

INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

IIT BOMBAY

**NATIONAL PROGRAMME ON TECHNOLOGY
ENHANCED LEARNING
(NPTEL)**

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**MOLECULAR SPECTROSCOPY:
A PHYSICAL CHEMIST'S PERSPECTIVE**

**PROF. ANINDYA DATTA
DEPARTMENT OF CHEMISTRY,
IIT BOMBAY**

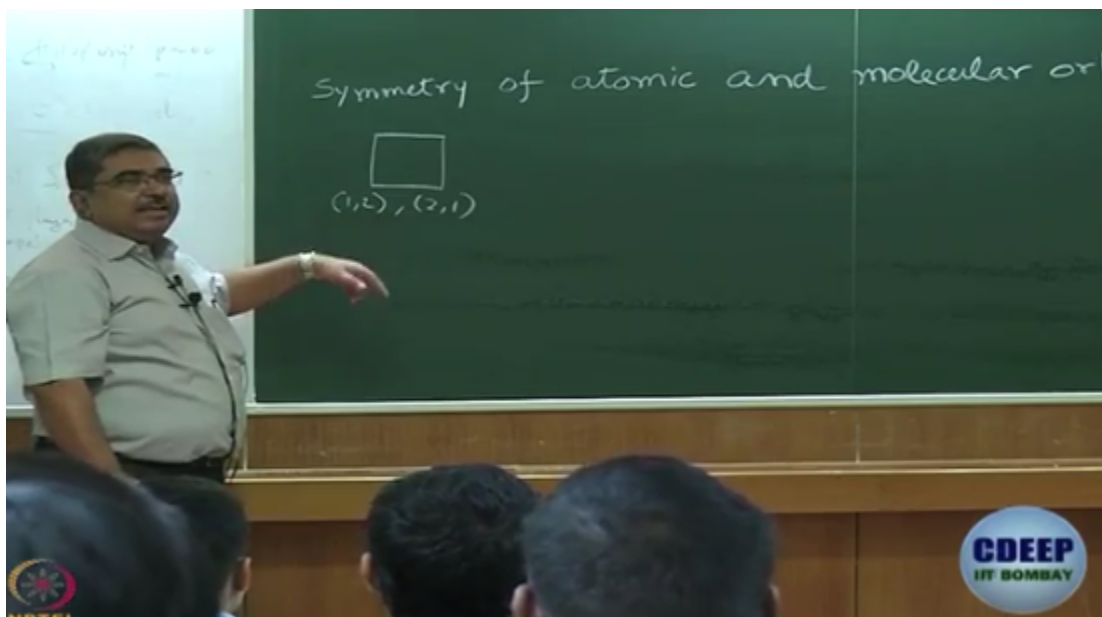
**Lecture no. – 39
Symmetry of Atomic and
Molecular Orbitals**

We've started our discussion on how wave functions can form bases for the irreducible representations of different symmetry point groups.

So today to start with we will focus on electronic wave functions, atomic and molecular orbitals, but then we will leave that discussion and after this we will go on to vibrations, we'll come back to electronic wave functions maybe next week, towards end of next week or week after.

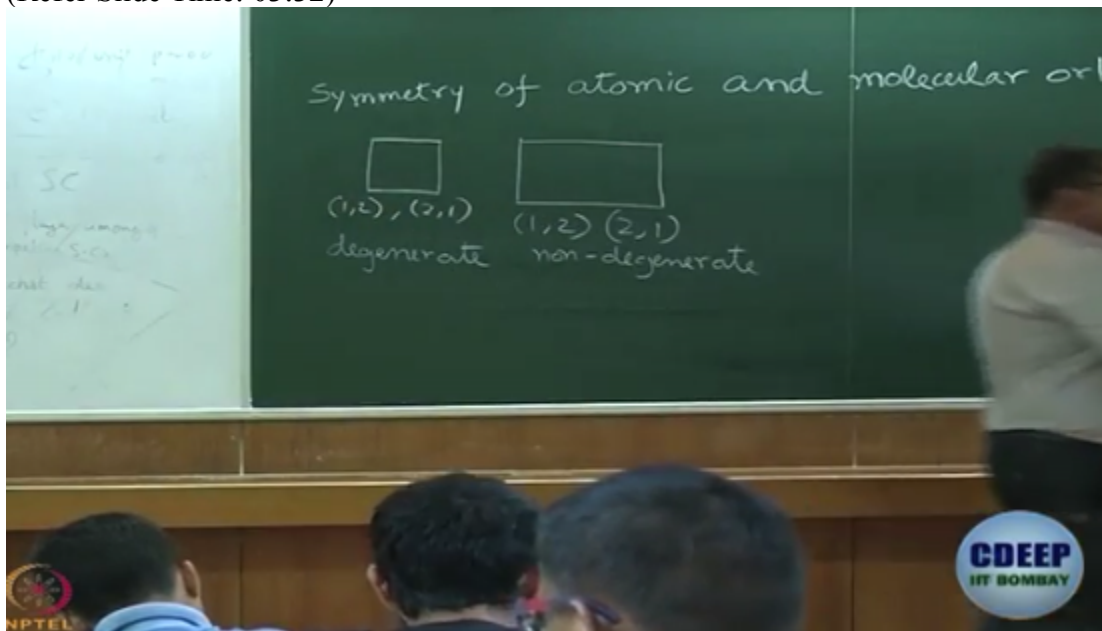
So before we'll proceed any further tell me what an orbital is? What is an orbital? Yes, right, it's an acceptable one electron wave function, so if you are talking about an atom then we talk about atomic orbitals, and when we talk about molecular orbitals there also acceptable one electron wave functions for not the atom but the molecule, so in principle you should be able to get molecular orbitals by solving, Schrodinger equation in electrical polar coordinate for something like H_2^+ , but then nobody does it because it's pointless, you wouldn't be to solve the Schrodinger equation for anything else, so what you do is you have different ways of preparing the molecular orbitals.

So let's talk a little bit about atomic orbitals first, but even before that why do we even care? Why do you care about symmetry of orbitals atomic or molecular? We care because symmetry and degeneracy go hand in hand, this is something that we've learnt when you discussed particle in say 2D box, remember particle in 2D box, right, if you have a square box then the 1, 2 and 2, 1 states are degenerated, does that ring a bell? Do we remember? $N_x = 1$, $N_y = 2$, and $N_x = 2$, $N_y = 1$,
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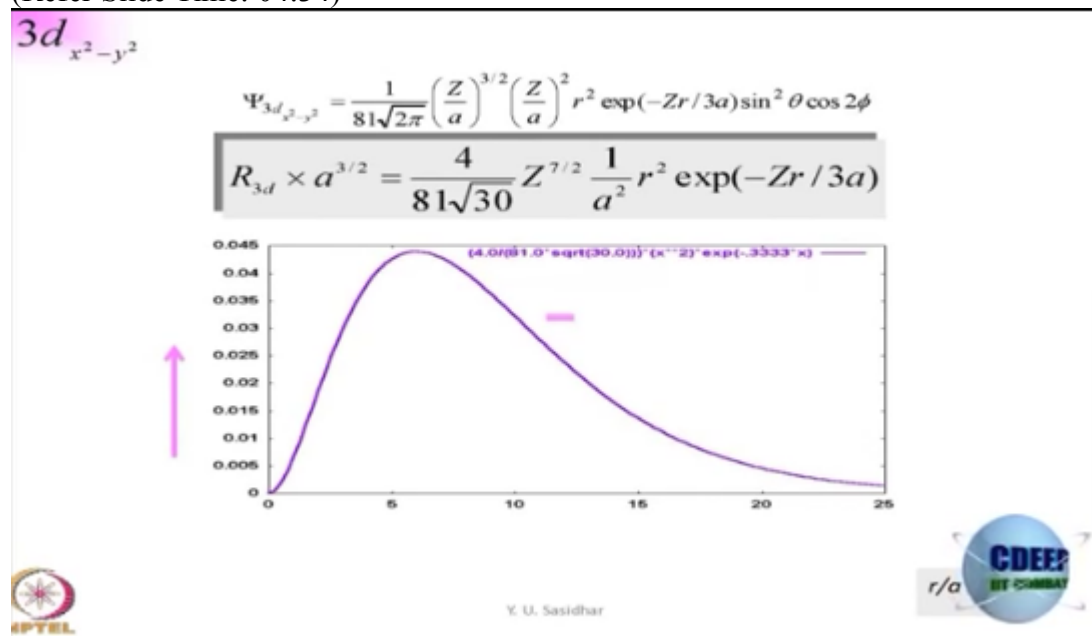
these two states have the same energy because it is $NX^2/LX^2 + NY^2/LY^2$ in this case $LX = LY$ so this $LX^2 + LY^2$ both can be equated to L^2 and you can take it outside the bracket, do we remember this?

What about rectangular box? Now 1, 2, and 2, 1 these are non-degenerate, here they were degenerate, degenerate as you know means same energy, so we build upon that concept (Refer Slide Time: 03:32)



and now that we know about character tables and now that we know about irreducible representations we can do a little more detailed discussion of this phenomenon that symmetry and degeneracy go hand in hand, so the reason why we do this is that it helps us simplify the actual quantum mechanical problem if you think of symmetry, a lot of terms become 0 and all so we can handle it a little easier.

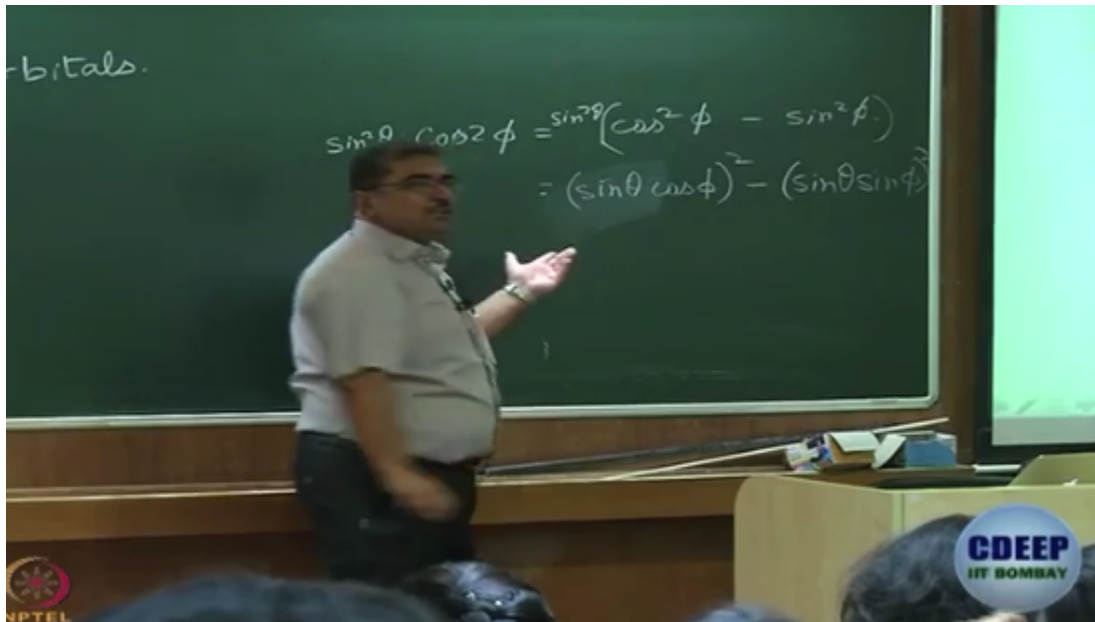
So we'll start with something that is very, very familiar to us. Let us talk about say D orbitals to start with, okay, we know very well that in free metal ion the D orbitals all have the same energy, right, they're degenerate, however if you put the same metal ion in an octahedral field, then what happens? They separate into EG and T2G sets, okay. Now if I want to do this discussion from the point of view of symmetry what I need to do first of all is,
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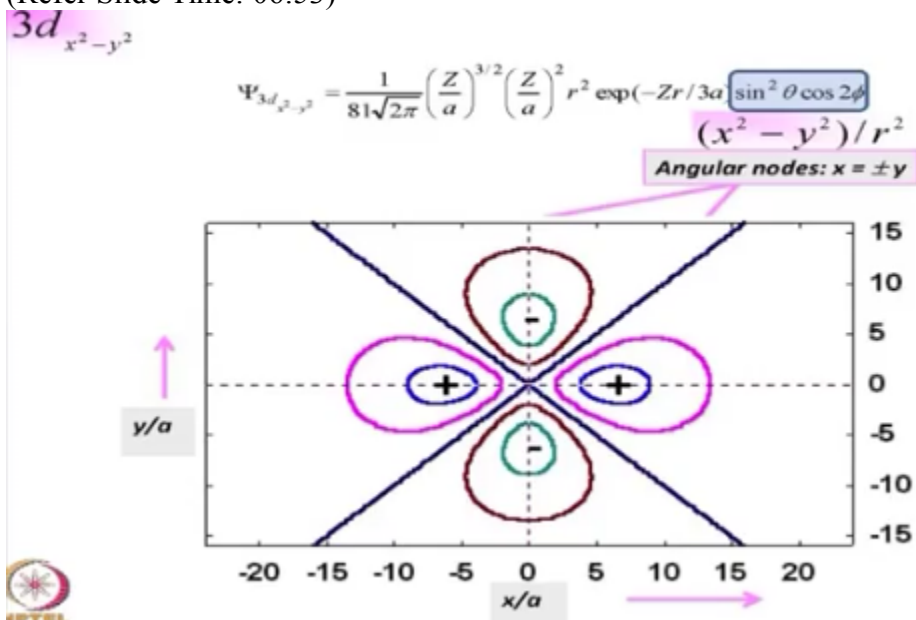
I need to remind ourselves of the form of the wave function of the D orbitals, this is the wave function for 3D X square - Y square, so why do we call it 3D X square - Y square? Because if you look at the wave function, what do you have? You have a constant then you have R square that is the capital R, R dependent part of the wave function multiplied by E to the power $-ZR/3A$ that also is part of capital R, R dependent part of the wave function. The angular part is sin square theta cos 2 phi, okay, this is your DX square - Y square orbital.

Now what is cos 2 phi? How can I write cos 2 phi? Cos square phi - sin square phi, what do you have in the wave function? You have cos 2 phi multiplied by sin square theta, okay, so this whole thing is multiplied by sin square theta, sin theta cos phi whole square - sin theta sin phi whole square, now what is sin theta cos phi? What is sin theta sin phi?

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Remember $R \theta \phi$, right, so $R \cos \theta = Z$, $R \sin \theta \cos \phi$ is X , $R \sin \theta \sin \phi$ is Y , okay, so $\sin \theta \cos \phi$ is X^2/R^2 , isn't it? And what is $\sin \theta \sin \phi$ whole square? Y^2/R^2 , so it boils down to $X^2 - Y^2/R^2$. (Refer Slide Time: 06:53)



Let's not bother about the notes for the moment, let's not bother about the picture for the moment, let's just look at the function, so you can write the function as something in R multiplied by $X^2 - Y^2$ that is why you call the orbital $DX^2 - Y^2$. So if I want to know how this orbital transforms in response to different symmetry operations, what do I have to do? I have to see how $X^2 - Y^2$ transforms? Are we clear? Okay.

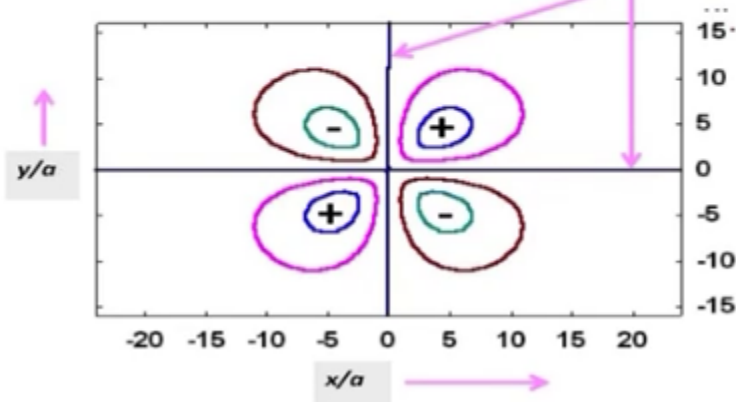
Similarly if you go to XY , XY is R dependent part multiplied by constant, (Refer Slide Time: 07:29)

3d_{xy}

$$\Psi_{3d_{xy}} = \frac{1}{81\sqrt{2\pi}} \left(\frac{Z}{a}\right)^{3/2} \left(\frac{Z}{a}\right)^2 r^2 \exp(-Zr/3a) \sin^2 \theta \sin 2\phi$$

$$xy/r^2$$

angular nodes: x=0, y=0



multiplied by sin square theta, sin 2 phi, what is sin 2 phi? 2 sin theta cos phi, so what do you have? One sin theta multiplied by cos phi, multiplied by one sin theta, multiplied by sin phi, that is XY, YR square, that is why this is called DXY orbital, so this orbital is going to transform in the same way as the function XY transforms.

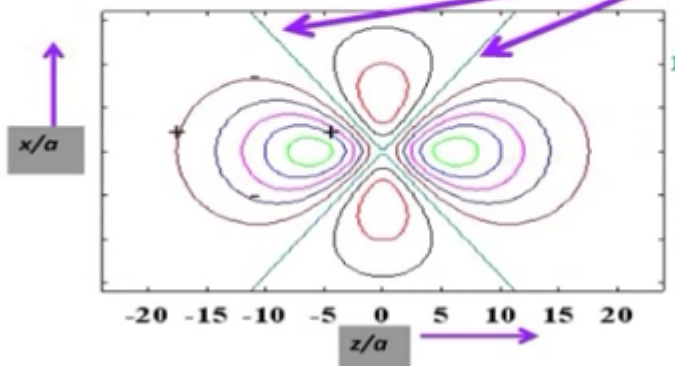
Z square is the one I like most,
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3d_{z²}

$$\Psi_{3d_{z^2}} a^{3/2} = \frac{1}{81\sqrt{6\pi}} Z^{7/2} r^2 \frac{1}{a^2} (\exp(-Zr/3a)) (3 \cos^2 \theta - 1)$$

$$\left(3 \frac{z^2}{r^2} - 1\right)$$

2 angular nodes

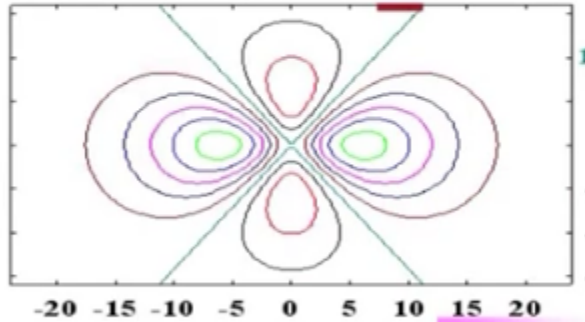


right, in Z square what you have is 3 cos square theta - 1, and you can say right away that it is 3Z square/R square-1, okay, that is why you call it 3DZ square, but let me also tell you that Z square is actually a nick name, what is the full label for DZ square? Yes, because instead of R square you can write X square + Y square + Z square, so from there you can get full level is going to be 2Z square - X square - Y square, okay,

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$3d_{z^2}$ is only a nickname

$$\Psi_{3d_{z^2}} a^{3/2} = \frac{1}{81\sqrt{6\pi}} Z^{7/2} r^2 \frac{1}{a^2} (\exp(-Zr/3a))(3\cos^2\theta - 1)$$



$$(3\frac{z^2}{r^2} - 1)$$

$$(x^2 + y^2 + z^2)$$

Full label: $3d_{2z^2 - x^2 - y^2}$



now this in different point groups you use either Z^2 or $2Z^2 - X^2 - Y^2$.

Now let us look at the character table for the octahedral group, (Refer Slide Time: 08:51)

Octahedral group

	E	$8C_3$	$6C_2$	$6C_4$	$3C_2=(C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear, rotations	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

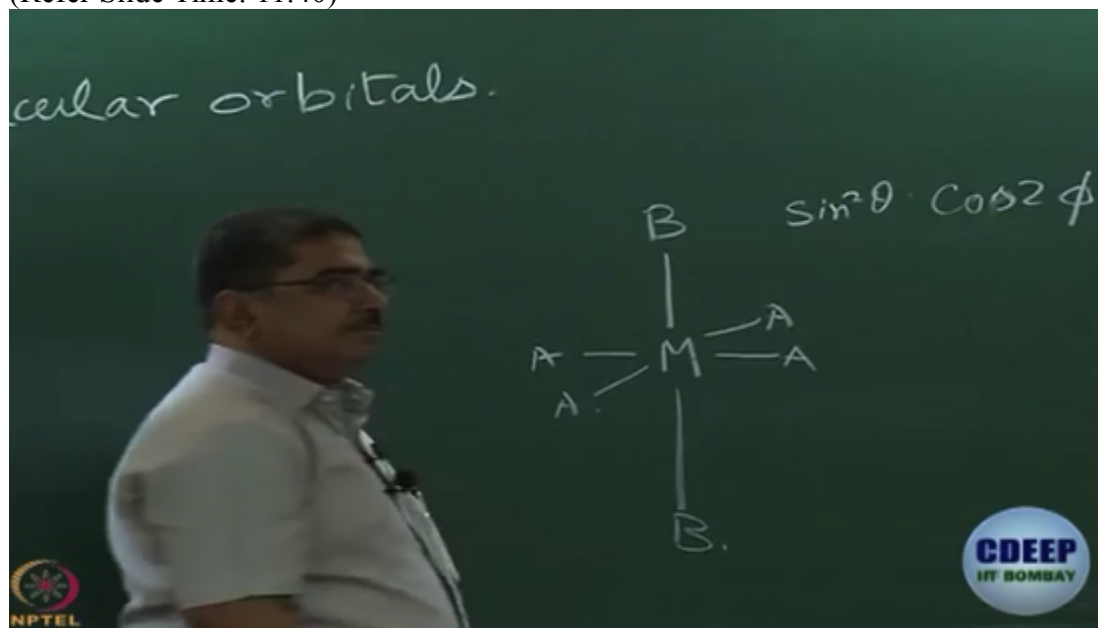
okay, remember what we have learnt here that symmetry and degeneracy go hand in hand, so if we have functions that belong to a 2 dimensional or 3 dimensional representation then they are going to be degenerate, okay, but if you look at the character table, see XZ, YZ, XY belong to T_{2g} , okay, and $2Z^2 - X^2 - Y^2$ and $X^2 - Y^2$ jointly form the bases for E_g , okay, what does that mean? That these 2 D orbitals are going to have the same energy, this 3D orbitals are going to have the same energy, so just by using symmetry without anything else I can tell that D orbitals should get split into two different groups, one is T_{2g} , one is E_g ,

okay, and this is why you call them T2G and EG, because it comes from the Mulliken nomenclature of the symmetry species.

Now what I cannot tell just by using symmetry is which one we will have higher energy, which one will have lower energy. For that you have to use electrostatics or commonsense or quantum mechanics depending on the degree of figure that you want, so from commonsense understanding of electrostatics I think in class 11 or 12 we learnt, which one will be lower? Which one will be higher? Yeah, EG will be higher in energy than T2G, why? Because these are, if you take this DX square – Y square and DZ square then they are along the axis, so electrostatic repulsion will be more that way you can figure out which will be higher, which will be lower, okay, so EG is higher and T2G is lower.

Now let us think of Jahn Teller distortion, Jahn Teller distortion means you have a nice octahedral complex and by some means you pull out two of the axial ligands or you can do a compression also, you pull them out, so the moment you pull them out it is not AB₆ anymore, so it's something like, this is central metal ion A, A, A, A, I hope my diagram is not difficult to understand, but I'm saying is the four A ligands are in a plane that is perpendicular to the plane of the board, and these I'll just call them B, which point group is it now?

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What is the principal axis of symmetry? C₄, do we have a perpendicular C₂ axis? So you take this AMA line, you turn it by 180 degrees that is C₂, this is another one and you think of the bisector of the AMA angle that is also a C₂ axis, so you have these four C₂ axis, okay, so what will it be? It will be D₄.

And next thing to ask is do I have a horizontal plane. I do have a horizontal plane, so it is D_{4h}, okay. In octahedral case we had this EG and T_{2g}, okay, the moment you have Jahn Teller distortion you, the symmetry point will changes from an octahedral to D_{4h}. Now let us see whether EG and T_{2g} remain intact upon going to D_{4h},

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Jahn Teller Distortion: from O_h to D_{4h}

	E	$2C_4(z)$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linears, rotations	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

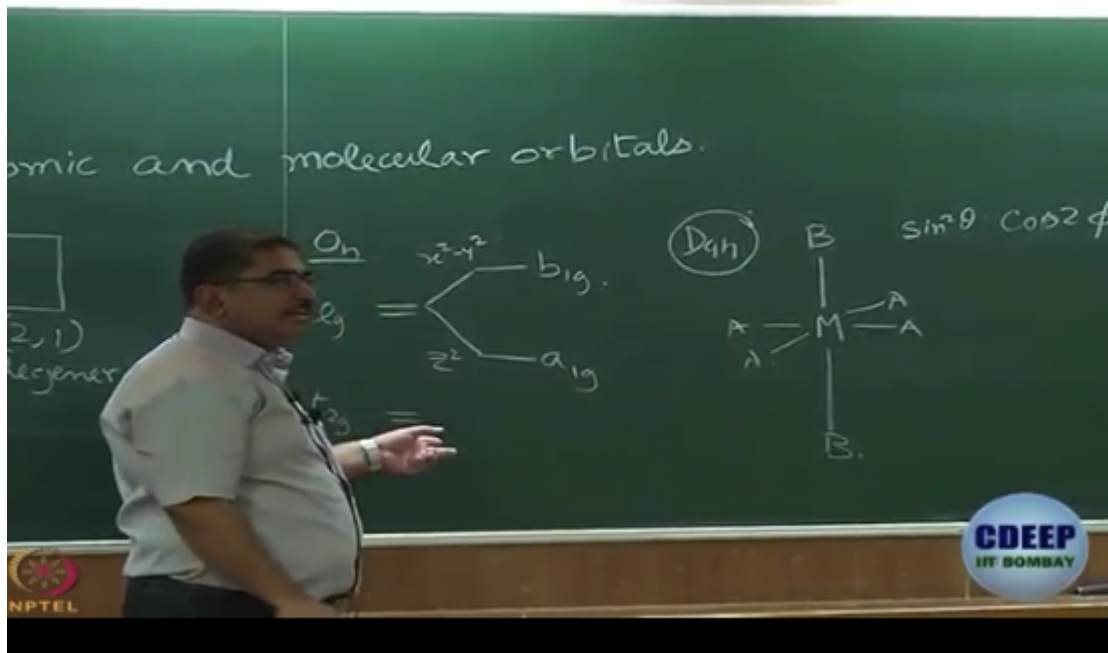


this here is D_{4h} and see what we have, I think I'll go there that is better.

Now see XZ and YZ belong to the same symmetry species, XY is different, right, earlier we had a triply degenerate symmetry species that is where XZ, YZ, ZX belong, not anymore, now XY belongs to a different symmetry species than XZ, YZ. And what about your X square – Y square and Z square, X square – Y square is here and Z square is in a different point group, so what this implies is that you cannot have these what used to be the E_g orbitals you cannot have them degenerate when you have Jahn Teller distortion, from symmetry itself I can tell that, okay.

So which one will be higher, which one will be lower if I pull the ligand out? Yes, one is gesture this is Z direction, this plane is XY, so I'm pulling the ligands along Z out, so increase electrostatic interaction for Z or decrease? Decrease, right so will that be stabilize or destabilize? Stabilize right, so it will be something like this, which one is this? Z square or X square – Y square, and this is X square – Y square, what I can do is, now that I know I can say that the lower one is A_{1g} , and the higher one is B_{1g} orbital.

Similarly there'll be a splitting here,
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so here XZ and YZ is in one symmetry species, XYZ another symmetry species, by similar arguments which one will be lower in energy, which one will be higher in energy? Right, if I want to write the Mulliken nomenclature what will I write? EG is the lower one and the higher one is P2G, so you see just for using symmetry we can get at least a qualitative idea of what to expect in the energetics of orbitals in different kinds of symmetries, okay.

Now what about your tetrahedral complex? For that I have to look at the character table for TD, (Refer Slide Time: 00:28)

Tetrahedral complexes

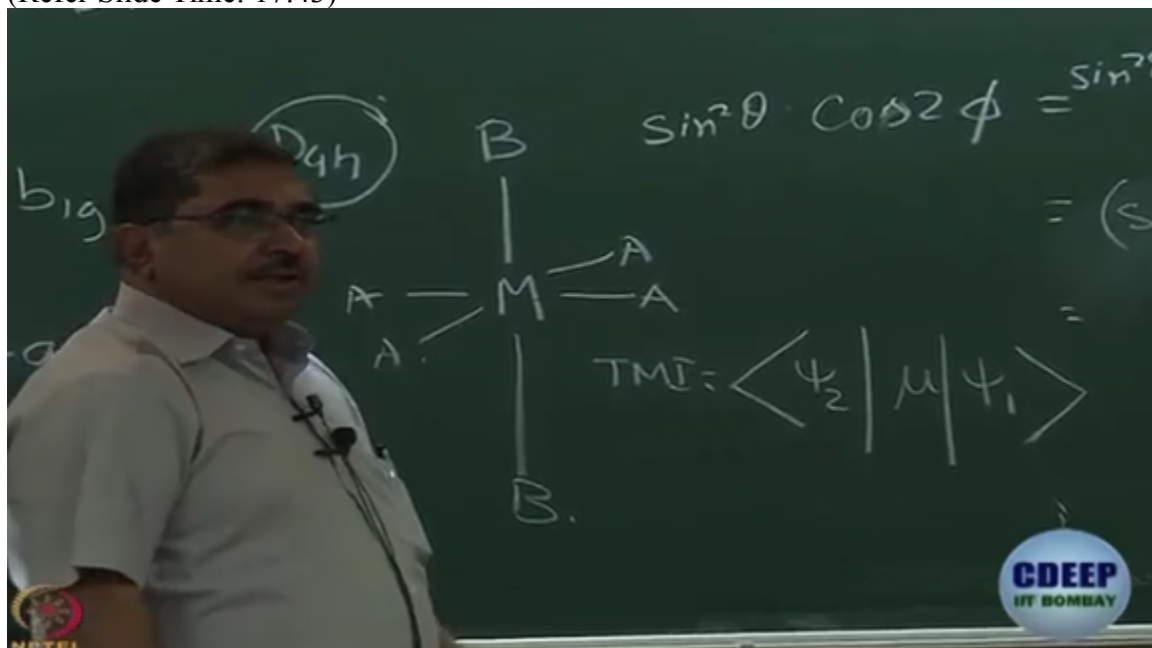
	E	8C ₃	3C ₂	6S ₄	6σ _d	linear, rotations	quadratic
A ₁	1	1	1	1	1		x ² +y ² +z ²
A ₂	1	1	1	-1	-1		
E	2	-1	2	0	0		(2z ² -x ² -y ² , x ² -y ²)
T ₁	3	0	-1	1	-1	(R _x , R _y , R _z)	
T ₂	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

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see here once again what you have is 2Z square – X square – Y square and X square – Y square belong to E, now you don't call it E2G because there is no center of symmetry, and there is no need to use 2 also because there is only one 2 dimensional symmetry species, you just call it E,

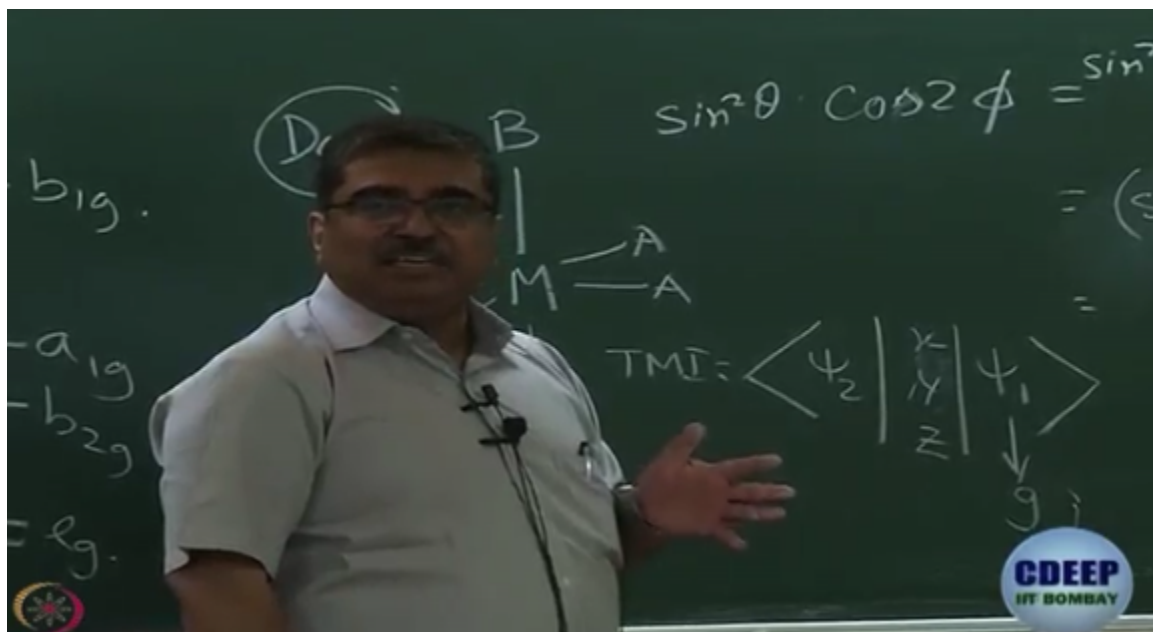
and XY, YZ, ZX jointly form the bases of E2 point group, okay, so once again you'll have two groups of D orbitals in a tetrahedral complex, but which one will be lower which one will be higher? Will the order be the same for octahedral? It'll be exactly the opposite because now the ligands are disposed between the axis, there is no along the axis approach, okay, so for that so what I am trying to say is that symmetry tells you what to expect, it tells you groups of how many orbitals you'll get, but it does not give you the last word, you still have to think of electrostatics to understand which orbitals will have lower energy, which orbitals will have higher energy, okay, so this is how symmetry can make quantum mechanical problems simpler, right.

To close this discussion we are, in this course we are trying to study spectroscopy, so now what we have understood is that this D orbitals can have different energies in different fields, right, and we can rationalize it in terms of symmetry, what about the transition moment integrals? Let us see, let's talk about the octahedral field, octahedral case. You have T2G, you have EG, what is the transition moment integral going to be? $\langle \psi_2 | \mu | \psi_1 \rangle$, right, (Refer Slide Time: 17:43)



as usual instead of mu we'll work with the X, Y and Z components, okay, and do you find it difficult to understand if I write like this? What I've done is that I have essentially written 3 integrals together, in any case E orbitals or so the wave functions are the same, so I have just written X, Y, Z, so what I mean is that this is the short form of writing integral $\langle \psi_2 | X | \psi_1 \rangle$, integral $\langle \psi_2 | Y | \psi_1 \rangle$, integral $\langle \psi_2 | Z | \psi_1 \rangle$, three integrals just written together. Are we clear with this notation?

Now see in octahedral case it is very simple to tell you that DD orbitals are actually symmetry forbidden. Is it octahedral, octahedron you have a point of inversion, right, so this is a gerade orbital, isn't it? EG, T2G both are G, symmetric with respect to inversion, (Refer Slide Time: 18:42)



this is also G, it doesn't matter from which orbital to which orbital transition you are talking about.

What about X? What about Y? What about Z? Where do they belong? In octahedral field, X, Y, Z jointly form the bases for T1U, right, and in fact if you are only talking about inversion you don't have to talk about X, Y, Z together, just think of X, isn't it anti-symmetric with respect to inversion? Same is true for Y, same is true for Z, so this is U, so what is the product of G, U and G, it is U, right, that means the integrand is anti-symmetric with respect to inversion, and therefore it does not survive, the integral does not survive, the integrand is anti-symmetric with respect to inversion that is why the integral doesn't survive that is why as you know DD transitions are actually symmetry forbidden, alright.

Of course what happens when I go to an octahedral field, now it is not so easy right I cannot, I don't have a center of inversion, there I have to consider everything, all symmetry operations and see whether the triple product contains a totally symmetric representation, okay. For now we will not go into that, we'll come back to this in later class, okay, but before we leave this topic let us quickly remind ourselves where we stopped yesterday about molecular orbitals.

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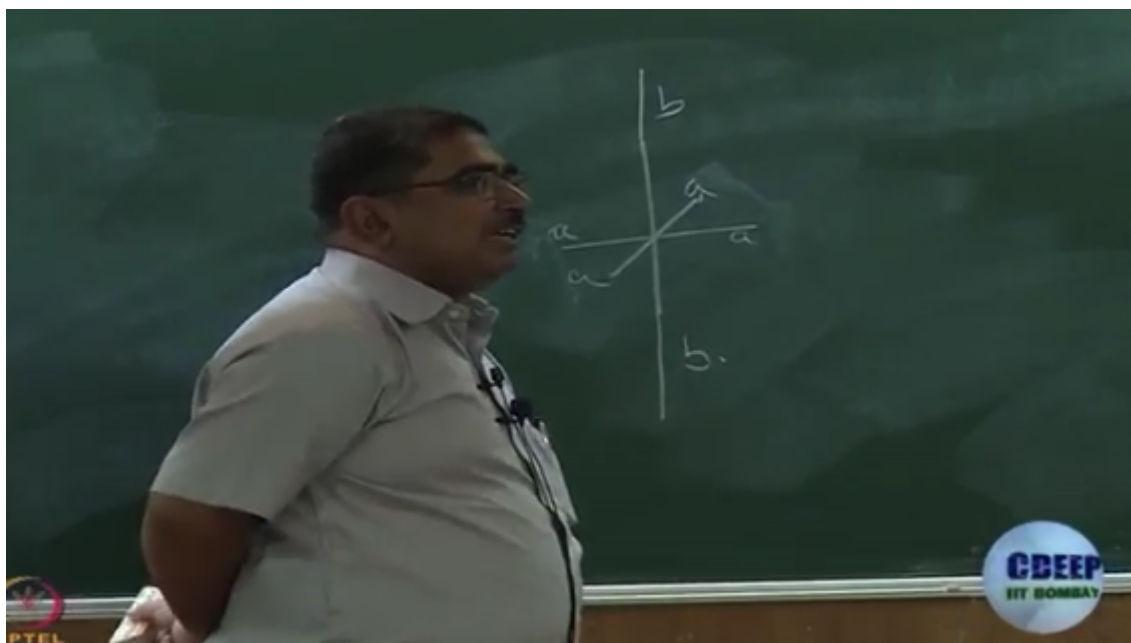
Homonuclear Diatomic Molecules: $D_{\infty h}$

	E	$2C_{\infty}$...	$\infty\sigma_v$	i	$2S_{\infty}$...	∞C_2	linear functions, rotations	quadratic
$A_{1g} = \Sigma_g^+$	1	1	...	1	1	1	...	1		$x^2 + y^2, z^2$
$A_{2g} = \Sigma_g^-$	1	1	...	-1	1	1	...	-1	R_z	
$E_{1g} = \Pi_g$	2	$2\cos(\phi)$...	0	2	$-2\cos(\phi)$...	0	(R_x, R_y)	(xz, yz)
$E_{2g} = \Delta_g$	2	$2\cos(2\phi)$...	0	2	$2\cos(2\phi)$...	0		$(x^2 - y^2, xy)$
$E_{3g} = \Phi_g$	2	$2\cos(3\phi)$...	0	2	$-2\cos(3\phi)$...	0		
...		
$A_{1u} = \Sigma_u^+$	1	1	...	1	-1	-1	...	-1	z	
$A_{2u} = \Sigma_u^-$	1	1	...	-1	-1	-1	...	1		
$E_{1u} = \Pi_u$	2	$2\cos(\phi)$...	0	-2	$2\cos(\phi)$...	0	(x, y)	
$E_{2u} = \Delta_u$	2	$2\cos(2\phi)$...	0	-2	$-2\cos(2\phi)$...	0		
$E_{3u} = \Phi_u$	2	$2\cos(3\phi)$...	0	-2	$2\cos(3\phi)$...	0		
...		



Molecular orbitals, so what we have shown you yesterday is that even molecular orbitals actually form basis for irreducible, before we go there is there any question in what we discussed so far? Yes, we erased it, this you don't have a problem right if I just write A everywhere, now if I write A A A A well in Jahn Teller distortion what I'm saying is that this two axial ligands have been pulled out that means they are distinct from the equatorial ligands, right, sorry, the bond is longer right, so what you can also do is you can talk about the bonds, you can name the bonds like that, I'll exaggerate a little bit, this is the figure so I call these bonds A A, A A, I call this bond B, I call this bond B, now it's not very difficult to see that B and B are equivalent but different from the 4 is, we just talked about the bonds, think of bonds as vectors, the lengths are different, sorry, we'll look at the shape of the molecule not just ligands, so bond length is also important right, so of course I mean what you expect is that if you have say A B A, then A B bond length should be the same, right, but then if you do a distortion here, why does Jahn Teller distortion take place anyway?

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Yes, so the bonds, bond lengths are not the same, isn't it, so since bond lengths are not the same, think that we are looking at the bonds, we've a way of looking at the bond lengths, this is what the picture is.

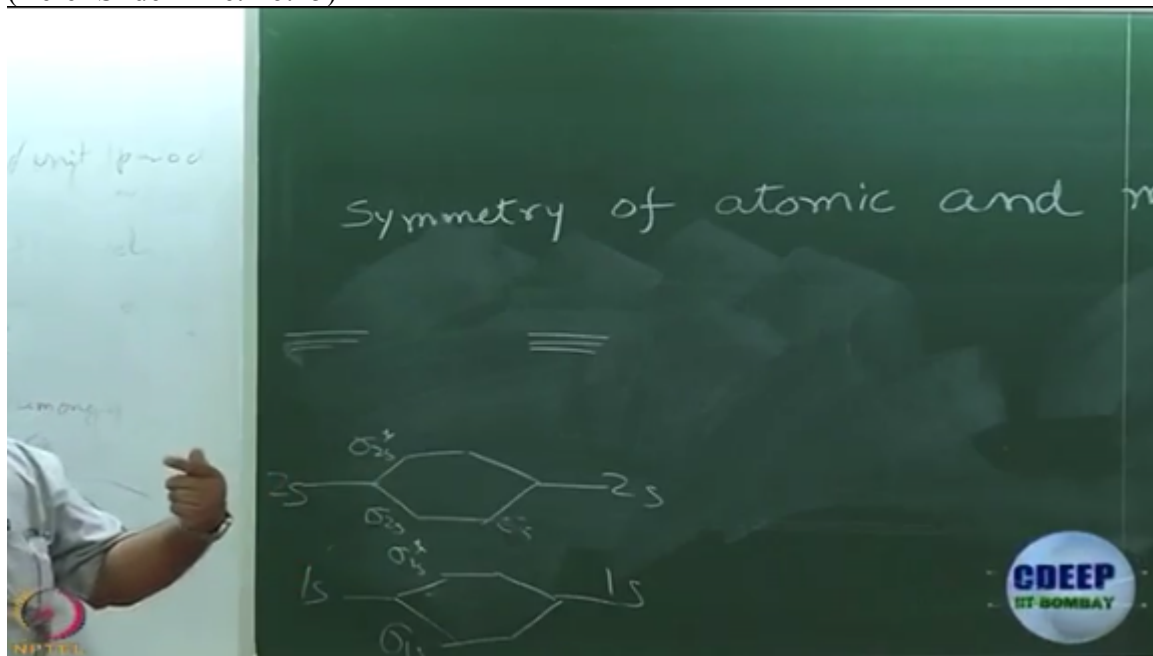
So if you work with the bond lengths do you understand there is going to be D_{4h} , that's good enough, it's not only ligand, see it is a shape of the molecule don't forget, if the ligands are for some reason placed at a larger or smaller distance then the symmetry changes, so it's equivalent to replacing the axial ligands by two different ligands.

Yes, sometimes we get slight DD transition, see we'll come back to that, wait until we do a little more detailed discussion of electronic spectroscopy, so what happens is forbidden transitions are not always for, I mean there are ways of working around forbidden transitions, so you can have things like spin orbit coupling by which the wave function is not what you would expect it to be without any correction, so the wave function itself is little changed, perhaps we can understand it if we think of what happen for un-harmonic oscillator, see for harmonic oscillator what was a selection rule? $\Delta V = \pm 1$, right, what about un-harmonic oscillator? The selection rule was $\Delta V = \pm 1, \pm 2, \pm 3$, but probability of transition kept going down steadily from ± 1 to ± 2 to ± 3 , why? Because in harmonic oscillator it is a part of system right, you don't have pure wave functions anymore, due to mixing of wave functions the transitions like $\Delta V = \pm 2$ that were forbidden earlier, now become allowed to some extent, right.

Similarly you can have mixing of orbitals by different means, spin orbit coupling being one of the most major reasons, we'll come to that or you can also have something called vibronic coupling, so when we talk about benzene for example you will see that a transition that is supposed to be forbidden is actually the most prominent transition in benzene that we see and that is because of what is called vibronic coupling, coupling of electronic and vibrational motion, okay. Let's wait for that we'll come there, okay.

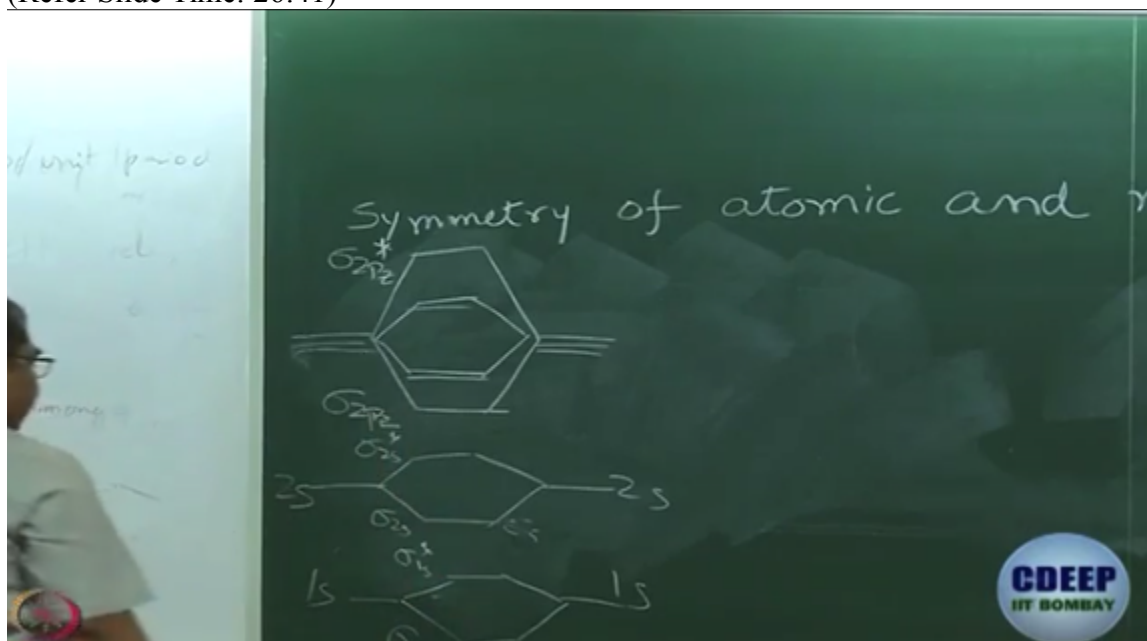
So where we stopped yesterday was this molecular orbitals, right, so let us just quickly see where the molecular orbitals would belong, we've already worked out in the previous class, let us take a simplistic scheme here, what we are saying is this 1S and 1S give you linear combinations to give you say sigma 1S and sigma 1S star, then 2S and 2S atomic orbitals give you, there is no space on the top that's the problem. 1S and 1S give you sigma 1S and sigma 1S star, 2S and 2S give you sigma 2S now I'll write here, sigma 2S and sigma 2S star, what about 2P?

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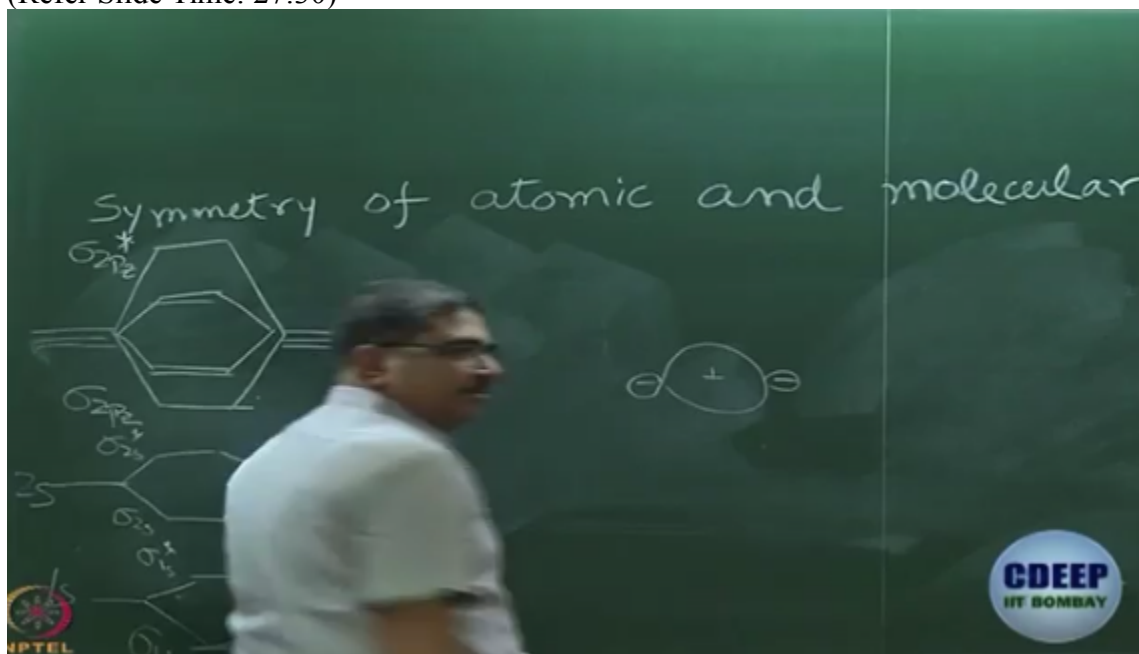
We consider the direction of approach of the two atoms to be the Z direction so 2Pz and 2Pz give you sigma interaction, and these give you pi interaction Px and Py, okay.

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So this we've already established right, that whenever you have bonding orbitals between two S orbitals what is the symmetry species? What is the irreducible representation? It's totally symmetric right, what do you call a totally symmetric representation in D infinity H? Sigma G+, so I can say that this is, there are different ways of writing this, I can say this is sigma G+, this is also sigma G+, this, what about this? When 2P orbitals give you a sigma bond, what is the symmetry? What does the molecular orbital look like?

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Something like this, right, right, so let us see quickly what the characters would be? For E character is 1, for C infinity what is the character? 1, what is the next symmetry operation? Sigma V, where is sigma V? This, plane of the board, of course there are many or I can take the plane of the board. What is the character? 1, what is the next one? S infinity, S infinity means you turn by this and reflect with respect to this,

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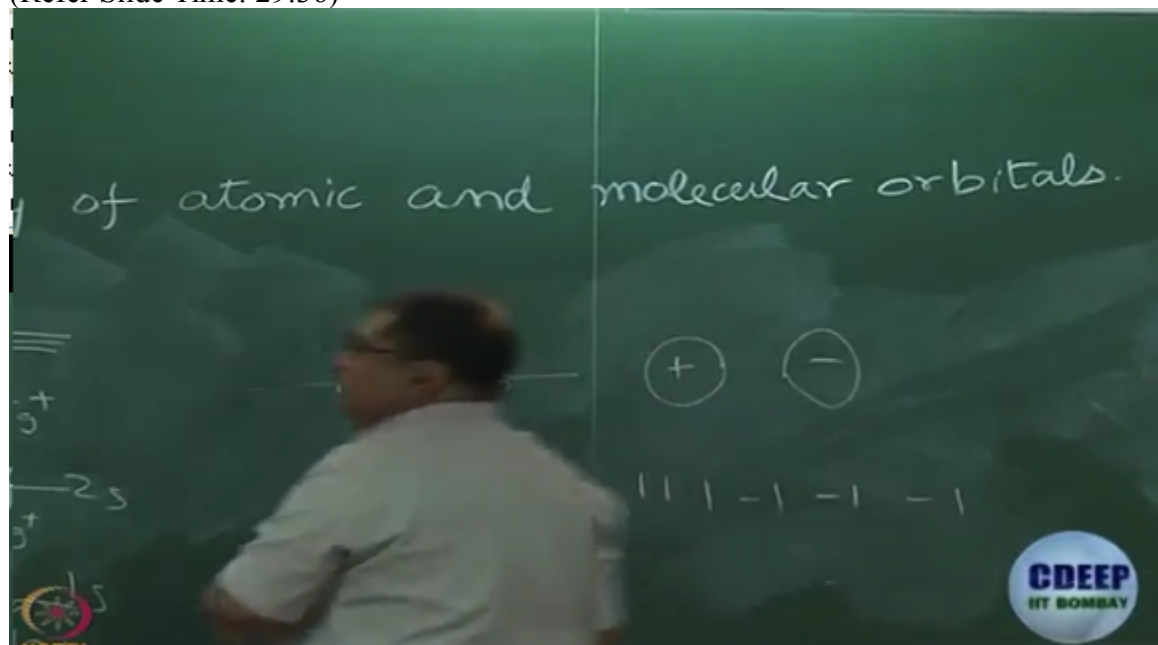
Homonuclear Diatomic Molecules: $D_{\infty h}$

	E	$2C_{\infty}$...	$\infty\sigma_v$	i	$2S_{\infty}$...	$\infty C'_2$	linear functions, rotations	quadratic
$A_{1g} = \Sigma^+_g$	1	1	...	1	1	1	...	1		x^2+y^2, z^2
$A_{2g} = \Sigma^-_g$	1	1	...	-1	1	1	...	-1	R_z	
$E_{1g} = \Pi_g$	2	$2\cos(\phi)$...	0	2	$-2\cos(\phi)$...	0	(R_x, R_y)	(xz, yz)
$E_{2g} = \Delta_g$	2	$2\cos(2\phi)$...	0	2	$2\cos(2\phi)$...	0		(x^2-y^2, xy)
$E_{3g} = \Phi_g$	2	$2\cos(3\phi)$...	0	2	$-2\cos(3\phi)$...	0		
...		
$A_{1u} = \Sigma^+_u$	1	1	...	1	-1	-1	...	-1	z	
$A_{2u} = \Sigma^-_u$	1	1	...	-1	-1	-1	...	1		
$E_{1u} = \Pi_u$	2	$2\cos(\phi)$...	0	-2	$2\cos(\phi)$...	0	(x, y)	
$E_{2u} = \Delta_u$	2	$2\cos(2\phi)$...	0	-2	$-2\cos(2\phi)$...	0		
$E_{3u} = \Phi_u$	2	$2\cos(3\phi)$...	0	-2	$2\cos(3\phi)$...	0		
...		

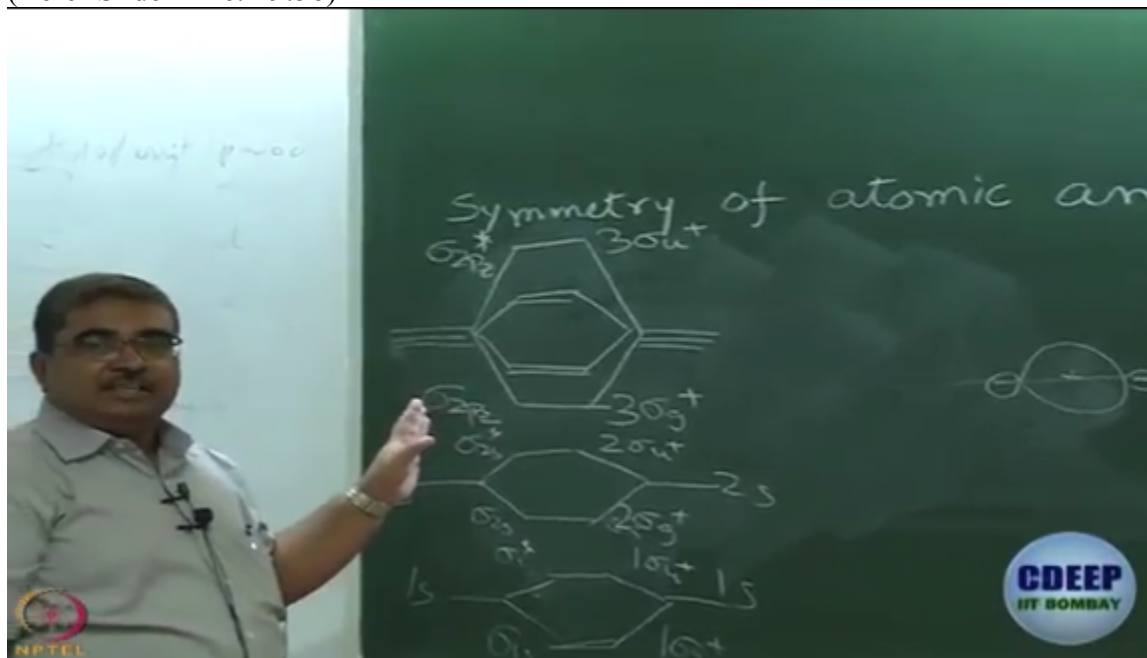
so what is the character? 1, and finally C_2 , this is C_2 , what is the character? 1, right, so even this is sigma G^+ . So what I can do is I can write this as 1 sigma G^+ , 2 sigma G^+ , 3 sigma G^+ , different books use different notations, you can use whatever is convenient for us.

What about the anti-bonding orbitals? Remember what was the anti-bonding orbital we worked it out yesterday, anti-bonding orbital sigma, something like this, for E the character is +1, for C_{∞} the character is +1, what is the next one? Yes, sigma V yes, sigma V what is the character? 1, then what is it? I, oh I missed I in the previous one but no harm, for I what is the character? -1. Then S_{∞} , what is the character? S_{∞} is also -1. And finally C_2 , C_2 -1, so 1 1 1, -1 -1 -1, 1 1 1,

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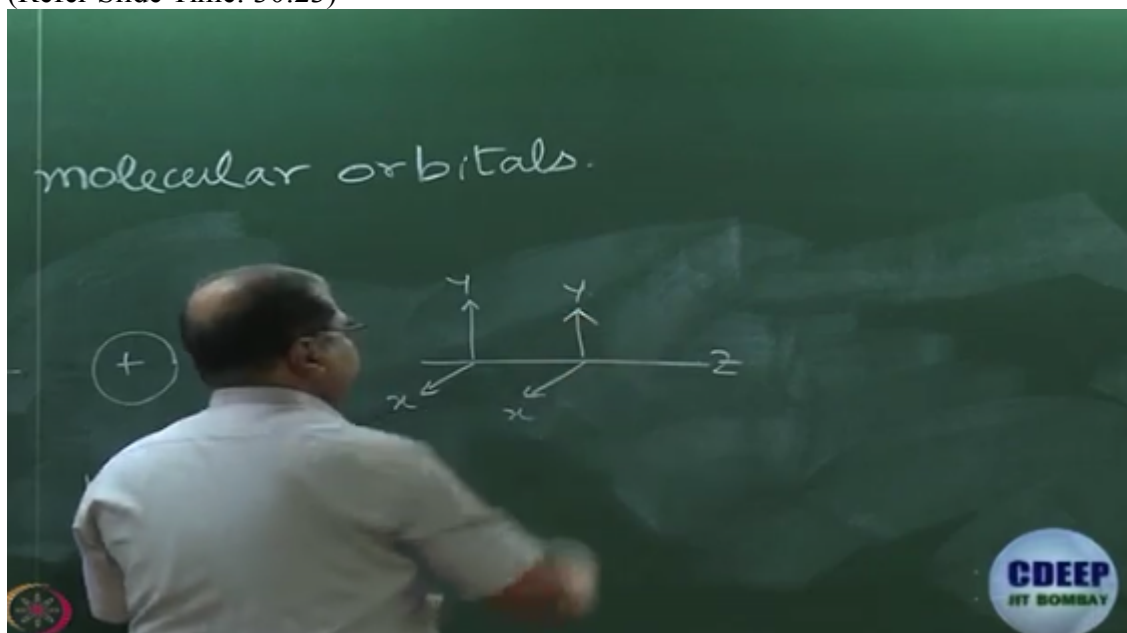


-1 -1 -1 it is sigma U+, so all this anti-bonding sigma orbitals can be written as say 1 sigma U+, 2 sigma U+, 3 sigma U+, I'm only left with the pi orbitals now,
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pi orbitals do not belong to a 1 dimensional representation.

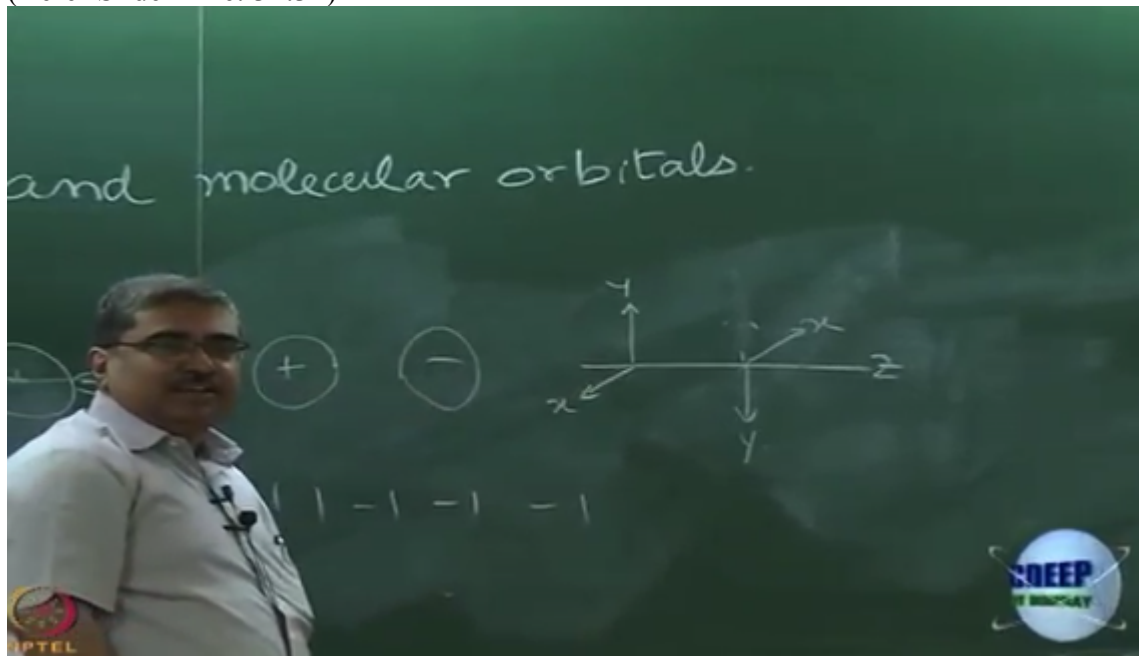
Let me draw them like this, this is Z that is defined okay, is it difficult to understand if I draw the P orbitals as arrows?
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These two arrows denotes the P orbitals of the two atoms and this two arrows denote, sorry this two arrows denote the PX orbitals of the two atoms, the vertical arrows denote the PY orbitals of the two atoms, are we clear? How will they transform? They'll transform exactly like X and Y axis, we don't even have to work it out it's given here.

Where do X and Y belong? Pi U, alright, pi U, so the bonding orbital here is actually pi U, you can work this out yourself and convenience yourself that this two PX and PY, two sets of PX and PY actually form bases for pi U when it is bonding.

What about the anti-bonding ones? When I write XY I mean PX, PY,
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this is the situation for anti-bonding, where will they belong? Once again they cannot be your, they cannot be bases for a one dimensional representation because the issue is this, this is X, this is Y right, like this, where is C infinity? C infinity is towards you, see if I do a rotation with respect to C infinity what does it happens? This transform coordinates cannot be written in terms of only PX or only PY, the transform coordinates have to be written as a linear sum of PX and PY, there is no other way that is why they jointly form the bases for a 2D representation, now this is the situation that we have done already, what I am asking you to do is this, 2D representation work out where it'll belong, one thing you can tell me right away, is it G or is it U? It is G isn't it? Look at my thumbs, and look at my index fingers, do you see the center of inversion? Right, right, so it's G, actually it is pi G, the anti-bonding pi orbital is pi G, so this is how you write it, how you write the names of the molecular orbitals in terms of symmetry.

The next thing to do is symmetry of states, okay, but before I go there I think it is better if we complete our discussion of vibrations of polyatomic molecules, then we'll comeback to this, okay, so we close this discussion here, we'll begin vibrations after this.

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