as well we talk about discrete energy levels and these are the molecular orbitals of the quantum dots. So, once a quantum dot is formed specially the outer shell electrons the loose electrons in the atoms they interact with each other and they form molecular orbitals and. So, these orbitals will have discrete energies because electrons are confined in all the directions.

And the electrons will be filled in these orbitals from the bottom from the lowest energy to higher energy. So, there are several important terms here one is the molecular orbital which is the up to which electrons are filled in a quantum dot in an or in a molecule is known as highest occupied molecular orbit or highest occupied molecular orbital or H O M O HOMO one.

Similarly, the lowest unoccupied orbital is known as LUMO orbital lowest unoccupied molecular orbital. So, this is the orbital that is that has energy just above the highest occupied molecular orbital ok. So, these two orbitals are extremely important HOMO and LUMO, orbitals HOMO is the orbital up to, which electrons are filled LUMO is the one which is just above the filled orbitals.

And depending on the number of electrons in the system there might be one electron in the LUMO or there might be two electrons as well. So, as all of us know that one orbital can take at max two electrons of different spins. So, this HOMO can take either one or two electrons. So, generally in most of the cases in stable quantum dots generally there are two electrons in HOMO because if there is one electron in highest occupied molecular orbital.

In that case that becomes quite a reactive quantum dot because it has a tendency to give one electron or to take an electron from the external environment essentially. So, generally we assume that generally in this discussion we assume that HOMO is completely filled two electrons are there of opposite spin LUMO is completely empty although in some cases HOMO might be half filled as well.

So, it is not that always HOMO, is completely filled, but that is the case in most of the situations. Now there are several terms that we need to understand the notion of Fermi level is not properly defined in these systems because there are very less number of electrons in this system and this statistics of electrons cannot be done properly.

However, we define the notion of Fermi level from the basic definition of Fermi level, which is it is the level it is the energy level at which the probability of being occupied is half.

So, the Fermi level is the level at which the probability of an electron being found is 1 by 2. So, in this case the probability of an electron being found at HOMO level is 1 because it is completely filled the probability of electron being found in LUMO is 0. So, the Fermi level will be right in the middle of LUMO and HOMO. However, if we have a system in which this is the way electrons are filled.

So, in which HOMO has one electron and LUMO does not have any electron in this case the Fermi level is assumed to be at the HOMO energy level, because HOMO is half filled highest occupied molecular orbital is half filled, which means that the probability of this state being occupied is half now. So, this becomes the Fermi level of the system.

So, this is how we define the Fermi level in quantum dots we also have a notion of ionization potential, which comes from the atoms actually this comes from atoms. So, this means ionization potential is essentially the energy that we need to ionize the system to take out an electron from the system into the free space. And the free space energy of the electron is defined by this vacuum energy level. So, this is the level at which the electron becomes totally free from the system.

So, the difference between the vacuum energy level and the HOMO energy is known as the ionization potential and this is the energy that is required to take one electron out of the system or to ionize the quantum dot or the molecule.

Similarly, we have another parameter, which is known as electronic affinity and that is the amount of energy that is released when an electron is occupied or electron is taken by the system. And that is the difference between the vacuum energy level and LUMO energy level because any additional electron will be taken in LUMO energy level.

And the energy that will be released will be the difference between the vacuum energy level and the LUMO energy level. So, that is known as the electron affinity of the quantum dot the difference between vacuum energy level and HOMO energy level is known as the ionization potential ok.

So, these are some basic terms the notion of highest occupied molecular orbital and lowest unoccupied molecular orbital and if you have a give a careful consideration LUMO is like the bottom of the conduction band and HOMO is like the top of the valence band you know in a bulk material. So, these are quite analog ideas analogous to each other. So, this is a very brief introduction to quantum dots.

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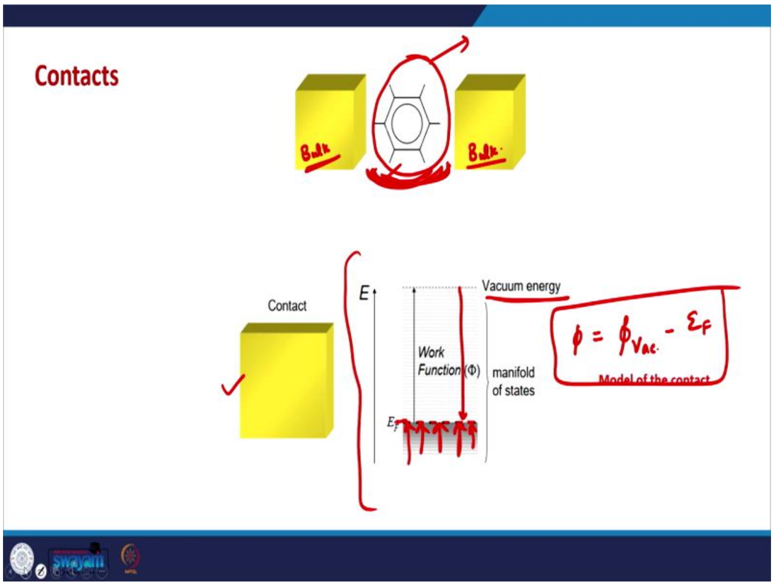

Contacts

$\phi = \phi_{Vac.} - \varepsilon_F$

Model of the contact

Now, in devices we need to put these quantum dots between two contacts between the metal contacts essentially. And as usual these contacts are bulk and metallic contacts fabricating these devices entirely different matter. So, we will not go into that here. Generally we need to grow on top of.

So, if, so this quantum dot or this 0D material could be an organic molecule as well or this could be a semiconductor nano structure as well and there are different ways to fabricate these different nanostructures essentially.

So, how does a contact look like a metal has a Fermi level E_F and generally what we assume is that all the energy levels up to this Fermi level are occupied, which means that metal has lot of electrons and all the energy levels up to this level are filled.

So, electrons are there in surplus up to this energy level metal has additional electronic states as well even above the Fermi level, but those are empty states. So, these states are empty above the Fermi level are empty ok. And the energy required to take out an electron from the metal to vacuum, which means to free an electron is known as the work function.

So, the difference between the vacuum energy level and the Fermi level is the work function of the metal that will also be the ionization potential of this metal in a way because that is also the same amount of energy. Because if we if this metal takes an extra electron in it the energy that will be released will be this vacuum energy level minus the Fermi energy level.

And this is known as the work function, which is essentially the difference between the vacuum energy level and the Fermi level ok. So, just to summarize the contacts are metallic contacts these are bulk contacts they have lot of electronic states there is a continuum of electronic states in a way and up to this energy level the Fermi level all the electronic states are filled. And above this energy level all the electronic states are empty. So, that is a key point here and that is what we need to keep in mind ok.

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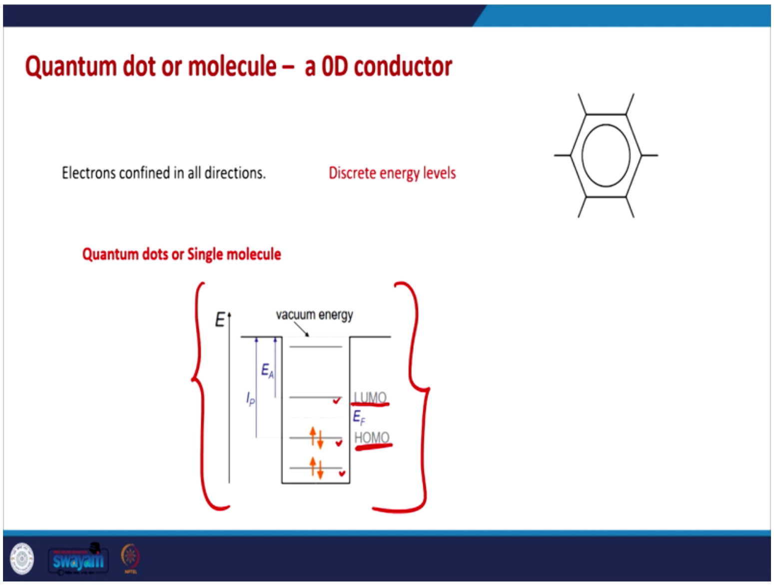

Quantum dot or molecule – a 0D conductor

Electrons confined in all directions.

Discrete energy levels

Quantum dots or Single molecule

So, that is a; that is a very general model of the contact and just to quickly remind you a general model of a quantum dot or a nanostructure or an organic molecule or any general structure that is in which electrons are confined in all the directions is this in which we have molecular orbitals.

And these orbitals are occupied by electrons in the order of increasing energy, the highest occupied molecular orbital is known as the HOMO orbital the lowest unoccupied is known as the LUMO orbital. And depending on the occupancy of homo the Fermi level can be defined in these systems.

Now, while making a device we need to put this contact in touch with the quantum dot. Generally, this is the way we symbolize a quantum dot or any organic molecule or just this symbolic representation this actually means an organic molecule, but this means any nano structure in which electrons are confined in all directions.

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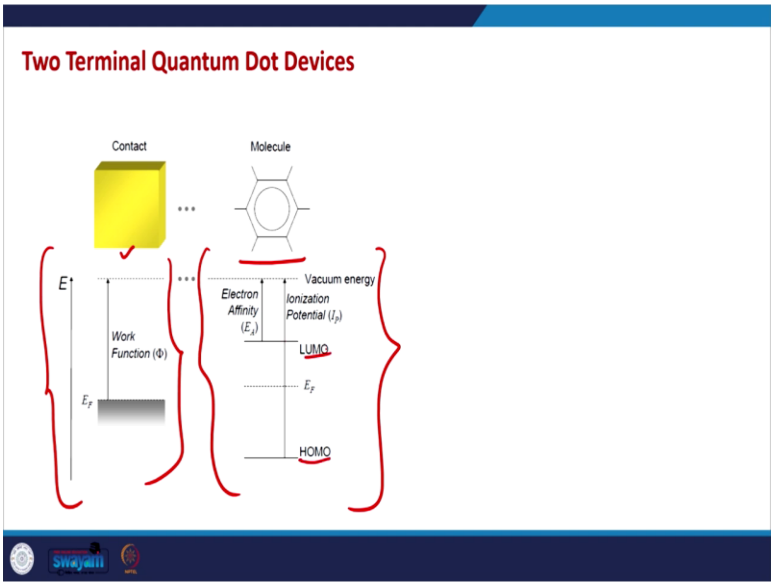

Two Terminal Quantum Dot Devices

So, what happens when we put a metallic contact in touch with this molecule or quantum dot? So, on one side on the metallic side electrons have this kind of energy profile on the right side in the molecule in the quantum dot electrons are like this on the left side they are in a continuum of energy and the occupancy is governed by the Fermi level. On the right side they are in discrete energy levels and occupancy depends on the number of electrons in HOMO and LUMO orbitals ok.

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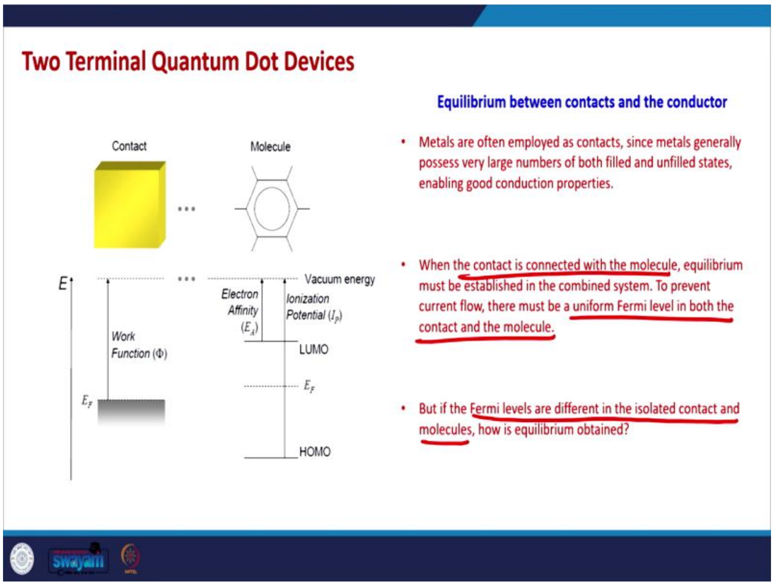

Two Terminal Quantum Dot Devices

Equilibrium between contacts and the conductor

- Metals are often employed as contacts, since metals generally possess very large numbers of both filled and unfilled states, enabling good conduction properties.
- When the contact is connected with the molecule, equilibrium must be established in the combined system. To prevent current flow, there must be a uniform Fermi level in both the contact and the molecule.
- But if the Fermi levels are different in the isolated contact and molecules, how is equilibrium obtained?

So, it is interesting what happens when these two are combined when we put a quantum dot in touch with the metal in equilibrium what happens is when a metal is connected to the molecule.

First of all equilibrium should establish equilibrium means very soon electrons will rearrange themselves across this metal and quantum dot in such a way that there is no net current in the system, which means that the Fermi levels of both the systems are aligned to each other. So, that is the first basic thing that happens whenever we put any two materials in contact with each other.

What happens is very soon equilibrium is achieved and in equilibrium a uniform Fermi level must be established between the both the materials. The interesting thing happens when the Fermi levels are different in isolated contact and quantum dots now we need to understand how this equilibrium is obtained.

How the electrons will rearrange themselves in such a way that there is a uniform Fermi level across the metal, across the contact and quantum dot and as expected electron rearrangement needs to happen in order to do that ok.

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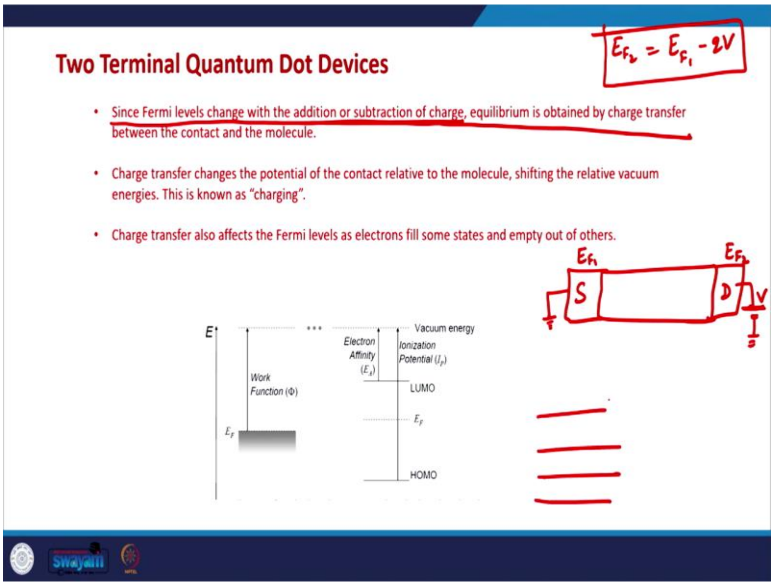

Two Terminal Quantum Dot Devices

$\boxed{E_{F_2} = E_{F_1} - 2V}$

- Since Fermi levels change with the addition or subtraction of charge, equilibrium is obtained by charge transfer between the contact and the molecule.
- Charge transfer changes the potential of the contact relative to the molecule, shifting the relative vacuum energies. This is known as "charging".
- Charge transfer also affects the Fermi levels as electrons fill some states and empty out of others.

So, the Fermi levels actually change with addition or subtraction of charges and equilibrium is obtained equilibrium means that both the Fermi levels need to be aligned. So, which means that now we need to have a rearrangement of charges between the two systems between the metal and the quantum dot or the molecule. And the Fermi levels depend on the, if you remember the Fermi levels actually depend on the applied voltage as well if you remember in a in our two terminal device.

If this is the left contact this is the right contact and if we apply a voltage V here and the left contact is grounded the Fermi level on the left contact is E_{F1} the Fermi level on the right contact is E_{F2}, then E_{F2} will be E_{F1} - qV. So, any voltage that is applied across the system will change the Fermi levels.

So, what it means is if there is or in other words if we deposit a charge here because of the voltage difference the Fermi levels will be changed also from quantum statistics the position of the Fermi level depends on the number of electrons in the system.

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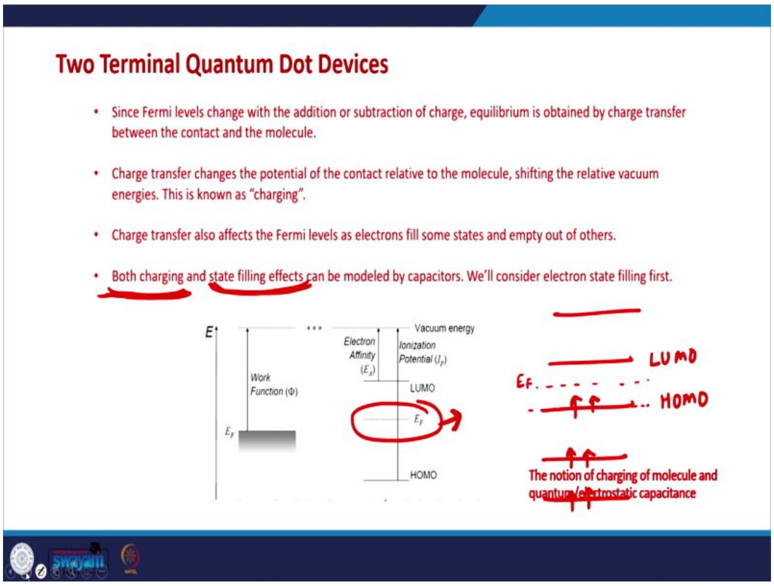

Two Terminal Quantum Dot Devices

- Since Fermi levels change with the addition or subtraction of charge, equilibrium is obtained by charge transfer between the contact and the molecule.
- Charge transfer changes the potential of the contact relative to the molecule, shifting the relative vacuum energies. This is known as "charging".
- Charge transfer also affects the Fermi levels as electrons fill some states and empty out of others.
- Both charging and state filling effects can be modeled by capacitors. We'll consider electron state filling first.

The notion of charging of molecule and quantum/electrostatic capacitance

Because if the number of electrons in a quantum dot let us say if we have a quantum dot whose molecular orbital are organized in this way. If the number of electrons in this system are just 5 this becomes the HOMO orbital and this becomes the LUMO orbital and the Fermi level lies at HOMO.

On the other hand if the electrons in this system are 6, the Fermi level lies between HOMO and LUMO. So, this Fermi level apart from the electrostatic voltage the Fermi level also depends on the number of charge carriers or number of electrons in a particular system ok.

So, there are two factors. So, this is a very subtle point I would like to remind you that the Fermi level the position of the Fermi level depends on two factors. One is the electrostatic voltage second is the number of electrons in a system generally in large systems we do not or we ignore the dependency of Fermi level on number of electrons because number of electrons are already huge. So, adding one or two electrons does not make any significant difference there.

And moreover as we will see that there is a role of density of states as well. So, if the density of states is significant in that case this number of electrons does not make much impact here, but there are two points that we need to keep in mind that the position of Fermi level depends both on number of electrons and the charge or the electrostatic voltage.

So, whenever any electron rearrangement happens in the system whenever we put a metal in touch with a quantum dot electrons are transferred from one system to another system, let us say then the number of electrons change in the system as well as there is an electrostatic voltage that appears electrostatic voltage difference that also that is also produced.

So, both of these needs to be taken into account specially in quantum dot devices. So, that is a subtle point I would like to repeat it again that the Fermi level position depends on the electrostatic voltage and that depends on the amount of charge that is present or if we have applied a negative voltage or a positive voltage on certain terminal.

It also depends on the number of electrons because it is the Fermi level is also the chemical potential of the system it is also a function of the number of electrons in the system in equilibrium. And if the number of electrons change then both of these factors change both electrostatic voltage change across the system because electrons are now getting transferred from one system to another system.

So, there is a positive charge is being produced at one place negative charge is getting accumulated at another place. So, there is this electrostatic voltage difference that appears across the system.

Also since the number of electrons are changing in the quantum dot just by the numbers in the Fermi level might also change. So, Fermi level will change because of two factors one is because of the charging because of the electrostatic effect and second is the because of the number effect which is known as the state filling effect.

Because if we fill this homo state this Fermi level changes significantly even if there is no applied voltage in the system. So, these are termed as charging effect and state filling effects.

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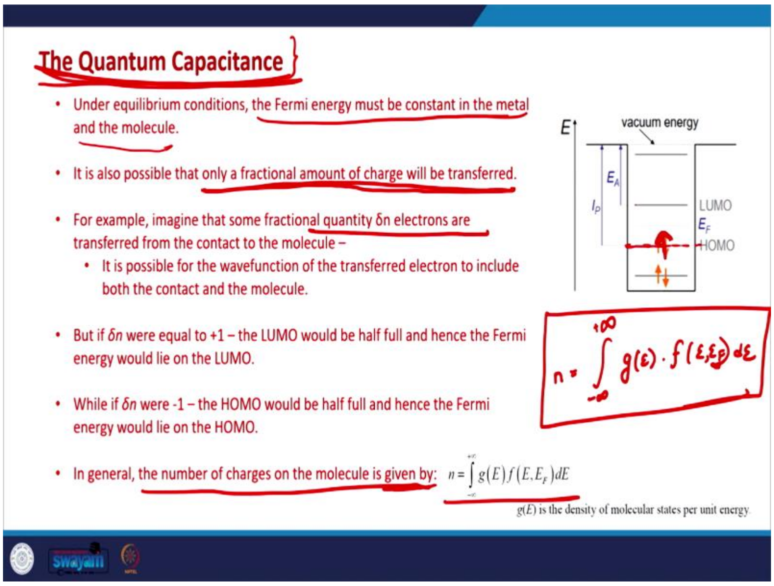

The Quantum Capacitance

- Under equilibrium conditions, the Fermi energy must be constant in the metal and the molecule.
- It is also possible that only a fractional amount of charge will be transferred.
- For example, imagine that some fractional quantity δn electrons are transferred from the contact to the molecule –
  - It is possible for the wavefunction of the transferred electron to include both the contact and the molecule.
- But if δn were equal to +1 – the LUMO would be half full and hence the Fermi energy would lie on the LUMO.
- While if δn were -1 – the HOMO would be half full and hence the Fermi energy would lie on the HOMO.
- In general, the number of charges on the molecule is given by: $n = \int_{-\infty}^{+\infty} g(E) f(E, E_F) dE$

$g(E)$ is the density of molecular states per unit energy

$$\boxed{n = \int_{-\infty}^{+\infty} g(\varepsilon) \cdot f(\varepsilon, \varepsilon_F) \, d\varepsilon}$$

So, let us first consider the what is known as the charge the state filling effect which means how does the Fermi level depends on number of electrons in a system because whenever we put a metal in touch with a quantum dot the number of electrons will change in both the systems.

So, we need to first understand how is the number of electrons govern the Fermi level and this is the notion of charging of the molecule and from here the idea of quantum capacitance and electrostatic capacitance actually comes up.

So, quantum capacitance is essentially this idea comes from the dependence of the Fermi level on the number of electrons in a system ok. So, let us see where it comes from under equilibrium the Fermi level in metal molecule system metal quantum dot system must be uniform and in order to achieve that uniform Fermi level certain amount of charge needs to be transferred across the system sometimes if the Fermi level are not aligned before joining them.

And it is also possible that only a fractional amount of charge is transferred, what it means is that it may not be necessary that entirely a full electron is transferred to the from metal to the quantum dot it might happen that the electronic wave function is now such that part of it is on metal and part of it is on quantum dot.

So, there is a non zero probability of a certain electron being found both on the metal contact and the semiconductor quantum dot or a molecule. So, that way we can say that only a fractional amount of charge is transferred and sometimes that is also the case ok.

So, we will consider the case in which delta n electrons are transferred from the contact to the molecule ok. If delta n is plus 1 which means that one electron is transferred from metal to the quantum dot and in that case LUMO will be half filled if the homo was already fully occupied and that is what we assume.

And that is why the Fermi energy or the Fermi level will now be at LUMO level. Similarly, if delta n is minus one, which means one electron is transferred from quantum dot to the metal in that case in that case there will be only one electron left at the HOMO orbital.

And the Fermi level will now be at HOMO energy level. So, that way Fermi level changes as a function of number of electrons. In general let us say in general the total number of charges on a molecule is given by this relationship which is a fundamental relationship.

So, the number is given by density of states times the Fermi function and integrated over all possible energy values. So, if we take this E_F to be the equilibrium Fermi function, which means this is the Fermi function after joining the metal to the quantum dot. In that case this number will be the number of electrons in the system at equilibrium after the molecule is in touch with the metallic contact.

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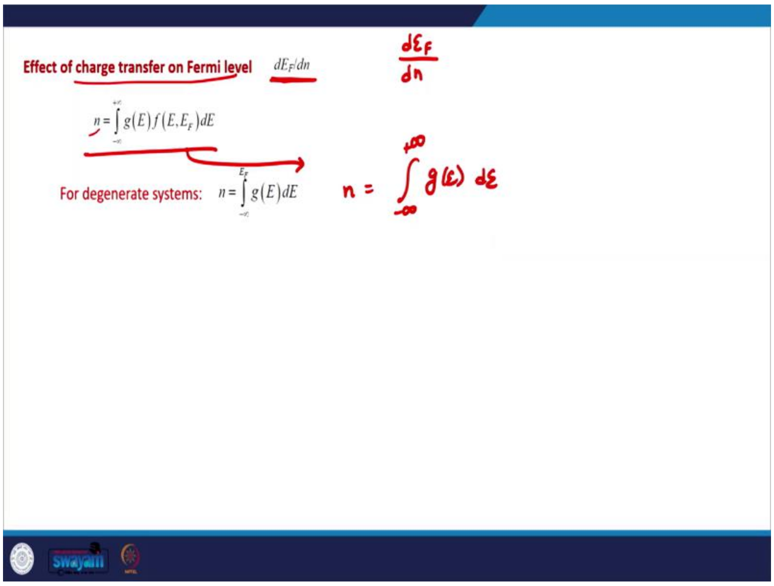

Effect of charge transfer on Fermi level dE_F/dn

$$\frac{d\mathcal{E}_F}{dn}$$

$$n = \int_{-\infty}^{+\infty} g(E) f(E, E_F)\, dE$$

For degenerate systems: $n = \int_{-\infty}^{E_F} g(E)\, dE$

$$n = \int_{-\infty}^{+\infty} g(\mathcal{E})\, d\mathcal{E}$$

So, in order to understand the effect of charge transfer on the Fermi level we essentially need to calculate this quantity how does the Fermi level changes with respect to the change in charge. And this will come from this relationship, which is the relationship between the number of electrons to the Fermi function.

So, if we take a derivative or generally in most of the systems the derivative will be taken little later most of the systems for example, in metals only the states up to the Fermi level are occupied.

So, this integration is taken only up to E_F and up to E_F this Fermi function is 1. So, n is can be rewritten as this f(E) becomes 1 and instead of +∞ it becomes the Fermi level.

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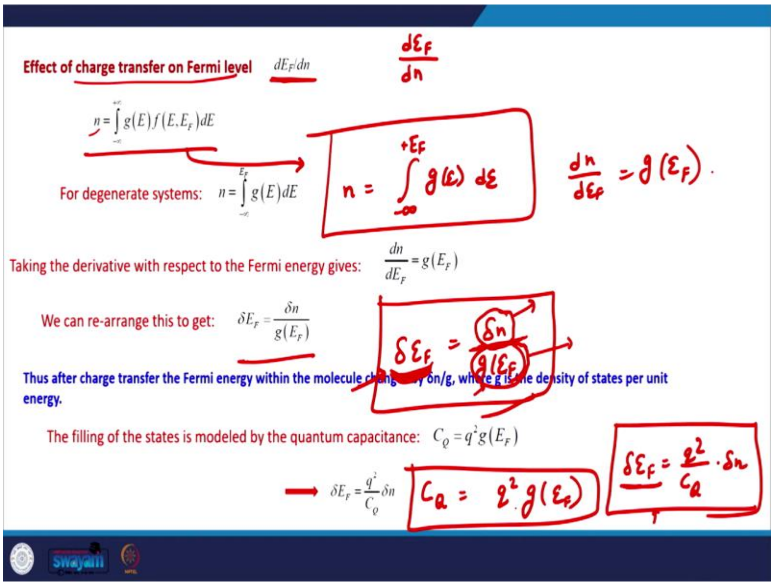

Effect of charge transfer on Fermi level dE_F/dn

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$$\boxed{n = \int_{-\infty}^{+E_F} g(\mathcal{E})\, d\mathcal{E}}$$

$$\frac{dn}{d\mathcal{E}_F} = g(\mathcal{E}_F).$$

Taking the derivative with respect to the Fermi energy gives: $\frac{dn}{dE_F} = g(E_F)$

We can re-arrange this to get: $\delta E_F = \frac{\delta n}{g(E_F)}$

$$\boxed{\delta\mathcal{E}_F = \frac{\delta n}{g(\mathcal{E}_F)}}$$

Thus after charge transfer the Fermi energy within the molecule changes by δn/g, where g is the density of states per unit energy.

The filling of the states is modeled by the quantum capacitance: $C_Q = q^2 g(E_F)$

$$\rightarrow \delta E_F = \frac{q^2}{C_Q}\delta n \quad \boxed{C_Q = q^2 . g(\mathcal{E}_F)} \quad \boxed{\delta\mathcal{E}_F = \frac{q^2}{C_Q} . \delta n}$$

The way the reason we can write it like this is that generally, the Fermi level of the metal does not change with the change does not change with the number of electrons because there are already a lot of electrons in the metal. So, even if few electrons go to the contact or few electrons come from the contact the Fermi level does not change much. And generally the equilibrium Fermi level is at the Fermi level of the metal and that is why this integration limits boil down to this level.

Now if we take the derivative of this with respect to E_F, (dn/dE_F), this is what we obtain this is the density of states at the Fermi level or δE_F becomes $\delta n/g(E_F)$. And this is what I would like you to think about this is the change in the Fermi level when we change the number of electrons in the system by δn. And this depends on the density of states of electrons at the Fermi level. So, the density of states in electrons is quite huge. So, that is why δE_F is almost 0.

But in quantum dot systems or in nanostructures density of states is not much and in that case δE_F is significant as a function of δn as well. So, that is why this change in the Fermi level as a function of the number of particles this is specially important in nanomaterials in quantum dots specially in which the density of states is very small. And from here comes the notion of quantum capacitance.

So, the quantum capacitance is defined as q square times the density of states. So, we will come back to this idea of quantum capacitance in the next class where it comes from. So, if we define it like this in that case δE_F becomes $q^2\delta n/C_Q$ and this is an very important relationship for quantum dots.

So, we will stop here, but the take away from today's discussion on quantum dots is that the Fermi level of quantum dots or nanostructures it depends on both the number of electrons and also the electrostatic voltage that is applied across the system ok.

And first we are considering just considering the impact or the effect of number of electrons on the Fermi level and here comes the notion of quantum capacitance with which we will begin our next class ok.

So, thank you all and see you in the next class.