Introduction to Molecular Thermodynamics
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Lecture - 25
Statistical Thermodynamics of Ideal Gases

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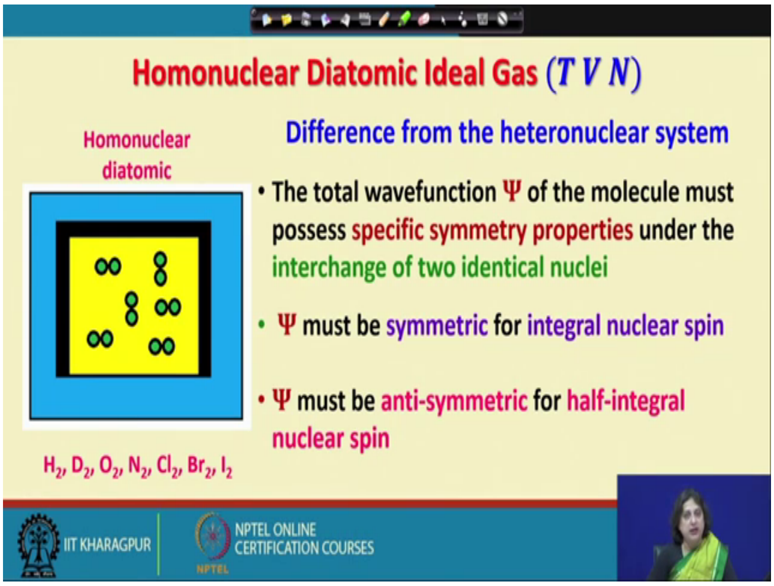

Homonuclear Diatomic Ideal Gas ($T\ V\ N$)

Homonuclear diatomic

H_2, D_2, O_2, N_2, Cl_2, Br_2, I_2

Difference from the heteronuclear system

- The total wavefunction Ψ of the molecule must possess specific symmetry properties under the interchange of two identical nuclei
- Ψ must be symmetric for integral nuclear spin
- Ψ must be anti-symmetric for half-integral nuclear spin

Welcome, we will continue our discussion of the statistical thermodynamics of an ideal gas comprised of diatomic molecules. And in today's lecture we are going to talk about the homonuclear diatomic ideal gas. So, as discussed before the homonuclear diatomics system is comprised of molecules like this, where both the atoms forming the molecules are of the same type. So, examples are hydrogen, deuterium, oxygen nitrogen and so on and other halogens. In this case, before we go into the discussion of how to work out the statistical thermodynamics of a system like this, it is very important to understand the difference between this case from the heteronuclear system. In this case, simply because the two nuclei are the 2 atoms constituting the molecule are identical, there are additional demands of symmetry from in this system.

So, the first thing that we should note down that the total wave function size of the molecule must possess rather specific symmetry properties under the operation where we interchange the two identical nuclei. Now, later we are going to have a very detailed look at these two terms first what I mean by this interchange of the two identical nuclei, and second what kind of specific symmetry properties am I talking about if I want to just show you highlight the kind of symmetry property I am talking about here. We would like to have this overall total wave functions psi symmetric with respect to interchange of two identical nuclei for integral nucleus spin.

But if it so happens that the nuclear spin is half-integral, in that case psi must be anti-symmetric with respect to interchange of the two nuclei. And therefore, let us take up these little different concepts of interchanging of the two identical nuclei and what effect it has on the overall wave function as well as the single particle partition function. And then we consider how to assign what is the specific symmetry requirement for different nuclei having integral or half-integral spins.

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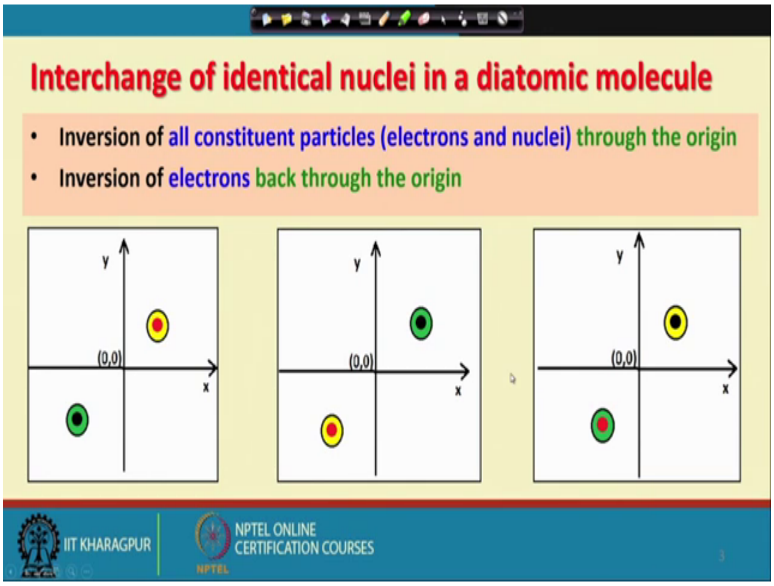

Interchange of identical nuclei in a diatomic molecule

- Inversion of all constituent particles (electrons and nuclei) through the origin
- Inversion of electrons back through the origin

So, the first thing that we would talk about is something that has been shown here in this approximate diagram. For the sake of simplicity, I will confine my discussion here in a two-dimensional space. So, this is the direction of my x-axis, and this is the direction of my y-axis. This is something that represents the nuclei and the electron cloud in the diatomic molecule, which is given here. Now, the red portion corresponds to the nuclei and the yellow portion corresponds to the electron cloud surrounding it. So, this is obviously a rather approximate representation of the diatomic molecule. And now if I carry out an interchange of the identical nuclei in a diatomic molecule, what I will do is I will do this in two steps. So, the first step is we will invert all the constituent particles of the molecule including the electrons and the nuclei through the origin.

So, in this picture, where is the origin, this point is my origin. So, if I want to invert this at this body or this point through this origin, I should appeared here. And therefore, what I am trying to say is this is an inverted image of this and vice versa. Now, as you see that I have this particle one and this particle two, and here for the sake of our understanding, I have coloured the nucleus of the particle one as red and the electronic cloud as yellow. Here for this particle two, what I have done is I have used as the center black and as the electron density green.

Now, so the in the first step this even this is my starting configuration I have one here, two here and I would like to invert all the constituent particles through the origin, and this would definitely result into something like this. So; obviously, this go will go to this position as we see in this picture, and this will come to this position as we see in this picture. Now, after this, we would have a second step of inverting the electrons back through the origin. And this is what we will get.

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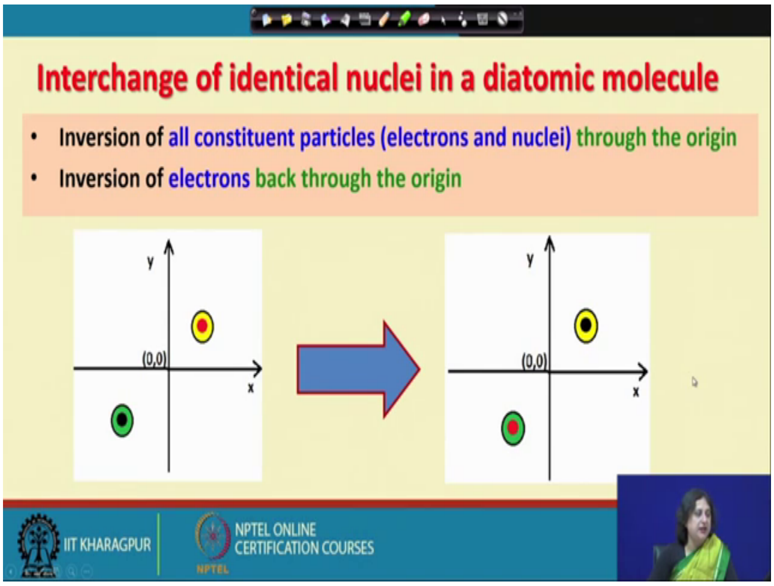

Interchange of identical nuclei in a diatomic molecule

- Inversion of all constituent particles (electrons and nuclei) through the origin
- Inversion of electrons back through the origin

So, now, if I compare these two pictures what I get is through this interchange of these nuclei, what I have obtained is starting from this structure simplified highly simplified structure, I have landed up in a structure like this. Where as you see that it is the same electron density at these two positions, it is the same electron density at these two positions, but only the nuclear positions have been exchanged. So, this is a pictorial representation of what I mean by interchange of the identical nuclei in a diatomic molecule, which means that if to start with I had a configuration like this. I am going to a configuration like that as a result of the interchange of the identical nuclei.

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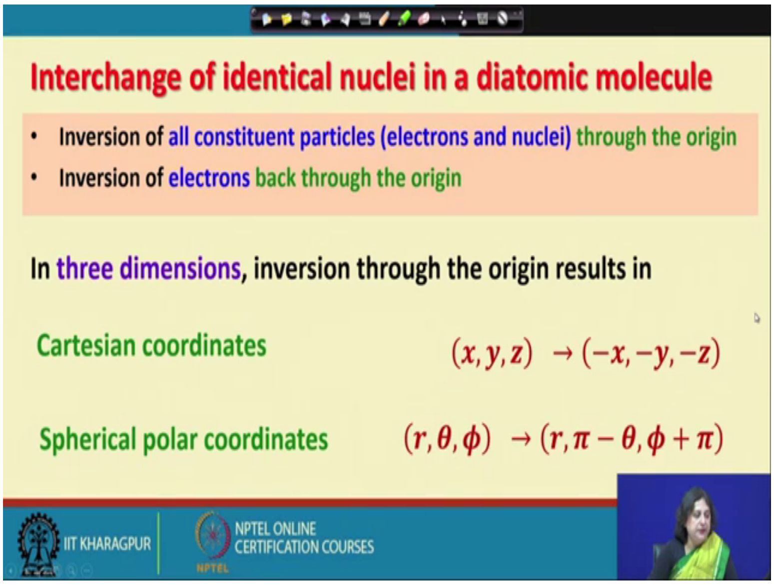

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- Inversion of all constituent particles (electrons and nuclei) through the origin
- Inversion of electrons back through the origin

In three dimensions, inversion through the origin results in

Cartesian coordinates	$(x,y,z) \rightarrow (-x,-y,-z)$
Spherical polar coordinates	$(r,\theta,\phi) \rightarrow (r,\pi-\theta,\phi+\pi)$

Now, under such condition, under such operation - this inversion, we would like to talk about what happens in three dimensions. Now, obviously, in three dimensions you can work in the Cartesian coordinates. In the case of the Cartesian coordinates, what you will find is that inversion through the origin results in transformation of the coordinate x, y, z into minus x, minus y, and minus z. In many cases in quantum mechanics, the exactly solvable models involve solution of the Schrodinger equation using the spherical polar coordinates just as in the case of hydrogen atom. So, in that case instead of x, y and z, one uses the three coordinates for each point r, theta and phi. Now, inversion through the origin results in the following conversion.

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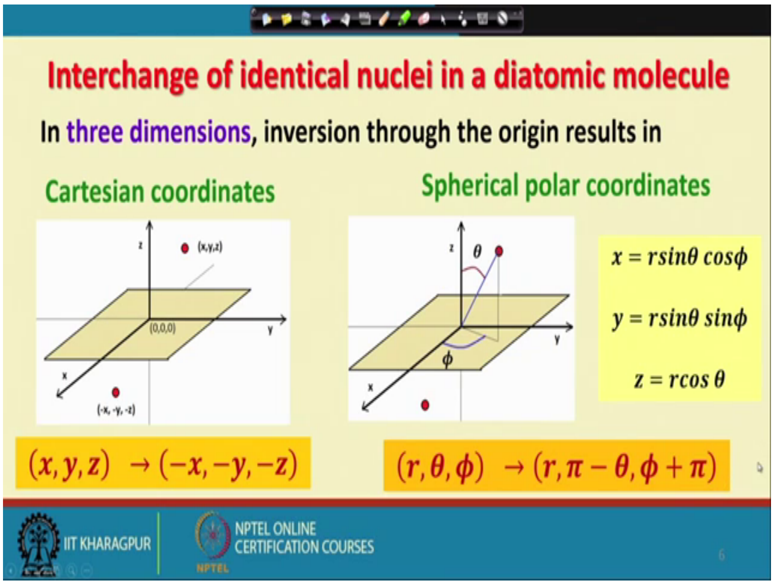

Interchange of identical nuclei in a diatomic molecule

In three dimensions, inversion through the origin results in

Cartesian coordinates

Spherical polar coordinates

$x = r\sin\theta\cos\phi$

$y = r\sin\theta\sin\phi$

$z = r\cos\theta$

$(x, y, z) \rightarrow (-x, -y, -z)$

$(r, \theta, \phi) \rightarrow (r, \pi - \theta, \phi + \pi)$

So, let us have a pictorial look at what these conversions mean and then proceed further. So, this is a representation of the Cartesian coordinates in the three-dimensional space this is the direction of my x-axis, this is the direction of my y-axis, and this is the direction of my z-axis. So, this plane is nothing but the x, y plane. Now, if I have one point here with which when inverted through the origin will land up here. So, if this point is above the x, y plane towards the direction of positive z by inversion through the origin, it will land up below the x, y plane and near and in the direction of the negative part of the z-axis.

Now, if I introduce here the spherical polar coordinates, and define them as x is r sin theta cos phi, y is r sin theta sin phi, and z is are cos theta, where I have taken the same point having the coordinates x, y, z. And I define it is radial distance from the origin as r. So, this distance between this point, and this point is my radial distance r. Now, what is theta? If I take this straight line and find out the angle made by it with the positive side of the z-axis that is given by theta. So, this is where it appears in the relationship between x, y, z, and r, theta, phi.

And there is another coordinate which gives you the if you take a projection of this vector on the x, y plane and then you find out the angle made by this particular line which is the projection of this r vector on the x, y plane that is phi. And phi also appears in the relationship between the two sets of coordinate systems, but z is independent of phi. Now, with this definition, we understand that if we replace now x by minus x, y by minus y, and z by minus z, there are only certain relationships, which are allowed for the new values of r, theta prime, and phi prime. And these values are given in terms of the changed numbers that I have noted here obviously, inversion preserves the distance from the origin and therefore, r remains unaltered. Then if you think about theta instead of being here, now for this theta is going to be this distance, and the angle it makes with the positive side of the z axis, so that would be pi minus theta. And similarly you can very easily show that phi will be replaced by phi plus pi.

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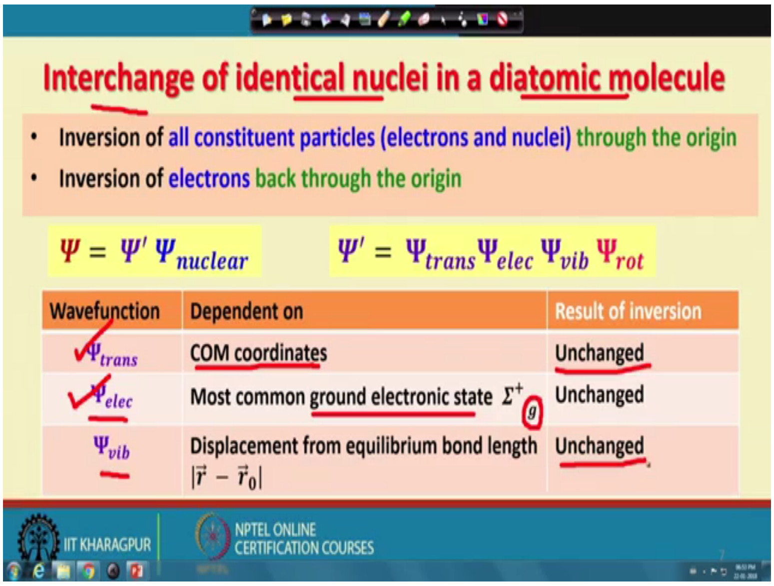

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- Inversion of all constituent particles (electrons and nuclei) through the origin
- Inversion of electrons back through the origin

$\Psi = \Psi' \Psi_{nuclear}$ $\Psi' = \Psi_{trans} \Psi_{elec} \Psi_{vib} \Psi_{rot}$

Wavefunction	Dependent on	Result of inversion
✓ Ψ_{trans}	COM coordinates	Unchanged
✓ Ψ_{elec}	Most common ground electronic state Σ^{+}_{g}	Unchanged
Ψ_{vib}	Displacement from equilibrium bond length $\lvert\vec{r} - \vec{r}_0\rvert$	Unchanged

Under such condition, let us now try to think about what happens when I carry out this inversion or which means that a change of the coordinate system such that x goes to minus x, y goes to minus y, and z goes to minus z or some equivalent coordinate transformation as far as a spherical polar coordinates are concerned. Now, we have already noted that my total wave function is a product of something like psi prime and a psi nuclear. Now, psi nuclear is the nuclear wave function and it is associated with the solution of the Schrodinger equation for the nuclear energy Eigen states. Now, what is psi prime in our discussion of the heteronuclear diatomic molecule, we actually looked at the different dependences of this psi prime on the translational degree of freedom, and electronic degrees of freedom, then vibrational and rotational degrees of freedom.

So, under the approximation of rigid rotor simple harmonic oscillator, I can write down that psi prime is a product of these individual wave functions psi trans corresponding to the translational motion of the center of mass of the molecule on the whole. Psi electronic is corresponding to the solution of the electronic energy Eigen states corresponding to the molecule that we have at hand. Psi vibration corresponds to the vibrational fine structure associated with this diatomic molecule. And finally, psi rot corresponds to the rotation of the molecule like a rigid rotor.

So, once we have this in hand, then the question is when I do the inversion or carry out some kind of a coordinate transformation, then what would be the result of such transformation on the different parts of psi prime. So, let us investigate the different parts of psi prime to start with. And this is what we get. Now, psi trans - the first term, psi trans it depends only on the center of mass coordinates. And therefore, when you carry out the inversion of the coordinates the center of mass coordinate actually remains unchanged. And therefore, I would say that through this interchange of identical nuclei, psi trans is going to remain unchanged. So, psi trans is symmetric with respect to interchange of identical nuclei in this diatomic molecule.

Similarly, if I look at psi electronic, what I find is that in most of the cases, in most of the diatomic molecules, in general the ground electronic state is supposed to be symmetric with respect to inversion through the origin. As a result I would say that under this interchange of identical nuclei in this inversion process that will also leave psi electric electronic in most cases unchanged. Therefore, this is symmetric with respect to this operation.

Now, think about psi vibration, in the case of psi vibration, this depends on displacement from the equilibrium bond length. So, this is some kind of an internal displacement which does not depend on where exactly what has happened whether you are looking at it in the after inversion or before inversion. So, once again these displacement within the molecule will remain unchanged when I interchange the two nuclei. As a result all the three wave functions that are shown here, psi trans, psi electronic and psi vibration will remain unchanged at this is a symmetric with respect to interchange of identical nuclei in the diatomic molecule. But of course, I have not talked about psi rot, so let us go and see have a look at a closer look at what happens psi rot. And if at all it has any it shows any effect as a result of this interchange of identical nuclei.

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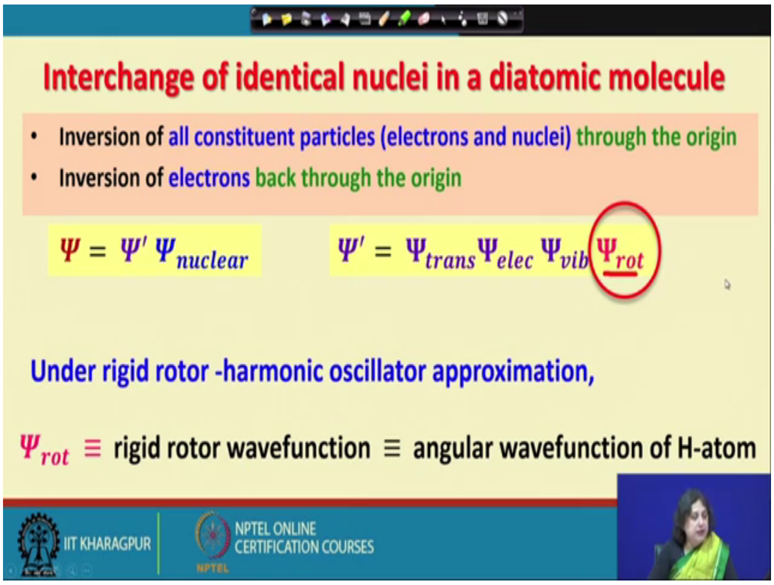

Interchange of identical nuclei in a diatomic molecule

- Inversion of all constituent particles (electrons and nuclei) through the origin
- Inversion of electrons back through the origin

$\Psi = \Psi' \Psi_{nuclear}$ $\Psi' = \Psi_{trans} \Psi_{elec} \Psi_{vib} \Psi_{rot}$

Under rigid rotor -harmonic oscillator approximation,

Ψ_{rot} ≡ rigid rotor wavefunction ≡ angular wavefunction of H-atom

So, the next thing that I do here is focus on this. Now, under the rigid rotor harmonic oscillator approximation, I understand that psi rot is nothing but the rigid rotor wave function. And this has the same property as the angular part of the wave function for hydrogen atoms. Now, in this particular observation tells us that I can use the properties of hydrogen atom orbitals to understand the symmetry nature, the nature symmetry properties of the wave functions for a rigid rotor case.

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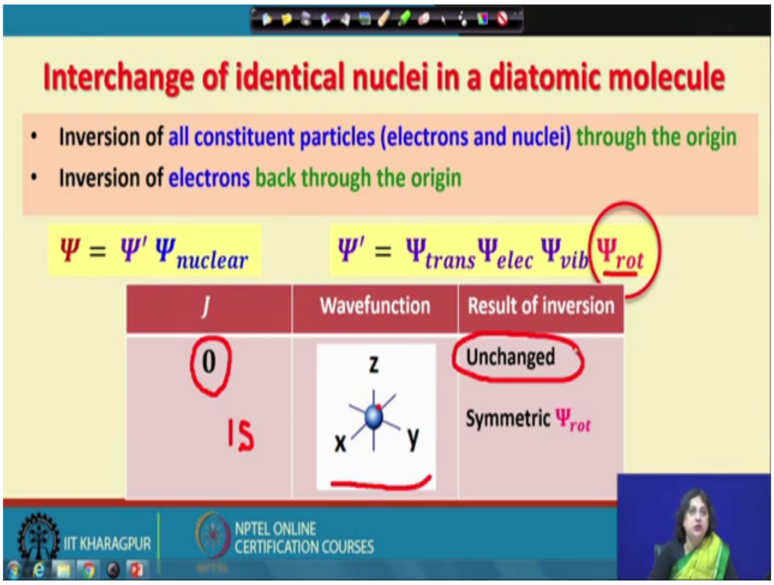

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J	Wavefunction	Result of inversion
0 1S		Unchanged Symmetric Ψ_{rot}

So, this is the first case. So, where what happens psi rot different rotational wave functions are associated with different rotational quantum numbers J. We have seen that these values of J they can vary from zero then take up values like 1, 2, 3 up to infinity. Now, let me take this first case where J is equal to 0, now when J is equal to 0, the symmetry properties of the wave function is like the 1 s orbital of the hydrogen atom. And in this case what we have done is we have shown you what happens to the s orbital when this is the direction of x-axis, this is the direction of positive y-axis, and this is the direction of z-axis.

Now, if I take a point here and I invert it through the origin which is at the center of the orbital that will there be any change in this wave function in the sign, the answer is no. And therefore, the result of inversion is that it will leave the wave function of J equal to 0 unchanged and therefore, we conclude that whenever I am talking about the J equal to 0 wave function of a rigid rotor I must be having a symmetric psi rot. Now, let me also look at the other cases like when J is equal to 1.

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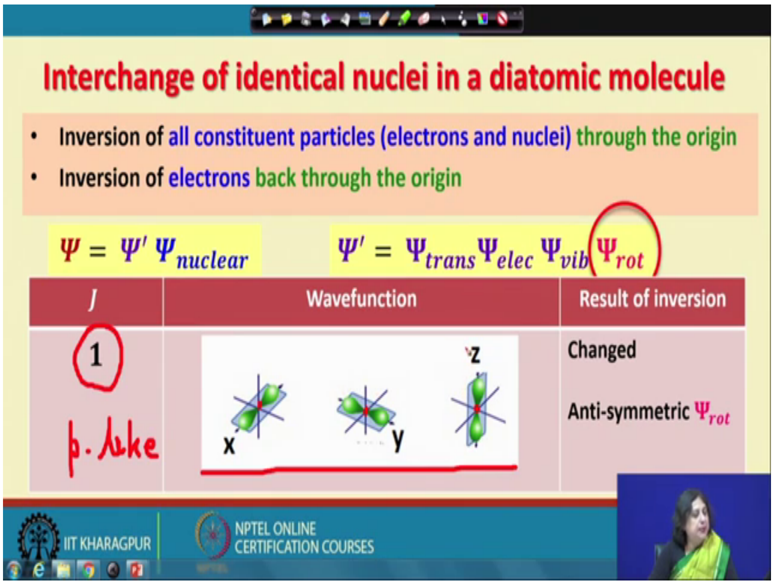

Interchange of identical nuclei in a diatomic molecule

- Inversion of all constituent particles (electrons and nuclei) through the origin
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$\Psi = \Psi' \Psi_{nuclear}$ $\Psi' = \Psi_{trans}\Psi_{elec}\Psi_{vib}\Psi_{rot}$

J	Wavefunction	Result of inversion
1 p. like		Changed Anti-symmetric Ψ_{rot}

Now, when J is equal to 1, this is the case where I have the rigid rotor wave function displaying symmetry properties exactly like the p like. So, now, if it is p like then here we have shown the dependence of the orientational dependence of the different solutions which are associated with J equal to 1. There are three solutions. And as you see the point is that here if I carry out an inversion through the origin, which are here at the nodal points of the p orbitals I know that the wave function changes sign as it goes from x to minus x, or plus y to minus y, or plus z to minus z. And therefore, I would say that for J equal to 1, the wave function undergoes a change in a change in shows a change in the way it is projected across the row center and here the associated psi rot must be anti-symmetric.

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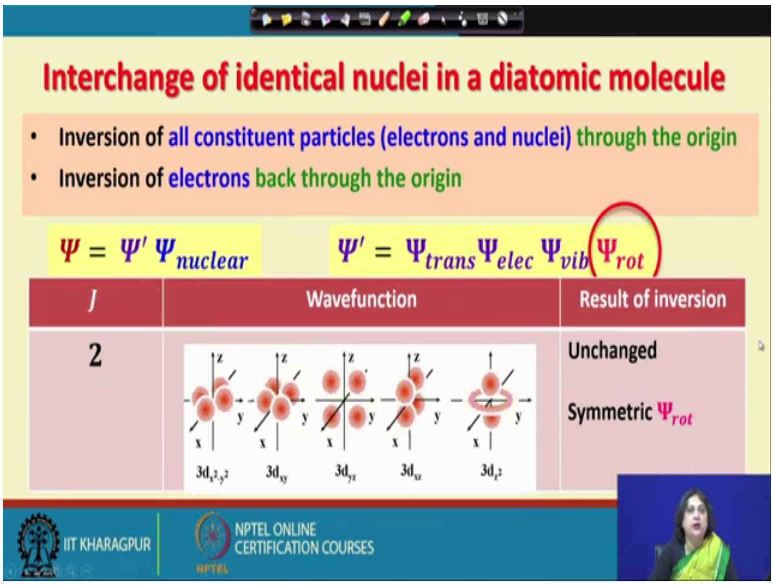

Interchange of identical nuclei in a diatomic molecule

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$\Psi = \Psi' \Psi_{nuclear}$ $\Psi' = \Psi_{trans}\Psi_{elec}\Psi_{vib}\Psi_{rot}$

J	Wavefunction	Result of inversion
2	$3d_{x^2-y^2}$ $3d_{xy}$ $3d_{yz}$ $3d_{xz}$ $3d_{z^2}$	Unchanged Symmetric Ψ_{rot}

Similarly, if I go ahead and look at what happens to j equal to two once again these are d like properties and therefore, the wave function is shown to be symmetric with respect to the interchange of identical nuclei.

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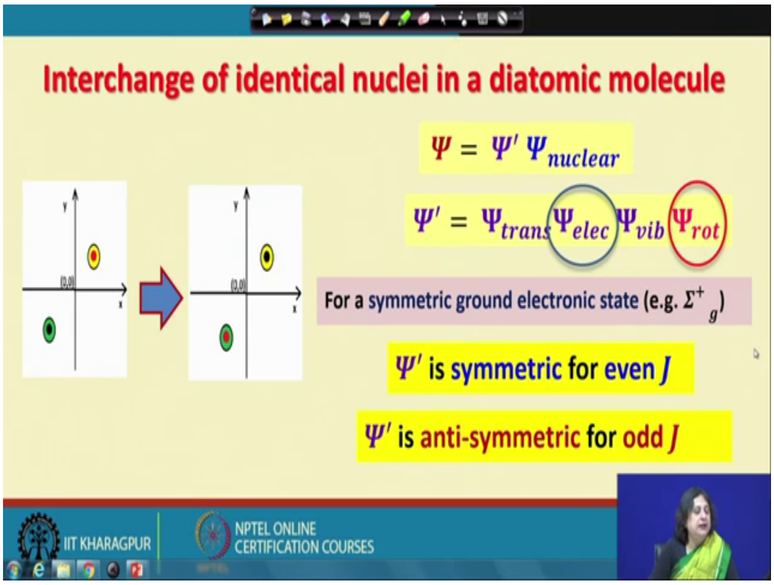

Interchange of identical nuclei in a diatomic molecule

$\Psi = \Psi' \Psi_{nuclear}$

$\Psi' = \Psi_{trans}\Psi_{elec}\Psi_{vib}\Psi_{rot}$

For a symmetric ground electronic state (e.g. Σ^{+}_{g})

Ψ' is symmetric for even J

Ψ' is anti-symmetric for odd J

Now, with all these results in hand then what we can do is we can say the following. I am looking at this kind of a process where I am going to look at the interchange of the identical nuclei. And I am going to groove this through an inversion by an inversion through the origin which is the midpoint as shown over here. Now, the pre symmetry property of overall psi will now depend on the symmetry property of psi prime and psi nuclear. I will come to the case of psi nuclear a little later, but let me first look at the symmetry properties of psi prime. Now, psi prime depends on these four factors of which this and this these are clearly symmetric with respect to the interchange of the nuclei. So, we are left with these two terms psi electronic and psi rotational.

Now, as I have already mentioned that in most of the cases psi electronic is a symmetric ground electronic state which remains unchanged with respect to inversion through the center. Therefore, we find that the symmetry requirement on psi prime is imposed entirely by psi rot. And then we can say that psi prime is symmetric if you are looking at rotational energy states associated with even values of the rotational quantum number. Now, psi prime will be anti symmetric with respect to interchange of the identical nuclei in a diatomic molecule, if we are looking at the rotational energy states associated with odd values of J. So, this is the most common scenario as far as the behaviour of psi prime is concerned in response to interchange of identical nuclei in this diatomic molecule.

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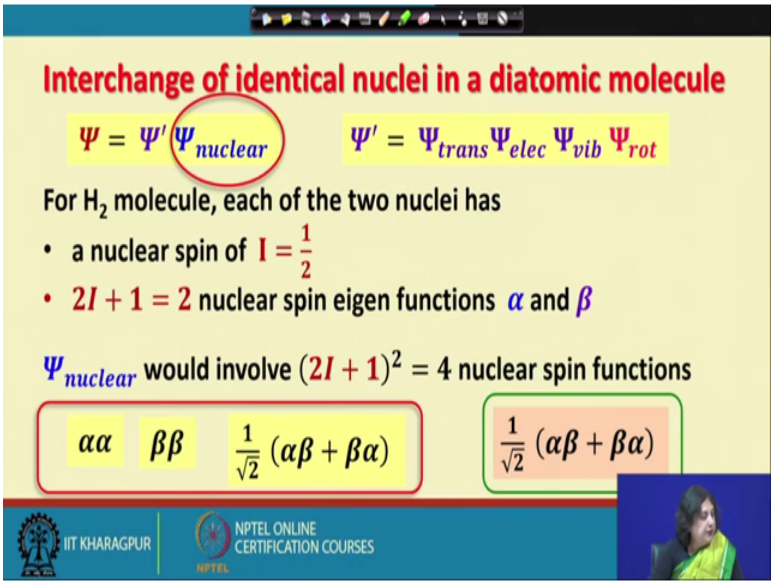

Interchange of identical nuclei in a diatomic molecule

$\Psi = \Psi' \Psi_{nuclear}$ $\Psi' = \Psi_{trans}\Psi_{elec}\Psi_{vib}\Psi_{rot}$

For H_2 molecule, each of the two nuclei has

- a nuclear spin of $I = \frac{1}{2}$
- $2I + 1 = 2$ nuclear spin eigen functions α and β

$\Psi_{nuclear}$ would involve $(2I+1)^2 = 4$ nuclear spin functions

$\alpha\alpha$ $\beta\beta$ $\frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$ $\frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$

Obviously, then the next part is to consider psi nuclear. Now, when I consider psi nuclear will go very slowly here. Because there are several concepts which are associated in this treatment where we find that it is not enough to talk in terms of the electronic energy states, overall translation of the molecule as well as the as an electronic nuclear as well as the translational energy of the molecules. But we have to very closely look at the consequence of having two identical nuclei which must preserve certain symmetry requirement depending on what the nuclear spin is.

Now, going back let me take an example. Let me take the simple example of hydrogen molecule. In the hydrogen molecule, there are two nuclei; the two nuclei corresponding to the two hydrogen atoms. Now, if I ask you the question what is the nuclear spin on each of these hydrogen atoms? You would say that from our initial knowledge about atomic structure. I know that each hydrogen atom nucleus is associated with a nuclear spin of half. And then I would say that then there will be nuclear spin eigen functions alpha and beta there will be two such nuclear spin eigen functions and they are up tend by saying that well if you have a nuclear spin I, how many spin nuclear spin eigen functions do you expect to I plus 1.

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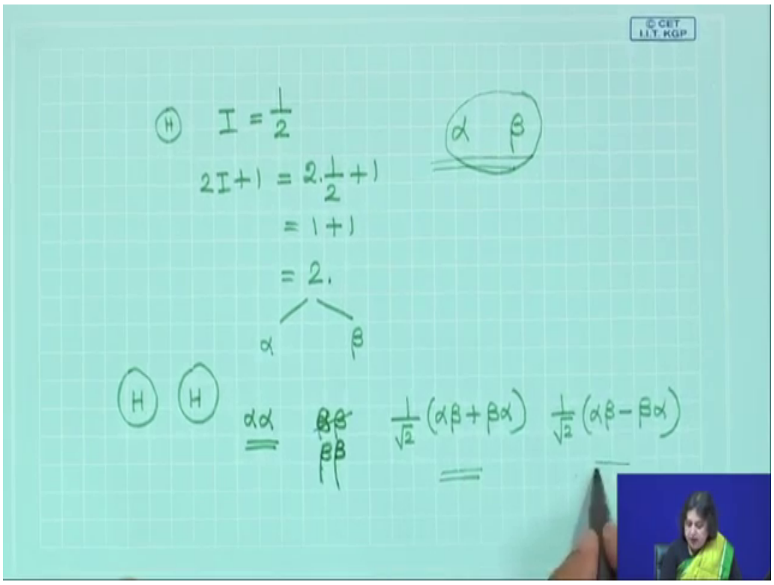

Now, when I have I is equal to half, I understand that 2 I plus 1 is equal to 2 into half plus 1 that is equal to 1 plus 1 that is equal to 2. So, one of these nuclear spin states is give the wave function is given this symbol alpha and the other one is given the symbol beta. Now, I have two such nuclei. So, this is for one hydrogen atom nucleus, and I have two such hydrogen atom nuclei. Then the question is if I can assume that the nucleus states of each hydrogen atom are occupied independent of each other, then the psi nuclear will involve how many nucleus spin functions, it will involve four nuclear spin functions. And these are alpha-alpha, beta-beta, 1 by root 2 alpha-beta plus beta-alpha, and 1 by root 2 alpha-beta minus beta-alpha. So, this means that both the nuclei are existing in the state such that it has spin wave function alpha and this has spin wave function beta.

Now, there is the second possibility is that both of them are existing in the state corresponding to beta spin wave function for the nucleus one and beta spin function for the nucleus two. It may so happen that one of them have alpha spin wave function, the other one has beta spin wave function. In and quantum mechanics requires that under such condition you take a linear combination of these two and these are the probable combinations that are allowed by this in this particular case.

So, these four nuclear spin wave functions are alpha-alpha, beta-alpha then a combination of alpha-beta, and beta-alpha; Out of these as you see that I have clubbed these three together. And I have labelled the fourth one separately. Do you understand why? That is because if you closely look into the symmetry properties of each of this nuclear spin wave functions, you will find that these three wave functions are symmetric with respect to interchange of the identical nuclei.

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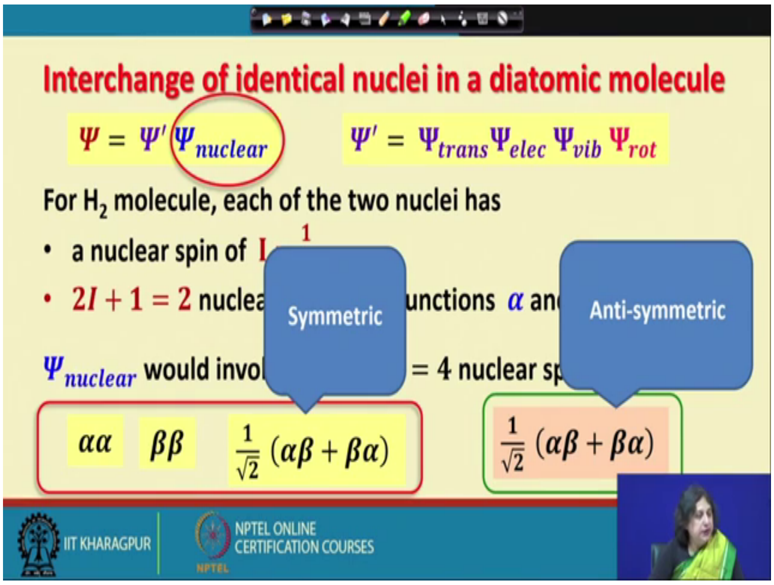

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For H_2 molecule, each of the two nuclei has

- a nuclear spin of I 1
- $2I + 1 = 2$ nuclea unctions α an

$\Psi_{nuclear}$ would invol = 4 nuclear sp

$\alpha\alpha$ $\beta\beta$ $\frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$ $\frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$

Symmetric

Anti-symmetric

And here these two are anti-symmetric with respect to interchange of the two identical nuclei. Now, this is some concept that we are going to use further where we use it to understand what are the symmetry properties of psi nuclear would be. In the next lecture, we shall once again start from this particular example, and discuss the general symmetry requirement of psi nuclear, and then the overall symmetry requirement of psi in a homonuclear diatomic molecule.

Thank you.