Electronic Theory of Solids
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Lecture - 09
Bonding and Band Formation: N=2 solid Molecular Orbitals, Linear combinations of Atomic Orbitals (LCAO)

As we have been discussing, we are introducing the quantum corrections to the properties of electron gas in a solid.

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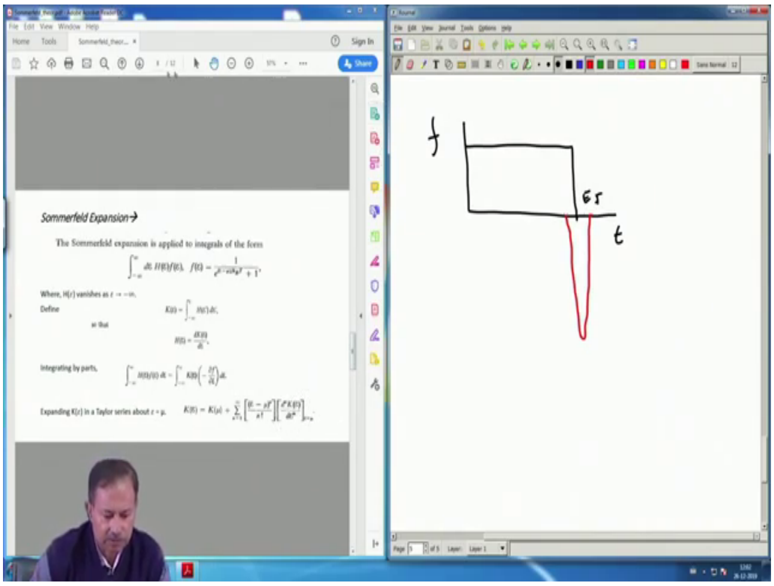

Sommerfeld Expansion→

The Sommerfeld expansion is applied to integrals of the form

$$\int_{-\infty}^{\infty} d\varepsilon\, H(\varepsilon) f(\varepsilon), \quad f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/k_B T} + 1},$$

Where, $H(\varepsilon)$ vanishes as $\varepsilon \to -\infty$.

Define

$$K(\varepsilon) = \int_{-\infty}^{\varepsilon} H(\varepsilon')\, d\varepsilon',$$

so that

$$H(\varepsilon) = \frac{dK(\varepsilon)}{d\varepsilon}.$$

Integrating by parts,

$$\int_{-\infty}^{\infty} H(\varepsilon) f(\varepsilon)\, d\varepsilon = \int_{-\infty}^{\infty} K(\varepsilon)\left(-\frac{\partial f}{\partial \varepsilon}\right) d\varepsilon.$$

Expanding $K(\varepsilon)$ in a Taylor series about $\varepsilon = \mu$,

$$K(\varepsilon) = K(\mu) + \sum_{n=1}^{\infty} \left[\frac{(\varepsilon-\mu)^n}{n!}\right]\left[\frac{d^n K(\varepsilon)}{d\varepsilon^n}\right]_{\varepsilon=\mu}.$$

And so, the first thing that we have just shown is that, the specific heat for example, which had a problem; because the classical theory did not meet the experimental results. This has been corrected by introducing Pauli exclusion principle and quantum statistics. And sort of an approximate calculation settled the matter, the two most important factors; the linearity in temperature at low temperatures and the factor of nearly hundred or more that the actual experimental result gives a value less than the classical value. And the both these accounts were settled by an approximate calculation and very physical calculation also gives similar kind of results.

Now, and the both of these basically use quantum statistics; by quantum statistics I mean the statistics that is Fermi Dirac statistics appropriate for electron gas. Now as I said, the calculation that I just shown gives me a factor, gives me all the factors correctly except by that it is only linear in temperature term is what we could get.

Now, if you want to go beyond that and want to get the numerical factors and the corrections to T square all that correctly, then you have to account for the fact that the chemical potential itself is a function of temperature. At zero temperature only it is equal to the Fermi level Fermi energy and so, that correction has to be put in. And the fact that Fermi function itself does not give you a delta function like derivative at E f should also be corrected.

So, it, so what Sommerfeld did was that, he to this general kind of integrals where you have to solve this d some function H of E times the Fermi function f of E. The condition is that this H of E has to vanish at epsilon, at energy is going to minus infinity; of course, that is true of almost all physical functions. And there is also the other conditions that at very large energies it has to be less than some powers in epsilon, so it can at best diverge at some powers of energy. So, those are conditions that are more or less obeyed by most of the physical quantities that we encounter. And so, that condition is not a prohibitively difficult or restrictive condition for a physical system.

Now, let us define this quantity basically it is the H is now defined as a derivative of another function which is K and so, one can integrate it by parts. And remember the fact that H vanishes at the boundaries. And so, the this integral will now give me this H of E f E d E integral is just the second term in the integral which is minus K E del f del E; that minus is now taken inside. As I wrote the, as I showed in the previous one that the advantage of; at 0 temperature the advantage we have is that the Fermi function f versus E at E f at E f, the derivative has this derivative has a delta function kind of structure, the negative direction.

So, minus del f del E is a very sharply peaked function across around the Fermi level and it is an even function. So, this is very important that you can actually calculate and take the derivative and see that check that it is an even function with respect to E; that means, if E goes to minus E the function the derivative does not change. So, these two facts are going to be used.

So, this integral can be written as this right hand side K E times minus del f del E into d. Now K e is expanded in a Taylor series and this about the chemical potential, ok. So, this is the standard chemical, the Taylor series expansion, ok. So, let us go ahead and see what we do next.

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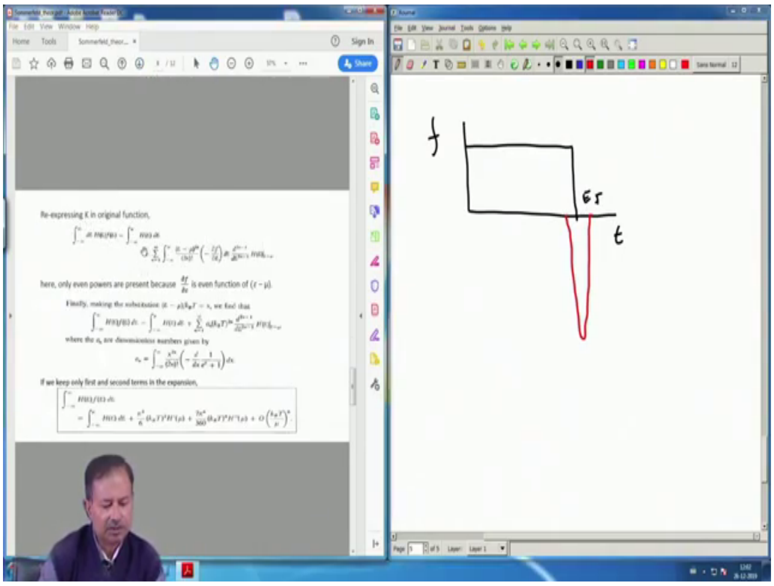

Re-expressing K in original function,

here, only even powers are present because $\frac{\partial f}{\partial \varepsilon}$ is even function of $(\varepsilon - \mu)$.

Finally, making the substitution $(\varepsilon - \mu)/k_BT = x$, we find that

where the a_n are dimensionless numbers given by

$$a_n = \int_{-\infty}^{\infty} \frac{x^{2n}}{(2n)!}\left(-\frac{d}{dx}\frac{1}{e^x+1}\right)dx$$

If we keep only first and second terms in the expansion,

$$\boxed{\begin{aligned}&\int_{-\infty}^{\infty} H(\varepsilon)f(\varepsilon)\,d\varepsilon\\&\quad = \int_{-\infty}^{\mu} H(\varepsilon)\,d\varepsilon + \frac{\pi^2}{6}(k_BT)^2H'(\mu) + \frac{7\pi^4}{360}(k_BT)^4H'''(\mu) + O\left(\frac{k_BT}{\mu}\right)^6.\end{aligned}}$$

.

So, this integral now can be rewritten in terms of this integral, first part up to mu which came from the first term; remember the this term is K of mu only it is a constant term. So, that will give me this term and because this is H is d K d remember. So, this integral will give me only K at mu, remember that is what I should get. The other terms are important now.

Now, you see that these in this other terms this part, what has been retained is only the even parts of epsilon minus mu to the power 2 n, 2 to the power n into 2. So, 2 n; because the odd powers all vanish because as I said that derivative, remember the derivative is a this derivative is of Fermi function is an even function.

So, I can only, I will even into odd over the entire minus infinity to plus infinity if you sum will give you 0 and that is exactly what has been used here, only the even terms have been written; which is just written below. Only even powers are written, because del f del E is an even function of epsilon minus mu, ok.

So, finally, you can substitute this one. So, this is just a substitution you do here this one, sorry epsilon minus mu by K B T is substituted by x. So, that then becomes an integral where you can term by term start integrating and that is what is being shown here. These are the coefficients, these integrals are not yet done, but this is an integral, remember this quantity x is a dimensionless quantity. So, whenever you have a quantity of this kind, integral these are dimensionless integrals.

So, that is that finally, leads to a, so the temperature dependence comes out and the final result that one gets is a result of this kind. So, this is the so called Sommerfeld expansion which is, sorry. Look at this result. So, this result for example, this gives me minus infinity to mu H E d E and then there are these corrections. These corrections are the order of order T square is the second term for example which is K B T whole square into pi square by 6 into H prime of mu.

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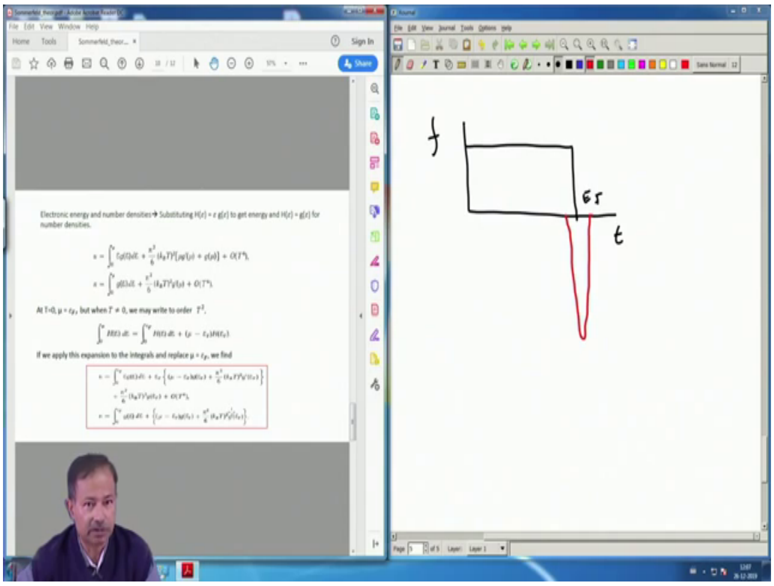

Electronic energy and number densities→ Substituting $H(\varepsilon) = \varepsilon g(\varepsilon)$ to get energy and $H(\varepsilon) = g(\varepsilon)$ for number densities.

$$u = \int_0^{\mu} \varepsilon g(\varepsilon) d\varepsilon + \frac{\pi^2}{6}(k_B T)^2[\mu g'(\mu) + g(\mu)] + O(T^4),$$

$$n = \int_0^{\mu} g(\varepsilon) d\varepsilon + \frac{\pi^2}{6}(k_B T)^2 g'(\mu) + O(T^4).$$

At $T=0$, $\mu = \varepsilon_F$, but when $T \neq 0$, we may write to order T^2.

$$\int_0^{\mu} H(\varepsilon)\, d\varepsilon = \int_0^{\varepsilon_F} H(\varepsilon)\, d\varepsilon + (\mu - \varepsilon_F)H(\varepsilon_F)$$

If we apply this expansion to the integrals and replace $\mu = \varepsilon_F$, we find

$$\boxed{\begin{aligned} u &= \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon + \varepsilon_F\left\{(\mu - \varepsilon_F)g(\varepsilon_F) + \frac{\pi^2}{6}(k_B T)^2 g'(\varepsilon_F)\right\} \\ &\quad + \frac{\pi^2}{6}(k_B T)^2 g(\varepsilon_F) + O(T^4), \\ n &= \int_0^{\varepsilon_F} g(\varepsilon)\, d\varepsilon + \left\{(\mu - \varepsilon_F)g(\varepsilon_F) + \frac{\pi^2}{6}(k_B T)^2 g'(\varepsilon_F)\right\}. \end{aligned}}$$

.

So, this, if you now use this Sommerfeld expansion to our problem which is the calculation of specific heat of an electron gas, degenerate electron gas, then you will basically get this kind of a result. So, the final result, as I said when T is not equal to 0; remember this second equation n equal to 0 to mu g d plus whatever it is, can be used to find the value of mu also in terms of n. It is can, it is often inverted to find mu in terms of n and it is correct to order T square.

So, finally, if you do all that and carry on doing the calculation as shown here; this integral you can this is up to E f plus the correction, the first correction to E f mu minus E f term. So, that has been incorporated and if you do it, you can finally, get these expressions for both u and n. As you can see they are still of the order of two order T square; beyond T squared terms are not included.

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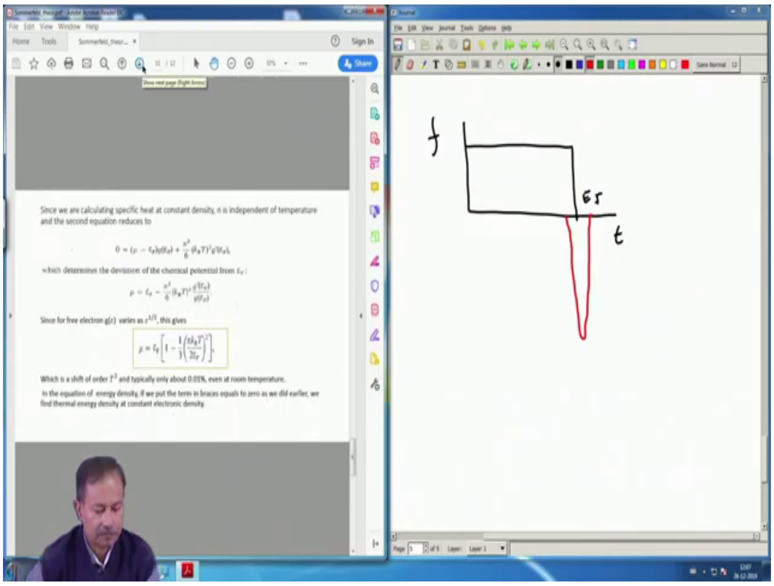

Since we are calculating specific heat at constant density, n is independent of temperature and the second equation reduces to

$$0 = (\mu - \varepsilon_F)g(\varepsilon_F) + \frac{\pi^2}{6}(k_B T)^2 g'(\varepsilon_F),$$

which determines the deviation of the chemical potential from ε_F :

$$\mu = \varepsilon_F - \frac{\pi^2}{6}(k_B T)^2 \frac{g'(\varepsilon_F)}{g(\varepsilon_F)}.$$

Since for free electron g(ε) varies as $\varepsilon^{1/2}$, this gives

$$\boxed{\mu = \varepsilon_F\left[1 - \frac{1}{3}\left(\frac{\pi k_B T}{2\varepsilon_F}\right)^2\right],}$$

Which is a shift of order T^2 and typically only about 0.01%, even at room temperature.

In the equation of energy density, if we put the term in braces equals to zero as we did earlier, we find thermal energy density at constant electronic density.

So, finally, you can actually make a correction, make the correction for the chemical potentials temperature dependence, chemical potential comes out to be of this one. So, remember see at zero temperature this is still E f, but there are corrections which are of order T square. So, order T, linear in T there is no correction to the specific heat to the chemical potential and beyond that the first correction appears to order T square in the chemical potential as a function of temperature.

And it is very very small actually, even at room temperature it is less than 0.01 percent. So, that is the reasons the correction to chemical potentials are generally ignored in most calculations, where you do not require extremely precise results. And that is why the linear in temperature dependence and the use of mu as E f in the approximate calculations that we did give us reasonably good results. And the factors of the T square dependence and in numerical corrections are far less than this first term that we already got.

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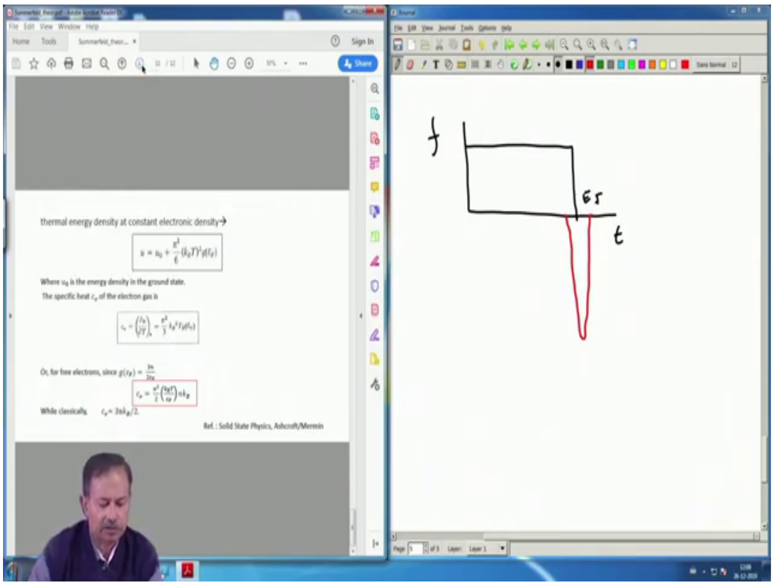

thermal energy density at constant electronic density→

$$\boxed{u = u_0 + \frac{\pi^2}{6}(k_BT)^2 g(\varepsilon_F)}$$

Where u_0 is the energy density in the ground state.

The specific heat c_v of the electron gas is

$$\boxed{c_v = \left(\frac{\partial u}{\partial T}\right)_n = \frac{\pi^2}{3}k_B^2 T g(\varepsilon_F)}$$

Or, for free electrons, since $g(\varepsilon_F) = \frac{3n}{2\varepsilon_F}$

$$\boxed{c_v = \frac{\pi^2}{2}\left(\frac{k_BT}{\varepsilon_F}\right) n k_B}$$

While classically, $c_v = 3nk_B/2$.

Ref. : Solid State Physics, Ashcroft/Mermin

But nevertheless for this is a historically important scheme of things, where you can systematically go and calculate higher order temperature dependences.

So, finally, the fact the result that you get for specific heat is this from Sommerfeld correction; this is the first term. And this term, see there you have to take a derivative of this and this will give you the first temperature dependent correction which is linear in T. So, as you can see that this is very very close to what I what our approximate calculation gave us.

And again if you can, if you put this free electron value g of E F equal to 3 by 2 3 n by 2 E F per unit volume here the small n is n by v. So, that will give you this final this boxed in red value of the specific heat in terms of the ratio KBT by E F which again I said takes care of the factor of hundred that we needed from the classical value.

Remember the classical value is just 3 by 2 n k B and so, you have a factor 100, one of 1 over 100 sitting here and that is exactly what we got from our previous calculation as well. But the advantage here is that in using these expansions you can go to higher order and calculate the corrections to chemical potential by temperature as well to order T square. You can actually go beyond that by retaining higher terms in the expansion; but then they become more and more complicated and cannot be handled analytically at all. So, that is the precise scheme of things that Sommerfeld adopted and he obtained these results correct to order T and then T square of so, ok.

So, let us now go over to a topic which is a fairly important for what we are going to do from now on. And that topic is the topic of bonding in solids and eventually the formation of a band. Now to do that what I will start doing is to just pretend that I have a solid of two hydrogen atoms.

Now, this is of course, a highly embellished version of a real solid; real solid has 10 to the power 23 atoms and many electrons in each atom and then of course, many orbitals to accommodate them. But, as we as I will demonstrate a very simple calculation of formation of a; for example, of hydrogen molecule starting from two hydrogen atoms which are far separated initially and brought close together, this kind of an approach gives you the basic idea that runs behind the formation of bands.

And there are many ways one can calculate these kind of things, there are many approximations; the simplest one is called the linear combination of atomic orbitals. And that in the context of band structure can be it is termed as tight binding approximation. And that is the simplest one that one actually does in most of the solids; of course, if you have bands large number of orbitals involved, then of course; you have to do a full blown calculation which we will come back later.

But for the moment we will just discuss the fact that when two protons with the two electrons in hydrogen atoms come close together they form a hydrogen molecule and why should they form it. And then carry on that idea the physical understanding they are off to the formation of bands in a solid of very large number of atoms, ok.

So, let us just start thinking about two hydrogen atoms.

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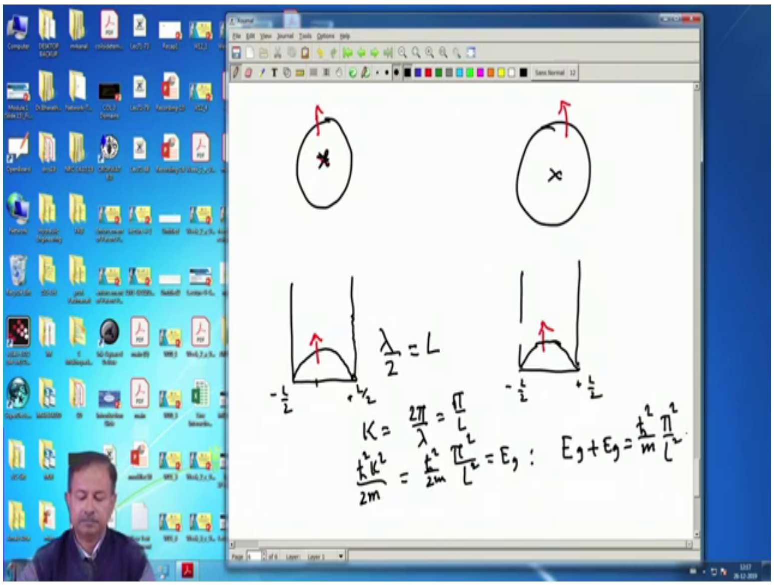

$$\frac{\lambda}{2} = L$$

$$K = \frac{2\pi}{\lambda} = \frac{\pi}{L}$$

$$\frac{\hbar^2 K^2}{2m} = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2} = E_g \; : \quad E_g + E_g = \frac{\hbar^2}{m}\frac{\pi^2}{L^2}$$

So for example, if I have in proton here an electron around it, another proton somewhere here and an electron around it. Now these are of course confined, they are confined within their orbitals. So, you can replace these two as I just to make a physical idea; let us first start with replacing these two electrons which are here, they may be in any direction in spins may. So, these two electrons are confined in a region of say Bohr orbit.

So, we can think of writing them just as a particle in an infinitely deep box here and here for example. This problem is solved everywhere in quantum mechanics books, it is a first problem you solve more or less. So, that is why I just want to bring out the physics of formation of a molecule; why should a molecule form for example.

Now, we all know how to solve this problem we can write the Schrodinger equation and we can then calculate the energies and so on and so forth, it is very straightforward. So, for example, minus L by 2 to plus L by 2 and if the electron is, because this is infinite potential the electron will be confined within the, was when the potential is zero inside. So, the we know also that the wave function will look like this, it has to vanish at the boundaries, right.

You will have this electron here, sorry. So, let us put these electrons here and here. We also can calculate the energy of these electrons trivially, very straightforward, because I know that this is the lower ground state wave function. So that means, lambda by 2 has to be equal to L, right.

Now, K is 2 pi by lambda. So, h cross square K square. So, this is 2 pi by 2 L. So, this is pi by L ok; h cross square K square by twice m is h cross square by twice m pi square by L square. So, this is the energy of the ground state, the lowest state at each of this infinite potential box. So, and this you have done in your class many times.

The now the question is, so the two electrons their energy is E g plus E g equal to h cross square by m pi square by L square. So, this is now the total energy of the system of two protons, two electrons with their parent protons in my blemished version of the theory, it is two electrons confined in infinitely deep potential electrons, deep potentials ok. So, particles in a box.

So, two such particles in a box problems I added their energies, because they do not contact each other, they do not see each other; there is no connection between these two. So, the total energy is this. Now, the question is what happens if I bring one close to the other if one approaches the other. So, let us see what we get.

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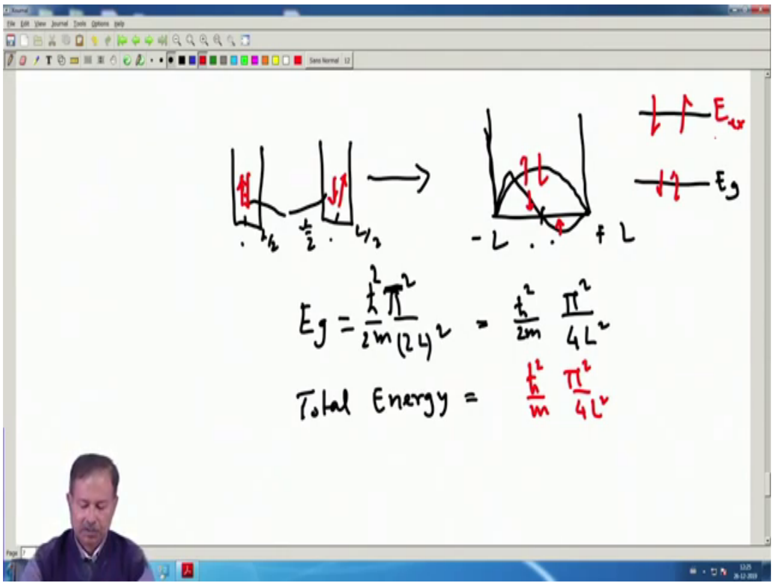

$$E_g = \frac{\hbar^2 \pi^2}{2m (2L)^2} = \frac{\hbar^2}{2m} \frac{\pi^2}{4L^2}$$

$$\text{Total Energy} = \frac{\hbar^2}{m} \frac{\pi^2}{4L^2}$$

.

So, now once they start coming closer; of course, the actual hydrogen atom, the potential is not infinite. So, the electron is in a finite potential. So, there is some leak of the wave function beyond this and there will be some overlap between this wave functions; this nuclei that are sitting here, here and here they will also start talking to the other electrons, so and then to themselves.

So, there is a mixing that takes is called mixing. So, this is, these two wave functions of the two electrons are now going to mix. And so, in the eventual scenario when a molecule is formed, then what one has is basically, a you can mimic it by these were both L by 2 from minus L by 2. Now, I have minus L to plus L and both the electrons are in the, under the influence of the two nuclei which are sitting below, they are pretty close now. So, I am forming a molecule, trying to form a molecule. So, it is two nuclei and then the two electrons will now go to this lowest ground state of the molecule.

Now, if I think of this again as an infinite potential problem, then I know the energy of this system. The energy is E g now is pi square h cross square by twice m pi square by 2 L square, right. Remember the energy that we got was, pi square by the total length square, h cross square by twice m into pi square by total length square.

Now, I will have the same thing here, h cross square by twice m into pi square; h cross square by twice m into pi square by the 2 L square which is h cross square by twice m pi square by 4 L square. Now both the electrons are in the same orbital now; so, this orbital total energy is basically just 2 times, this energy which is h cross square by m into pi square by 4 L square.

So, now you can see that compared to the previous one where I had where our energy was h cross square by m into pi square by L square. Now, we have the energy which is h cross square by m into pi square by 4 L square. So, the energy has gone down compared to the two independent atoms sitting far apart from each other.

So; that means, the formation of a molecule when these two electrons start talking to each other is the most appropriate solution for this problem, because you reduce the energy. Of course, this argument has two interesting aspects, which I do not know if you have noticed; one is that this when I had electrons here, they could be in any direction in spin. This could be up, this could be down or this could be down, this could be up and so on, right. So, this or both could be up, both could be down in the respective boxes when they were not talking, but when they start talking and they come to the same orbital, now you do not have that choice, ok.

So, what has happened is that, the eventual molecular or by, this is called the molecular orbital; in this orbital the both the electrons are to be put. And, Pauli Exclusion Principle tells us that you cannot have up and up or down and down kind of states, you can only have up down states or down up. The electrons are indistinguishable, so up down is the same as down up.

So, this system is now a spin singlet, it has no net moment; whereas, here in the when they were not talking to each other, they could be in any possible states, because they are completely different spins, right. So, they could be both off means the total moment you will find is 1, both down total moment you will find minus 1; total moment is 1, the projection is minus 1 and so on and so forth; up down will be 0 and down up will also be 0.

But here, there is only one choice that you have to put the electrons. So, the moment of the electrons now are not to be seen, it is in a singlet state. The other interesting thing is that, supposing I was not dealing with hydrogen but say helium; helium has two electrons and two protons of course. And then of course, I could still do the same calculation, but now I had these two electrons in these boxes.

So, I have to put in four electrons then of course, I have to go to the next higher energy state; and which the wave function looks like this and the energy is somewhere here. So, this is the lower energy E g, but now I have to put two electrons in this orbital. And so, these are all filled up, all four electrons has to be. So, this is the E excited, write it with red.

So, the few you can calculate the total energies and you will find that the there is not much again. So, this means that this kind of treatment that I am doing is restrictive; it is two helium atoms forming a molecule is completely different scenario that this theory will never give you that. And so, you have to remember that this is true for situations where you I have less than fully filled orbitals to deal with, for other cases we will take care of them separately.

But, this is just a caveat I wanted to you to remember that, for helium this kind of treatment will not give me the lowering of energy that I was looking for in a molecule.

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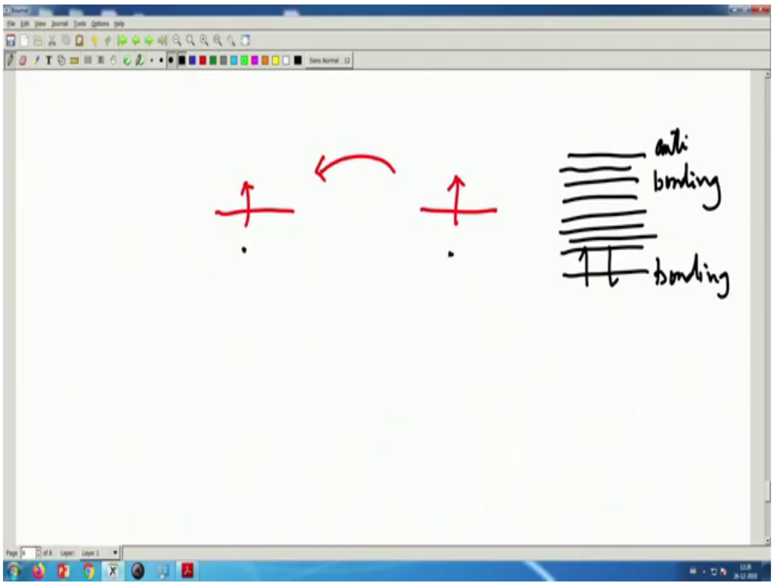

So, the point that I am trying to make is that, if you have two separate energy levels of two electrons sitting here. And if you bring them close, start approaching each other; then of course, you will mix them, these orbitals there is an interaction coming from their nuclei. And they also interact with each other, this right nuclei will interact nucleus will interact with the left electron and vice versa. And so, they say Hamiltonian that you have to write which involves terms, which are the kinetic energies of each of the electrons and then there the terms which are the interaction between the nuclei of the two electrons and of course, finally, the electron-electron interaction and the nucleus-nucleus interaction.

So, all that has to be written down and then one can start making approximation. And the idea that we got from the previous calculation is that, eventually you will get states which are one is below the state the two energies and the other is above these states. And you can now put two electrons in this state and gain energy.

Whereas if you have to, if you have more electrons you had to put it in the upper orbital and then you do not get much energy. This kind of a scenario which I will discuss in my next class by writing down the Hamiltonian, it is very common in chemistry and these are called bonding and anti-bonding molecular orbitals.

So, you can see already that there are now, I started with two orbitals, I got two orbitals; but there is a lowering in energy, because I could put two electrons in the bonding orbital which is the lower energy orbital. And that leads to formation of molecules and eventually if you increase the number of sites, number of such atoms to very large number. Then of course, you will get band formation, where you will have all sorts all the orbitals coming in between these all the wave functions from each of these atoms will come within this range. And there will be 10 to the power 23 orbitals states within this range, between the bonding and the anti-bonding orbital and you will have a so called band formation. So, that is what I will come to in my next class.

Thank you.