Principles and Applications of Electron Paramagnetic Resonance Spectroscopy

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Lecture -14
Theory of First-order EPR Spectra - I

Hello. Today we are going to discuss the quantum mechanical treatment of various interactions of an atom. And the atom is the simplest possible atom we can think of that is hydrogen atom. Why you discuss this? Because the simplest system which is paramagnetic. So, to discuss any quantum angle properties we must start with Hamiltonian.

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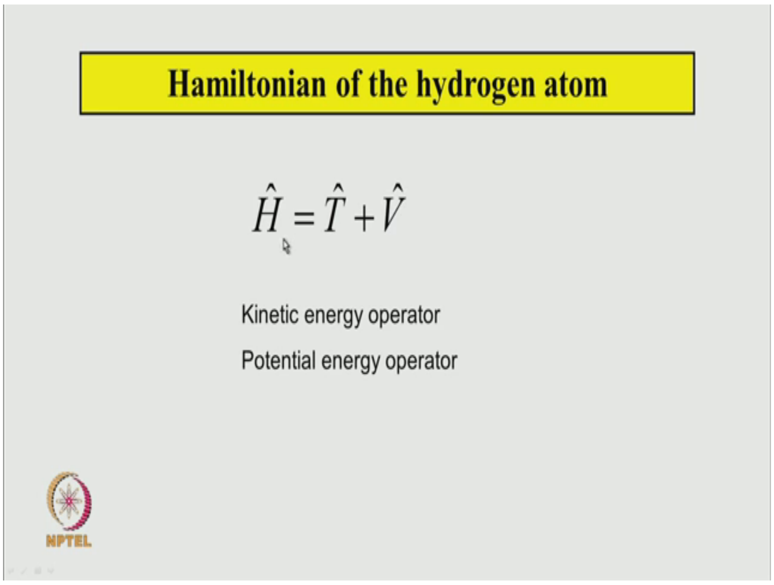

Hamiltonian of the hydrogen atom

$$\hat{H} = \hat{T} + \hat{V}$$

Kinetic energy operator
Potential energy operator

So, what is Hamiltonian of the hydrogen atom? As you all know Hamiltonian operator is a sum of this kinetic energy operator and the potential energy operator. What the hydrogen atom?

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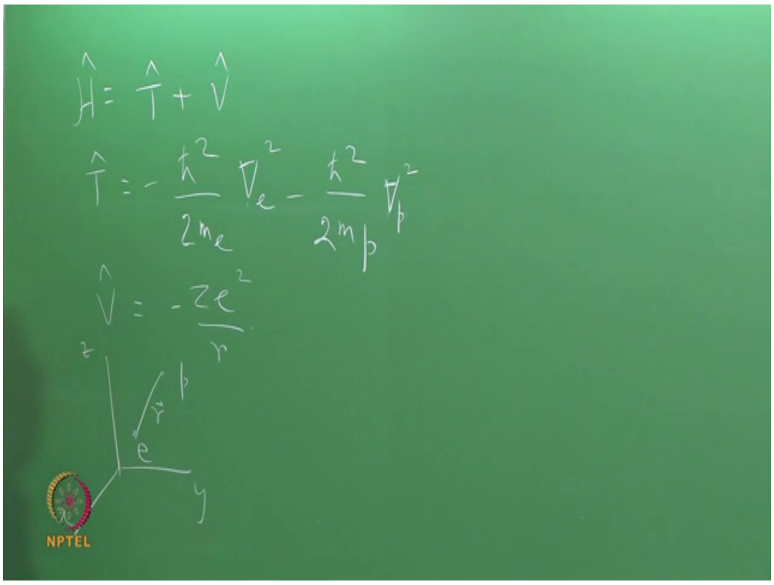

$$\hat{H} = \hat{T} + \hat{V}$$

$$\hat{T} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_p}\nabla_p^2$$

$$\hat{V} = -\frac{Ze^2}{r}$$

It is T and v can be written as the kinetic energy operator is kinetic energy of the electron, and the kinetic energy of the proton. So, this will be this is the kinetic energy operator for the electron, and kinetic energy operator of the proton. This at the laplacian operator and the potential energy v is the coulomb attraction, between the 2 say this is minus z e square by r; where r is the distance between the electron and proton; so in particular coordinate system, if I have x y and z. Let us say here the electron is sitting here proton is sitting then this distance is r. And for each of this coordinates here and here. I have got corresponding operators.

Now, in magnetic resonance, we really do not worry at all about these type of interactions. These are treated to be a constant energy that the system has. What we are interested in is over and above this interaction, what are the magnetic inter sense, which are responsible for the magnetic resonance spectrum in general, and EPR spectrum in particular. So, these terms are not used at all they are just giving rise to a constant energy of the system. So, what are the magnetic interactions that this atom has? So, if we put this hydrogen atom in magnetic field, then the interactions that we can think of is the Zeeman interaction here.

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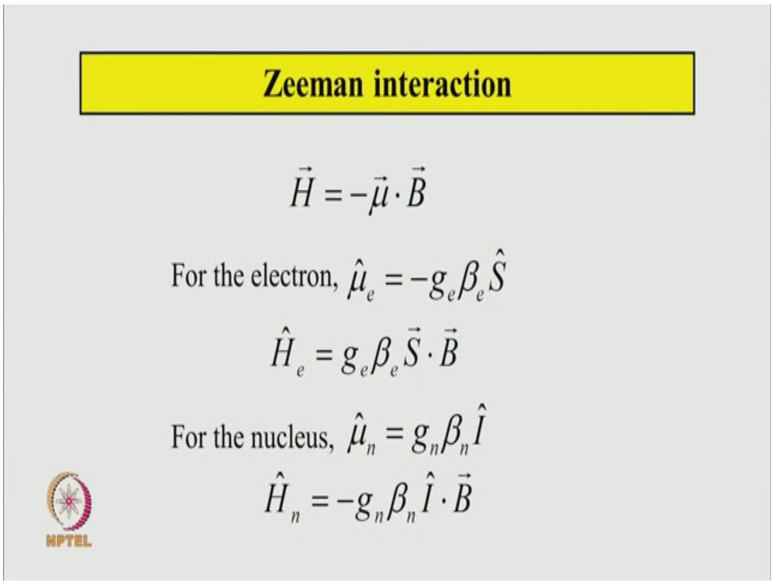

Zeeman interaction

$$\vec{H} = -\vec{\mu}\cdot\vec{B}$$

For the electron, $\hat{\mu}_e = -g_e\beta_e\hat{S}$

$$\hat{H}_e = g_e\beta_e\vec{S}\cdot\vec{B}$$

For the nucleus, $\hat{\mu}_n = g_n\beta_n\hat{I}$

$$\hat{H}_n = -g_n\beta_n\hat{I}\cdot\vec{B}$$

So, this is the magnetic moment interacting with the magnetic field give rise to the corresponding operate energy. So, for electron the magnetic moment comes from the spin angular momentum and this is the relationship. So, it is operator for Zeeman interaction is g e beta e S dot B. Similarly, for the nucleus it is g n beta n I is the magnetic moment of the nucleus. So, that gives the Hamiltonian for the nuclear Zeeman interaction which is g n beta n I dot B

In addition, there is another interaction that is possible which comes from the magnetic dipole dipole interaction I one that is a magnetic dipole coming from the proton, another magnetic dipole coming from the electron. So, this 2-magnetic dipole can interact. And that is shown here.

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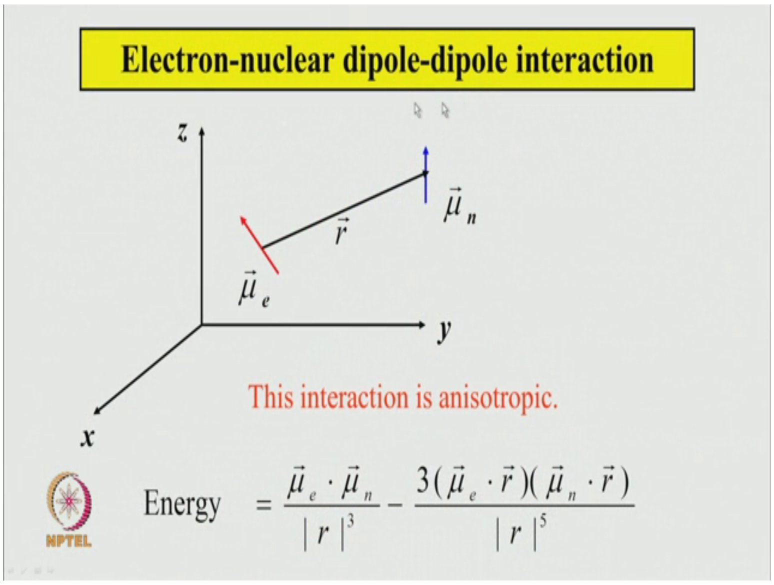

Electron-nuclear dipole-dipole interaction

This interaction is anisotropic.

$$\text{Energy} = \frac{\vec{\mu}_e \cdot \vec{\mu}_n}{|r|^3} - \frac{3(\vec{\mu}_e \cdot \vec{r})(\vec{\mu}_n \cdot \vec{r})}{|r|^5}$$

This slide, this is the it is a direction of the electron dipole moment it is the direction of the magnetic dipole moment in sudden x y z coordinate system, and there is a distance between the 2. So, this energy of this 2-magnetic dipole depends on the orientation of this 2 dipole. In fact, it is the relative orientation of them that matters.

Energy is given as this. So, it not only depends on the magnitude of the dipole, but also distance between them and the orientation of mu with respect to r, mu with respect to r. Therefore, this interaction is directional dependent, then you call it anisotropic interactions.

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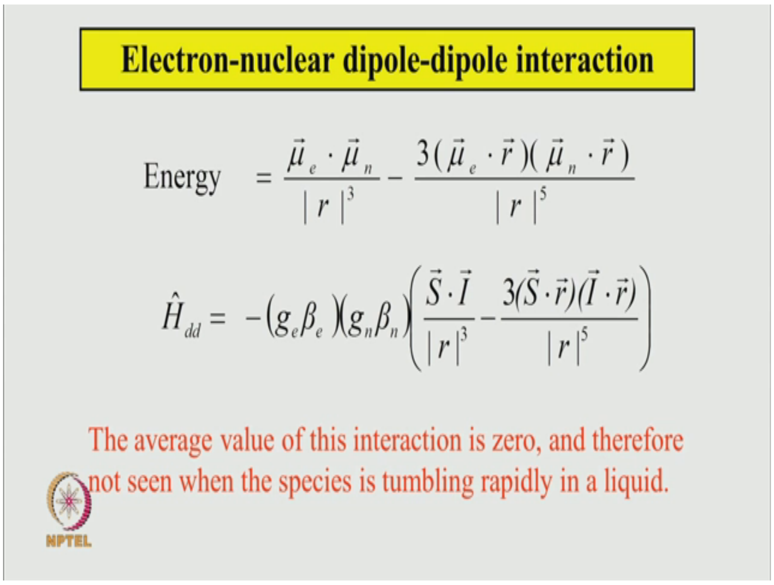

Electron-nuclear dipole-dipole interaction

$$\text{Energy} = \frac{\vec{\mu}_e \cdot \vec{\mu}_n}{|r|^3} - \frac{3(\vec{\mu}_e \cdot \vec{r})(\vec{\mu}_n \cdot \vec{r})}{|r|^5}$$

$$\hat{H}_{dd} = -(g_e\beta_e)(g_n\beta_n)\left(\frac{\vec{S}\cdot\vec{I}}{|r|^3} - \frac{3(\vec{S}\cdot\vec{r})(\vec{I}\cdot\vec{r})}{|r|^5}\right)$$

The average value of this interaction is zero, and therefore not seen when the species is tumbling rapidly in a liquid.

Now, what will be the corresponding operator for this? We simply replace the magnetic moment of each of them by their corresponding operators in terms of the angular momentum. So, mu e is replaced by g e beta e S mu n is replaced by g e n beta n I and a singular fashion.

This is the expression for the dipole dipole Hamiltonian operator for electro nuclear interaction. Now this dipole dipole interaction is such that it is average value turns out to be 0. So, when the species tumbling rapidly, let us say liquid or gas their collisions of atoms.

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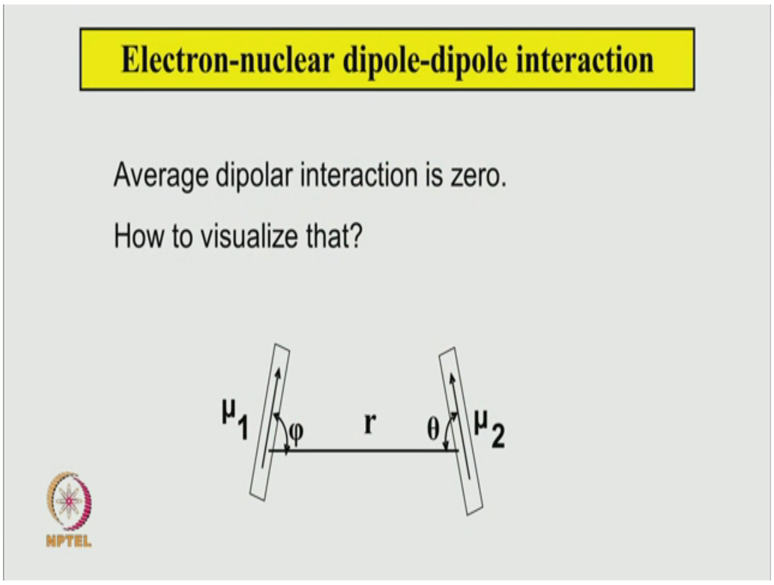

Electron-nuclear dipole-dipole interaction

Average dipolar interaction is zero.

How to visualize that?

Then the average value of this energy becomes 0. How do you visualize that this energy of interaction becomes 0? It is not very obvious from this type of operator; or this type of energy expression for that. Of course, one can calculate and turn and find out the indeed that is 0, if we take care of all possible orientations. Now let us try to understand at least qualitatively whether this energy can be 0.

So, for that this is the schematic representation of 2 magnets, let us say mu 1 and mu 2, they are kept at a distance r, and they are aligned such a way that mu 1 function angle phi with respect to r and mu 2 forms an angle theta.

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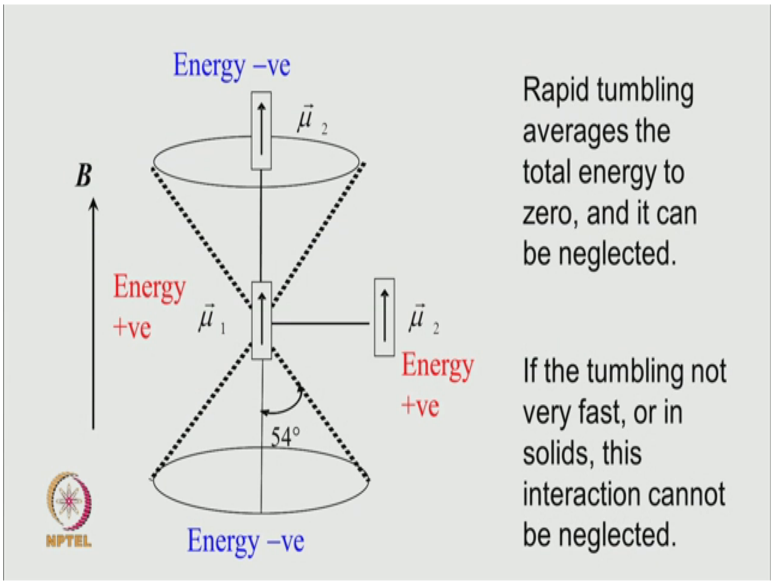

Rapid tumbling averages the total energy to zero, and it can be neglected.

If the tumbling not very fast, or in solids, this interaction cannot be neglected.

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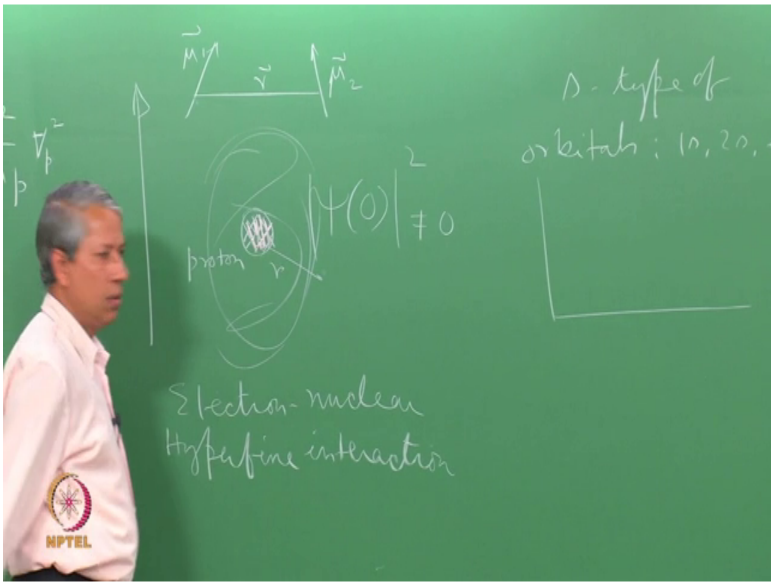

Then what we have here is mu 1 mu 2 and this is r vector. So, if I keep this in a magnetic field, then both of them will get aligned along a magnetic field, once we have put it here. Then what will be the corresponding energy of interaction? If their orientation changes, and also go from let us say one alignment to other alignment, and this is shown here. This is the direction of the external magnetic field.

And let us say one magnetic moment is fixed here and other one is moved from this arrangement to this arrangement. Here these 2 magnets are parallel to each other. So, North Pole is pointing North Pole; South Pole is pointing South Pole. So, this energy will be repulsive. So, you call the energy is positive, same is true if this magnet is brought here on the other hand when second magnet is pointing in this direction. And at the top of this first magnetic moment mu 1 then you see here the north here north south are pointing in such a way that they will be attractive interaction.

So, this north is pointing to south. So, the energy of interaction will be negative here. Same is true here. So, approximately in this region the energy of interaction is negative and same is true here and in this region, is positive and this energy is positive. So, it turns out that if we really look at the interaction operator in detail, the angle of approximately 54 degree is the defining angle within which is rather within this cone of the interaction region, where the energy is negative here also energy is negative, and exactly in this along this region the energy of interaction becomes 0; so the 2 regions as divided such a way that somewhere energy is positive and somewhere energy of interaction is negative.

So, here now if the system is tumbling very rapidly, that all possible regions are covered equally. Then one could consolably assume that this total energy actually becomes 0. That is indeed the case, if we do the calculation exactly for all possible orientations; so in solution EPR spectrum. For example, when the species is tumbling very, very rapidly then one can ignore this interaction. But it cannot be ignored if let us say solution is viscous and tumbling is not very rapid, or if the species is held in a solid state or in a frozen solution, then the tumbling is restricted very severely. So, we cannot neglect this interaction, but for our purpose right now let us neglect this.

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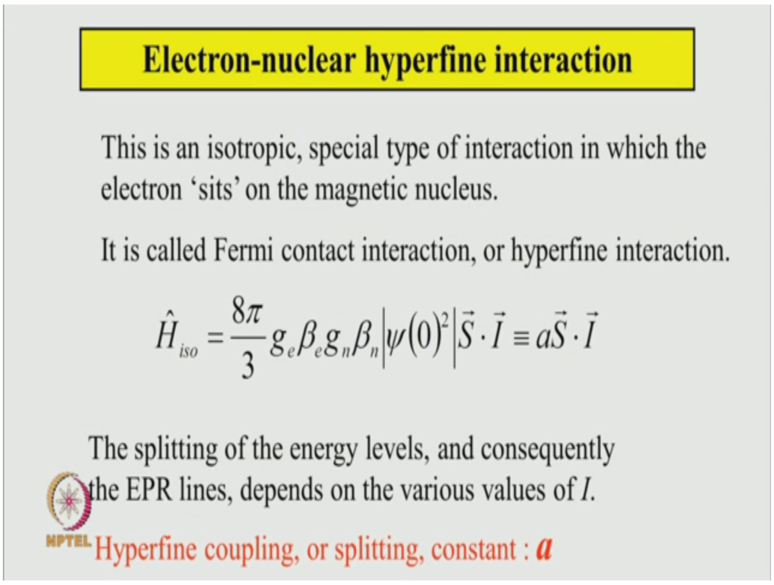

Electron-nuclear hyperfine interaction

This is an isotropic, special type of interaction in which the electron 'sits' on the magnetic nucleus.

It is called Fermi contact interaction, or hyperfine interaction.

$$\hat{H}_{iso} = \frac{8\pi}{3} g_e\beta_e g_n\beta_n \left|\psi(0)\right|^2 \vec{S}\cdot\vec{I} \equiv a\vec{S}\cdot\vec{I}$$

The splitting of the energy levels, and consequently the EPR lines, depends on the various values of *I*.

Hyperfine coupling, or splitting, constant : ***a***

So, what other type of interaction this electro nuclear can have? That is call electron nuclear hyperfine interaction. It is a special type of interaction which does not depend on the direction. It is called an isotropic interaction. And also, special requirement is that the electron sort of sits on the magnetic nucleus. So, unlike here the dipole dipole interaction, there here if this is the nucleus which is proton, but hydrogen atom of course, electron is moving all over. This is decide by the orbital of the electron.

Now if there is some finite probability that electron actually occupies this place. This is what I call sitting on the proton. Then that is interaction is a special type of interaction that is called the electron nuclear hyperfine interaction. It was proposed by fermi, in the expression is given here. Just like dipole dipole interaction is also depends on the strength of the magnetic moment of electron and the magnetic moment of nucleus. But it also depends on this probability of finding the electron at the nucleus.

So, if the psi is the wave function of this. Electron which is describing it is motion around the nucleus, then psi 0 and the square of that if the probability of finding the electron at the nucleus. Now for those orbitals which satisfy this requirement, that this has to be nonzero. Then this expression shows that this isotropic electronic (Refer Time: 12:28) will be nonzero.

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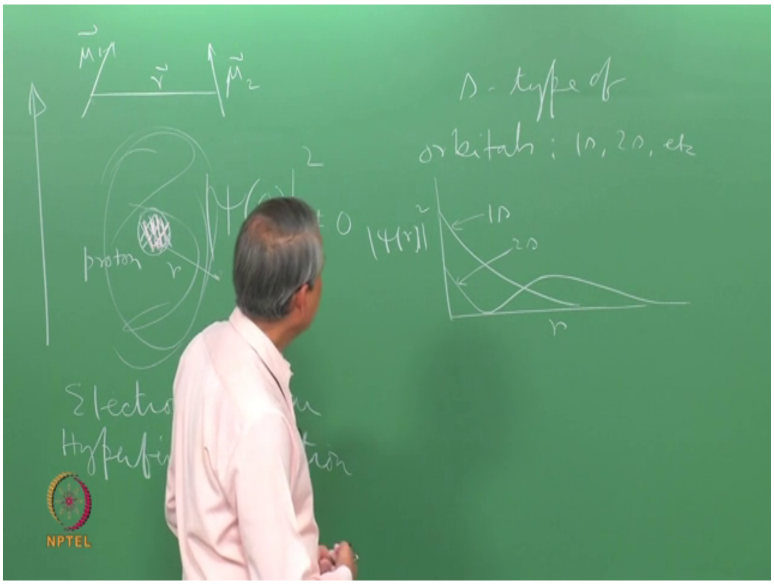

So, not all orbitals have this property, we know from the property of the hydrogen orbitals, it is that S type of orbital. For example, 1 S 2 S etcetera on the; so here if you plot the wave functions square as a function of the distance from this nucleus r. Then this is psi r square. So, this for 1 S orbital, it goes on exponentially. So, at r equal to 0, this is value is nonzero.

Similarly, for 2 S orbital, it looks like something like this this could be 2 S orbital. So, for all the S orbital there is finite probability of finding the electrons at the nucleus.

In contrast if you take other type orbital.

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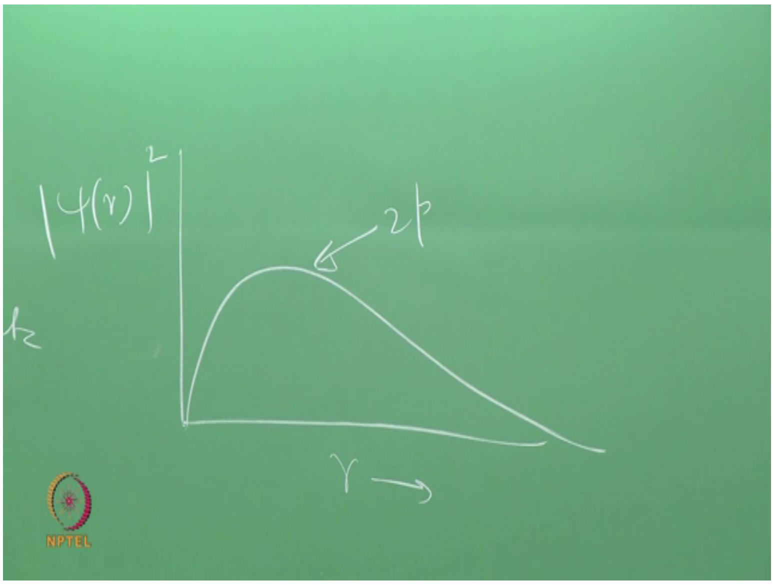

There is a p orbital, this is a 2-p orbital, similarly, d and other orbitals there. Here at the nucleus a probability is exactly 0. So, for this set of orbitals there will not be any such electron nuclear hyperfine interaction, but for these orbitals it will be.

So, for hydrogen atom this is of course, the exact form. But for other system let us say, theoretical species this will be the corresponding wave function of their electron which is producing the interaction, and probability of finding their electron at the particular nuclear site has to be used here. So, this whole of this term here is replaced by a constant called a is a parameter. In fact, so, this constant is called hyperfine coupling constant or hyperfine splitting constant.

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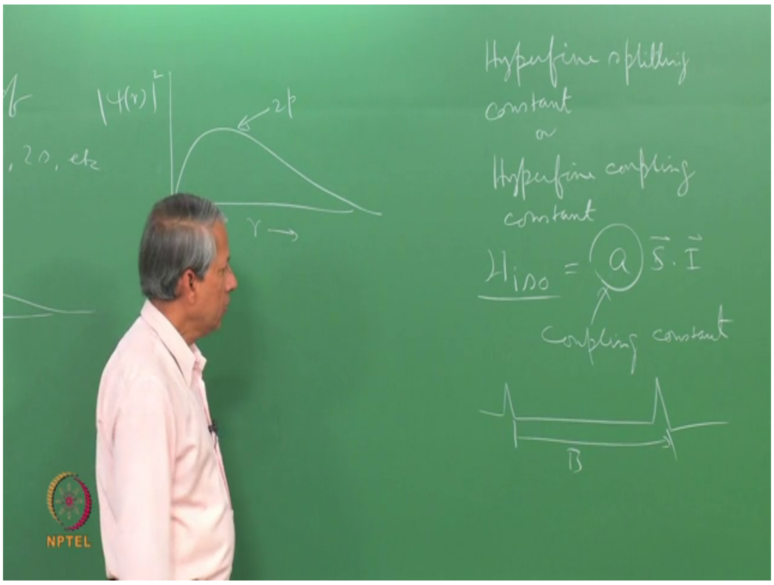

Now, these 2 terms (Refer Time: 15:02) though they are used often synonymously, they may not mean exactly the same, thing this right now let us understand the just a certain difference what I mean by that. In this Hamiltonian isentropic Hamiltonian write a S dot I. So, here there is an energy of interaction. So, here is a is the strength of the interaction. The a gives the strength of interaction. So, here I will be calling it as hyperfine coupling constant, with coupling interaction between the electron dipole and the nuclear dipole. So, when it is measured in the units of energy, this is the call coupling constant. Now we will see that this will of course, so, it is presence by splitting the EPR spectrum. So, in EPR spectrum is measured the function of magnetic field generally. So, we measure something from the experiment which is the measure of the splitting in terms of the magnetic field.

So, this interaction causes splitting in the spectrum. So, whatever property will measure from here, the measure of the splitting that is of course, related to this one, but that splitting that is measured from the experiment will be called the hyperfine splitting constant. And we will see how they are related later.

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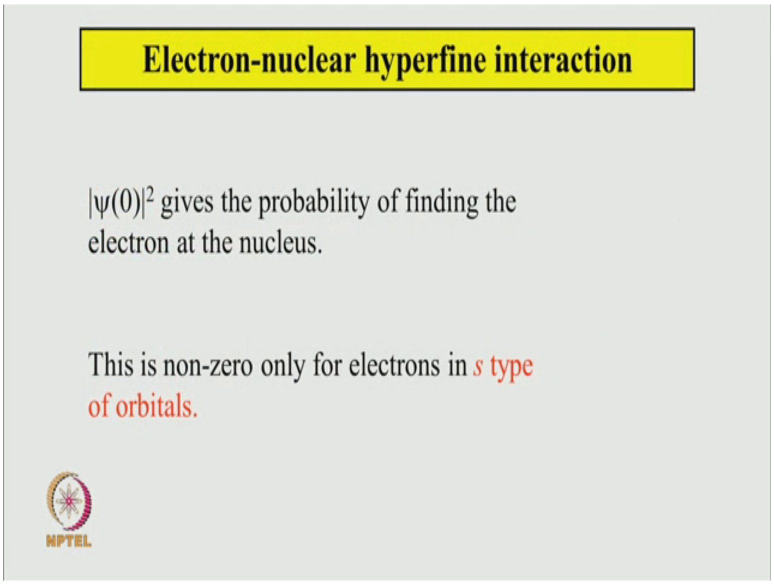

Electron-nuclear hyperfine interaction

$|\psi(0)|^2$ gives the probability of finding the electron at the nucleus.

This is non-zero only for electrons in *s* type of orbitals.

So, I have already said that psi 0 square gives the probability of finding the electron at the nucleus. And this is nonzero only for electrons in S type of orbitals.

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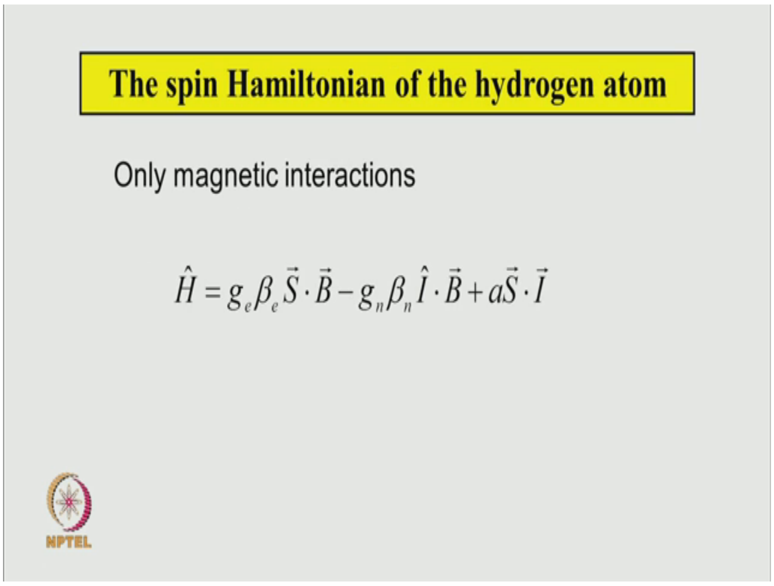

The spin Hamiltonian of the hydrogen atom

Only magnetic interactions

$$\hat{H} = g_e\beta_e\vec{S}\cdot\vec{B} - g_n\beta_n\hat{I}\cdot\vec{B} + a\vec{S}\cdot\vec{I}$$

So, this Hamiltonian where we are dealing only with the magnetic interactions, such as this electrons even interaction nuclears even interaction, and the hyperfine interaction. So, so this type of Hamiltonian are called spin Hamiltonian where we see you see there, we do not include the kinetic energy of various constant particles or potential energy that they have only this interaction energies are included in the spin Hamiltonian.

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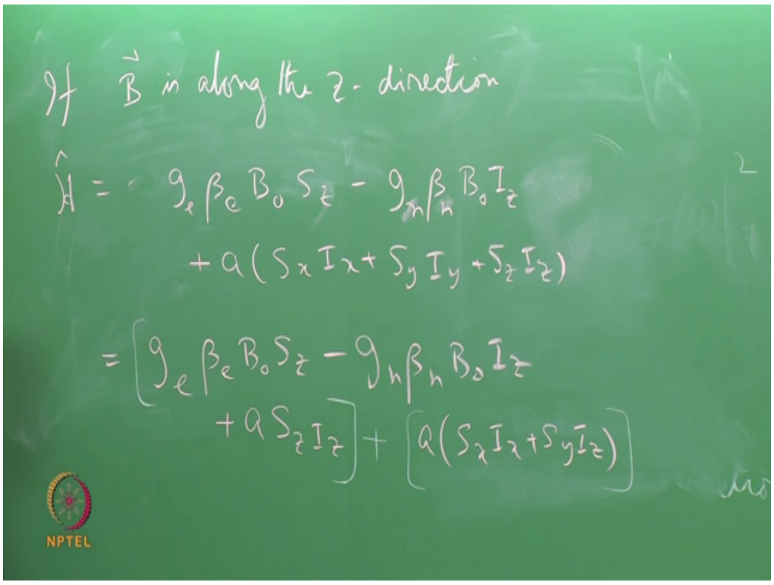

If $\vec{B}$ in along the z- direction

$$\hat{H} = g_e \beta_e B_0 S_z - g_n \beta_n B_0 I_z + a(S_x I_x + S_y I_y + S_z I_z)$$

$$= \left[g_e \beta_e B_0 S_z - g_n \beta_n B_0 I_z + a S_z I_z\right] + \left[a(S_x I_x + S_y I_z)\right]$$

Now, if the magnetic field B is along the z direction. Then this Hamiltonian operator (Refer Time: 18:25) can be written as B 0 S z minus g e, g electric nuclear Zeeman S z I z. This can be written as sum of 2 components, plus this is one component plus another component. We will see why you do that in the moment. This term which involves the x and y, there is a mistake.

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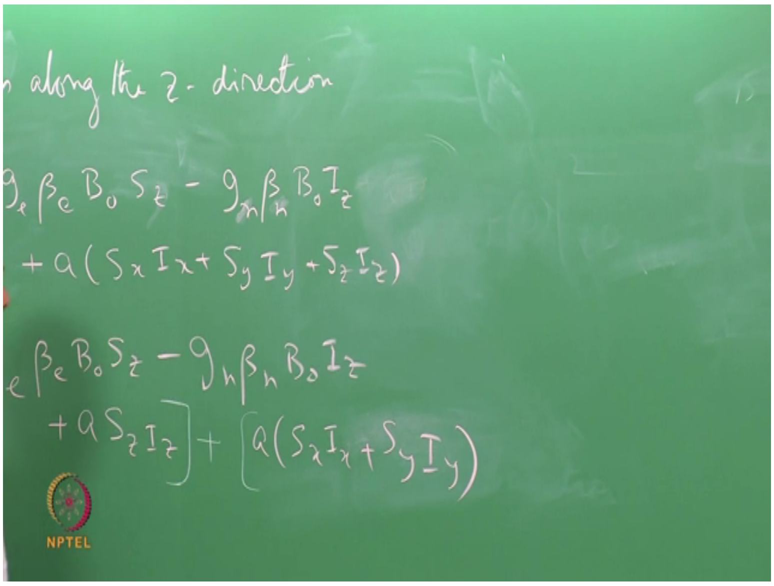

along the z- direction

$$g_e \beta_e B_0 S_z - g_n \beta_n B_0 I_z$$

$$+ a(S_x I_x + S_y I_y + S_z I_z)$$

$$\beta_e B_0 S_z - g_n \beta_n B_0 I_z$$

$$+ a S_z I_z\Big] + \Big[a(S_x I_x + S_y I_y)$$

S x I x plus S y I y; so this can be written in terms of the raising.

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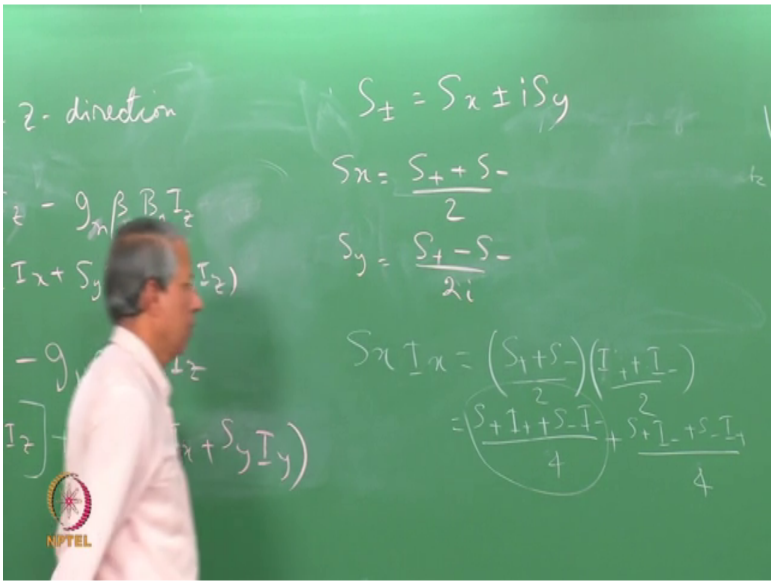

$$S_\pm = S_x \pm iS_y$$

$$S_x = \frac{S_+ + S_-}{2}$$

$$S_y = \frac{S_+ - S_-}{2i}$$

$$S_x I_x = \left(\frac{S_+ + S_-}{2}\right)\left(\frac{I_+ + I_-}{2}\right)$$

$$= \frac{S_+I_+ + S_-I_-}{4} + \frac{S_+I_- + S_-I_+}{4}$$

And lowering operator S plus minus equals to S x plus minus I S y. So, S x gives S plus plus S minus by 2.

S y is equal to S minus minus by 2 I. Similarly, we can write for the I x and I y. Then S x plus I x variable is becomes S plus plus S minus by 2 into S gives S x plus I x plus. Similarly, if you take the other one, by putting this one then this term will cancel out.

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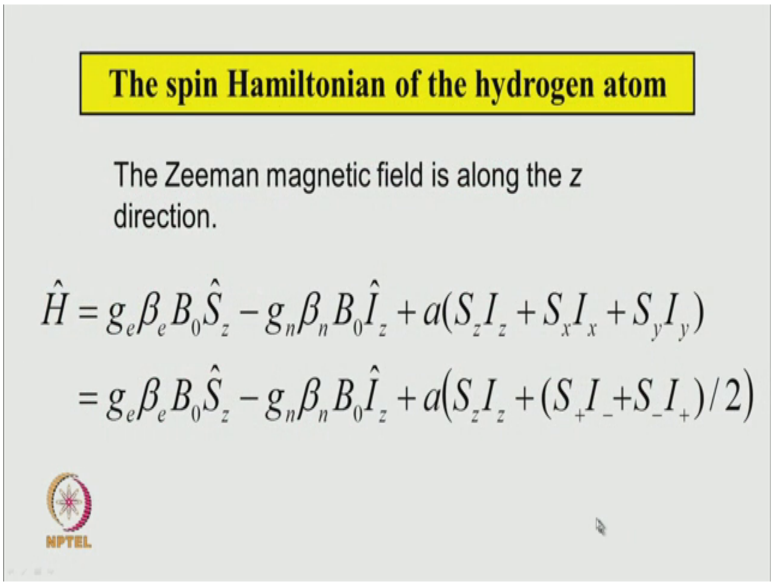

The spin Hamiltonian of the hydrogen atom

The Zeeman magnetic field is along the z direction.

$$\hat{H} = g_e\beta_e B_0\hat{S}_z - g_n\beta_n B_0\hat{I}_z + a(S_zI_z + S_xI_x + S_yI_y)$$

$$= g_e\beta_e B_0\hat{S}_z - g_n\beta_n B_0\hat{I}_z + a\left(S_zI_z + (S_+I_- + S_-I_+)/2\right)$$

So, what we see here, that the simplification of this will turn out to be this way that electrons even nuclears even and this S z I z plus this is a term that comes out S plus I minus plus S minus I plus by 2.

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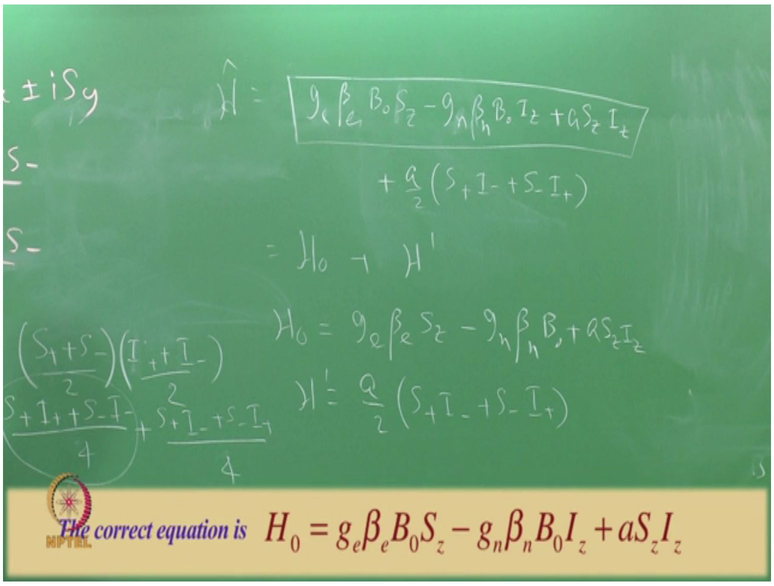

The correct equation is $H_0 = g_e\beta_e B_0 S_z - g_n\beta_n B_0 I_z + aS_zI_z$

So, we have the total Hamiltonian time 0 B 0 S z I z plus a S z I z plus a by 2 S plus I minus plus S minus I plus. Here, now let us see the relative magnets of the various interactions, which is the electron is a one term and here nuclear is a one. So, we know there magnetic moment of electron is about 2 thousand times higher than this. So, this will be the most dominant interaction. This will be very, very small compared to that one. And this magnitude of the hyper fine coupling constant is also not very large. So, this will still be the dominant interaction.

This is usually very small. So, what we do now is that we treat these as the (Refer Time: 23:19) Hamiltonian or main Hamiltonian plus this is the perturbation. So, h 0 is equal to z, this is the main Hamiltonian and perturbation Hamiltonian is a by 2 minus plus S minus I plus this one.

With this approximation we will see how the energy level that appears what hydrogen atom in the next discussion. We stop here now.