Symmetry and Group Theory

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Lecture - 28
Character Table and Mulliken Symbols

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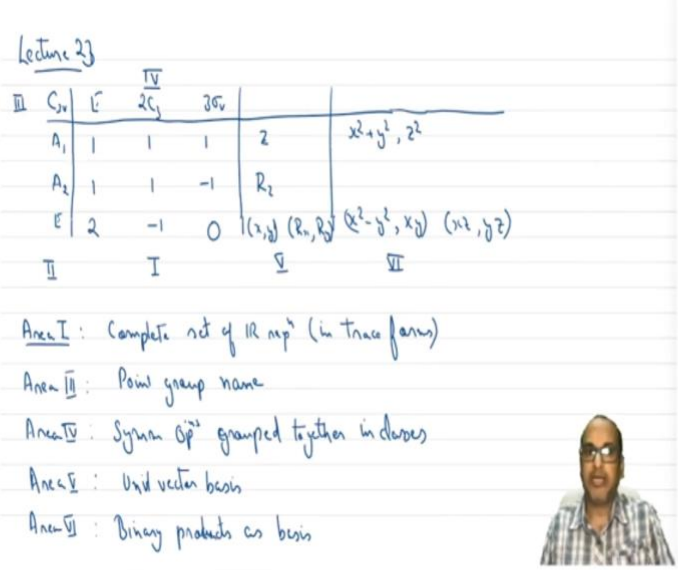

So, welcome to lecture 23. So, so far we have learned how to write a reducible representation, irreducible representation from scratch, and then how to convert a reducible representation into a linear combination of irreducible representations. So, now, we are well versed with what is a character table, which is a complete set of irreducible representations. So, now, let us look at what is the complete character table.

So, far we have been looking at actually a partial character table. So, now, let us again take the example of C3v, because we now know all the elements of this character table, at least some of it. So, let us see what are the different areas in the center? What are the meanings of those areas? So, if you look at any textbook, what you will see is, character table is divided into certain areas which are like this.

So, for example, here you would find written some characters like A1, A2, E in this case mostly A, B, E and with some subscripts and superscripts. Now this one we are aware of already and here you will find some x y z written on it which is the basis set, that also be have some idea and here you will see something written as again x y in some functions of x y. So, x square - y square.

So, what are the meaning of all this? Let us see. So, let us divide this into different areas. So, let us call this as area 1, let us call this as area 2, area 3, area 4, area 5, and area 6. This is all in most of the character tables you will see it is divided into different areas. So, let us talk about area 1 first. This we already know it is a complete set of irreducible representations in trace forms, so trace of these vectors.

So, area 1 is we are well versed with, so let us also see what we know so far. Area 3 we know, so area 3 here is the point group name, then area 4 also we know, area 4 is the symmetry operations or group elements, grouped together in classes. So, for example, here 2 C 3 is one class, C 3 and C 3 square are combined into one class sigma v 1, sigma v 2, sigma v 3 are combined to another class. So that is also very well we know.

Now area 5 also we know, because we have done unit vector transformation. So, these are unit vectors, unit vector basis set basis. So, for example, if I am writing z here that means, unit vectors z will be transformed as this particular representation. If I am writing Rz here that means, Rz will transform as 1, 1, - 1 this particular IR representation, and when I say x, y within braces, these brackets, so it is, it basically means that x and y are not separable and thus are forming a degenerate representation.

So, this would be a 2-dimensional representation. So, whenever you have x, y like that, that means, x and y both together form the basis for this particular representation. We have seen this case earlier. Similarly in this case Rx, Ry would also be inseparable and Rx, Ry together would form basis for this. So, x and y, Rx and Ry together will form basis for this. Now here these are, so unit vector basis and then area 6 is binary products as basis.

So, these are if you see that x square + y square if you take, x square + y square will form basis same as z. Similarly, z square will also form basis for A1. If you take now x square minus y square, xy that means, this and this together will not be separable and put together form basis for E. Similarly, xz and yz together will form basis for this. So, typically these binary products, why are we discussing these binary products?

Because these binary products actually have, some of these binary products have properties as d-orbitals. So, d-orbitals properties if you want to know then you would want to know the binary products, how these binary products would be transformed under a particular symmetry operation. So, these are binary products. So, if we want to know, so let us say that we have written this set of irreducible representations and now we want to know, we want to understand which unit vector form basis of which representation that is easy. So, what you do is you create a matrix. For example, if you want to know what is x, y and z what you do is?

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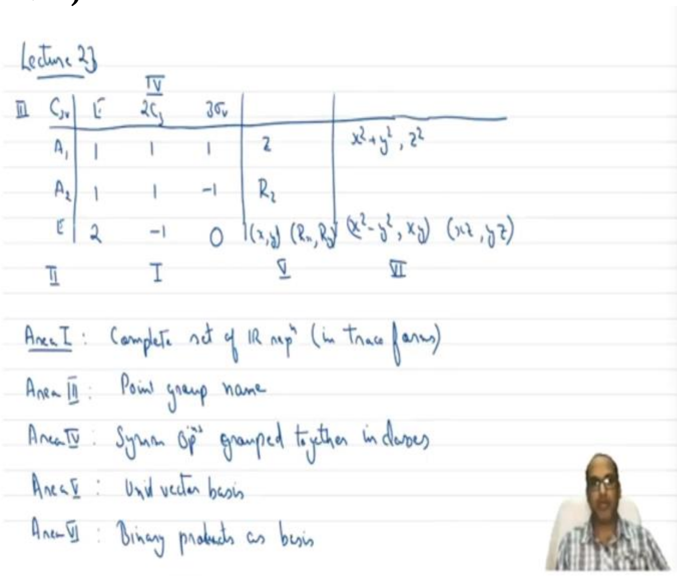

You carry out the transformation E on x, y, z together and then find out the resultant matrix, this we have seen already, find out the resultant matrix and then find out the matrix for the operator, so this we have already seen. So, we can do it for E, C 3, sigma v any operation given, we can do it on x y z matrix and then find out the resultant matrix and that will help you find out the what will be the matrix for the operator.

The point to remember because, to start with we do not know whether a particular representation would be 1-dimensional or 2-dimensional or whether it will be degenerate with respect to xy or xz or yz we do not know to start with. So that is why we generally take x y z together and then we reduce it then we see which 2 vectors are going together and which one particular basis set is going separate right.

So, for example, in this case, if we see that xy would not be separable, so xy would form a 2 cross 2 matrix corresponding to this and then this will be 1 cross 1 matrix, this case we have already seen. So, finding which unit vector is the basis for which particular IR representation is easy and we have done that already. Now to find which binary product is the basis for which particular this thing, IR representation is forming the basis, it is little tricky and then it is better if we what we do is, we take the various binary products as d-orbitals.

So, for example, if I am taking d x square - y square and then I take the shape of these orbitals, as let us say, so because this is x square - y square, so I will just draw x, y and z is coming out of the plane of the board. So, x square - y square would be lined along, the loops will be lying along the axis. And these 2 will be positive and this will be negative. We know what is the shape of d x square - y square.

Similarly for d xy again we know this will be, again let us not draw the z, x, y, -x, -y. Now d - xy that will be lying in between the axis and these will be 2 opposite ends will be negative and these will be positives. Similarly, we can do it for d-yz which will be in y z plane and d-zx which will mean in xz plane. So, it will be same. So, if you want me to draw, if you draw it quickly. So, you have if you have yz that means, this will be y, z, -y, -z and this will be like between yz.

Now x will be coming out of the plane of the plane of the board. And then this will be 2 negatives and 2 positives. Now for d-zx this will be xz will be like this x, z, -x, -y and when you have one, so - xz will be negative, so this will be z minus positive positive. So, this is easy and then you also have the z square which will be if I want to draw may be something like this with a ring of positive intensity and this will be negative negative, x, y, z, - z, - y, - x.

So, now, what you have to do is if you want to identify what is a matrix for E for example, you have to carry out the operation E onto this and see how it is transformed and then accordingly write the matrix for E. Similarly, you do it for all 5 together and see what happens to each of this and then accordingly write the matrix representation for E. So, this again I leave it as home exercise. So, try to do it yourself if not, we can discuss during the interaction session.

So, try to identify what will be the, assignment, try to identify what will be the IR representation for each of this as the basis set and then we have each of these as the basis of what will be the IR, find IR representation for d-orbital as the basis, so in C3v case for example. So, do it for yourself and then you will see that how it is transformed. So, we will be able to identify it easily. So, now that we have seen, so now we know that area 1, area 1 is clear area 3, 4, 5 and 6 is clear.

Now let us look at these symbols over here A1, A2, A3. So, far we have been referring to all these IR representations as tau i where as any ith representation as tau i which is a generic symbol, but these symbols were actually given names by Mulliken and hence these symbols are called as Mulliken symbols.

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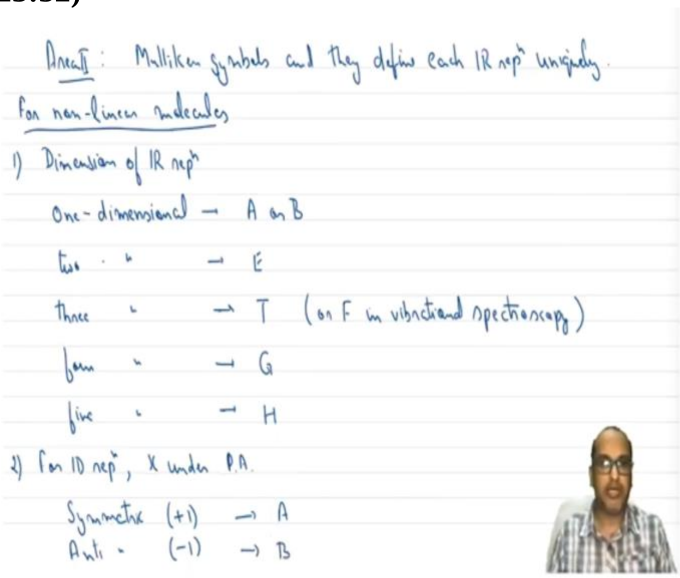

So that is area 2, these are called as Mulliken symbols and they define each IR representation uniquely. So, now, let us look at what are the different rules for this. So, the molecules can be divided for these rules into linear and nonlinear. So, let us first look at nonlinear molecules, for nonlinear. So, the first is dimension defines the characters, the Mulliken symbol, so dimension of irreducible representation.

If it is one-dimensional the symbol is A or B. We will also differentiate between A and B based on some other property. If it is 2-dimensional the symbol is E, if it is 3-dimensional the symbol is T, and sometimes in vibrational spectroscopy this is used as F. F symbol or F in vibrational space, within group theory it is used as T but in vibrational spectroscopy it is used as F. For 4-dimensional which is rarely used in group theory, but still for completeness I will define the full, G and for 5-dimensional I have never seen any example of 4 and 5.

For completeness, this is the complete set of nomenclature. So, for the dimension of IR representation then the symbol will be defined as A or B for 1, E for 2, T for 3 and so on so forth, 4 G and 5 H, so now between A and B. So, let us do it for between A and B. So that is for 1d representations if, so symmetry defines let us say, character under principal axis. So, if the character is symmetric what do you mean by symmetric?

The trace is + 1 then the symbol is A. If it is anti-symmetric, that is the trace is – 1, it is called as B. So, here dimension was not able to classify between A or B. So, the character under principal axis rotation defines it within 1 dimensional representation whether it is going to be classified as A or B. So that is 1. And now, let us look at various subscripts which are written.

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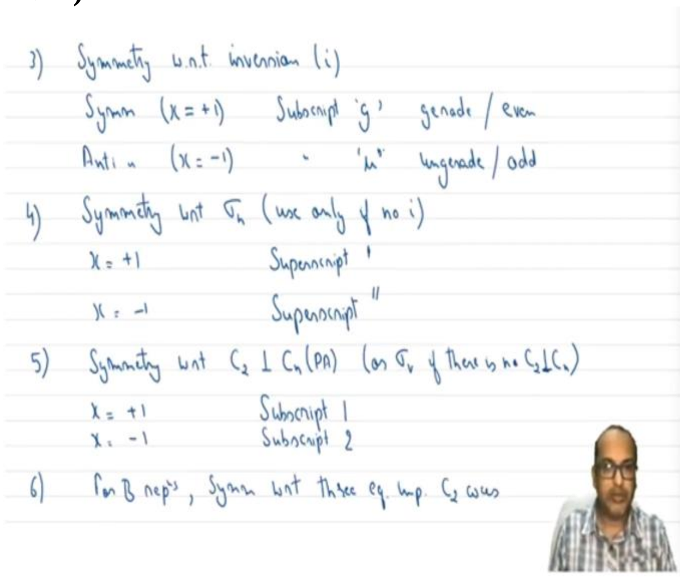

So, the third rule is symmetry with respect to inversion, center of inversion. So, if it is symmetric again character equals plus one, the subscript is g. If it is anti-symmetric that is character is minus one, the subscript is u. So, this actually stands for gerade and ungerade. This you would have learnt somewhere. Which is basically meaning of that is even or odd. So, you would have seen that in group theory or in inorganic chemistry somewhere.

So, symmetric with respect to inversion i and if it is symmetric + 1 characters there goes a subscript called g otherwise it is u, for example, Ag, Au, Bg, Bu, Eg, Eu and so on and this goes as a subscript. So, forth is symmetry with respect to sigma-h, horizontal plane of symmetry. When? this has to be used only if no i is present. So, symmetry with respect to sigma h, if so I will not write now symmetric and antisymmetric, I will just say character + 1 then the superscript is prime.

If character is - 1 then the superscript goes as double prime. This will be confusing so let me write it as superscript, so prime in double prime superscripts. Now also, if symmetric with respect to C2 perpendicular to Cn, which is principal axis or sigma v if there is no C2, no such C2 is there. So, again chi = + 1 then you have subscript 1, if chi = -1, then you have subscript 2. Now let us also look at if there are 3 equally, important perpendicular and this happens only for B.

So, for B representations, symmetry with respect to 3, lets call them equally important because you do not know which one is principal axis, for example, we have seen the case of D 2h where it is C 2 z, C 2 x, C 2 y we do not know which one is principal axis, many a times they do not define it. So, 3 equally important C2 axis then let us go to next page.

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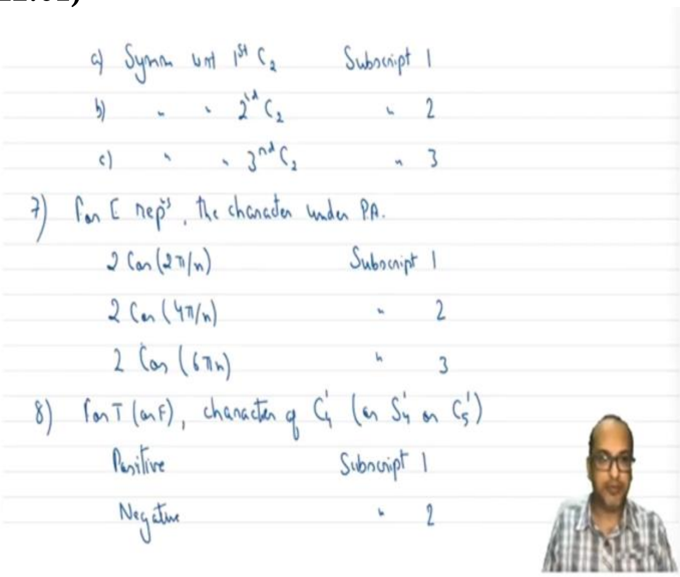

Symmetric with respect to first C2, subscript 1; B part is symmetric with respect to second C2 subscript 2, 3. Rule number 7, I think this is 2 more rules. So, for E representations the character of C or we just write, character under principal axis. If the character is 2Cos 2pi / n, where n is the order of the principal axis, we all know that, then it takes subscript 1. If the character is 2Cos 4pi / n, it takes subscript 2 and if the character is 2Cos 6pi / n it takes subscript as 3 and can go on.

And the last rule for nonlinear molecules is and this is for T or F. If you are looking at vibrational spectroscopy, character of C4 or S4 or C5 in that order. So, if there is no C4 then you look for S4, if there is no S4 then you look for C5 and the first operation, I mean the first order, so you do not have to look for C4^3 if it is different, so only character under C4^1, S 4^1 or C5^1. If it is positive then the subscript is 1.

If it is negative then the subscript is 2. So, if you follow all these rules, you can actually you neatly define the symbol for each and every irreducible representation in the point flows. So, we will take some examples, but let us first complete the rules if they are not complete yet, because we also have to cover linear molecules.

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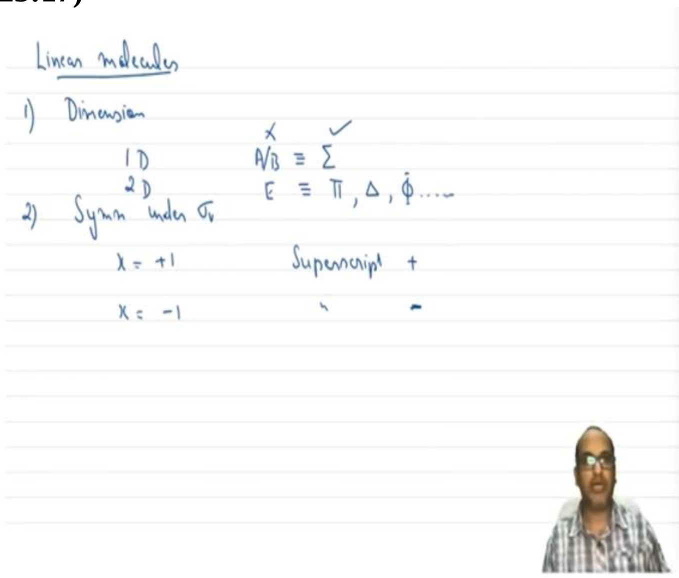

So, for linear molecules they are much lesser number of rules. So, for linear molecules what do we have? So, the dimension defines the symbols as, if it is 1 dimensional then usually it is called as A, in A or B in nonlinear molecules which in this case is equivalent to called as sigma. So, we do not write A or B here, we write sigma here in linear molecules and for 2 dimensional molecules, in other molecules like nonlinear molecules, we used to write E.

In this case we write it as capital pi, capital delta, or capital phi and the symbols you can take up different symbols. So, there are only 1 or 2 dimensional representation in case of linear molecules, 1d are denoted by sigma and 2ds are denoted by pi, delta. Because these are mostly infinity point group, so you can keep on having more number of 2 dimensional representations symmetry under sigma v.

We have seen that symmetry under sigma-v in case of linear molecules also here. Here we have seen sigma-v case, where if it is positive it takes subscript 1, if it is negative it takes subscript 2. So, here what happens, here if it is character is plus one or character is minus one or we can say positive and negative, it takes superscript instead of subscript 1, 2, it takes superscript plus and superscript minus that is the only difference.

Rest all the rules will remain same for these molecules also. So, this defines the complete character table. So, now, let us look at the example with these rules, let us look at the example of C3v that we have been discussing. So, these are a 1 dimensional representations, the first 2 are, this is one dimensional, this is one dimensional, the symbols have to be either A or B and this is 2 dimensional. So, symbol has to be E. So, now, if you see, both of them have been given letter A and not B, why?

Because for both of them the principal axis is positive and that is why both are A, now 1 and 2 because character under sigma v is positive for this one. So that is why it is subscripted as 1 and negative for this one, so that is why it is subscripted as 2. So, for E there is no superscript, subscript required because there is only one E and that uniquely defines this particular IR representation. So, we will take up more examples in next class and we will see how we will take at least 2 examples?

But meanwhile, you will also try to solve, to try to look at different character tables and see based on these rules, can you actually uniquely determine the Mulliken symbol for each given IR representation. We will see how it is done for at least 2 examples in next class but let us do it at home yourself and then see if we have any doubts. So that is all for today and see you in next class.