Principles and Applications of Electron Paramagnetic Resonance Spectroscopy

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Lecture - 23
Theoretical Basis of isotropic Hyperfine Coupling

In these series of lectures we have seen many EPR spectrum, we have analyzed some of them and measured the isotropic hyperfine coupling constant for some of the spectra. We found the values are different for different nuclei.

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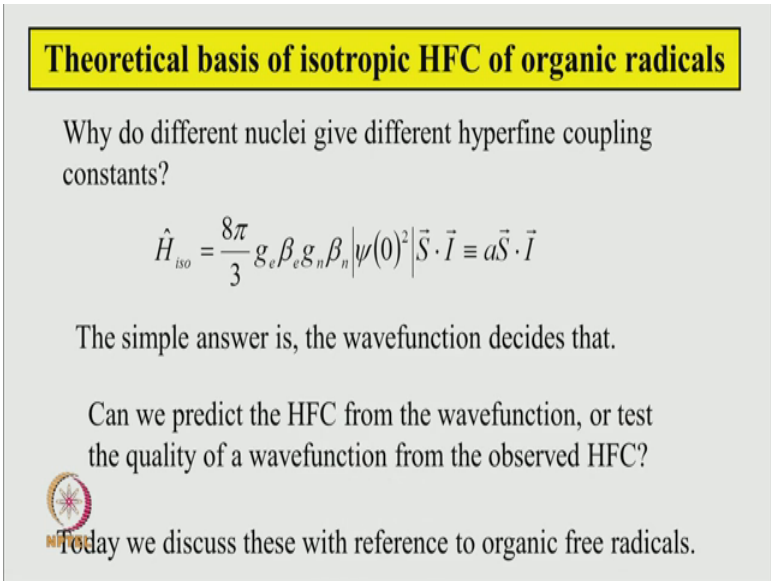

So, today we are going to ask this question why the different nuclei give different hyperfine coupling constants. So, what is the theoretical basis for isotropic hyperfine coupling constants? Of course, the simple answer will be that these type of interaction; that is contact interaction which give rise to hyperfine coupling constant.

So, here the wave function decides the hyperfine coupling constant. Then can we predict the hyperfine coupling constant from wave function? Or if you have the measured value of coupling constant, can we test if the theoretically calculated wave function gives similar values? So, today we are going to discuss these issues in reference to organic free radicals.

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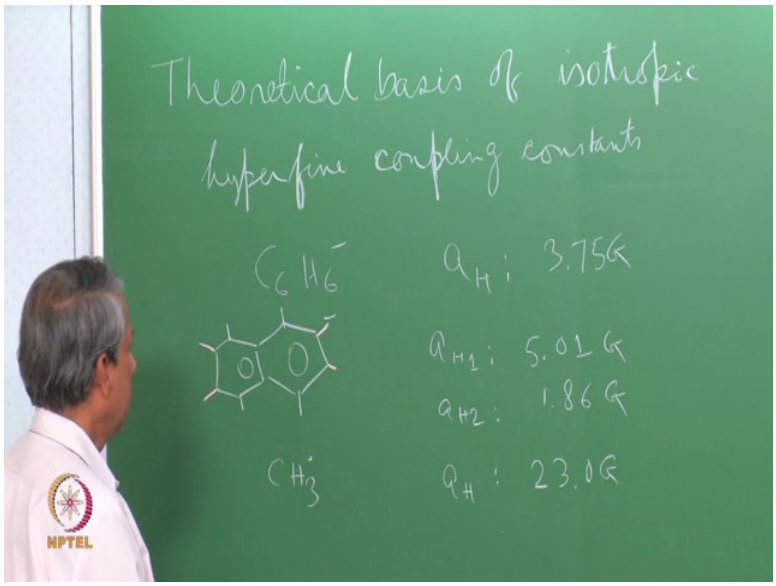

Let us take a few examples of some known coupling constants, this benzene anion radical; this we know that it gives; several line spectra and the hyperfine coupling constant is, let us call a H is equal to 3.75 Gauss. If you take naphthalene anion radical is got two sets of equivalent nuclei, so the coupling constants are; it is equal to a H 1 is 5.01 Gauss and a H 2 equal to 1.86 Gauss.

Compared to that, if we take the case of methyl radical, which is 3 equivalent nuclei; this coupling constant is equal to 23.0 Gauss. So, you see the values are quite different; here this two coupling constant corresponds to of course, two different set up equivalent nuclei. So, if you mark them; we will use colour chalks; this, this, this, this they have one group of equivalent nuclei and these are other.

So, from the experiment we will get these values, but there is no way we can assign the value; that whether this belong to one set or this belong to other one. So, can theoretical calculation help us assigning this? So, that is the aim of today's lecture, try to connect the observed value to some theoretical model of wave function which can either credit this or help us assign this or we can check if this is the value; how good the wave functions are if it is able to make this sort of prediction.

Immediate major problem, if we take the stand that the hyperfine coupling constant that we have been saying again and again comes from this to the contact interaction.

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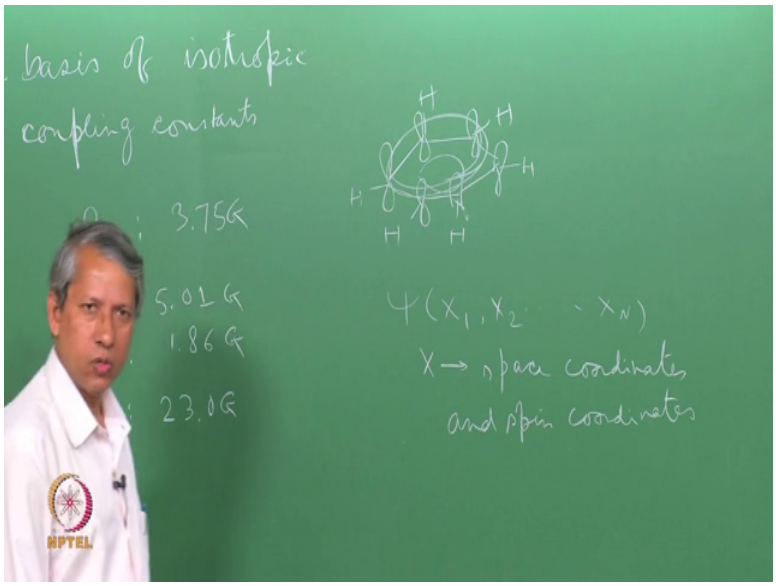

So, you mean the trouble is that if you take this aerobatic hydrocarbon for these; this protons which are coupled they in fact, lie in a plane where the molecular orbitals; the one which actually suppose to hold on the unplugged electron that molecular orbital has exactly a nodal plane, where this protons are lying. So, in this simple minded molecular orbital; these protons cannot give any splitting, but we do see splitting. So, you see that immediately there is a problem that the wave function which gives this set of electron distribution cannot predict these hyperfine coupling constants.

So, does it mean that we have to do very sophisticated quanta numerical calculation to arrive at that? Luckily there are very simple molecular orbital concepts, which can be used to make very good predictions of the coupling constant that this sort of nuclei can give, we need to understand a few simple key concepts.

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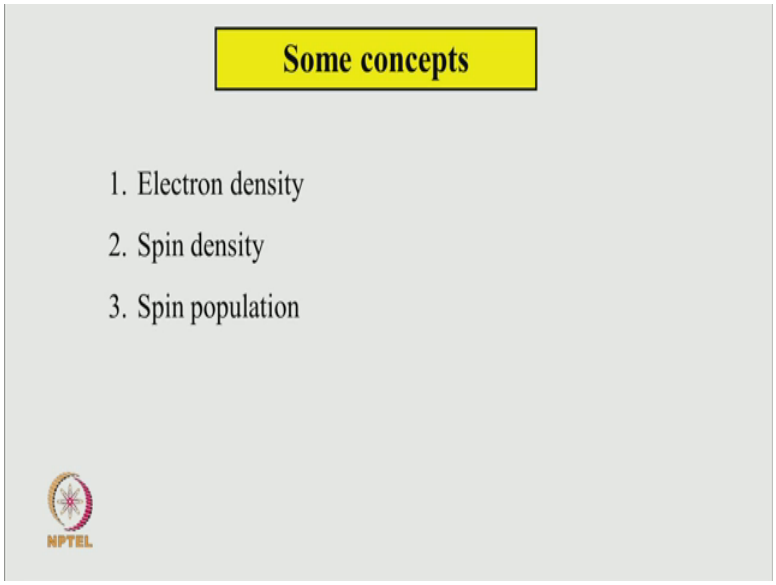

That is here; the concepts are electron density, spin density and spin population, let us see what they are. So, if we have an N electron system they are given by a Y function of these kinds, which will have coordinates of all the electrons. And this coordinate X include the space coordinate and spin coordinates; by spin coordinates I mean whether it is alpha or beta spin. And this should have all the information that we can think of; about the system.

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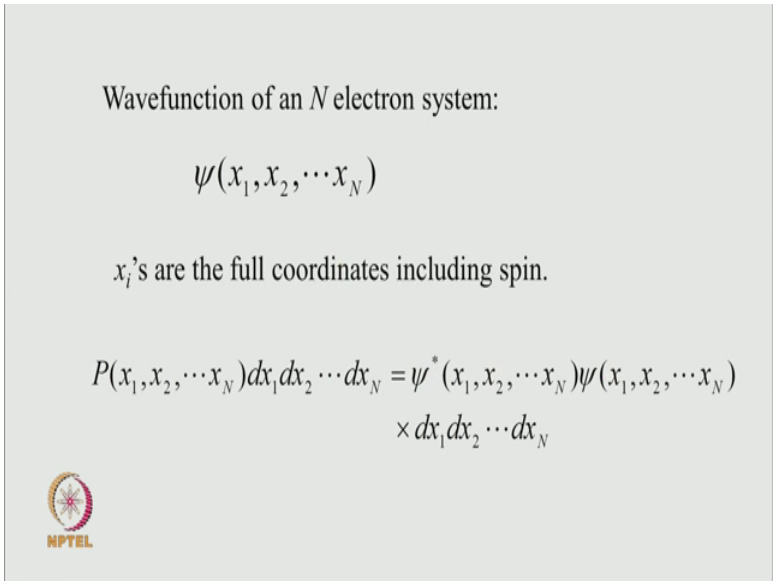

So, wave function for N electron system can be written in this fashion, now here the x i are the full coordinates.

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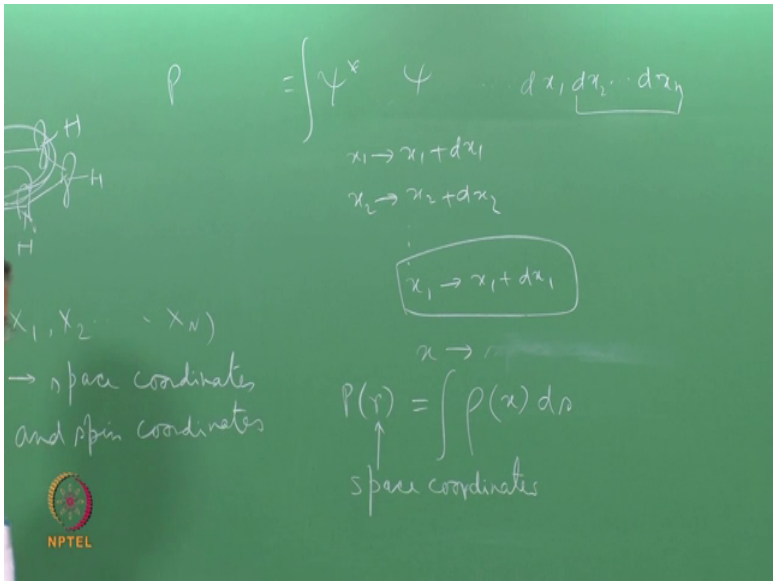

So, for this the meaning of this psi star psi is that; psi star psi with all the coordinates here is that you have a volume element given by d x 1, d x 2, d x n; this gives the probability that electron number 1, will appear in the volume x 1 to x 1 plus d x 1; electron 2 will appear in a volume x 2 to x 2 plus d x 2 and so on. Again this x's are the full coordinate constitute space and spin; so, that is the meaning of this psi star psi.

Now, if I want to find out the probability of finding electron 1 in a space x 1 to x 1 plus d x 1; irrespective of where the other electrons are, then what I should do? Is to integrate this function, with respect to all the rest of the coordinates; leaving this aside.

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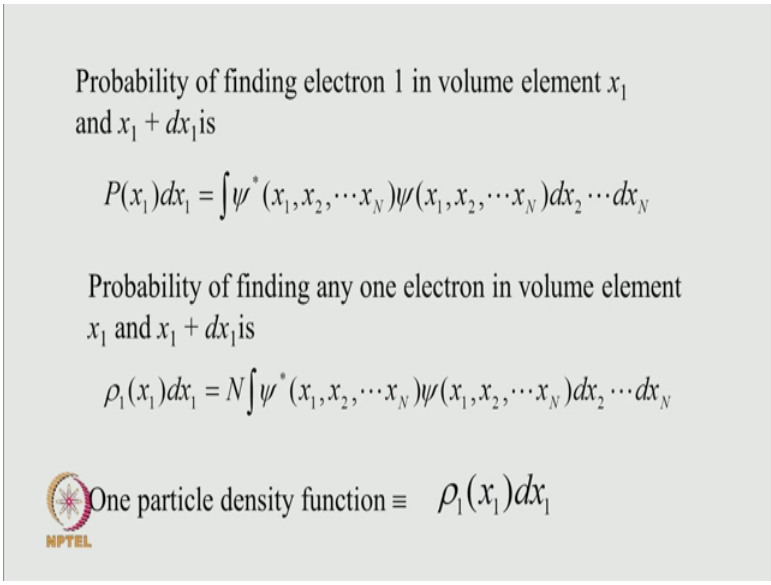

That is written here; that is probability of finding electron 1 in a volume element x 1 and x plus d x 1 is given by this integral central, where integration is done with respect to all the coordinates other than the electron number 1.

Now, from this I can ask the next question is that what is the probability in this volume now? Not the electron number 1, but any electron can come. Since there are N electrons, then any of the electron 1 to N can appear there. So, that probability of finding any one electron in a volume element x 1 and x 1 plus d x 1; N times this value and we call this one particle density function; written as rho 1; x 1, d x 1.

So, this gives the density function for any electron to be available in the volume element x 1 to x plus d x 1. As I said that x has space and spin coordinate, so if I integrate this rho with respect to only the spin coordinate; then I will get a function which will be function of only the; let us call it r, this is the space coordinates.

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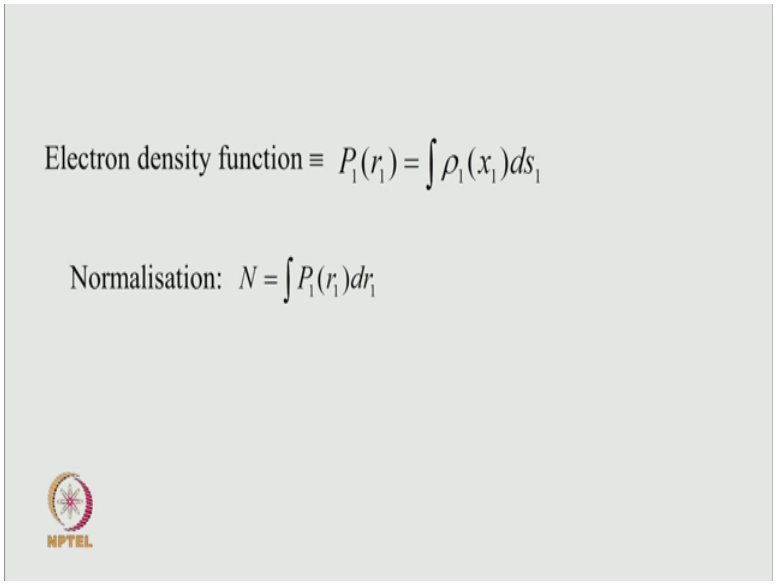

And that is nothing but the charge density, where having integral respect to the spin coordinate here. So, this is called electron density function P 1, r 1 integrate respect to this space. So, this gives a probability of finding any electron in this range of volume given by r 1 to r plus d r 1; naturally now somewhere all possible space that will give me the number of electrons that in normalisation condition.

So, to understand this abstract concepts; let us take a simple example of 3 electron system.

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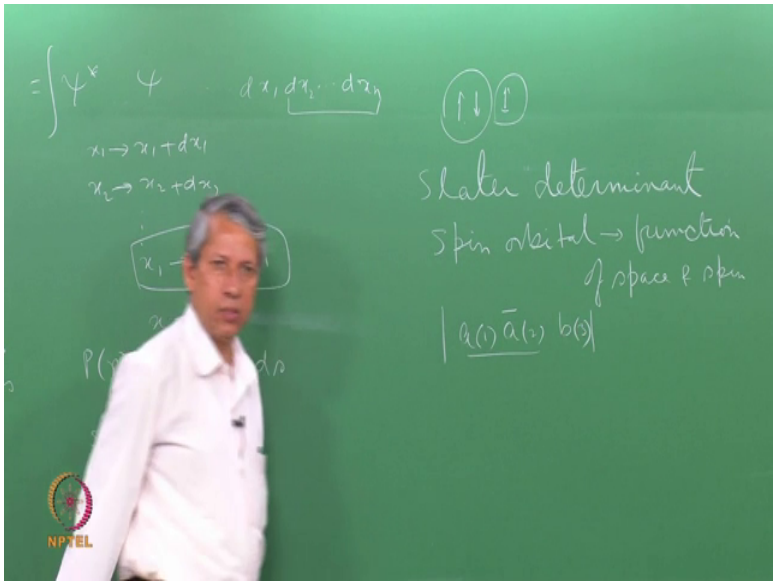

3 electrons such that two are paired, one is unpaired. Though a function for a many electron system are written as a determinant form called slater determinant; in which for each electron, we use a spin orbital; which is a function of, again this function of space and spin and the determinantal form is written in terms of this, if there are 3 electrons we need 3 spin orbitals.

So, here we use this a, a bar and b and electron number 1, number 2 and electron number 3. So, these are the spin orbitals and where the difference between a and a bar is that; this has alpha spin function, this has beta spin function this also has alpha spin function; so, that is shown in this slide.

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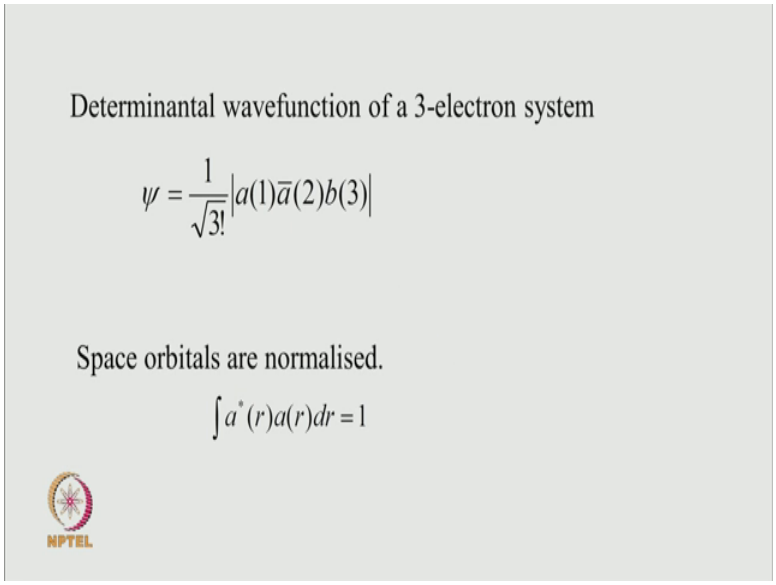

If we expand this determinant, then you get the full form of the function. We also use the space orbital a and b; they are orthogonal and normalised to 1. So, you see that because of this same space part is used for 1 and 2, this electrons are paired and a only one electron unpaired which is by a spin orbital b or the same the same thing differently space orbital b with and alpha spin function.

So, here now we again go through this set of calculation that to find the one particular density function and then charge density function or electron density functions; we expand it and multiply psi star psi type of form here and integrate respect to the other two electrons. So, what is the one particle density function we can find out from these 3 electron system.

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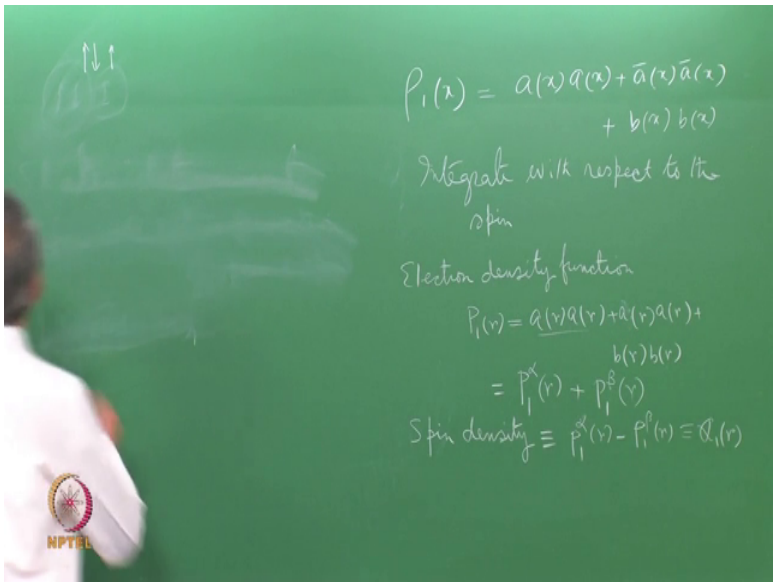

And if we do that; one particle density function turns out to be a x, a x plus that is how it turns out to be. So, in a sense it should be implicitly clear that is how it should be; that electron 1 stays is spin orbital a, electron 2 stays in spin orbital a bar, electron 3 stays in spin orbital b. So, one particle density function has exactly square of this, square of this and square of this one but that will come out; naturally if we simply multiply with the function with this conjugate and integrate respect to coordinate 2 and 3.

So, if I integrate now this with respect to the spin part; we get the charge density or electron density, function a r, a r plus; this is also understandable that this one integrate with respect to electron spin, this alpha spin will integrate to 1, this beta spin will also integrate to 1 and this will integrate to 1, so this third concept to be; this is the charge density electron or electron density function which looks like this.

Now this is same as you see that; this comes from the alpha spin this also comes from alpha spin; these comes from the beta spin. So, you can write it as; the electron density function coming from the alpha electron plus again 1 electron density function coming from the beta electron.

So, with this in mind that the electron density ultimately comes to be a sum of densities that come from the alpha electron and the density that come from the beta electron, we define spin density; is defined as p alpha; r minus p beta r; that is the difference of the

density of alpha and beta; that is the spin density function. So, what we have here now for this 3 electron system?

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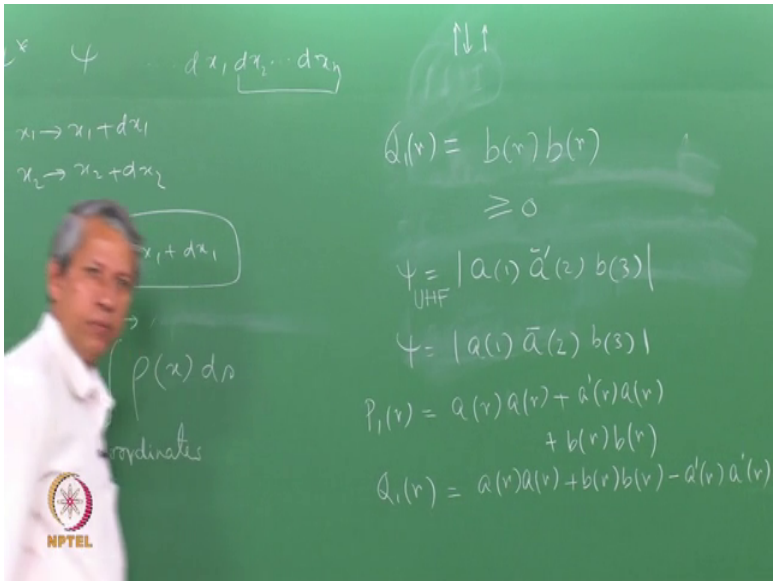

Paired and one unpaired electron; here the spin density function, this is written as Q 1; r. Q 1; r becomes, so the difference between alpha and beta spin state. So, alpha comes from this, this and this is the beta; so we subtract alpha and beta this comes out to be beta beta, this is the spin density.

So, the value that I can get for such type of expression you see; it will be the always the square of some number. So, this is always going to be greater than or equal to 0; so, you cannot get a negative spin density for such type of wave function. We will see later that spin density, the way it is actually going to influence the observed hyperfine coupling constant; can be negative.

So, this picture therefore is not sufficiently broad to predict negative spin density because is going to (Refer Time: 18:55) the square number positive therefore, so we can immediately think of improving this wave function; a 1; a this is prime bar and b 3 what is the difference? The earlier wave function was; this here the alpha and beta this paired electron have the same spatial part, only difference in the spin part; by putting a prime here, I use a different spatial part for the alpha spin and beta spin. So, this is a method which is called unrestricted (Refer Time: 19:59) of method where the alpha and beta electrons, which are paired need not occupy the same spatial orbital.

So, now with this one; if we do the same calculation now p 1; r will be and then the Q 1 r will become; again the same definition, they are the difference between the alpha and beta population that will be here. So, in this condition as the spatial part for alpha and beta are different, this need not be same as that. So, these can be both positive and negative; so this is the one way of having the possibility of generating negative spin density.

Other way would be that instead of having a single determinant to represent the wave function, one can get more than one determinant and some of that which is called the configuration interaction type of wave function; that can also predict a negative spin density. So, the spin density the way it is defined now that Q; if we integrate with respect to all space.

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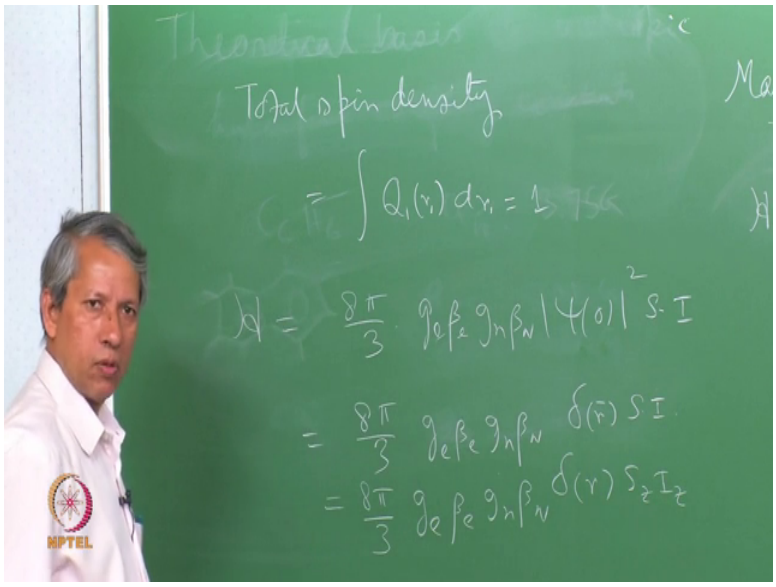

That is total spin density; that will give me just the number of unpaired electrons, this particular case only 1 is there; so, this is only 1. So, that way total spin density must sum to 1.

Now, for calculating the hyperfine coupling constant; how do we go about? The Hamiltonian for that is g e; beta e, g n beta N; psi 0 square; S dot I, this was for a single electron and the probability of find the electron and the nucleus. Now here we are going to integrate over that space; so we should immediately make some modification here that when integrate whenever it is necessary, this will give the same result.

So, this could be written as g e beta e g n; beta N, delta r sum delta function with respect to space coordinate r; S dot I. So, this will have precisely same result like that, the way delta function gives non zero contribution; only when the r itself is 0. Again this is for 1 electron case; if I have many electron, then I must do the same thing for all the electrons therefore, that I can write; I will write it here.

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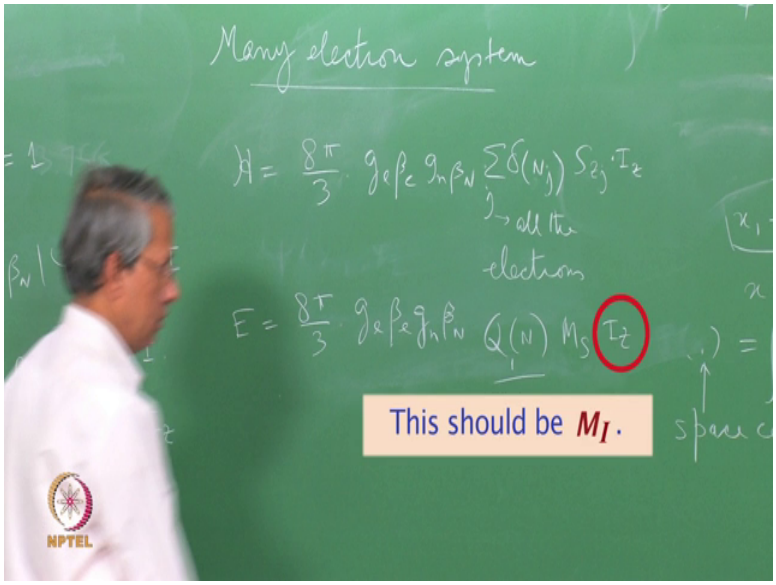

I basically sum over all possible electrons which are going to interact with one nucleus. What does it mean? It is a simple generalised of this; that this j is corresponds to all the electrons. And this is the electron density at the nucleus for the j-th electron; that is the meaning of this. And this is the spin angular momentum, operator of the j-th electron. So, what I have done here and going from here to here is that I have put a z; I z here; that is possible if the interaction is not very strong.

So, that the first order calculation is good enough then this same thing could be written as S z; I z; first order calculation, so this give rise to the expression which is here. So, if you calculate the energy; this Hamiltonian that energy will be beta N and what it will give? It will give me, this will give me this, spin density; one particle spin density at the position of the nucleus.

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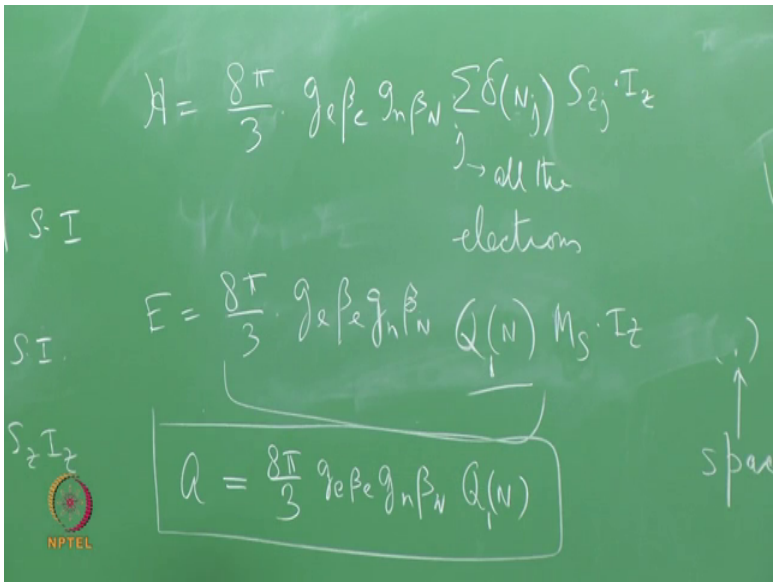

So here therefore, we can associate this to our hyperfine coupling constant a; therefore, can be written equated to this part of this expression, but this is the one we are trying to arrive at.

This connects now, the observed hyperfine coupling constant to the calculated spin density at the nucleus. Now this calculation will depend on the type of wave function we can use here; that is either this or even better than that. So, the connection between the theory and experiment is this; that this is experimentally measured, these is theoretically calculated and see how well they match.

So, I can use the theoretically calculated value to assign its various coupling constant to various different nuclei in a molecule. Or having measured the value and assign it, I can see how well my calculations are; are they well to predict such measured values. So, theory and experiments are breezed in this relationship. From this, few ideas that is spin density, electron; charge density we need to extend this concept just little bit more, where we deal with the wave function which is of course written as a determinantal form.

But often these determinantal forms are made up these molecular orbitals and molecular orbitals are in turn written in terms of atomic orbitals. So, we want to relate these concepts to ultimately the spin population in an atomic orbital. Now let us look at the slide now.

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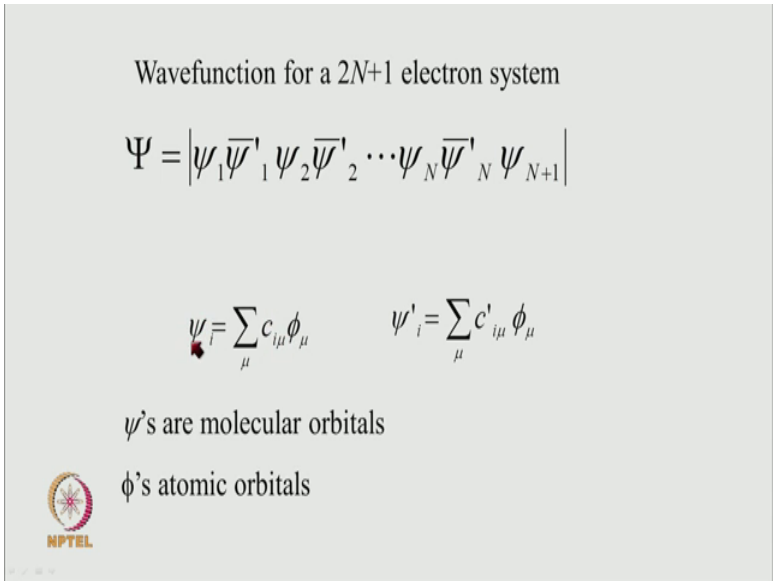

So, this is let us say total wave function for a 2 N plus 1 electron system; here psi 1, psi 1 bar with prime, psi 2, psi 2 bar with the prime. Each of them have paired electron only one is unpaired at the end here. So, this electron is unpaired; all the other electrons are paired, we have put the beta electron; molecular orbitals with the prime, we will see in a moment; why it is convenient to distinguish them; not just by bar, but also with the prime.

So, these molecular orbitals are written now in terms of the atomic orbitals; this phi's are the atomic orbital. So, they are the corresponding coefficients for I have given molecular orbital here.

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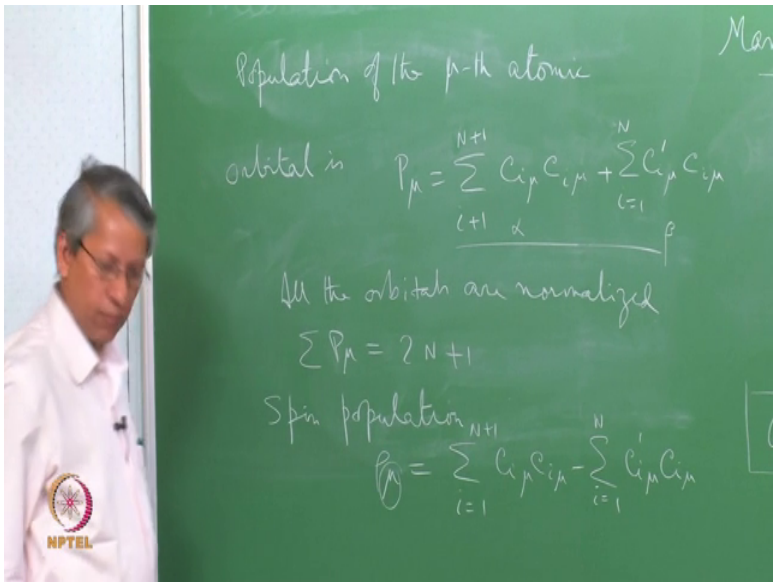

So, with this or population of the mu'th atomic orbital; orbital will be given as the coefficients of this here; see the mu'th in the psi I molecular orbital, the phi mu has the coefficient C i mu. So, here see that our wave function has 2 N plus 1 electron and all this N electron; 1 to up to this N; they have got alpha spin plus one more extra also is alpha spin.

And other N electron; psi 1 prime, psi 2 prime; they have got better electron. So, this population of the mu'th atomic orbital is actually sum of the alpha electron and the beta electron and square of this is a coefficient of the atomic orbital there. So, as all the orbitals are normalised, so we can get this is equal to 2 N plus 1. So, with this type of atomic orbital population, I can write now the spin population.

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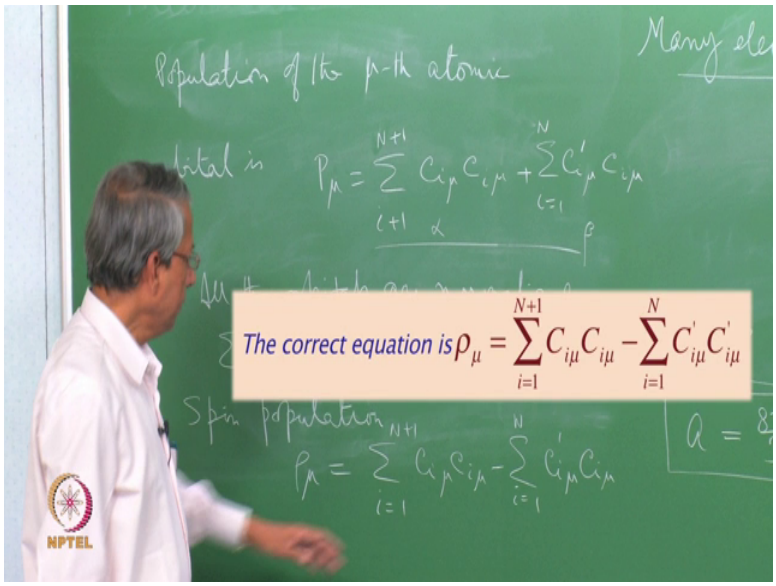

Which is the difference between alpha and beta spin state; spin population. So, exactly same thing we did earlier, when we took the difference between alpha (Refer Time: 33:04) spin density. Now it is spin population on a particular atomic orbital mu here that is the way it is. What we have in mind is that if we know the atomic orbital and the corresponding coefficients, we can calculate the spin density or and spin population on a particular atom.

Now in a Huckel molecular orbital; all the paired electrons they occupy the same space orbital.

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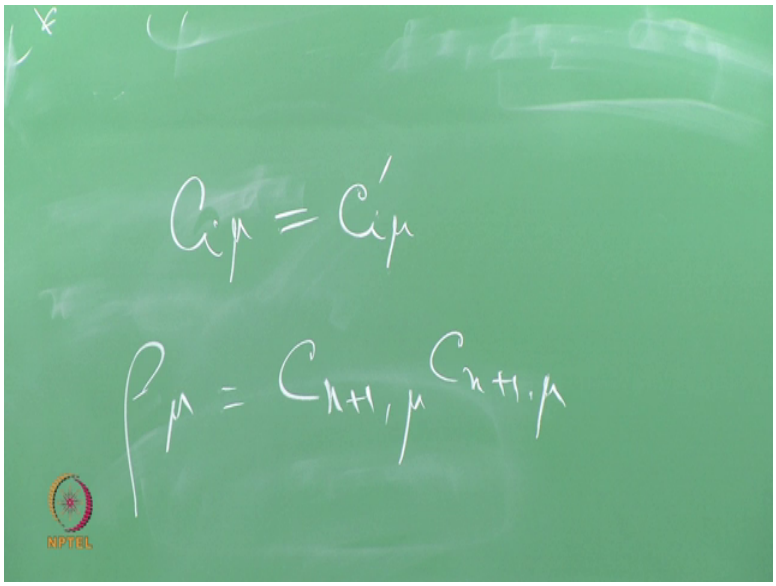

So, for them the C i mu and C prime they are same; so, this will all cancel each other and only thing that will be left here is the single electron, which is unpaired. So, the rho mu will be C n plus 1; mu and C n plus 1 mu. So, with this now let us make some connection to Huckel molecular orbital see how much it can predict the observed splitting constants.

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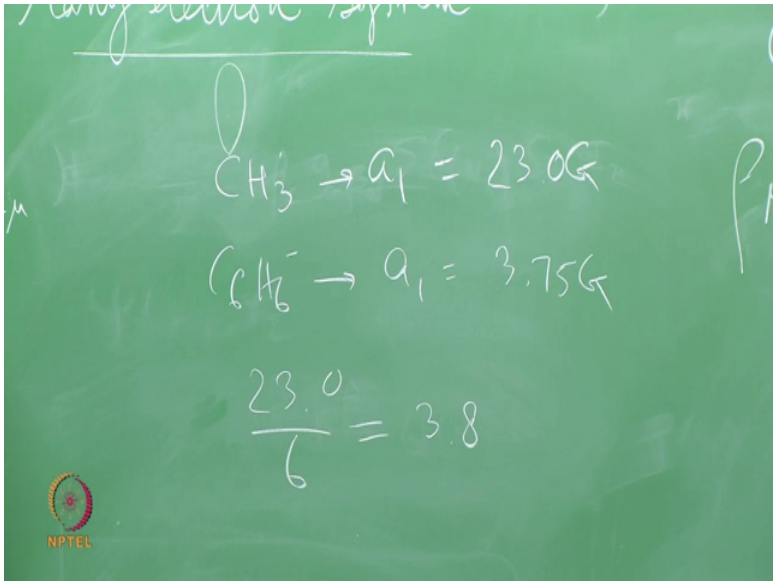

When we have seen earlier; methyl gives a hyperfine coupling constant equal to 23 Gauss and benzene gives the a 1 equal to 3.75 Gauss and methyl radical; the electron is basically staying in one 3 hybrid orbital. And here this one electron is occupying a pie

orbital; so, 6 such protons are there. So, it will spend one sixth of its time around this 1 proton.

So, from this relationship the one sixth of this happens with this you see; this very nearly equal to 3.8; so value is very similar. So, it somewhat shows therefore, that the spin density near the carbon atom is correlating with the observed hyperfine coupling constant. Is it true for other organic radical or not?

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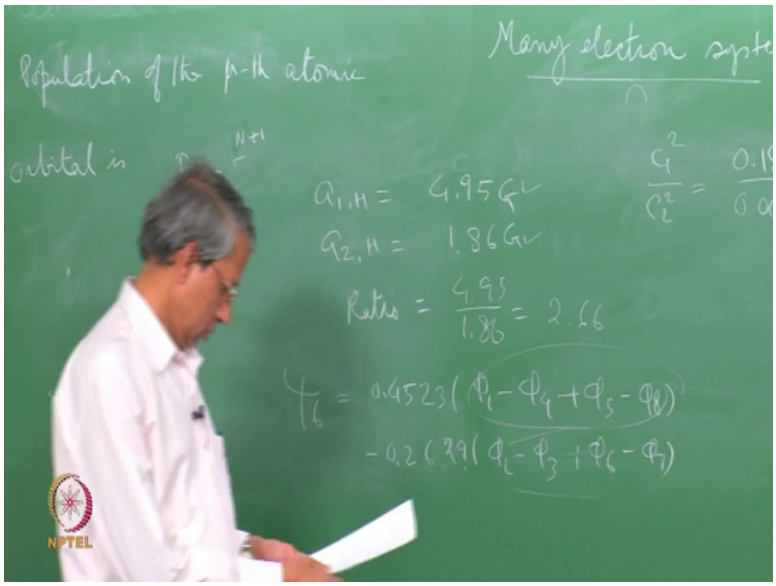

Naphthalene, which we saw earlier the a 1; H was 4.95 Gauss and a 2; H was 1.86 Gauss between the ratio of this ratio, which is 2.66. For naphthalene, the orbital which occupies the unpaired electron here; that is why this sort of contribution from various atomic orbitals, the ratio of this spin density will be square of this divide square of this.

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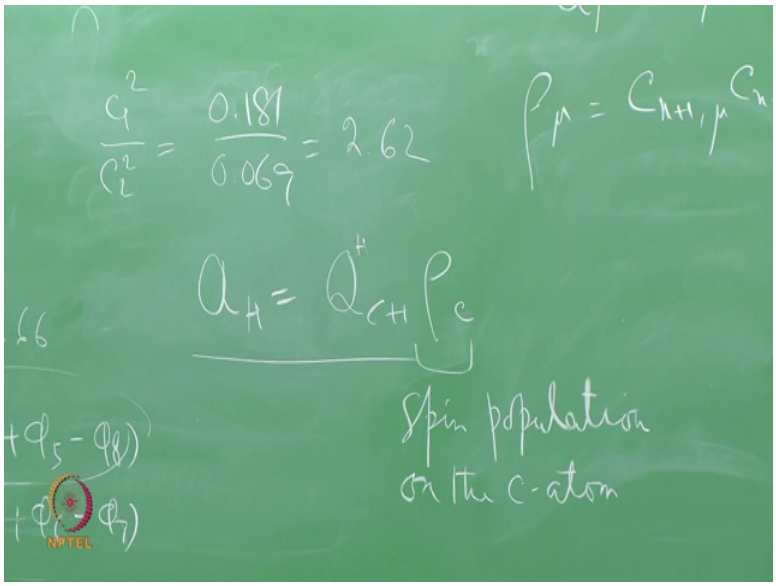

So this will be; when you a come to 0.181 by 069 which is 2.62 and you see how well these are matching. So, this also shows that the spin density of the carbon atom, governs the observed hyperfine coupling constant. And here because all four have a same coefficient, they have also similar coupling constant. So, I can associate therefore, that these four have this coupling constant and these four have this coupling constant.

So, from this; this has been found for many many such organic aromatic hydrocarbon, a radical. So, I can write a of H; the observed hyperfine coupling constant is some sort of constant times, the carbon hydrogen parameter; some Q parameter, times the spin population on the carbon atom; this stands for the photon hyperfine coupling constant, this is the spin population on the carbon atom.

Thus, form imperially true; so, though it is imperially true; how does it work? Because our fundamental problem still remains that the molecular orbitals has a nodal plane where the atom is sitting there, so it just cannot give rise to such splitting. So, the wave function has to further improve to take that into account and the way it is done is now shown here.

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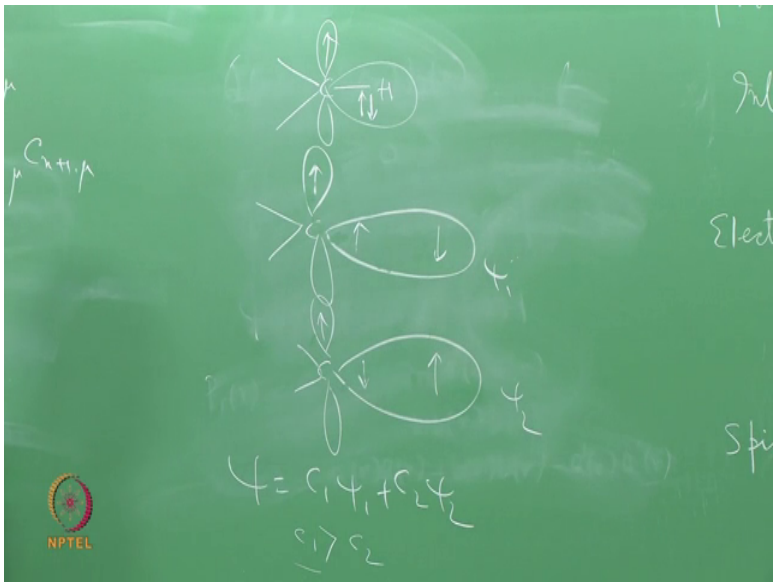

Let us just consider only the fragment of this benzene type of fragment; only 1 electron is sitting in this p orbital, which is part of the p molecular orbital and this sigma bond has the C H group, which gives the hyperfine splitting. So, the way it goes is that; because this is plane a nodal plane here, this cannot give any splitting because of this. Let us see whether I can get some spin density here. So, for that it is this electron is here and this move the electron are paired, but I can think of a situation that expand this one; one electron here, other electron there and other is that; this electron down, this electron up and here.

So, both are same essentially; so nothing different, but if there is no difference in energy between these two, of course they will contribute equally to the; these are the wave function that I can write here, which is linear combination of let us say psi 1 and psi 2 and total psi can be written as C 1, psi 1 plus C 2; psi 2. And if they are equally energetic, then this will be same as this one and there will be no resultant spin density here.

But it so happened that this one is just a little bit more stable than this one. So, that C 1 is just a little bit more than C 2; why is that? Simple qualitative argument is that you see these two electrons are parallel here, these are anti parallel. The two electrons are parallel, give rise to more stability that concept is used here.

When two electrons are parallel give more stability, there is a (Refer Time: 41:09) rule of fact, so even though these two either is looking very similar; this little possibility that

these two parallel being slightly more stable; give rise to this. So that means, I can get a net spin population appearing here, these are not cancelling now.

So, that way one can generate a net spin population here which can give rise to hyperfine splitting, so it is possible. This has to be now implemented in the wave function, so we define the wave function by; not just sticking to the ground state configuration that we have, but we can mix some (Refer Time: 41:50) state and get a better quality wave function, which will give this sort of spin population, which is appearing here.

What is more? This also shows that if the overall space system has a alpha spin state; these produces a better spin state here. So, the spin density here is negative for psi system that also has been seen experimentally. So, here this lecture we have seen how the wave function can be used to predict the spin densities or the calculated values can be used to assign the various observed values to different nuclei. And the wave function can be improved, if there is no matching between the observed value and the calculated value by doing improved calculation.

Now, with this we come to the end of this lecture and it is taken from this textbook.

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