Symmetry and Group Theory
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Lecture -40
Symmetry Adapted Linear Combinations

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Lecture 32 Let us take a C_{3v} point group

We will consider a general function $xz + yz + z^2$. and see how to obtain a function out of this function which forms basis of 'E' representation.

C_{3v}	E	C_3	C_3^2	$\sigma_{v1}(xz)$	σ_{v2}	σ_{v3}
E	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}$	$\begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix}$	$\begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix}$

Now let us apply Sym Operations on x, y, z

So, in the previous lecture we have seen the derivation part of projection operator and now let us see an example and see how the actual projections can be calculated out of a given function. See the job of a projection operator is to project out a part of function onto a irreducible representation so that we know that whatever function comes out is the basis of a given irreducible representation. So, without wasting time, so let us actually try to take an example and see. C3v point group example because we have seen all the matrices.

And we have no difficulty understanding how the matrices are obtained for this particular point group now. So, let us take an example of this point group and what we are going to do is we will consider a general function. As of now we are not taking any of the atomic orbital wave functions we will just consider a general function. Let us say xz + yz + z square and this particular example I am taking this is a solved example in Cotton book.

So, if you have any difficulty understanding you can also refer to Cotton but once we do this example, we should be through with how to use projection operator and then we will take up unsolved examples also. So, we will consider general function this under the C3v point group. And see how to obtain function let us say out of this function which forms basis of E representation.

So, this E is the Mulliken symbol E not the Symmetry element E or symmetry operations. So, let us first write down all the matrix elements for E representation for C3v point. And now we have to expand on all the symmetry operations because the matrices are different, so C3v. This is the E representation which we are talking about. So, for E symmetry operator we have it is a two-dimensional representation because it is E.

So, this is for C3, we have minus half, minus root 3 by 2, root 3 by 2 and minus half. For C3 square, so I am not going to show you how to do this now because we have already discussed this, C3 square is minus half and this becomes plus and this element becomes negative this remains as minus half, then we have sigma. Let us call this xz let us say sigma v1 which is basically xz and one of the vertical planes we can take along the axis and rest of the two will be in the middle of the axis.

So, this will be 1, 0, 0, minus 1, and for the other two sigma v2 this also we have learnt how to write the matrices, so I am just writing it straight away. So, you can work it out to yourself how to do this. So, now these are the matrix elements now let us apply operators onto x, y, z.

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C_3	$-\frac{1}{2}x \; -\frac{\sqrt{3}}{2}y$	$\frac{\sqrt{3}}{2}x \; -\frac{1}{2}y$	z
C_3^2	$-\frac{1}{2}x \; +\frac{\sqrt{3}}{2}y$	$-\frac{\sqrt{3}}{2}x \; -\frac{1}{2}y$	z
$\sigma_{v1}(xz)$	x	$-y$	z
σ_{v2}	$-\frac{1}{2}x \; +\frac{\sqrt{3}}{2}y$	$\frac{\sqrt{3}}{2}x \; +\frac{1}{2}y$	z
σ_{v3}	$-\frac{1}{2}x \; -\frac{\sqrt{3}}{2}y$	$-\frac{\sqrt{3}}{2}x \; +\frac{1}{2}y$	

So, let us do it systematically so that; because we are going to be using all of this, so let us make a table out of it. So, here I am going to write the function or the operator and here I am going to like the function what happens to x what happens to y and what happens to z. So, when E is applied on x, it is x and correspondingly y, and z so nothing changes. Now for C3 now we can use this matrix over here to be able to save what happens if we apply C 3 onto x to get minus half x + minus root 3 by 2 y.

When C3 is applied on y we get root 3 by 2 x, so you have the matrix if you do it on x y whatever resultant you get you just try to over here. This is minus half y so these two matrix elements are coming from here and here these two matrix elements are coming from here and here and z remains as it because C3 is lying along z axis. So, similarly I am just going to write all the resultants of various operators on to this.

So, x and z does not change y goes to minus y, so this is simple. For sigma v2 we have the matrix so just use that minus half x + root 3 by 2 y, root 3 by 2 x + half y all the planes are along z axis so nothing change is there. Sigma v3 minus half x, minus root 3 by 2y, minus root 3 by 2 x + half y and z.

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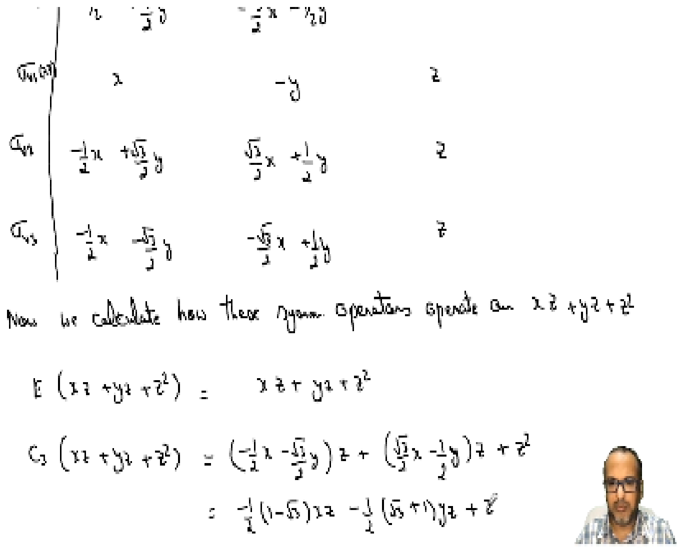

So, we now know what happens to each and every function upon these operations. So, now we calculate effect of these operators on to the given function. So, here we are calculating the projection out of the given function, which will have the symmetry or which will form the basis for E representation, so that is why we have taken E representation matrix. So, let us say what happens if we apply E onto xz + yz + z square so this remains same. Now what happens for C3? Let us calculate for C3.

So, we first have to calculate we already have listed down. So, we will first put here what happens to x multiplied by what happens to z. Similarly, what happens to y and what happens to z and so on. So, this is easy, it is just tedious calculation minus half x minus root 3 by 2 y multiplied by z. So, C 3 on x gives you this C 3 on z gives you z. So, that is how xz becomes this. Now C3 on y gives you root 3 by 2 x minus half y and z remains as z.

So, now we can separate this out, separate out the variables, so if you take xz common, so we will have xz coming from here also so we can write this as minus half 1 minus root 3 xz somewhere here I can take yz from here minus half root 3 + 1 yz plus z square. So, this is the effect of C3 onto this function, which is written over here. So, similarly this; calculate for the rest of the symmetry operators.

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$$C_3^2\,(xz + yz + z^2) = \left(-\frac{1}{2}x + \frac{\sqrt{3}}{2}y\right)z + \left(-\frac{\sqrt{3}}{2}x - \frac{1}{2}y\right)z + z^2$$

$$= \left(-\frac{1}{2} - \frac{\sqrt{3}}{2}\right)xz + \left(\frac{\sqrt{3}}{2} - \frac{1}{2}\right)yz + z^2$$

$$\sigma_{v1}(xz + yz + z^2) = xz - yz + z^2$$

$$\sigma_{v2}\,(xz + yz + z^2) = -\frac{1}{2}(1-\sqrt{3})\,xz + \frac{1}{2}(\sqrt{3}+1)\,yz + z^2$$

$$\sigma_{v3}\,(xz + yz + z^2) = -\frac{1}{4}(1+\sqrt{3})\,xz + \frac{1}{2}(-\sqrt{3}+1)\,yz + z^2$$

So, for C3 square, so now I will just write down the answers, ok let us do it completely. So, you should able to calculate, this one is easy. So, again I will just write down final answer, so that is what the calculation is tedious, but it is not difficult. This was minus half 1 plus root 3 xz + half minus root 3 + 1.

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$$_{2}\,(xz + yz + z^2) = -\frac{1}{2}(1-\sqrt{3})\,xz + \frac{1}{2}(\sqrt{3}+1)\,yz + z^2$$

$$_{3}\,(xz + yz + z^2) = -\frac{1}{4}(1+\sqrt{3})\,xz + \frac{1}{2}(-\sqrt{3}+1)\,yz + z^2$$

now let us calculate projection of E IR rep on the f $xz + yz + z^2$

$$P_{11}^{E}\,(xz + yz + z^2) = \frac{2}{6}\left[1\,E(f) + \left(-\frac{1}{2}\right)C_3(f) + \left(-\frac{1}{2}\right)C_3^2(f) + \cdots\right]$$

$$= \frac{2}{6}\left[xz + yz + z^2 + \left(-\frac{1}{2}\right)\left[-\frac{1}{2}(1-\sqrt{3})\,xz - \frac{1}{2}(1+\sqrt{3})\,yz + z^2\right] + \cdots\right] = xz$$

So, now let us calculate the projection of E IR representation on to this function. So, let us calculate different matrix elements. So, projection of E matrix element 1 1 xz + yz remember that this is 2 cross 2, so we will have 4 elements of this 1 1, 1 2, 2 1, 2 2. So, we will calculate 1 by 1 because this is a complete projection of four elements coming out of this. So, this one should have so the dimension will come over here order of the group is six so that will go here 2 by 6.

So, remember the formula Li by h and then I have summation over all R, so that means summation I have to take for all R. Now we have to take go back to the matrix element this matrix element over here and multiply it with the effect of E on to the given function and put multiply that with this one. So, let us see how to do that in short, I will write the function, now next will be the corresponding matrix element of C3.

So, C3 will have minus half and then the effect of C3 onto that function, that is what the projection operator formula says. So, now I will have minus half and effect of C3 on to the function. Similarly for C3 square matrix I have minus half again, and effect of C3 square on to the function. And so on let us do it for one so that it is very, very clear. So, 2 by 6 E effect of e will give you xz + yz + z square + minus half effect of C3 on to the function was minus half square root 1 minus square root 3 xz minus half 1 plus root 3 yz + z square.

So, this is the matrix element of C3 multiplied by effect of C 3 all the functions. And similarly, you do this. So, if you do this complete calculation the answer here what you will get will be xz. You have to trust me on this because I have done this calculation and it is also solved in Cotton. Here due to lack of time so will not do it here so I expect you to completely do it by hand.

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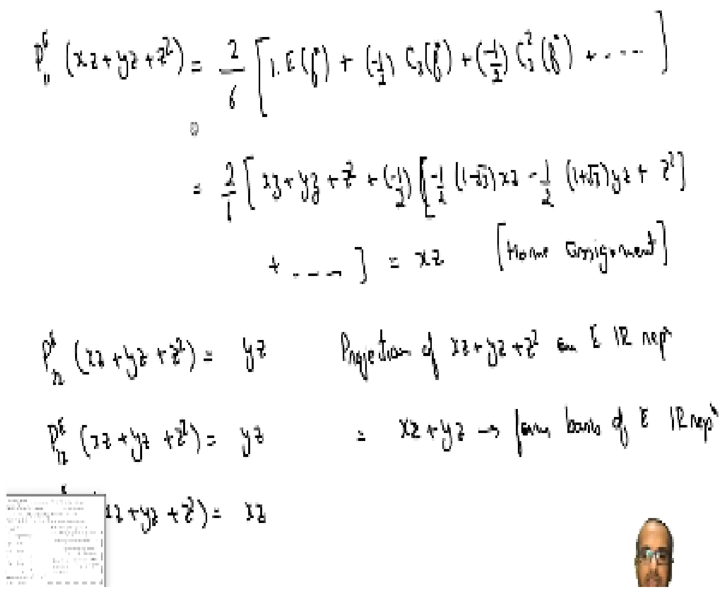

So, please take this as home assignment and do this calculation. Similarly, so the way we have calculated for P11 that is the 1 1 element of E irreducible representation of this, so let us also calculate P E 22 xz + yz + x square and if we do the same thing what we will get is yz without any coefficient. So, this one gives you xz 22 element will give you yz. Similarly, we can do it for 12 and 21. So, they will also be the same thing so P I think 12 E on projection operating function gives you yz and P 21 xz + yz + x square gives you xz.

So, all of this gives you this thing. So this implies that this particular projection, projection of xz + yz + z square on E IR representation is nothing but a linear combination xz + yz and if you want to normalize you can divide square root of the sum of squares of coefficient which will give you 1 by root 2. So, this is how the projection of this will be calculated on a given IR representation. So, now if we try to use this as the basis, we will see that this thing forms basis of E IR representation.

So, out of a given function, we have what we have achieved here is, we have achieved the part which is relevant for E representation and rest of the part is basically neglected. So, when we take this projection what we get is this and we know that now this thing will form the basis of E representation. So, that is the job of a projection operator. So here we are dealing with full matrix elements like this.

So, we needed the whole all matrices, but in this particular case when we deal with incomplete projection operator will be dealing with only traces and the calculation is much simpler. So, that is all for today. So, please do calculate all the components yourself and complete this calculation and see for yourself if you are getting this thing as a result, thank you very much.