INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

IIT BOMBAY

NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING (NPTEL)

CDEEP
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MOLECULAR SPECTROSCOPY: A PHYSICAL CHEMIST'S PERSPECTIVE

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IIT BOMBAY

Lecture no. – 38
Wave functions as basis

We are going to talk about wave functions as bases.
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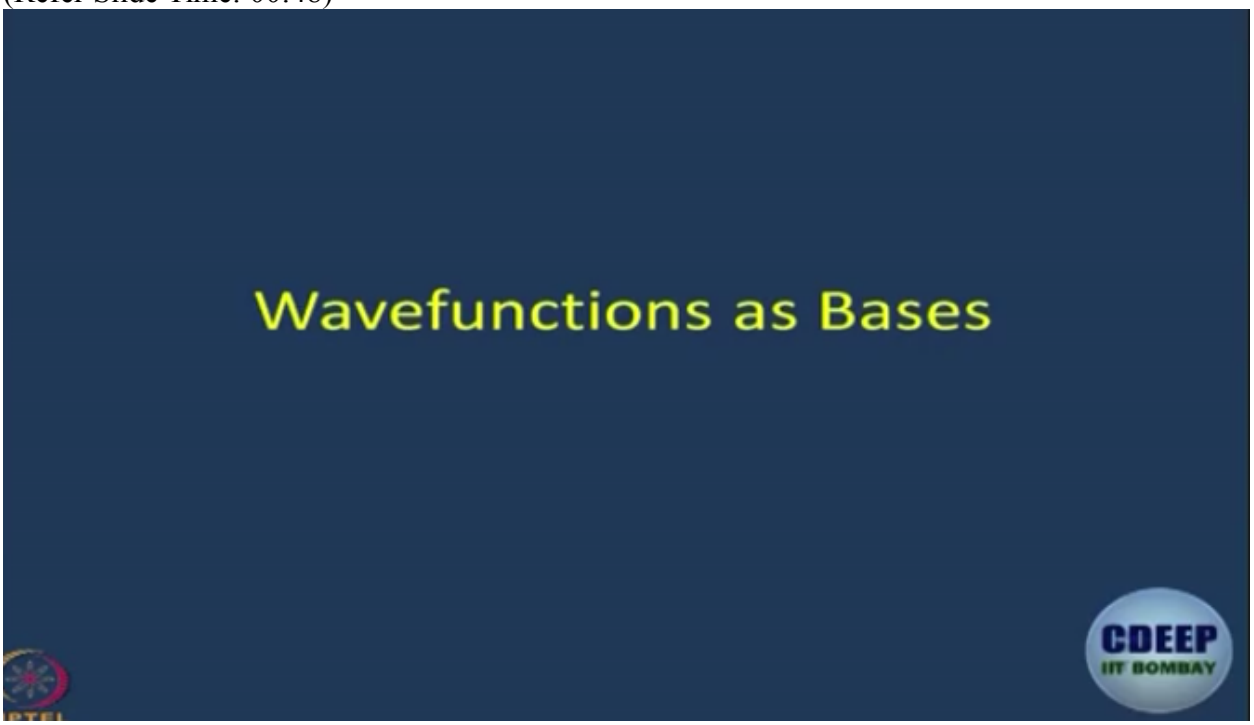

See so far we have been using X, Y, Z and so on and so forth as the bases, but the reason why we studied is that we want to work with wave functions.

Before we start talking about wave functions as bases, I'll briefly bring, I'll briefly draw your notice to special character tables rather character tables or twos very special symmetry point groups, one is D infinity H, the other is C infinity V, okay. Think of H2 for example, so far before we started this discussion on symmetry we have restricted ourselves to diatomic molecules, right, so the simplest diatomic molecule you can think of is H H, di-hydrogen isn't it? Right, let us see what are the elements of symmetry or operations of symmetry that are there in this di-hydrogen molecule, first of all you have an axis of course, this is an axis, okay.
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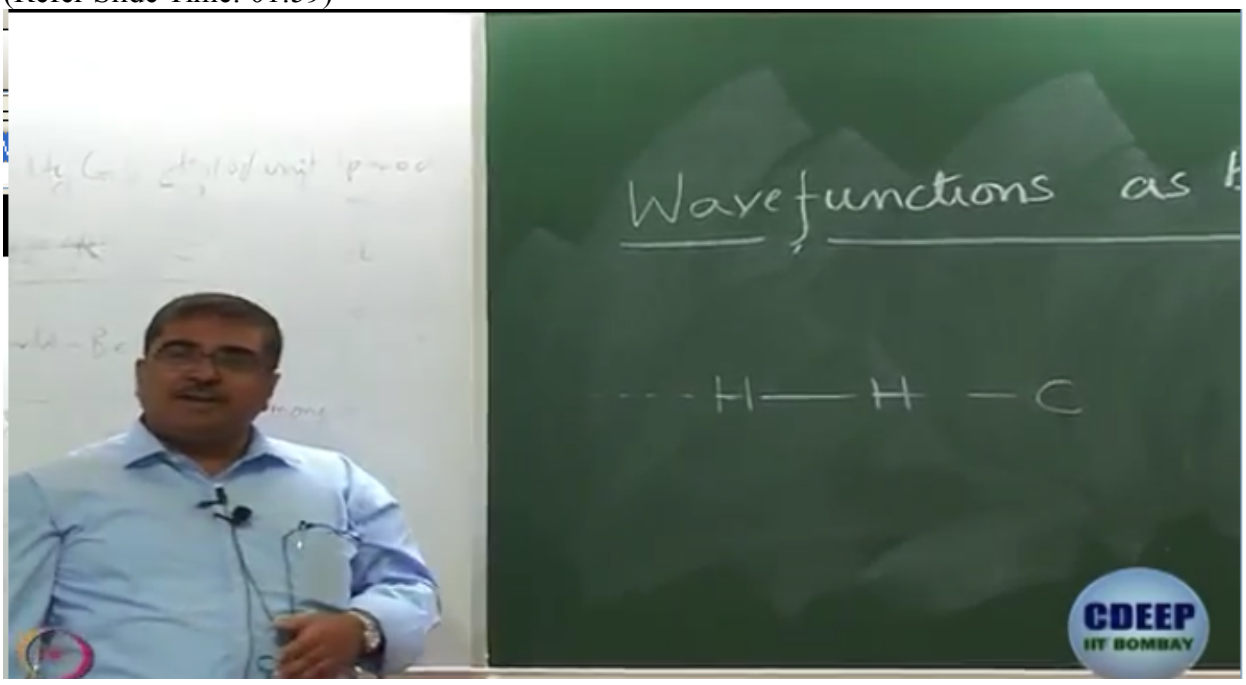

CN, what is N here? Infinity, what does that mean? If you rotate by a very small amount at 0.0000000 as many 0's as you think 1 degrees, then also you get a symmetry operation right, this is my di-hydrogen molecule, I rotate by any amount, small amount or large amount doesn't matter, I get back the same di-hydrogen molecule in the same configuration, so this here is CN, don't forget rotation is by 180 degrees/N, so if I rotate by a very amount then N goes up, if I rotate by an infinity decimal amount, N is infinity, are we clear with that?
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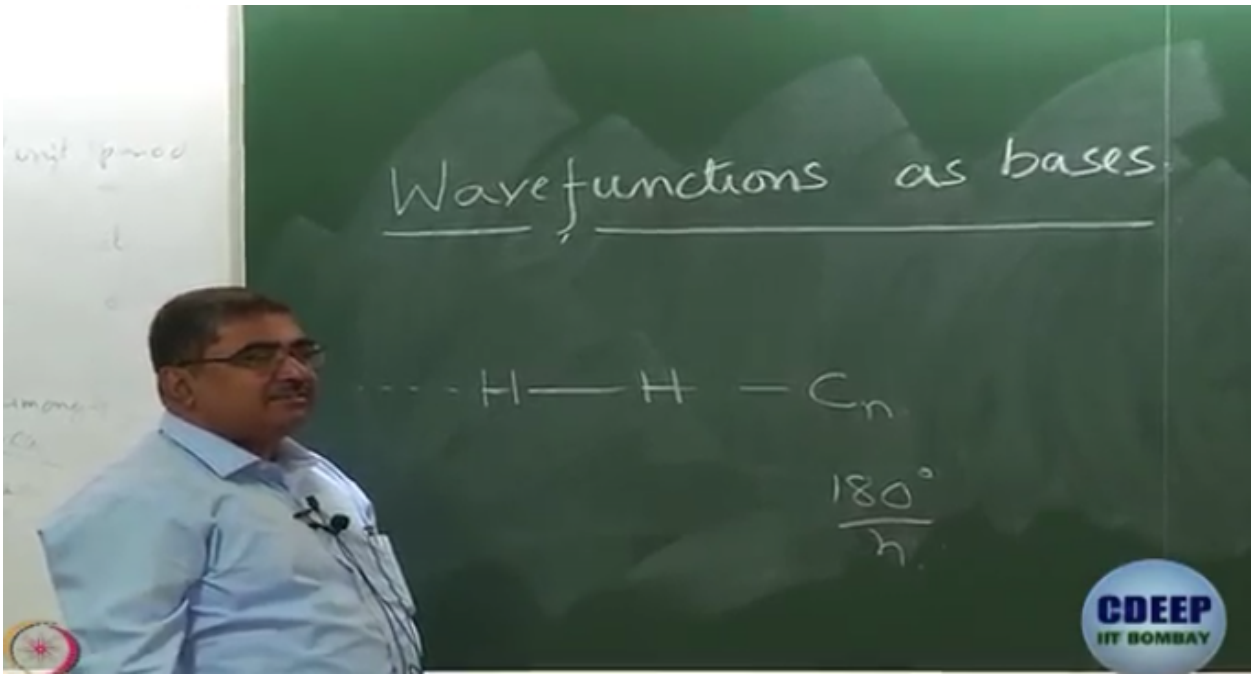

Now, is there any other axis of symmetry? If I go through the mid-point and I drop perpendicular line I get a C2, right, di-hydrogen rotate by 180 degrees, the two hydrogen atoms change places. Now since my rotation is restricted, it's better to use this pen, this pen is not really like di-hydrogen, it's more like HCL, but assume that it's di-hydrogen, this is a C2 axis right, how many such C2 axis can I think? First of all the C2 axis is perpendicular to the CN axis, isn't it, C infinity, how many such C2 axis are there? Infinite, this is C2, this is C2, anywhere you can have a C2, so there are actually infinite number of C2's, what is the name then from these two? N is infinity, and you've perpendicular C2's, so the name becomes D infinity already,

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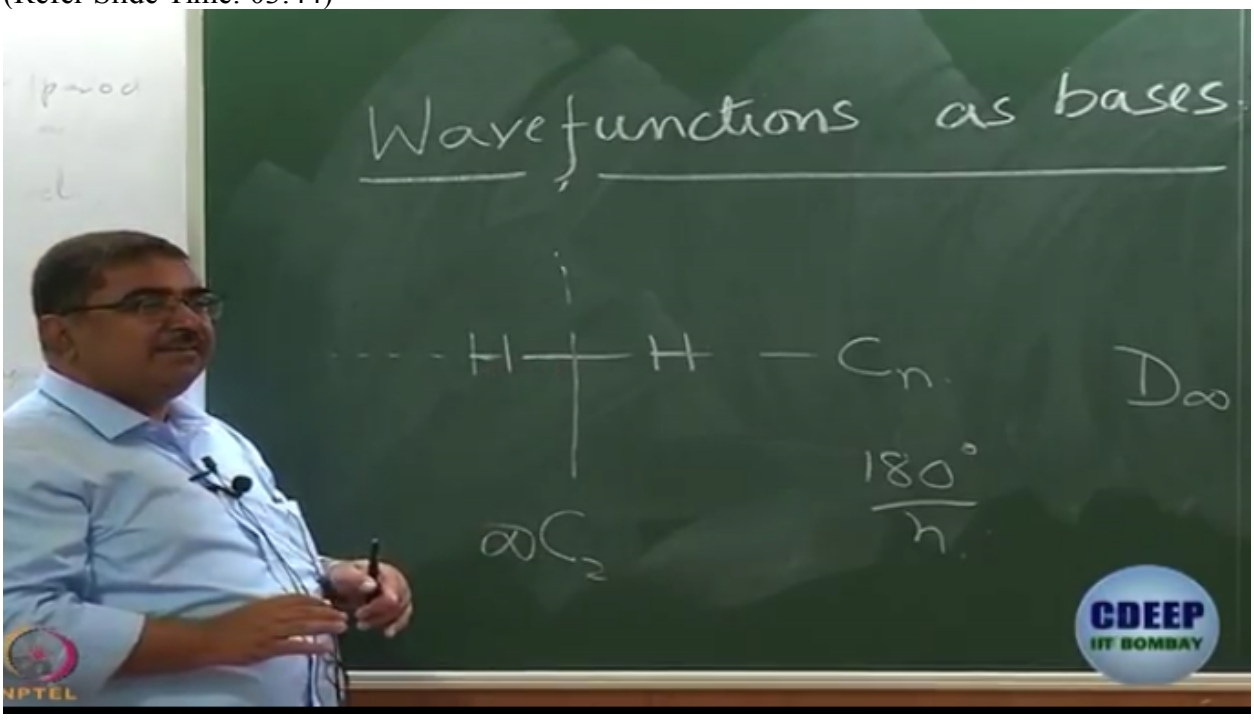

next thing to look for is a horizontal plane, do I have a horizontal plane here? Where is it? This or this? This is a horizontal plane right, this here is your sigma H, so this is the D infinity H point group.

Which are the symmetry operations are there, point of inversion is there? Right, the sigma V's will be there, okay, many things, okay.
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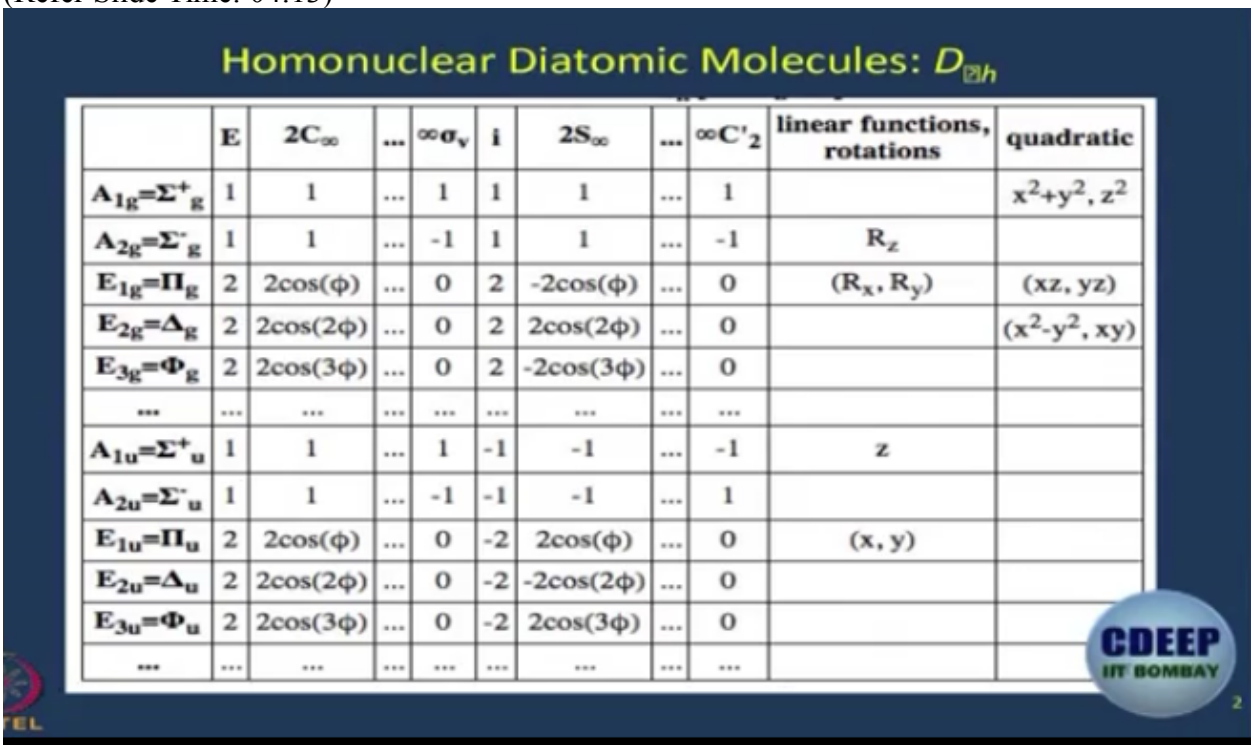

	E	$2C_\infty$	...	$\infty\sigma_v$	i	$2S_\infty$	...	$\infty C'_2$	linear functions, rotations	quadratic
$A_{1g}=\Sigma^+_g$	1	1	...	1	1	1	...	1		x^2+y^2, z^2
$A_{2g}=\Sigma^-_g$	1	1	...	-1	1	1	...	-1	R_z	
$E_{1g}=\Pi_g$	2	2cos(ϕ)	...	0	2	-2cos(ϕ)	...	0	(R_x, R_y)	(xz, yz)
$E_{2g}=\Delta_g$	2	2cos(2ϕ)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

So then how do you write the character table for such an infinite point group? See H2 is the simplest molecule that we can think of, but its character table turns out to be as complex as it can be, maybe not all that complex also, so the only way in which you can work out this character table is by inspection, right? So these are the irreducible representations, this dot dot dot means there are many more, okay.

Since there are infinite number of symmetry operations we cannot of course right that, so what we do is we only write a representative few E, 2C infinity, why have I written 2C infinity? Where is the other C infinity? C infinity +, C infinity -, right I can rotate this way or I can rotate this way, then infinite number of sigma V's, I there is only one, S infinity is also there, C infinity doubles as S infinity, 2S infinities and infinite number of C2's, C2 dash means C2 that is perpendicular to your C infinity axis, and you can work out this characters by inspection.

What is this phi? Phi means the small angle or maybe not small angle by which the rotation is performed with respect to your C infinity, okay, so this here is the character table for D infinity H, and since it's a special character table Mulliken nomenclature is also special. See the first one, first irreducible representation you have that is of course totally symmetric, so you usually call it A1G but you don't. To recognize the fact that it is a special character table you call it sigma G+, this one is A2G, A2G means what? Symmetric with respect to C infinity therefore A, anti-

symmetric with respect to sigma V therefore 2, and symmetric with respect to I therefore G, okay, don't call it A2G you call it sigma G-, G is the same, it's just that instead of A1 I'm writing sigma +, instead of A2 I'm writing sigma-, okay.

And then next we come to the two dimensional representation, this one 2 here, 2 cos phi means it is still kind of symmetric with respect to the rotation, and it is symmetric with respect to I, how do you get 2 character? 1 and 1 along the diagonal, so X remains X, Y remains Y that kind of a situation, so it is E1G instead of that you call it pi G, instead of E2G you call it delta G, so its important to remember that pi G and delta G or pi U and delta U for that matter are actually 2 dimensional representations.

Instead of E3G you write phi G, and then for all these you have the corresponding on gerade representations as well. Have you understood? At least roughly, how this character table is written and how the Mulliken nomenclature is performed, okay, first of all the character table is worked out not fully only partially by inspection. Secondly Mulliken nomenclature is sort of special, okay, and this is a good character table to start our discussion of your functions orbitals as bases elements, okay, let us see.

We are talking about H2, aren't we? D infinity H is H2, so do you remember the molecular orbitals that we've all studied somewhere or the other, right, what is the lowest energy molecular orbital? One is atomic orbital, okay, some sigma orbital right, what does it look like? This 1S + 1S, right? Actually it's okay if I simply write this,
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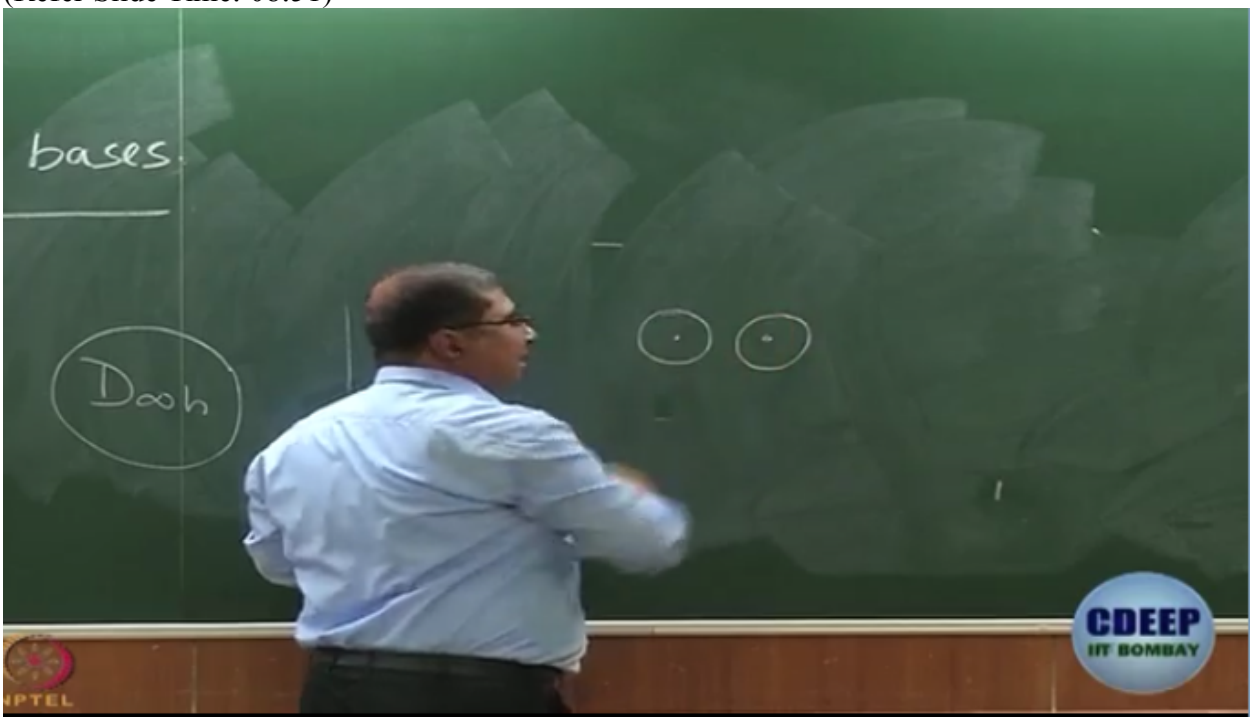

I don't really have to draw an ellipse or something like that, but it's important that I write the signs of the wave function,
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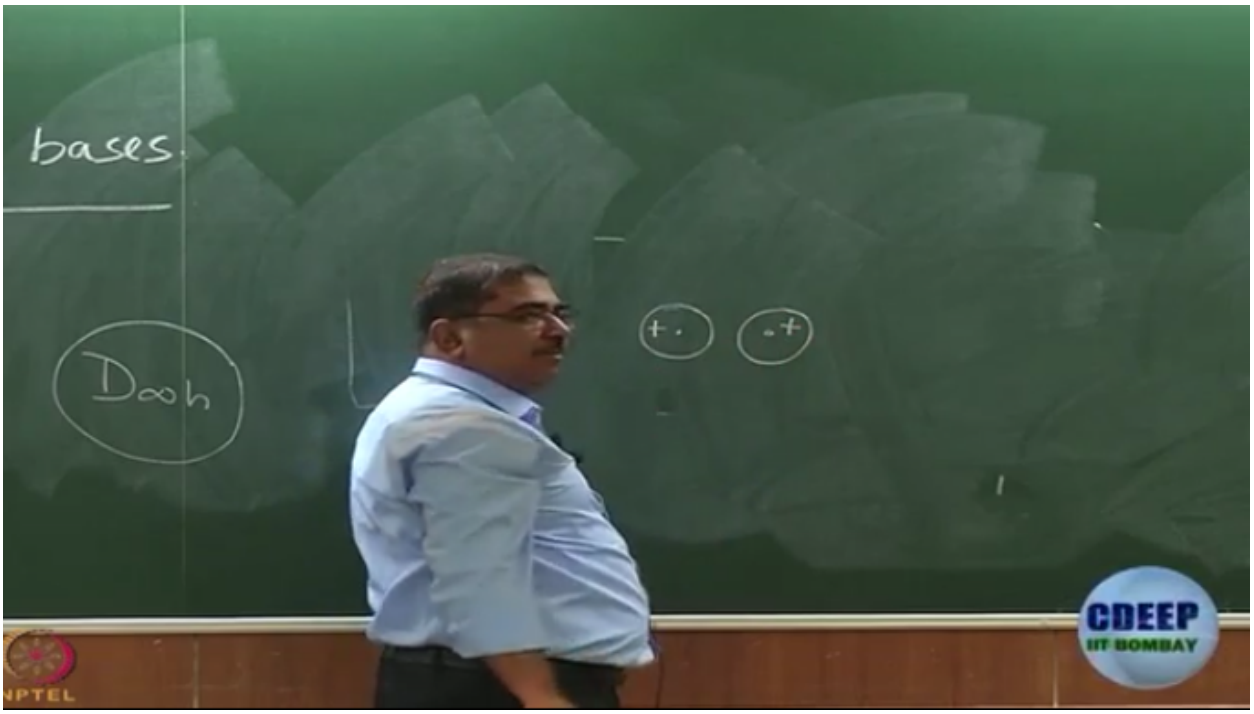

this is your bonding orbital and neglect the size, sizes are supposed to be the same, it's just different levels of enthusiasm while drawing the wave function, one is plus, one is minus, okay,

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now take this, can you tell me to which symmetry species it belongs? The bonding orbital, let's see, with respect to E of course it is, the character is 1, with respect to C infinity character is 1 or -1? The bonding orbital character is 1,

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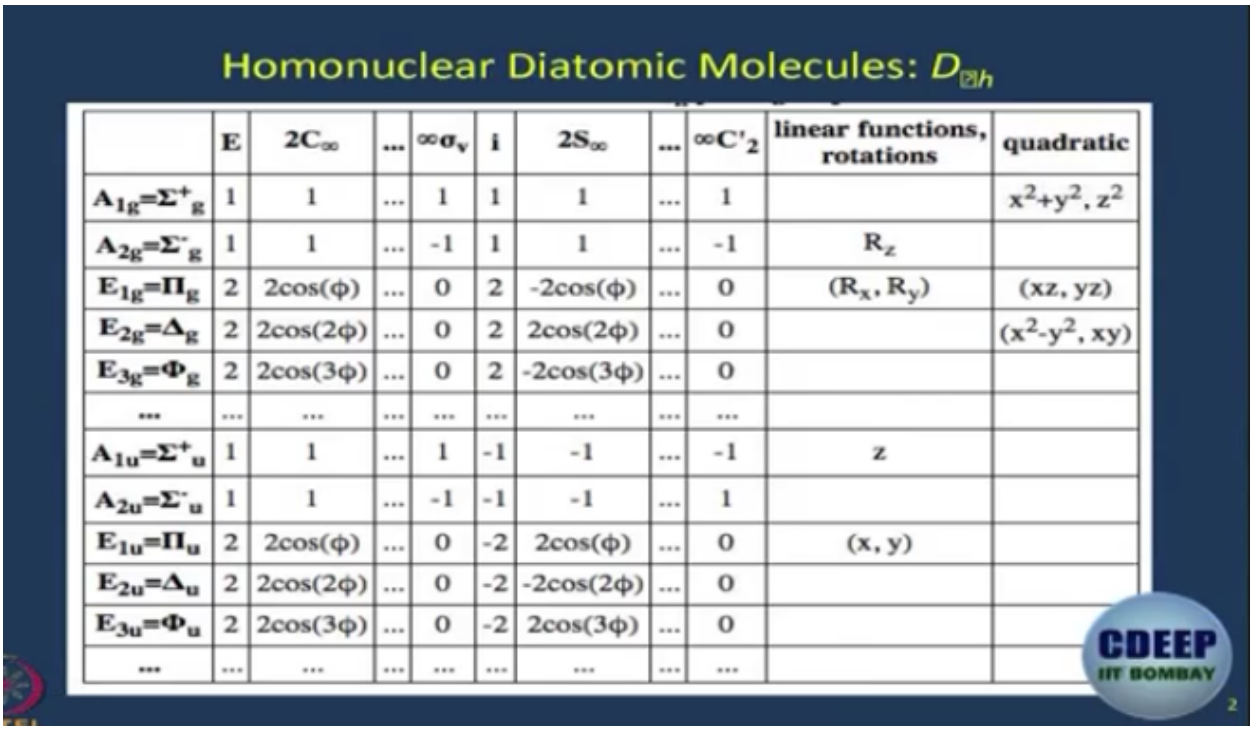

	E	$2C_\infty$	...	$\infty\sigma_v$	i	$2S_\infty$	...	$\infty C'_2$	linear functions, rotations	quadratic
$A_{1g}=\Sigma^+_g$	1	1	...	1	1	1	...	1		x^2+y^2, z^2
$A_{2g}=\Sigma^-_g$	1	1	...	-1	1	1	...	-1	R_z	
$E_{1g}=\Pi_g$	2	$2\cos(\phi)$	...	0	2	$-2\cos(\phi)$	...	0	(R_x, R_y)	(xz, yz)
$E_{2g}=\Delta_g$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

with respect to sigma V, is the character +1 or -1? +1, with respect to I? +1, S infinity? C2, but everything is +1 right so it belongs here, sigma G+ right, so what I do is I call it this sigma G+ orbital.

What do you call this kind of a bonding? Sigma bonding, isn't it? You call it, this orbital is a sigma bonding molecular orbital, this is why, this is where the name comes from. This well-known sigma name comes actually from the character table, that's why you call it sigma, okay, so this orbital from now on we are going to call it sigma G+ orbital, you might note that I have used small sigma here, right, that is the other convention we are going to follow, whenever we write a wave function we'll use small letter, whenever we talk about a state we use a capital letter, that is going to come very handy in our discussion of electronic spectroscopy, okay, that being said where does this belong? The anti-bonding orbital, anti-bonding orbital, what is the character for E? -1, 1, what is the character for C infinity? 1 or -1? Not -1 be careful, 1, confident 1? Okay, then it's 1.

What is the character for sigma V? Where is sigma V? Sigma V, this is your C infinity, right, so don't forget horizontal plane is like this and sigma V is the plane of the board,
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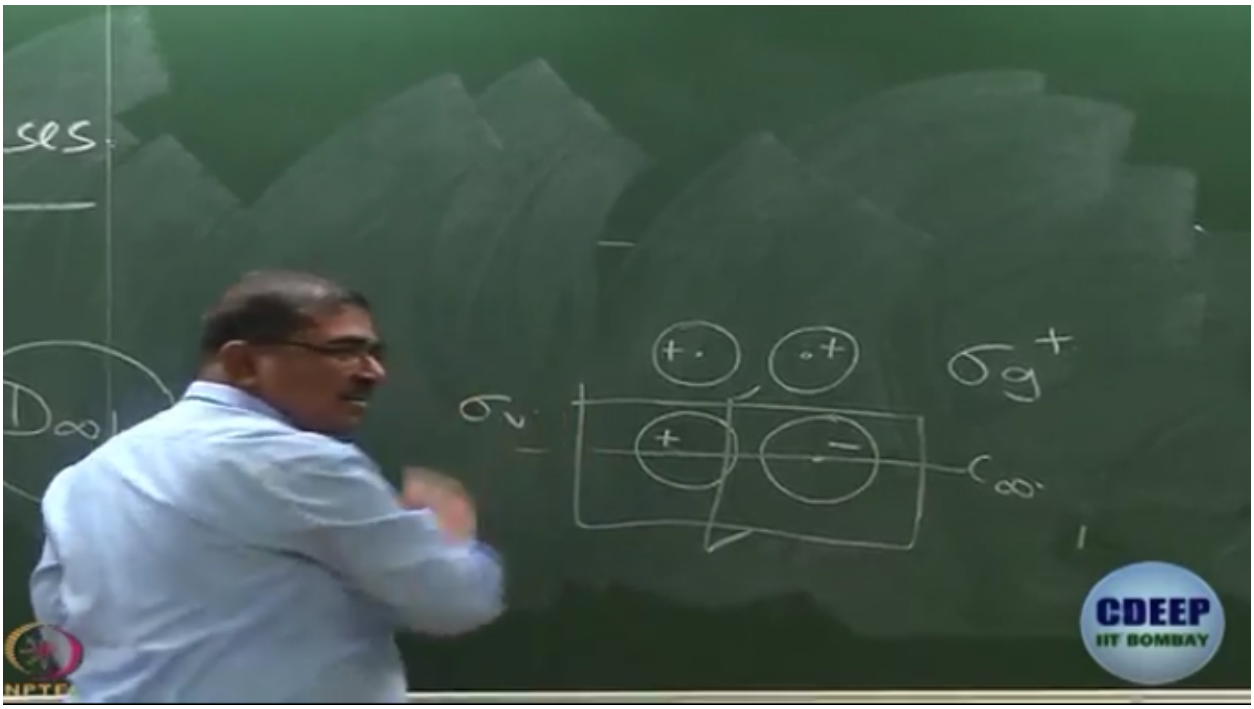

so let's try again, what is the character for sigma V? +1, see this plus and minus right, so you can think of them as spheres, okay, and basically bisecting as sphere, this plus you can think is a rate sphere, minus you can think is a blue sphere, but red interchange red and red hemispheres, blue and blue hemispheres interchange, are we clear? So that is -1 remember.

So now 1, 1, -1 what about I? Symmetric or anti-symmetric with respect to inversion, we are talking about the bonding orbitals, sorry anti-bonding orbital, symmetric or anti-symmetric? Anti-symmetric convinced, are we convinced? Start from any point, go to the center extrapolate the sign changes, so -1, what do we have? 1 1, -1 -1, F infinity, F infinity, rotation and then reflection, so the loops interchange, okay, -1, C2 dash C2 dash, C2 dash, exactly with other, don't forget this is C2, right, so you do a C2 dash + and – loops interchange, okay, plus minus, where is C2? Here so interchange like this, okay, so what are the characters? 1 1, -1 -1 -1 everywhere else, where is it? Where is it? Oh, then it must be somewhere here, right, first of all it has to be U, A1U, A1U is something we don't use, we use sigma U+. Yes sir, sorry, sorry, sigma V is +1 not -1, if it is -1 I've made a mistake, don't forget what sigma V is, actually we discussed it correctly but then in the heat of the moment I change the sign, this is sigma V right plane of the board, so as you agreed for sigma V the character is +1 not -1, so I made a mistake here, so character of E is 1, character of C infinity is 1, sigma V is 1, I-1, S infinity -1, C2 dash is -1, okay, so this orbital is called the sigma U+ orbital. If you want to add a star to denote that it's anti-bonding it is up to you. Are we clear? Are we clear?

So what we have demonstrated is that at least molecular orbitals, wave functions of a molecule, electronic wave functions of a molecule can form bases for the irreducible representations and that is what forms the bases of symmetric classifications of wave functions, okay.

Let us close today's discussion with this D6H, no not D6H actually I want to do octahedron, okay, for the moment I don't want to show you the last column, okay, let us talk about the atomic orbitals of the central metal ion in an octahedral complex,
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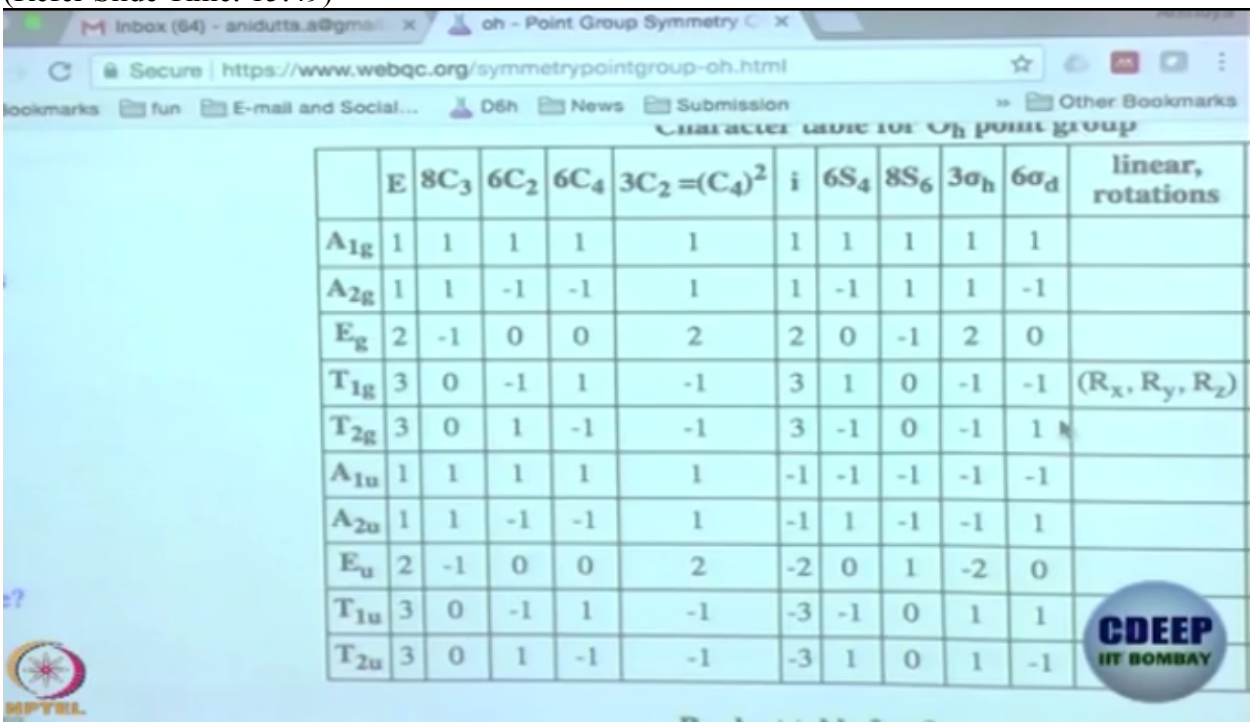

	E	$8C_3$	$6C_2$	$6C_4$	$3C_2=(C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear, rotations
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	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	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	

okay, S orbital of course is totally symmetric, right, S sphere, now it's important to understand that a sphere is the most symmetric object you can think of right, it has infinite number of symmetry operations of infinite kind, only one symmetry operation is there which is only one in number for a sphere that is point of inversion, otherwise you think of any line that goes through a close to the center it is CN and N can raise from anywhere to anywhere, right, there are infinite such, you can think of infinite planes going through the center and so on and so forth, right, so well if you think of the S orbital, any S orbital of the central metal ion in an octahedral complex it will be A1G, right. Think of the P orbitals, P orbitals are along X, Y, Z axis, right, where will they belong? Same symmetry species, same irreducible representations as your X, Y and Z and here as you see X, Y, Z jointly form the bases for T1U, so for an octahedral complex S is A1G, PX, PY, PZ jointly form the bases for T1U.

What about the D orbitals?
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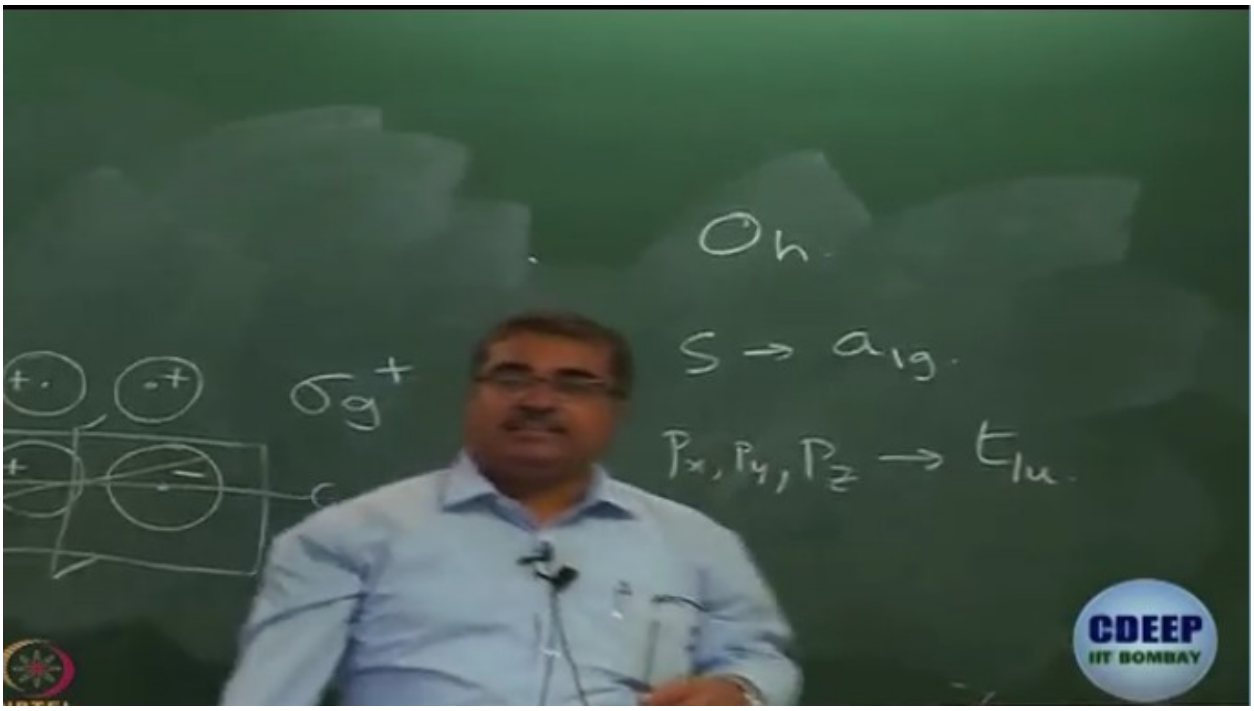

Do you remember the names of the D orbitals? DZ square, DXY, DYZ, DZX, so these are all your quadratic functions isn't it? And can you tell me why DZ square is called DZ square, or DZ, XZ, ZX is called DZX? Because in this wave functions those functions are actually there, there is something like 3 cos square theta YR square -1 in DZ square, okay, and that when equated to 0 gives you the equation of the node, maybe what we'll do is we'll stop here and we'll start from here next day and go on to vibrational wave functions, first we'll talk about the D orbitals then only we'll go on to vibrational wave functions.

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